Processing and properties of MSM based hybrid materials

Frans Martin Christian Nilsén
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Abstract

Magnetic shape memory alloys, such as the Ni-Mn-Ga Heusler alloy, have been studied intensively for the last twelve years due to the high and reversible magnetic-field-induced strains (MFIS) exhibited by their twinned martensitic structure at room temperature. The large elongation and high cycling speed due to twin variant boundary movement, induced either by magnetic field or by mechanical stress, makes such materials an ideal choice for fast actuators and sensors in applications ranging from active damping elements to medical micropumps. However, the properties of MSM alloys are highly dependent on the chemical composition. The highest reversible MFIS have so far been found only in single crystals, which are troublesome and expensive to manufacture. Polycrystalline structures are easy to manufacture, but they usually have low or non-existent MFIS due to grain boundary constraints and are brittle. Researchers have tried to solve these problems by developing the single crystal manufacturing process so that it is more suitable for industrial scale production, and by reducing the grain boundary constraints by manufacturing magnetic shape memory foams with high porosity and texture. In this work, industrially viable Ni-Mn-Ga hybrid composites are manufactured in laboratory scale and their properties as actuators and vibration damping elements are studied. The first hybrid structure presented is a Ni-Mn-Ga-Co/WC-Co double dispersion metal matrix composite (MMC), with high cavitation resistance and damping properties. Though previous research on Ni-Mn-Ga composite structures has focused primarily on polymer composites, the results from the Ni-Mn-Ga/WC-Co MMC show that it is possible to produce a material with high damping and wear resistance by adding a metal dispersion such as WC-Co into a Ni-Mn-Ga matrix. The next objective was to develop a heat-treatment process with minimal chemical composition change for gas atomized Ni-Mn-Ga powder. This powder was further used to manufacture highly porous spark plasma sintered structures with pronounced MFIS comparable to previously manufactured textured polycrystals. Lastly, the powder was also used to produce cast Ni-Mn-Ga/epoxy composites with magnetically controllable vibration damping properties and pronounced MFIS. The vibration damping properties of these hybrid Ni-Mn-Ga/epoxy composites were found to be higher than previously reported structures, even though pronounced damping is usually associated with disorganized Ni-Mn-Ga/polymer composites. In comparison to other Ni-Mn-Ga powder manufacturing methods, the results from this thesis work show that the heat-treated gas atomized powder method can be used to produce hybrid composite structures with comparable and at times even better properties than with other methods.

Keywords Ni-Mn-Ga, ferromagnetic shape memory alloys, hybrid composites structures, damping, magnetic-field-induced strain

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Helsinki, 4 April 2018
Frans Martin Christian Nilsén
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# List of Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>Austenite</td>
</tr>
<tr>
<td>at.-%</td>
<td>Atomic percentage</td>
</tr>
<tr>
<td>(A_s)</td>
<td>Austenite start temperature</td>
</tr>
<tr>
<td>(A_f)</td>
<td>Austenite finishing temperature</td>
</tr>
<tr>
<td>(a, b \text{ and } c)</td>
<td>Lattice parameters</td>
</tr>
<tr>
<td>Cu-K(\alpha)</td>
<td>K(alpha) radiation from Copper source, with wavelength (\lambda = 0.1542) nm, used in the X-ray studies for the analysis of materials crystal structure</td>
</tr>
<tr>
<td>Co</td>
<td>Cobalt in the alloys in atomic percentage</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>(d(0,5))</td>
<td>Median diameter</td>
</tr>
<tr>
<td>(\delta)</td>
<td>Phase lag</td>
</tr>
<tr>
<td>(\Sigma)</td>
<td>Sum</td>
</tr>
<tr>
<td>(E')</td>
<td>Storage modulus</td>
</tr>
<tr>
<td>(E'')</td>
<td>Loss modulus</td>
</tr>
<tr>
<td>(E^*)</td>
<td>Complex modulus</td>
</tr>
<tr>
<td>(\varepsilon_0)</td>
<td>Lattice dependent maximum field induced strain</td>
</tr>
<tr>
<td>(e/\alpha)</td>
<td>The average number of valence electrons per atom</td>
</tr>
<tr>
<td>EDS</td>
<td>Electron dispersive X-ray microanalysis</td>
</tr>
<tr>
<td>F</td>
<td>Applied force</td>
</tr>
<tr>
<td>Ga</td>
<td>Gallium in the alloys in atomic percentage</td>
</tr>
<tr>
<td>HF-DMA</td>
<td>High-frequency dynamic mechanical analysis instrument</td>
</tr>
<tr>
<td>H</td>
<td>Applied magnetic field</td>
</tr>
</tbody>
</table>
\( \frac{H_{avg}}{H_o} \) Normalized applied magnetic field

\( K_{\mu} \) Magnetocrystalline anisotropy

MFIS Magnetic-field-induced strain

MMC Metal matrix composite

MSM Magnetic shape memory

MSMA Magnetic shape memory alloy

\( M_s \) Martensite starting temperature

\( M_f \) Martensite finishing temperature

\( \text{Mn} \) Manganese in the alloys in atomic percentage

\( \text{Ni} \) Nickel in the alloys in atomic percentage

\( \text{NM} \) Non-modulated martensite (in literature also known as 2M)

NHT Not heat-treated

OMMD Optical magneto-mechanical device

POM Polyoxymethylene

SPS Spark plasma sintering (in literature also known as pulsed electric current sintering, PECS)

SEM Scanning electron microscopy

\( \sigma \) Stress

\( \sigma_{mag} \) Magneto-mechanical stress

\( \sigma_{tw} \) Twinning stress

\( T_S \) Starting temperature of phase transformation

\( T_F \) Finishing temperature of phase transformation

\( T_A \) Average of start and finishing austenitic transformation temperature

\( T_C \) The Curie temperature

\( T_M \) Average of start and finishing martensitic transformation temperature

\( T_g \) Glass transition temperature

\( T_{mart} \) Martenstic transformation temperature in Kelvins

\( \tan \delta \) Loss tangent

UTS Ultimate tensile strength
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>VSM</td>
<td>Vibrating sample magnetometer</td>
</tr>
<tr>
<td>vol-%</td>
<td>Volume percentage</td>
</tr>
<tr>
<td>wt.-%</td>
<td>Weight percentage</td>
</tr>
<tr>
<td>WC</td>
<td>Tungsten carbide in the alloys in atomic percentage</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Magnetic susceptibility</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>10M</td>
<td>5-layered modulated martensite (in literature also known as 5M)</td>
</tr>
<tr>
<td>14M</td>
<td>7-layered modulated martensite (in literature also known as 7M)</td>
</tr>
</tbody>
</table>
List of Publications

This doctoral dissertation consists of a summary of the following publications that are referred to in the text by their Roman numerals.


IV. Frans Nilsén, Ilkka Aaltio, Simo-Pekka Hannula, Comparison of magnetic field controlled damping properties of single crystal Ni-Mn-Ga and Ni-Mn-Ga polymer hybrid composite structures, Composites Science and Technology, Volume 160, (2018), pp. 138-144, DOI: 10.1016/j.compscitech.2018.03.026
Brief Description of the Publications

Publication I: “Properties of the pulsed electric current sintered Ni-Mn-Ga-Co-WC composites”
In this publication the damping capabilities of two double dispersion composites of Ni-Mn-Ga/WC-Co, prepared with pulsed electric current sintering, were studied with DMA and cavitation erosion testing. Composite 1 consisted of 90 vol-% WC-12Co and 10 vol-% of non-modulated Ni-Mn-Ga-Co martensite, while Composite 2 consisted of 18 vol-% of WC-12Co and 82 vol-% of 10M Ni-Mn-Ga-Co martensite. The two different martensitic structures were chosen based on previous damping experiments and the two different fractions were used to evaluate the effect of increasing WC-Co content. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) studies showed that during sintering the cobalt had distributed almost evenly between the two different phases. The experiments showed that both composites are promising candidates as damping element materials in applications where high hardness and wear resistance is required. The damping ability of the composites is proposed to be derived from the combined effect of energy dissipation by twin boundary movement in the Ni-Mn-Ga matrix together with the high hardness and wear resistance arising from the tungsten carbides.

Publication II: “Characterization of gas atomized Ni-Mn-Ga powders”
In this publication the properties of the gas atomized Ni-Mn-Ga powder that was used for the following publications III and IV was studied. Gas atomization is a well-known high-volume powder manufacturing method for metallic powders, which produces round and smooth surfaced powder particles with a narrow and controllable particle size distribution. The microstructure, magnetic properties, phase transformation temperatures and the effects of heat-treatment of two gas atomized powders ATO1 and ATO2, with different compositions of Ni$_{10.7}$Mn$_{27.6}$Ga$_{22.8}$ and Ni$_{10.3}$Mn$_{28.8}$Ga$_{21.6}$Cu$_{0.3}$ respectively, were studied in the publication. The copper in ATO2 was introduced to the alloy from the precasting mold used in the gas atomization process. The phase transformation temperatures and magnetic properties of the as atomized powders were considerably lower when compared to conventionally prepared alloys. Additionally, X-ray diffraction (XRD) measurements showed that both as atomized powders had cubic crystal structure at room temperature. However, when the atomized powders were heat-treated in evacuated crystal ampoules both powders recovered the magnetic properties and the ATO2 powder was found to be 10M at room temperature. This recovery is probably due to the combined effect of released
residual strains and homogenization of the structure. Additionally, compared to ball milled Ni-Mn-Ga alloys the sintering temperature of the gas atomized powder was found to be lower.

**Publication III: “Highly porous spark plasma sintered Ni-Mn-Ga structures”**

In this publication, the previously studied gas atomized ATO2 powder was used to manufacture porous Ni-Mn-Ga structures from a mixture of as atomized 25 vol-% Ni-Mn-Ga and 75 vol-% NaCl powder. Once the NaCl was removed from the sintered pieces using water immersion, the solid Ni-Mn-Ga skeletons were heat-treated in vacuum to grow the grains to a size of 22-23 μm from the 1.7 μm found in the as atomized powder. X-ray texture measurements revealed that the crystal c-axis in the grains had aligned in the spark plasma sintering process close to the compression stress direction. Additionally, the magnetic field induced strain increased with the sample porosity, with highest MFIS of 1.24% found in the sample with porosity of 92%. As the measured MFIS is larger than previously reported value for magnetostriction for polycrystalline Ni-Mn-Ga, it is attributed to the magnetically induced twinning.

**Publication IV: “Comparison of magnetic field controlled damping properties of single crystal Ni-Mn-Ga and Ni-Mn-Ga polymer hybrid composite structures”**

Hybrid composites were manufactured from gas atomized and annealed Ni-Mn-Ga powder and Hysol 9455 epoxy. The combination of ductile polymer and gas atomized large grained Ni-Mn-Ga powder, has multiple advantages compared to bulk single crystals. These advantages include ease of manufacturing and freedom of shape, while still being magnetically controllable. In this publication, damping capabilities of hybrid composites manufactured at three different filling ratios 25, 30 and 35 vol-% in comparison to single crystal and steel filled hybrid composite are reported. The damping properties were characterized using a commercial dynamic mechanical analyzer (DMA) in single cantilever mode and a laboratory built high frequency dynamic mechanical testing instrument in uniaxial stress mode. Both experiments were done with and without magnetic field. The results showed that the Ni-Mn-Ga hybrid composites could be magnetically controlled and that the magnetic field has a comparable stiffening effect with single crystal Ni-Mn-Ga at forced cyclic tensile/compressive vibration with externally applied magnetic field. The magnitude of stiffening effect is directly related to the filling ratio of the composites. This stiffening can thus be utilized and controlled in damping applications.
Author’s Contribution

The Author of this Thesis is also the responsible author for all the Publications (I to IV) presented in this Thesis and has thus contributed the majority of the writing work for them. Of the experimental work, he has been responsible for the magnetic measurements, microstructural and chemical characterization, X-ray diffraction studies, porosity and density measurements. In addition, he has been responsible for the high frequency dynamic mechanical analysis (HF-DMA) measurements and for the redesign of that instrument.

In addition to participating in the preparation of the manuscripts of the Publications, the co-authors have contributed the following:

Publication I: Properties of the pulsed electric current sintered Ni-Mn-Ga-Co-WC composites

Dr. Ilkka Aaltio: Provided important scientific guidance and participated in planning of the experiments. Additionally, provided expertise for the magnetic measurements and resulting data analysis of the spark plasma sintered samples. Also participated in design and building of the laboratory built magnetic measuring systems (VSM, low-field ac susceptibility system) and conducted part of the Ni-Mn-Ga-Co/WC-Co DMA measurements and analysis.

Dr. Outi Söderberg: Conducted the differential scanning calorimetry (DSC) and thermal characterization of Ni-Mn-Ga-Co/WC-Co powders and spark plasma sintered samples.

Dr. Illya Glavastkyy: Conducted the manufacturing of Ni-Mn-Ga-Co/WC-Co powders and characterization using X-ray diffraction.

Dr. Mika Lahelin: Conducted part of the Ni-Mn-Ga-Co/WC-Co DMA measurements and the analysis.

Dr. Ryuji Maki: Conducted the spark plasma sintering of Ni-Mn-Ga-Co/WC-Co samples.

Prof. Simo-Pekka Hannula: Provided scientific guidance for the research work and participated in planning of the experiments.

Publication II: Characterization of gas atomized Ni-Mn-Ga powders

Dr. Ilkka Aaltio: Provided important scientific guidance and participated in planning of the experiments. Additionally, provided expertise for the magnetic measurements and data analysis. Provided guidance in writing the Publication
II. Also participated in design and building of the laboratory built magnetic measuring systems (VSM, low-field ac susceptibility system, HF-DMA magnetic circuit and DMA magnetic circuit).

Dr. Yanling Ge: Contributed to the X-ray diffraction and analysis. Provided expertise to scanning electron microscopy and chemical composition studies. Provided guidance in writing the Publication II.

M.Sc. Tomi Lindroos: Provided expertise in the gas atomization of the MSM alloy for the Publication II.

Prof. Simo-Pekka Hannula: Provided scientific guidance for the research work and participated in planning of the experiments, contributed to the development of heat-treatment procedure for the gas atomized powder and provided guidance in writing the Publication II.

**Publication III**: Highly porous spark plasma sintered Ni-Mn-Ga structures

Dr. Ilkka Aaltio: Provided important scientific guidance and participated in planning of the experiments. Additionally, provided expertise for the magnetic measurements and data analysis. Provided guidance in writing the Publication III. Also participated in design and building of the laboratory built magnetic measuring systems (VSM, low-field ac susceptibility system, HF-DMA magnetic circuit and DMA magnetic circuit).

Dr. Yanling Ge: Contributed to the X-ray diffraction and texture measurements and analysis. Provided expertise to scanning electron microscopy and chemical composition studies. Provided guidance in writing the Publication III.

M.Sc. Joonas Lehtonen: Provided expertise in spark plasma sintering for Publications III.

Prof. Simo-Pekka Hannula: Provided scientific guidance for the research work, provided insight for the manufacturing of the porous spark plasma sintered structures and provided guidance in writing the Publication III.

**Publication IV**: Comparison of magnetic field controlled damping properties of single crystal Ni-Mn-Ga and Ni-Mn-Ga polymer hybrid composite structures

Dr. Ilkka Aaltio: Provided important scientific guidance and participated in planning of the experiments. Additionally, provided expertise for the magnetic measurements and the magnetic measurement analysis. Also participated in design and building of the laboratory built magnetic measuring systems (VSM, low-field ac susceptibility system, HF-DMA magnetic circuit and DMA magnetic circuit).

Prof. Simo-Pekka Hannula: Provided scientific guidance for the research work, contributed to the development of the heat-treatment procedure for the gas atomized powder and provided insight for the manufacturing of the porous spark plasma sintered structures.
Magnetically controllable Ni-Mn-Ga Heusler magnetic shape memory alloys have been studied intensively starting from their discovery in 1996 by Kari Ullakko et al. [1] to this day. Compared to typical shape memory materials where the shape memory effect is achieved by phase transformation [2], which limits the speed of the transformation, the shape change in magnetic shape memory alloy Ni-Mn-Ga is due to twin boundary reorientation in the martensitic phase. The twin boundaries can be moved either by applying an external magnetic field or simply by mechanically straining the material. As such, continuous movement can be achieved either by rotating the field or by combining magnetic field with mechanical straining for example with a spring to compress the Ni-Mn-Ga crystal and an external magnetic field that is oriented perpendicularly to the straining direction to recover strain after compression.

One of the goals of magnetic shape memory material research has been to develop new types of materials, which utilize the elongation of MSM materials’ properties beyond those of piezoelectric [3] and magnetostrictive materials. As the aim is to develop ever lighter and smaller machines, materials able to act both as sensing and controlling elements would be highly beneficial. As such, magnetic shape memory alloys possess fast actuation capabilities [4] of up to 1 kHz range, good fatigue resistance [5] with recoverable strain even after $10^8$ magneto-mechanical cycles [4] and large magnetic-field-induced strains (MFIS) of up to 10% [6]. Because of the above properties, Ni-Mn-Ga alloy shows exceptional promise as a fast high-precision actuator, which could be used in multiple different applications from active damping elements [4] to medical micropumps [7, 8] and actuators [9].

However, some problems still need to be solved before the huge potential of magnetic shape memory alloys can be realized. The main disadvantage being that, to date, the high magnetic-field-induced strains have only been achieved in single crystals within a narrow composition and temperature range. Single crystal manufacturing is difficult and costly as the growth needs to be controlled carefully to prevent manganese evaporation and oxidation. Additionally, the grown crystals need to be evaluated using X-ray diffraction and then cut with precision to produce working MSM elements. Thus the whole process is difficult to automate, which keeps the working MSM element price high. Lastly, even in single crystals, the modulated crystal structures can become brittle due to impurities and are difficult and costly to shape into products. The reason why randomly textured polycrystals do not exhibit as high MFIS as single crystals, is due
to the grain boundary constraints imposed on twin boundary motion [10–13]. If the grains are not highly oriented and have large misorientation between nearby grains, the constraints for the grain deformation are high, as more hinging between the grains is required for accommodating the misorientation during deformation [13].

Researchers have approached these problems using three different methods. Firstly, some researchers and companies have tried to develop the single crystal manufacturing process to make it more reliable and capable for mass production [14]. Secondly, some researchers have tried to approach the problem from another angle by reducing the grain boundary constraints by, for example, manufacturing cast foams with preferred orientation [12, 13]. Both of these approaches have produced remarkable results, but a commercial breakthrough has not yet happened. A third approach is to first produce working Ni-Mn-Ga alloy powder, by either ball milling single crystals [15] and melt-spun strings [16] or with spark erosion [17]. The powder can then be used to manufacture working structures either by utilizing powder metallurgical methods, such as spark plasma sintering, or by manufacturing hybrid composite structures by combining it with a suitable polymer. Even though the properties that the powder metallurgical and hybrid composite structures [18, 19] exhibit are not close to the highest MFIS of the single crystal [20, 21] or the moderate MFIS achieved with textured foams [12, 13], the production of MSM powder and thus composites or other structures is far simpler and easier to scale up. Additionally, the use of Ni-Mn-Ga in powder form makes it possible to utilize brand new manufacturing methods such as selective laser sintering and binder jet printing [22]. The benefit of utilizing composite structures is the possibility of achieving any needed shape in the application by combining working composite elements together [23]. The use of ductile polymers in the composites also permits independent deformation of active MSM grains to some extent and acts as a spring to recover the MFIS after the applied magnetic field is removed. Thus, the composite works as an independent actuation/damping element without need for external springs. To make this possible, the polymer matrix should exhibit similar stiffness as the original alloy. To this end silicones, epoxies and polyurethanes have been previously studied [24] as possible matrix candidates.

In this Thesis, the manufacturing and properties of polycrystalline Ni-Mn-Ga structures including metal matrix composites [Publication I], porous spark plasma sintered structures [Publication III] and hybrid polymer composites are studied [Publication IV]. Additionally, a heat-treatment procedure suitable for gas atomized Ni-Mn-Ga powders is developed based on experiments in Publication II and the powder is used to manufacture the samples in Publication III and IV.

The literature review provides an overview of the properties of Ni-Mn-Ga alloys starting with different martensitic crystal structures (5m, 7M and NM) found at room temperature in Ni-Mn-Ga alloys. The impact of chemical composition is presented with the basic requirement for magnetic field induced strain. This is followed by an outline of different manufacturing methods that can be used for Ni-Mn-Ga alloys and hybrid structures. As there are problems related to the
mass production of single crystal structures, multiple different manufacturing methods have been previously used for producing magnetically active Ni-Mn-Ga structures. Finally, the principles of vibration damping and damping of Ni-Mn-Ga composite structures are presented.

In the experimental section, the heat-treatment process that was developed for the gas atomized powder is presented. As the gas atomization produces particles with extremely fine grain structure, the heat-treatment process was critical for increasing the grain size and reducing constraints to twin boundary movement. Additionally, the treatment homogenized the powder and reduced stresses created during the fast cooling in the atomization process. The basis for the developed heat-treatment procedure can be found in the heat-treatment experiments that were performed in Publication II. Then the different manufacturing and testing methods for the samples in Publications I, III and IV are reviewed.

In the results & discussion section, the results from Publications I-IV are presented together with the optical magneto-mechanical device (OMMD) measurements for the porous spark plasma sintered samples and hybrid composite samples, performed in Boise State University during a research visit. First, the vibration damping results of the Ni-Mn-Ga MMC are compared to the vibration damping capabilities of the hybrid epoxy composites. Secondly, the MFIS of porous spark plasma sintered structures are compared to the hybrid epoxy composites. The measurements are also compared to values found in literature. Finally, in the conclusions section the results are summarized and a brief outlook of future work is presented.

1.1 Aim of the work

The aim of the thesis is to manufacture, in laboratory scale, and study the properties of Ni-Mn-Ga hybrid structures that could be used in actuators or vibration damping elements. Additional goal is to develop a working heat-treatment procedure for producing spherical and large grained Ni-Mn-Ga powder particles, which can be used to manufacture said hybrid composites and other structures with pronounced MFIS and vibration damping capabilities. The specific aims are presented below:

Typically, in composite design, two materials with different but complimentary properties are combined together to create a multiphase material with a better combination of material properties [25]. Previous research on Ni-Mn-Ga composites has focused mainly on different polymer composites to offset the brittle behavior of Ni-Mn-Ga found in polycrystals and to create spring-like composite structures that return the Ni-Mn-Ga to its original shape after MFIS [23, 24, 26–40]. However, as the vibration damping capability depends on multiple material properties that can bind the vibrational energy to the structure, it is reasonable to assume that with correct filling ratio of Ni-Mn-Ga a metal matrix composite could have pronounced vibration damping capabilities.

Two double dispersion Ni-Mn-Ga-Co/WC-Co metal matrix composites are manufactured using spark plasma sintering. The samples are characterized
using vibrating sample magnetometer, low-field ac susceptibility measuring system, X-ray diffraction and energy-dispersive spectroscopy. The vibration damping capabilities are studied using DMA and with cavitation erosion measurements.

Previous research has shown that powder particle morphology [30], grain boundary constraints [12], texture [13] and composition [20, 21] all affect the twin boundary movement and thus achievable MFIS and vibration damping capabilities in Ni-Mn-Ga polycrystalline powder. Currently, most of the powder manufacturing methods that are used for producing Ni-Mn-Ga powder either produce randomly shaped particles with large shape anisotropy [15, 27] or powders with compositional inhomogeneity and large particle size distribution [17, 41]. It is reasonable to assume that a well-established industrial scale process such as gas atomization could be used to produce high quality Ni-Mn-Ga powder which should be suitable for manufacturing hybrid composite structures, with comparable properties to previously manufactured structures.

Two batches of gas atomized Ni-Mn-Ga are produced, heat-treated and analyzed. The powders are characterized using vibrating sample magnetometer, low-field ac susceptibility, X-ray diffraction, compositional analysis using energy-dispersive spectroscopy and by measuring the average grain sizes. Then the as-atomized properties of the Ni-Mn-Ga powders are compared to the heat-treated powder samples and to previously produced Ni-Mn-Ga powders found in literature.

The produced gas atomized powder is used to manufacture highly porous structures and hybrid epoxy composites. The samples are characterized using vibrating sample magnetometer, low-field ac susceptibility, X-ray texture measurements and finally by optical magneto-mechanical measuring device. The results of the porous structures are compared to previously manufactured Ni-Mn-Ga foams and (textured) polycrystals. Additionally, the damping properties of hybrid epoxy composites are studied using DMA and laboratory built high frequency mechanical measuring device and the vibration damping capability of the composite is compared to previously manufactured Ni-Mn-Ga polymer composites in literature and to the Ni-Mn-Ga-Co MMC.

1.2 State of the art

Magnetic shape memory alloys are a special subdivision of shape memory alloys that can change their shape reversibly with the application of either external magnetic field or mechanical stress. In comparison to the conventional shape memory alloys, where the shape change is related to the reversible phase transformation from martensite to austenite [2], the shape change in magnetic shape memory alloys is driven by the movement of the twin boundaries in martensite [1, 42]. These twin boundaries are coherent planar interfaces between twin variants that are formed in the self-accommodation of the martensite variants during austenite to martensite transformation [2]. Although these variants can
form in different orientations to each other, they still share the same martensitic structure [2, 43].

The reason these differently orientated martensitic variant regions are formed during cooling is to compensate lattice strain during the martensitic solid-state shear transformation, which involves a small shift in the atomic positions in the crystal lattice [2, 43]. When the material is cooled over the phase transformation region, the starting point for the phase transformation is marked as $M_s$ and the finishing point $M_f$. Correspondingly, when the material is heated back up, the martensite transforms back to austenite and the starting point for this transformation is marked $A_s$ and the higher finishing point the $A_f$. [2] If heating is continued, eventually the material reaches the so-called Curie temperature where the ferromagnetic properties of the material disappear as it changes into paramagnetic state, this temperature is marked typically as $T_C$ [44].

The transformation temperatures depend largely on the chemical composition of the alloy [45], which additionally defines the crystal structure of the martensite [45–47]. However, the internal stresses and dislocations can also affect the martensitic transformation [15]. The effect of chemical composition on the phase transformation temperature has been studied by Jin et al. [45] and they found that based on the manganese and gallium content the transformation temperature for the martensitic transformation can be defined, empirically, with the Formula 1 where Mn and Ga are the atomic concentration of the alloy in atomic percentages [45].

$$\frac{T_{Mart}}{K} = 1960 - 2110 \cdot Mn - 4920 \cdot Ga \quad (1)$$

The formula works when the atomic percentage of manganese is within the range from 20-35 at.% and that of gallium is 18-27 at.% [45]. The composition, mainly manganese content, also determines the type of martensite that is formed during transformation. The transformed martensite referred to as NM (non-modulated), 5M and 7M, has been named based on the different long period stacking order of martensite found in the martensitic structure, with the number denoting the shuffled layers and the letter M denoting monoclinic crystal structure in Ramsdel notation [48]. The modulation in the 5M and 7M martensite comes from the \{110\} basal planes of the unit cell that are periodically shuffled along the [1\ 1\ 0] direction as seen in Figure 1 [49].
In the 5M martensite, the tetragonal layered structure is 5 atomic planes long, however this has to be doubled due to the L2₁ ordering, and thus consists of two subcells and is called either 5M or 10M [47, 49–52]. The 7-layered martensite, with an orthorhombic structure, has a length of 14 atomic planes and thus two subcells and is called 7M or 14M [47, 49, 51, 53]. The non-modulated martensite has a layered structure that is two atomic planes long and is called non-modulated or NM [51]. However, the basic structure is more widely used, along with the cubic phase coordinates, than the larger modulated unit cell. The basic crystal lattice constants which are used in this work are, for the 5M martensite \( a = b = 5.0 \text{ Å} \) and \( c = 5.44 \text{ Å} \), while for the 7M orthorhombic martensite \( a = 6.14 \text{ Å} \), \( b = 5.78 \text{ Å} \) and \( c = 5.51 \text{ Å} \) and for the tetragonal non-modulated martensite \( a = b = 5.62 \text{ Å} \) and \( c = 6.44 \text{ Å} \) [49, 51]. The crystal structure of the martensite is important as it defines the behavior of the alloy from mechanical properties to phase transformation temperatures and the Curie point [50, 54–57].

The different martensitic structures and their properties such as phase transformation temperatures, have been systematically characterized as a function of the average number of valence electrons per atom [45–47], i.e., the so-called \( e/a \) ratio. Chernenko et al. [46] calculated this \( e/a \) ratio for each component of the Ni-Mn-Ga alloy using the Formula 2.

\[
\frac{e}{a} = \frac{10 \times (\text{Ni}) + 7 \times (\text{Mn}) + 3 \times (\text{Ga})}{(\text{Ni} + \text{Mn} + \text{Ga})}
\]  

(2)

The values for different elements are based on the number of electrons in the outer electron band 3d⁸4s² the value is 10, while for manganese it is seven as it has 3d⁵4s² and three for gallium as it has 4s²4p³. Figure 2 [58] shows the general compositional range and the \( e/a \) ratio for different martensitic structures and phase transformation temperatures for Ni at 50 at.%. For practical use the austenitic and martensitic phase transformation temperatures can be presented as average phase transformation temperatures \( T_A, T_M \) and \( T_C \) [2, 44, 57, 58]. These average transformation temperatures can be calculated using the
following Formula 3, where $T_S$ is the starting temperature and $T_F$ is the finishing temperature of phase transformation. By using $M_s$ and $M_f$ in the formula average phase transformation temperature for the martensitic transformation $T_M$ can be obtained. Similarly, using the $A_s$ and $A_f$ temperatures in the formula gives the average phase transformation temperature for the austenitic transformation $T_A$ [2, 44, 57, 58].

$$T_A \text{or } T_M = \frac{T_S + T_F}{2}$$

(3)

It is important to note that in Figure 2, the 5M martensite has a low phase transformation temperature and a large austenitic range below the Curie point, while in the 7M and NM the phase transformation temperature is close to or even higher than the Curie point [58]. This is important, as for application design it would be ideal to have a large martensitic region, with high phase transformation temperature and Curie point, since this would guarantee the largest working temperature region for the MSM application without the need to add cooling systems that would increase the weight, size and cost of the application.

![Figure 2](image)

*Figure 2. Composition dependence of martensite transformation temperatures and Curie temperature in 5M, 7M and NM structures, reproduced with permission from [58].*

The maximum extent of deformation achievable by the twin boundary motion in single crystal depends on the ratio of the lattice constants. The highest obtainable strain in single crystal can thus be estimated using a formula $\varepsilon = (1 - \frac{c}{a})$ [20, 21]. For 5M Ni-Mn-Ga the strain is about 6% [59], for 7M about 10-11% [20, 21] and for NM about 20% [60]. In practice some parts of the material are not able to contract or elongate, for example, due to external constrains like
sample attachment. Thus, the measured maximum strains are usually lower. The movement of twin boundaries can be achieved due to the high magneto-crystalline anisotropy and low twinning stress of the material e.g. stress required for twin boundary movement [9]. When the material is placed in a magnetic field, the magnetic anisotropy creates a magnetic stress $\sigma_{mag}$ [61, 62]. The magnitude of this stress increases with the field until it reaches maximum at the magnetic saturation point. This maximum value depends again on crystal structure and can be calculated using the formula $\sigma_{mag} = (1 - C/a)^{-1} K_{u}$, where $K_{u}$ is the magneto-crystalline anisotropy of the material [61, 62]. According to the magneto-mechanical model presented first by Likhachev [61, 62], the magnetic shape memory alloy can reorient by magnetically induced twin boundary motion only if the magnetic stress exceeds the twinning stress $\sigma_{tw}$. As the maximum magnetic stress depends on the magnetic anisotropy $K_{u}$ but cannot exceed the field induced strain $\epsilon_{0}$, we can formulate these requirements together into Formula 4 to get a model for the magneto-mechanical stress required for twin re-orientation [61, 62].

$$\sigma_{mag} = \frac{K_{u}}{\epsilon_{0}} > \sigma_{tw} \quad (4)$$

The twinning stress can be understood as the sum of internal stresses at zero applied field, which needs to be overcome for twin boundary movement [56]. The field induced strain $\epsilon_{0}$ can be evaluated experimentally from the stress-strain curve as the maximum strain of the twinning. The measured twinning, magnetic anisotropy and the induced strain for different martensitic structures are shown on the Table 1 [54, 63]. However, in practice, as the twinning stress is a defect-controlled property its magnitude depends on the obstacles the twin boundaries have to overcome such as defects and grain boundaries. Thus the observed twinning stress can exceed the theoretical calculated stress by several orders of magnitude [64].

<table>
<thead>
<tr>
<th>Alloy [at.%]</th>
<th>Crystal Structure</th>
<th>$K_{u}$ [10^5 J/m^3]</th>
<th>$\epsilon_{0}$ [%]</th>
<th>$\sigma_{mag}$ [MPa]</th>
<th>$\sigma_{tw}$ [MPa]</th>
<th>MFIS [%]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni50.7Mn28.4Ga20.9</td>
<td>5M</td>
<td>1.67</td>
<td>6.2</td>
<td>2.8</td>
<td>0.5-4</td>
<td>&gt;6</td>
<td>[54,63]</td>
</tr>
<tr>
<td>Ni50.5Mn29.4Ga20.1</td>
<td>7M</td>
<td>1.74</td>
<td>10.7</td>
<td>1.6</td>
<td>3-5</td>
<td>0.47</td>
<td>[54]</td>
</tr>
<tr>
<td>Ni50.5Mn30.4Ga19.1</td>
<td>NM</td>
<td>1.44</td>
<td>21.0</td>
<td>0.7</td>
<td>17-25</td>
<td>none</td>
<td>[54]</td>
</tr>
</tbody>
</table>

Temperature measurements carried out by Okamoto et al. [42, 65] and Glavatska et al. [66] have shown that the magnetic anisotropy constant increases in all martensitic structures with decreasing temperature, while the magnetic field required for twin movement and the MFIS increase. The increasing requirement for the higher magnetic field can be understood as increasing twinning stress due to decreasing temperature, which explains the lower temperature limit for the magnetic shape memory effect that is -108.15 °C [67].
1.3 Manufacturing methods for Ni-Mn-Ga alloys

Ni-Mn-Ga alloys can be manufactured in multiple different forms from single crystals [68], to melt-spun ribbons [26], to polycrystalline structures [69], to textured foams [12], to milled [29] or spark eroded powders [27] and gas atomized powders [Publication II]. The reason for interest in different manufacturing methods is twofold. Firstly, the highest MFIS has been found only in the single crystal structures, since in a small grained polycrystalline structure the grain boundaries constrain the twin movement by creating incompatible stresses between the deforming grains [13]. Thus in a randomly oriented fine-grained polycrystalline structure, the constraints lead to a near zero $\Sigma$MFIS. Secondly, the polycrystalline modulated martensitic structures are brittle and as the properties are dependent on the chemical composition [46, 70] even slight compositional inhomogeneity, as seen in Figure 2, can lead to formation of different crystal structure in the specimen [58].

The most typical way for manufacturing the single crystal is to use the Bridgman method, which is one of the oldest techniques used in crystal growth. In the process, a polycrystalline ingot is heated above its melting point and then transferred along its axis over a temperature gradient (Fig. 3). As the temperature lowers below the melting point, the crystal starts growing along the orientation of the seed crystal in the melt-seed interphase. [71]. The obtained single crystal ingot needs to be heat-treated for homogenizing and ordering of the structure. During the homogenization treatment, the chemical structure is made uniform by getting rid of concentrated alloying element irregularities that can form during crystallization through diffusion processes. During the following ordering treatment, the partly ordered B2’ structure, where Ni atoms are ordered and Mn and Ga atoms are randomly distributed on corresponding sublattice, transforms to fully ordered L21 structure, where the manganese atoms occupy the 4a positions, gallium atoms the 4b positions and nickel the 8c positions in the Fm3m space group structure [72, 73]. These heat-treatments can take considerable time as they are done at a lower temperature and need to be done in a protective gas atmosphere to minimize manganese evaporation and oxidation [14]. Finally, the crystals orientation needs to be measured using X-ray diffraction and then cut, while minimizing the wasted material [14]. Thus, the crystal growth process is difficult to automate and scale up commercially.
As such, the difference between the different manufacturing methods can be understood as the differences in the grain size and crystal orientation. The effect of the orientation and grain boundaries on MFIS are significant when the MFIS achieved with single crystal [74], melt-spun ribbon [26] and polycrystalline particles [27] are compared. The single crystal has only one crystal orientation and no grain boundaries. Thus, when sample is rotated in a magnetic field the whole sample changes shape as the twin structure reorients resulting in highest MFIS. Whereas, the melt-spun ribbon has a bamboo microstructure, which can be visualized as a string consisting of multiple single crystals [75, 76]. The bamboo-like structure in the wires means that the grain size of each grain in the wire is similar to the wire diameter. As this leads to large grain size in the wires, they are typically referred to as oligocrystalline wires with bamboo-like structure [77]. In each bamboo, the grain texture forms along the melt-spinning direction [78], so the orientation of the crystal structure is not random. Thus, when the oligocrystalline Ni-Mn-Ga wires are rotated in the field a MFIS of up to 1% [76] has been achieved, which is comparable to the highest MFIS of 1% [64, 79] achieved in polycrystalline Ni-Mn-Ga with strong texturing.

Even though these MFIS are lower than the 10% [21] measured in Ni-Mn-Ga single crystals, the MFIS of 8.7% [12] found in Ni-Mn-Ga foams, which has oligocrystalline bamboo-like struts, shows that it is possible to achieve higher MFIS with oligocrystalline wires than with even heavily textured polycrystalline structures. Lastly, in the polycrystalline particles, even though grain size can be increased with a heat-treatment, each grain has a different crystal orientation. Consequently, when the sample is oriented, for example during composite manufacturing, using a magnetic field, the particles orient according to the easy axis of magnetization of the largest grain in the particle [19, 27]. Thus, each grain likely has a different orientation and when the sample is rotated in a magnetic field. The achieved MFIS, which is the sum of all the magnetic-field-induced strains (ΣMFIS) of the differently oriented grains, is usually very small, as each grain strains at different direction.
Research attempts have been made to overcome these problems in polycrystalline structures by introducing porosity [12] and texture [12, 13]. The idea behind this approach is that compared to normal polycrystalline structures, the grains forming the porous struts are free to deform due to twinning as the empty space surrounding them does not constrain movement. As such, the porous foams act more like a three-dimensional structure of individual single crystals that are connected to other single crystal through rigid nodes. Thus, the resulting 2MFIS can be as high as in single crystal [12]. However, if the grains of the porous foam are not highly textured, the resulting MFIS is still smaller than real single crystals as the grains deform in different directions. Texture can be introduced for example by using directional solidification and can double the MFIS in porous foams [13]. However, even though these methods produce polycrystalline structures with increased MFIS the problem is still that the manufacturing method is not easy to scale up and requires a lot of specialized equipment.

Similar approach of minimizing grain boundaries is used in the preparation of Ni-Mn-Ga powder, as the particles are prepared by either mechanically crushing [18, 19, 24, 27–31], cutting [32] or by spark eroding [27, 80] single- or polycrystalline Ni-Mn-Ga or as in Publications II to IV with gas atomization. During mechanical milling, the intense mechanical deformation experienced by the milled particles can lead to accidental mechanical alloying and to the generation of crystal defects [15] and the resulting powder particles are randomly shaped. Whereas with spark erosion, the resulting particle size distribution is typically large and bimodal [17], consisting of particles with average diameter between one and tens of μm and from nanoparticles ranging from 1 to 20 nm [41]. The smaller particles also tend to react with the dielectric used in the process and thus require further treatments such as annealing [17, 41]. Additionally, likely due to the fast quenching rate of the molten droplets during the process, the resulting powder particles have inhomogeneous chemical composition, nonuniform lattice strains and are comprised of a mixture of disordered and ordered cubic phases [81].

Gas atomization is a high-volume manufacturing method for metallic powders. Compared to other powder producing methods gas atomized powder particles are round, have smooth surface and a narrow particle size distribution, which can be controlled by adjusting the atomization gas pressure [82]. In the gas atomization process the induction-melted alloy is sprayed through a narrow nozzle after which the melt is atomized into droplets using an inert gas, typically Argon [82]. Compared to other powder manufacturing methods [29, 81], gas atomization is already a well-established industrial process and the compositional homogeneity of the manufactured powder is high [82]. As the cooling in the process is severe, the resulting powder particles have an extremely fine grain structure [82]. This means that the powder needs to be heat-treated before working Ni-Mn-Ga structures can be produced [Publication II]. A similar effect has been observed with fast cooling spark eroded particles [81]. The heat-treated powder can then be used to manufacture structures either by powder metallurgical methods, such as spark plasma sintering (SPS) to create porous structures [Publication III], or by mixing it with polymer to create a composite
Spark plasma sintering is an electric current assisted sintering method where the heating and consolidation of the powder mixture occurs due to the Joule effect and pressure [83, 84]. A schematic of spark plasma sintering can be seen in Figure 4 [83, 84].

![Schematic representation of spark plasma sintering process](image)

**Figure 4.** Schematic representation of spark plasma sintering process [83, 84].

In the SPS process, the heating power is dissipated evenly through the contact points of the particles and the process has three distinct parts [83, 84]. In the first part, the powder is activated by the pulsed current - this refers to the elimination of adsorptive gas and surface impurities in the powder due to intense Joule heating [83, 85]. In the second part, a bridge is formed between the particles either through vapor transport or surface diffusion [83, 84]. Finally, the particles start to sinter together by lattice and grain boundary diffusion as the material seeks to minimize the grain boundary energy by decreasing the surface area [83, 85]. The external pressure in the process increases the densification by reducing the distance between the contact points of the particles, however sintering would happen even without the pressure [83, 84]. It is important to note that, if the sintered powders have a variable or inadequate electrical conductivity, then the Joule heating can lead to nonhomogeneous temperature gradient inside the powder compact. Thus, it is crucial to know the powder's electrical and thermal conductivity, particle size and the die wall thickness [83]. As the sintering process is fast and can be done in either vacuum or in a protective atmosphere it is suitable for Ni-Mn-Ga alloys as there is no risk for manganese evaporation or oxidation. Additionally, even though SPS usually leads to compacts with extremely low porosity [84], it is possible to manufacture highly porous foam structures using spaceholder material as in Publication III.
1.4 Composite manufacturing

In composites design, two materials with different but complimentary properties are combined into one system to create an artificially made multiphase material that is formed so that a better combination of the two individual materials' properties are realized [25]. As the combined materials typically have properties that can be regarded as contrary e.g. hardness and ductility, the materials are usually chemically dissimilar and have clear interfaces [25]. Compared to Ni-Mn-Ga single crystals, polycrystalline structures have smaller strains and behave more brittle [86]. While, in single crystals their intrinsic brittle behavior of the Heusler L2₁ type intermetallic compound at high temperatures is a problem in practical applications [39]. However, these intrinsic disadvantages of Ni-Mn-Ga alloys can be partly overcome by creating a composite structure, i.e. combining the Ni-Mn-Ga either with a suitable polymer [Publication IV] or with a Cermet such as WC-Co [Publication I].

1.4.1 Metal matrix composites

Metal matrix composites (MMCs) are a combination of metal and other, often a ceramic, material such as Al-Al₂O₃ composites. Also low metal content composites can be regarded as MMCs if the metal is as a matrix in the composite, such as in the well-known Cermets consisting of WC and Co as a matrix. Metal matrix composites can be divided into groups either according to their base metal reinforcement phase e.g. particles or fibers, or by the manufacturing process such as stir casting [87], infiltration [88], powder metallurgy [Publication I] etc. A wide variety of metal matrix composites can be manufactured [89]. The interest in MMCs is due to two different reasons. Firstly, the composite approach makes it possible to overcome previous limitations in material design of the main materials [25, 89]. For example, the performance of engineering materials can be modeled in uniaxial stress by using their value of elastic modulus divided by their density. A mapping of the elastic modulus and density of metal alloys and technical ceramics can be seen in Figure 5. For most engineering materials, the elastic modulus divided by density is close to 26 MJ/kg and the only way to increase it is by manufacturing a composite where the metallic material is replaced with ceramics such as Al₂O₃ or SiC [90]. Secondly, the composite approach makes it possible to utilize ceramics in forms that would otherwise be difficult to handle such as in fibers and particles, as many ceramics have far better properties in particle form than as large bulk materials [89].
The properties of MMC depend also on the reinforcement type and the interphase between the metal and the reinforcement particulates. When stiff ceramic particles are added to the metal matrix, the flow stress increases due to the more difficult load transfer across the interphase between the matrix and the reinforcement. Depending on the interphase, this can lead to formation of stress concentrations and damage due to decohesion and fracture. The critical failures depend on the reinforcement particle size, volume fraction of the reinforcement and the properties of the matrix [92, 93]. Some models [94] have been developed so that the formation of these stress could be predicted.

Not much work has been done to study Ni-Mn-Ga metal matrix composite structures. However, some theoretical model studies have been done with Ni-Ti particle alloyed aluminum [95]. Based on the model developed, by applying Eshelby’s equivalent inclusion method [96], it was found that by increasing the volume fraction of the shape memory particles, the Young’s modulus, yield stress and work hardening of the aluminum increased [95]. It was claimed, that these increases were related to the residual stress caused by the addition of the shape memory fillers into the matrix [95]. When the MMC is manufactured from powder using spark plasma sintering, as in Publication I, the manufacturing process is quick. Double dispersion composites [97] are obtained when the Ni-Mn-Ga matrix is reinforced by large hard metal particles consisting of small WC particles in Co matrix. In Publication I, the WC-Co is added to the Ni-Mn-Ga powder using mechanical milling, where kinetic energy for the milling process is utilized in the alloying of the WC-Co with Ni-Mn-Ga [98]. Double dispersion composites are of interest due to their high hardness and good wear properties. As the Ni-Mn-Ga material could be used as a vibration dampener, the increased wear resistance and hardness achieved from the WC-Co particulates in the double dispersion MMC structure were of interest and the compacts did exhibit increased damping and wear properties.
1.4.2 Polymer composites

To overcome the brittleness \(^{[39, 86]}\) of the Ni-Mn-Ga alloy, different composite structures have been previously manufactured using polymers, such as silicones \(^{[24, 33]}\), epoxies \(^{[24, 34]}\) and polyurethanes \(^{[35, 36]}\), as they can increase the ductility and also act as a spring to return the MFIS. The polymer used as a matrix needs to be chosen so that it is suitable for Ni-Mn-Ga alloys \(^{[24]}\) as the stress that is applied to the composite needs to be able to transmit into the Ni-Mn-Ga to overcome the twinning stress. A too stiff matrix will exceed the MSM alloys blocking stress, which renders the composite ineffective, while a too soft matrix accommodates the particle’s strain locally thus displaying no or minimal macroscopic strain \(^{[33]}\). Thus, for 5M Ni-Mn-Ga polymer composites the yield strength of the polymer should be between 0.5 to 4 MPa \(^{[54, 63]}\), while for NM composite the range is higher from 17 to 25 MPa \(^{[54]}\). Some polymers that have yield strength in the range of 0.5 to 4 MPa and Young’s moduli in the range of 1 to 1000 MPa are shown in Figure 6 \(^{[91]}\). Not all of the polymers in the figure are suitable for matrix materials, however as mentioned before many silicones, epoxies and polyurethanes have been widely tested \(^{[24, 33–36]}\). The shrinkage of the polymer during curing should be minimal \(^{[24]}\) as otherwise, the polymer can create compressive stress onto the powder particles.

![Material map showing potential matrix polymer materials suitable for Ni-Mn-Ga composites](image)

Secondly, when choosing the polymer, the contact strength between it and Ni-Mn-Ga should be studied. If the matrix does not stick to the particles, then the stress transfer will be inadequate. So far the contact between Ni-Mn-Ga and different matrix materials has not been studied that much \(^{[24, 37]}\), except for silicones \(^{[37]}\) and for few epoxies \(^{[24]}\). The final characteristic is the polymer’s suitability for composite manufacturing. This means that the working and curing time need to be adequately long so that the four manufacturing steps - mixing, degassing, casting of composite mixture and magnetic orientation of the particles - could be achieved. However, if the curing and working time are too long then the heavier Ni-Mn-Ga particles can settle to the bottom of the casting mold.
A potential polymer should fulfill all of these requirements if it were to be used as a matrix for Ni-Mn-Ga. Additionally, it should be readily available and relatively inexpensive.

Compared to other manufacturing processes used with Ni-Mn-Ga alloys, polymer composites are likely the easiest to manufacture once a suitable polymer is found. Typically, the prepared powder is just mixed into the polymer [27–30, 38], which is then degassed and cast to a mold. Degassing is an important step of the process, as gas bubbles in the matrix affect the mechanical properties and the stress transfer of the finished composites. Finally, particles are either oriented with a magnetic field or cured without orienting particles. Depending on the chosen polymer, curing e.g. cross-linking of the polymer chains, which leads to the hardening of the polymer material, happens either in room temperature or in an oven. For example, epoxies Hysol 9455 and 9492 cure fully in room temperature in 6 and 72 hours respectively [24]. If a heat-cured polymer is used it must be taken into account that when the composite is heated between 40°C and 80°C, the Ni-Mn-Ga powder becomes austenitic [99]. Thus, if particle orientation is done during the curing process [24, 33–36], the particles will still align into chains but once cooled down to martensite the crystallographic orientation of the particles will become random and thus the composite will not have texture [99].

1.5 Damping and Ni-Mn-Ga composite structures

Two different categories of damping are found in materials namely, static and dynamic hysteresis. The separation between these types can be done based on the loss mechanism and the frequency dependence [100]. The two main sources for static hysteresis are plastic deformation and magnetoelasticity, which have no frequency dependence [99]. In plastic deformation the damping is caused by dissipation due to nucleation and movement of dislocations. Thus, dissipation requires that the stress generated by vibration is higher than the yield stress and as expected the loss decreases with cycles until failure happens. In magnetoelasticity, the dissipation happens due to magnetic hysteresis as the stress generated by the vibration moves domain walls [99] and it is only found in magnetic materials. Compared to static hysteresis, the dynamic hysteresis has a strong time dependence and usually a temperature dependence as well. A good example of time dependent dissipation can be seen in viscoelastic materials, where the damping is due to the relaxation of polymer chains as they are stressed [99].

The Ni-Mn-Ga alloys ability to dissipate energy, and thus the high damping capacity, is based on the presence and the hysteretic mobility of the interphase and the intervariant planar interphases [28]. However, a more detailed research on the SMAs has shown that the whole defect structure, such as the internal defects of the martensitic variants, needs to be considered as they all contribute with different extent to the damping behavior [64, 101]. Thus, by adjusting the structure of the Ni-Mn-Ga alloy [28], the damping capacity can be optimized for different applications and requirements. The effect of the whole structure can
be evaluated using the twinning stress [102], as it is affected by the internal defect and the martensitic structure, and additionally gives the stress required, e.g. during vibration, for the twin boundary movement when the applied magnetic field is zero [61]. Thus, it is possible to evaluate the twinning stress indirectly by studying the vibration damping capabilities of the Ni-Mn-Ga alloy and composite structures.

The most typical way of studying the vibration damping is to use a dynamic modulus analyzer, where sample is stressed either with a set frequency or over a specific frequency range [103]. This gives us information on the materials response time e.g. phase lag (δ) to the stress, in addition we can measure the storage (E') and the loss modulus (E'') [103]. These three properties can be calculated from the materials response to the dynamic stress. Storage modulus gives us information on the materials ability to store the vibration energy for example by deforming, while loss gives us a value on the amount of energy that can be dissipated. The phase lag can be calculated as the the ratio of loss and storage modulus and is called tan δ. Together (Fig. 7) these can be combined into complex modulus (E*), which is comparable to, but not the same as, Young’s modulus from the classic stress-strain curve [103].

![Figure 7. Relation of storage modulus (E'), loss modulus (E''), complex modulus (E*) and tan δ](image)

As is with the magnetic shape memory effect, the vibration stress needs to overcome the twinning stress so that the vibration damping can occur with the twin boundary moment. Since stress is related to the strain by Hooke’s law, the vibration stress also creates a vibration strain. Thus, the effective damping amplitude is limited by the maximum achievable lattice deformation based on martensitic type, ε0, combined together with the 4% [104] from the martensite phase boundary damping effect. The damping properties of single crystals have been studied widely and can be relatively high even having the loss coefficient tan delta as high as 0.35 [4]. However, in addition to twin boundary motion damping in Ni-Mn-Ga composite structures can happen due to interfacial friction between the matrix material and the particles [19, 29]. A similar effect has been seen in carbon nanotube reinforced composites [105].
The shape of the Ni-Mn-Ga particles also affects the damping properties in composite structures. Spherical particles generally show larger damping than irregular particles, since they do not have a shape component in the magnetic anisotropy and minimize the pinning during twin movement [27]. Spherical particles are also easier to orient with magnetic field during the composite manufacturing process [27]. The effect of particle size, distribution and orientation on the damping properties, though lesser than the effect of particle shape, are also important [19, 27, 30]. Larger particles are more effective at dissipating energy due to larger volume-to-surface ratio, but with a wider particle size distribution the packing density along oriented particle chains improves as smaller particles fill the gaps between the larger particles. This improves the stress transfer along the particle chain. However, the larger particle size distribution also increase the volume of inactive smaller particles [27]. Additionally, when the volume fraction of Ni-Mn-Ga particles is increased in composite structures the damping properties of the composite increase, while with a low filling ratio the effect of the Ni-Mn-Ga particles disappears [27, 30]. However when the filling ratio increases over 40% in the composite, the yield strain of the composite starts to decrease and the composites start to exhibit brittle fracture behavior [29, 30]. Lastly, the effect the particle orientation in the composites is a complex one, since in composite with disordered Ni-Mn-Ga particles there are more particle-matrix interfaces, which dissipates the vibration energy due to interfacial friction [19]. In ordered composites, where particles are in chains, the ratio of particle-matrix interfaces is smaller but the chains transfer the applied stress better and can exhibit higher MFIS [19, 27].

In addition to the composite structure and defects, the frequency of vibration at applied magnetic field also affects the damping properties. At low frequencies, damping is mainly due to the hysteretic twin boundary movement, which dissipates the energy and converts it to heat. When the frequency is increased to hundreds of Hz, then eventually eddy currents can start appearing in the magnetic field [106]. These eddy currents can generate an internal magnetic field, which can partially offset the external magnetic field. If a dynamic magnetic field is used for the actuation, the eddy currents can enhance the damping as can be seen in Figure 8. The diffusion of applied magnetic field and external field increases the phase lag, which increases the damping capability while decreasing the amplitude.
The damping properties of the Ni-Mn-Ga also depend on the temperature, with a peak in the damping capability at the martensitic and austenitic transformation temperatures [24, 26, 28]. This reflects the effect that the change in temperature has on the mobility of the twin boundaries [107], respectively. When the alloys are heated up the damping effect increases up to the phase transformation temperature [24, 26, 28]. When the dominating damping mechanism is energy dissipation by moving twin boundaries in the 5M martensite, it can be seen that the tan δ is dependent on the strain in experiments performed at room temperature [4, 40]. Zheng et al. [108] have studied the effect of the martensitic crystal orientation on damping and have found that the highest damping coefficient can be observed between the a-c crystal configurations.

When damping properties of the composite are studied, it is important to remember that the polymers used as the matrix material also contribute to the damping, as their properties are typically time, deformation rate and temperature dependent. For example, while the twinning boundary movement is fast, as Ni-Mn-Ga single crystals can be mechanically cycled between 90-150 Hz [109], the behavior of the polymer matrix sets limits to the cycling in composites. Research with Ni-Mn-Ga polymer composites [19, 24, 26–28, 31] has shown that when temperature is increased during the DMA experiments, close to phase transformation temperature of the MSM alloy and glass transition temperature of the polymer, the composite exhibits increased damping properties as both effects increase the damping capability of the composite structure synergistically. When the combined effect of temperature and frequency were studied in MSM composites, it has been shown that decreasing temperature has a similar effect on the damping properties as increasing frequency, since below the glass transition temperature the loss modulus of the matrix starts decreasing [28]. Compared to other materials, the damping in polymers is strongly dependent on temperature and frequency [110, 111] and the vibrational energy is absorbed in the polymer in the form of heat [111].
polymer is studied in relation to temperature, three distinct regions can be observed. The first low temperature region is the hard glassy region with typically high modulus compared to the following regions [110]. When temperature reaches the glass transition temperature (T_g), the polymer softens by a factor of a thousand as it transitions from glassy to rubbery state [110, 111]. This transition is accompanied by a maximum value in the damping curve [110, 111]. In the temperature region above the glass transition point, if the polymer is crosslinked, it behaves like a rubber band [111]. The third and final region is the flow region, where the amorphous or semi-crystalline rubbery polymer transforms into freely flowing melted polymer [110]. The damping in viscoelastic polymers is also dependent on frequency [110, 111] and with constant load the deformation increases with time. Thus, it is important to keep the measuring times fast and give the polymer time to recover between measurements. Frequency dependency also means that at higher frequencies the transition temperature, T_g, starts shifting to a higher temperature which in turn affects the modulus [110]. Thus, correlation of the mechanical properties of polymers in a broad frequency range is not without problems since the maximum peak of the modulus increases and becomes broader with increasing temperature, as the polymer starts heating up at an average rate of 6-7ºC/10 Hz [110, 111]. However, the exact heating rate varies from polymer to polymer depending, for example, on molecular weight and the amount of crosslinking [110, 111].
2. Experimental

The three different types of Ni-Mn-Ga hybrid composites prepared and studied in this thesis are: (1) double dispersion Ni-Mn-Ga-Co/WC-Co metal matrix composites [Publication I], (2) porous spark plasma sintered Ni-Mn-Ga structures with interconnected porosity that could be filled with suitable polymer and act as active scaffolding [Publication III] and (3) Ni-Mn-Ga powder epoxy hybrid composites [Publication IV]. In Publication I, milled single crystal MSMA powder was prepared and used to enhance the damping properties of a MSM/metal ceramic composite. Recycled WC-Co was used to prepare the MSMA matrix composites by mechanical alloying, to obtain double dispersion composites having first dispersion of WC particles in the cobalt matrix of the WC-Co particles and then another dispersion of the WC-Co particles in the Ni-Mn-Ga matrix. The goal was to see if combining WC-Co, with high hardness and good wear resistance, with Ni-Mn-Ga, which can dampen vibrations by binding the energy to the movement of twin boundaries, would lead to a material with enhanced damping capabilities.

As Feuchtwanger et al. [27] have shown, mechanically milled Ni-Mn-Ga powder is not optimal for the polymer matrix composites. This is because, the irregularly shaped powder particles have more pinning sites that hinder twin boundary motion and do not orient as well with applied magnetic field as spherical particles, due to shape component of magnetic anisotropy. Therefore, polycrystalline Ni-Mn-Ga powder with 5M structure was manufactured by gas atomization of melt [Publication II]. The 5M powder was used for the spark plasma sintered porous structures [Publication III] and for the epoxy hybrid composites [Publication IV] as previous research has shown that Ni-Mn-Ga with 5M structure is the best candidate for magnetic-field-induced strain (MFIS) applications [57]. Gas atomization has the added advantage of being an industrially viable method to produce spherical powders with narrow but controllable particle size distribution in large quantities [82]. It would be a breakthrough if these kinds of Ni-Mn-Ga powder could be utilized in active damping solutions. The Hysol 9455 epoxy, used in the hybrid composites, was chosen based on its mechanical properties that matched the 5M structure and due to suitable short pot life that minimized gravitational settling of the powder to the bottom of the mold. The MFIS achieved with the porous spark plasma sintered samples [Publication III] were studied and compared to literature values of similar foam and polycrystalline structures [12, 13]. To compare the suitability of the polycrystalline powder for hybrid composite manufacturing [Publication IV], the damping properties
were compared to those of: (a) Ni-Mn-Ga-Co/WC-Co MMC [Publication I], (b) reference samples manufactured from regular Hysol 9455 epoxy and (c) hybrid composite containing Hysol 9455 epoxy and Ralloy® WR4 steel powder. Pure Hysol 9455 was used as reference to evaluate the effect that Ni-Mn-Ga had on the matrix, while the steel hybrid composite was used to evaluate how the effect of the Ni-Mn-Ga hybrid composite differed from the ferromagnetic attraction in steel composite. Lastly, the achieved change in strain due to applied magnetic field is studied by comparing the hybrid composite to a 5M single crystal.

2.1 Gas atomization, powder heat-treatment process and characterization

The gas atomized Ni-Mn-Ga powder was produced by VTT (Technical Research Centre of Finland) using Hermica gas atomization equipment [Publication II]. The powder was produced during multiple batches marked ATO1, ATO2 and ATO3 respectively [Publications II-IV]. The first batch, ATO1, was atomized at a temperature of 1080°C using chamber pressure of 0.3 bars and atomization pressure of 40 bars, while for ATO2 and ATO3, the atomization was done at 1308°C with 0.25 bars chamber pressure and with atomization pressure of 50 bars. The atomization nozzle size was 1.5 mm and the gas was argon. Before heat-treatments, powders were sieved mechanically, in the case of ATO1 below 150 \( \mu \)m, in the case of ATO2 below 75 \( \mu \)m and for ATO3 between 20 \( \mu \)m and 45 \( \mu \)m [Publications II-IV].

The heat-treatment had three goals [112]. First goal was to grow the grain size of the powder as large as possible, until powder particles would have optimally 1-3 grains, to minimize the grain boundary constraints [12] for the twin boundary movement. Second goal was to homogenize the powder composition and to remove residual internal strains created by the fast cooling [81] of the melted alloy during the gas atomization [82]. Lastly, the heat-treatment needed to be performed in a way that would not lead to the sintering of the powder particles [112–116, Publication IV] during the heat-treatment. To achieve these goals, it was concluded that a non-reactive separator material would be needed during the heat-treatment and that the heat-treatment should be done under a controlled atmosphere. Additionally, the batch size of each heat-treatment needed to be large enough to minimize possible differences created by the heat-treatment process. Thus, a large fluidized bed oven was used as the argon could be supplied easily through the bottom of the chamber. Multiple separation materials were tested for the heat-treatment including SiO\(_2\), Al\(_2\)O\(_3\) and NaCl [112, 113]. Finally NaCl was selected as it resulted in minimal changes in the chemical composition of the Ni-Mn-Ga powder and kept the powder particles separate so that no sintering could happen [112, 114–116, Publications III, IV]. The used Ensure® sodium chloride had a mean particle size of 330 \( \mu \)m [Publication III].

When using NaCl, the annealing temperature must be kept below its melting point (800.7 °C [117] for the NaCl) [113–116, Publications III, IV]. Before mixing NaCl with the gas atomized Ni-Mn-Ga powder it was dried in furnace (Nabertherm Muffle furnace, model L5/12/C6) by annealing it at 100°C for 2 hours on
a wide plate to maximize evaporation [Publication III-IV]. After NaCl was dry it was mixed with MSMA powder in the ratio of 90 vol-% NaCl/10 vol-% Ni-Mn-Ga powder, in a Willy Bachofen Turbula shaker-mixer at room temperature for 2 hours and kept overnight in Argon atmosphere [114, 115]. The powder mixture was then placed in an alumina crucible, then a 3 cm thick layer of sodium chloride was poured on top of the mixture and finally titanium and manganese flakes were placed on top of the NaCl layer [112, Publication IV]. The titanium acted as an extra oxygen getter during the annealing to stop the MSMA powder from oxidizing and the manganese flakes were added to create a manganese rich atmosphere in the oven to hinder manganese evaporation. The crucible was then placed inside the fluidized bed furnace, which was filled with argon and left to stabilize for an hour before the furnace was heated to 770°C and kept for 28 hours [112].

Once the crucible had cooled down, the NaCl was removed with water immersion [114–116, Publications III, IV]. Then the powder surface was cleaned in a 10 wt-% citric acid solution cooled down to 0°C by mixing the powder in the acid for 15 minutes [116]. The acid cleaning was done to remove the brownish manganese rich layer covering the powder, owing to the manganese rich oven environment, as the extra manganese layer would likely lower adhesion of the powder to the epoxy or delaminate during straining [116]. To reduce the twinning stress of particles inside the powder, it was trained magneto-mechanically after the annealing and cleaning step. Training was performed by packing 5 grams of the powder tightly into small nitrile bags, the bags were then placed into 1 T applied magnetic field to orient the particles along the field [114–116, Publications IV]. After orienting the particles in the magnetic field, the bags were placed carefully inside a compression jig of the Lloyd tensile tester and compressed perpendicularly to the previously applied field with 10 MPa. This cycle of magnetic orientation and compression was then repeated three times [114–116, Publications IV].

The phase composition and crystal structure of the gas atomized powder was measured with PANalytical X’Pert Pro XRD using Cu-Kα. For the elemental composition, a small amount of powder from each batch was cast into Epofix epoxy inside a conducting copper ring. Samples were then ground until the powder cross-section, and the conducting edge of the ring on the other side, were visible. To get quantitative results a Ni-Mn-Ga 5M sample with a known composition was used as a reference in the SEM EDX measurements [113–116, Publications I-IV]. Average grain size was measured from the EDX samples by etching the samples first with 10 wt-% Nital [Publication II] and in further publications, with a more specialized acid solution of 22.7 vol-% HCl, 22.7 vol-% HNO₃, 9.1 vol-% H₃PO₄ and 45.5 vol-% CH₃COOH [114–116, Publications III, IV]. The measurements were made from images taken with the optical microscope Leica DRMX using the ImageJ software for image analysis. The phase transformation temperatures were measured using a laboratory built low-field ac magnetic susceptibility measuring device [118, Publications I-IV], with heating and cooling rate of 5 °C/min. Magnetization of the powder was studied with laboratory built
Experimental

vibrating sample magnetometer [118] at room temperature by packing the powder tightly into cone shaped plastic holders [Publications II-IV]. A NIST standard nickel disk was used as a reference for the measurement. Relative density of the powder was measured by AccuPyc™1330 pycnometer, applying helium gas displacement method and the measured density was used in calculating the porosity by comparing the measured value for the powder with the relative density of each sample [Publication III].

2.2 Metal matrix composite

The metal matrix composite was manufactured from single crystal powder that was produced by mechanically milling single crystal ingots having compositions of Ni50Mn25Ga25 (Alloy 1) and Ni50Mn30Ga20 (Alloy 2). The single crystals were grown using the Bridgman method [71] by annealing polycrystals for homogenization and ordering. These crystals were then ball milled into powders using WC-Co pot and balls to form Ni-Mn-Ga+WC/Co powders designated as powder 1 and powder 2. The residual stresses from the ball milling [9] were removed by annealing the powder [Publication I]. The powder particle size was studied using Malvern Mastersizer 2000 and the phase structure with Philips PW3830 XRD diffractometer using Cu-Kα radiation. The samples were then compacted using FCT HP D 25-2 pulsed electric current sintering unit at a sintering temperature of 875°C and pressure of 50 MPa [Publication I]. The diameter of the finished compacts was 20 mm. Two different types of samples were cut from the sintered pieces using the slow speed diamond saw. For the DMA experiments, with TA Instruments Q800 DMA instrument in the single cantilever mode, samples were cuboids with dimensions of 1.88 mm x 0.52 mm x 16.59 mm, while for the cavitation erosion tests, small cubes with dimensions of 3 mm x 3 mm x 4 mm were utilized [119, Publication I].

2.3 Hybrid polymer composite

From among the potential polymer matrices, a Loctite Hysol 9455 was chosen [114–116, Publication IV] based on its mechanical properties which can be seen in Figure 6 in relation to some other polymers. It fulfilled all the before mentioned requirements for a suitable polymer matrix adequately, as its yield strength was over the 1 MPa limit and it possessed a Young’s modulus higher than 1 MPA. The working time for the two-component epoxy was 5 minutes, which meant the particles would not have time to settle due to gravity [24] while still long enough to be magnetically oriented [115]. Additionally, the epoxy was readily available and relatively inexpensive.

The hybrid composite manufacturing was done by first measuring the needed amount of the annealed gas atomized powder and then mixing it with epoxy [114–116, Publication IV]. Then the mixture was degassed in vacuum chamber for 3 minutes until no bubbles could be seen and cast into 5 x 6 x 25 mm³ poly-
oxymethylene (POM) mold carefully to prevent bubbles formation during casting [114–116, Publication IV]. Then the mold was closed tightly and placed in 1 T applied magnetic field, where the magnetic field was along the long axis of the sample. The sample was then rotated 180°, while the field was lowered, for nine times to ensure an equal distribution of particles in the particle chains formed in the composite [114–116, Publication IV]. The samples were then left to cure in room temperature for three days. To find the mechanically optimal filling ratio for the hybrid composite structures, a set of five composite samples with different filling ratios: 20 vol-%, 25 vol-%, 30 vol-%, 35 vol-% and 38 vol-% were prepared [116, Publication IV]. Samples were then tested using Instron 4204 Universal Tensile Tester to find out how the different filling ratios affect the mechanical properties such as ultimate tensile strength (UTS) and tensile strain at break by performing a standard tensile test. For the needed reference measurements, two different types of reference samples were prepared. First reference sample was a Loctite Hysol 9455 sample without any particles and the second reference sample was a hybrid composite, which had 35 vol-% of Ralloy® WR4 steel powder, that was prepared using the same procedure as for the regular samples [116]. For the high frequency mechanical analysis measurements, thin pieces with dimension of 0.6 mm x 2.5 mm x 15 mm were cut from the composite samples so that the long dimension was parallel with the particle chains. Additionally, thin pieces of paper were wrapped around the center of the samples to stop buckling of samples during measurements [Publication IV].

2.4 Porous pulsed electric current sintered structures

To produce the porous spark plasma sintered structures, a mixture of 25 vol-% as atomized Ni-Mn-Ga and 75 vol-% of coarse Ensure® NaCl powder was prepared and mixed at room temperature with a Willy Bachofen Turbula shaker-mixer for two hours. Five samples were prepared from the mixture by measuring 13 g of the powder mixture into SPS graphite molds. To prevent the NaCl powder from melting, the sintering temperature was kept at 700 °C, while the other process parameters i.e. room temperature compression pressure, sintering time and sintering pressure were varied [Publication III, Table 1]. The sintering was performed using FCT HP D 25-2 pulsed electric current sintering unit and during consolidation the pulse length was 10 ms with 5 ms pause between pulses. After sintering, the graphite foil surrounding the sample was removed and the salt was dissolved by immersing the sample into 1 l of deionized water at room temperature. The sample was held in the middle of the beaker using a net basket and water was circulated using a magnetic stirrer. Water was changed every 12 hours during the 48 hour long immersion and the sample weight was measured periodically so that immersion could be stopped once salt had dissolved i.e., when sample weight stopped changing.

The samples were dried using ethanol and air blower. At this step, it was evident that the samples would require an extra heat-treatment step as regular handling easily broke the resulting foams. To find the right heat-treatment while mini-
mizing the possibility of manganese loss, the first sample was annealed in evacuated quartz ampoule at 900°C for 24 hours. The resulting structure was not yet rigid enough so for the other samples the annealing temperature was increased to 1000°C and the time to 48 hours. This led to the formation of a firm porous structure, where the original boundaries between particles could no longer be seen. Rectangular cuboid samples were cut from the original 20 mm diameter samples, with dimensions \( x = 4.19 \pm 0.85 \text{ mm} \), \( y = 10.51 \pm 1.73 \text{ mm} \) and \( z = 3.70 \pm 0.89 \text{ mm} \) [Publication III]. The y direction (Fig. 9) of each sample was perpendicular to the compression stress during spark plasma sintering, while z direction (Fig.9) was parallel to the stress. The PANalytical MRD X-ray diffractometer (using Cu K\(_\alpha\)) was used to measure the texture of each sample. The porosities were measured using by AccuPyc™1330 pycnometer using the helium gas displacement method. Samples were placed to the cradle plate so that the y-side of the sample was along the x-axis of the cradle plate and the x-side of the sample along the y-axis of the cradle plate. Magnetization measurements were performed with the laboratory built vibrating sample magnetometer at room temperature. The magnetization was measured at three different orientations, in relation to the applied magnetic field, so that the direction of highest magnetization could be found. This information was used later to determine the starting position for the optical magneto-mechanical device (OMMD) measurements when the MFIS was measured.

Figure 9. Diagram showing how the porous SPS samples were cut from the SPS button [Publication III].

2.5 Optical magnetic-field-induced strain measurements

The magnetic-field-induced strain of the porous spark plasma sintered samples were measured using an optical measuring set-up. In this set-up, samples were attached to a rotating copper plate with a polyoxymethyle (POM) mold that had a laboratory glass cover plate window [Publication III]. The POM mold was small enough so that the samples could be rotated controllably between the
magnetic poles of the electromagnet, but still large enough so that the samples had enough room to change shape (Fig. 10). After the samples were attached to the plate, care was taken so that the lens of the Canon 60D camera was aligned directly at the sample so that the sample could be filmed while it was rotated.

![Figure 10. Schematic of the sample placement and rotation in relation to the applied magnetic field in the optical magnetic-field-induced strain measurements [Publication III].](image)

Before the experiment was started, the sample was filmed for 5 seconds to record the starting dimensions of the sample. Then the field was increased to 1 T and the sample was rotated first from 0° to 90° and then all the way to 180°. Then the sample was rotated back to 0° by stopping at 90°. This rotation was repeated 2 to 3 times for each sample so that enough data could be obtained for the image analysis. For the image analysis, still images were captured from the video and the dimensions were measured using ImageJ image analysis program [Publication III].

The MFIS of the porous spark plasma sintered foams [Publication III] and polymer composite samples [Publication IV] were measured using a dedicated optical magneto-mechanical measuring device (OMMD) in Boise State University. The difference between the measurements performed at Aalto University [Publication III] and those performed using the dedicated OMMD system is that, in the OMMD system the camera lens rotates with the sample stage and takes images at fixed rotation angles. Thus, the image quality is higher and the sample is directly at the focal point of the lens, and consequently, there is a smaller measuring error in the image analysis. For hybrid composite OMMD measurement, cuboid samples with dimensions of 4.0 mm x 5.3 mm x 1.9 mm were cut from the composites with three different filling ratios 25, 30 and 35 vol-%, using a tungsten carbide wire saw and SiC slurry. Both the spark plasma sintered foams and the composite samples were attached to the holder using double sided tape and rotated in 1 T field from 0° to 360° with images saved every 5°. The images were then analyzed using the ImageJ program.
2.6 Vibration damping measurements

Vibration damping capabilities of the material were tested with multiple different methods. These included cavitation erosion testing [Publication I], a laboratory built high-frequency dynamic mechanical analysis instrument [Publication IV] and a commercial TA Q800 dynamic mechanical analysis device [Publication IV]. In all the different testing methods, the principle is to study the mechanical properties of the samples under dynamic loading conditions. Of the three different testing methods, the cavitation erosion and the laboratory built high frequency dynamic mechanical analysis instrument measure the damping capability of the sample indirectly, while the commercial DMA [103] instrument yields the storage modulus, loss modulus and tan δ directly.

2.6.1 Cavitation erosion

In cavitation erosion testing, cavitation bubbles are generated using a magnetostrictive ultrasonic horn [120]. The oscillating movement of the horn at 20 kHz generates cyclic formation of high and low pressures, which in turn induces negative tension in liquid. This creates pressure oscillations that are larger than the ambient pressure, resulting in pressure drops during the negative point pulse cycles, which in turn creates a cavitation bubble cloud on the surface of the sample and as the bubbles collapse the resulting pressure wave erodes the sample [120]. Depending on the damping properties of the material, the resulting shockwave from the cavitation bubble collapse either starts to damage the material or with materials with good damping properties, the energy is dissipated resulting only in minor damage.

The test can be performed either directly, when the sample is attached to the vibrating horn, or indirectly with the sample attached to sample holder at a distance of 500 μm from the titanium horn [120]. For the cavitation tests, sample surfaces were ground with 600 grit sandpaper and a Misonix Sonicator XL2020 was used for the cavitation [120]. As the ASTM G32 method [120] calls for samples with diameter of 16 mm, a special brass sample holder was manufactured [Publication I, Fig.1a] so that the smaller samples could be fixed to the holder [Publication I, Fig.1b]. To analyze the erosion, the samples were weighed using Sartorius CPA224S at intervals of 30 minutes until cumulative time of 39 hours was reached. After 39 hours of cavitation, sampling time interval was increased first to one hour and finally to two hours, until cumulative cavitation duration of 60 hours was reached. Deionized water was used as the cavitation medium and the temperature was kept at 20 °C using a cooler for the test duration, while the peak-to-peak displacement of the tip was 76 μm. Since the titanium horns wear during cavitation erosion testing and as this can affect the peak-to-peak displacement and formation of the cavitation bubbles [120], a new tip was changed for each tested sample [Publication I].
2.6.2 High-frequency dynamic mechanical analysis

The damping properties of MSM composites were studied by comparing the amount of stiffening that happens in the sample due to the magnetic field. This stiffening is due to the hindering effect that the perpendicular magnetic field has on the movement of twin boundaries in the composite [Publication IV]. A laboratory built high-frequency mechanical testing instrument (HF-DMA) (Fig. 11) was used to measure the change in the strain with and without the applied magnetic field. The tested frequencies were 21, 41, 81 and 101 Hz and the vibration was load controlled. A. Soroka [121] did the original design for the instrument. In the instrument, the sample is attached between two grips, as in a tensile tester, and the lower grip is vibrated up and down using a sinusoidal drive signal from the TTi TG550 function generator and a speaker element [Publication IV]. Before the speaker, the drive signal is amplified using a QSC RMX 2450 audio amplifier, so that the desired stress level is reached, while the displacement of the sample is measured using a laser displacement sensor. The force generated by vibration is then measured with a piezoelectric load cell at the upper grip [Publication IV]. These three signals - displacement, force and drive signal, are then read and recorded using Agilent Technologies DSO-X 204A oscilloscope.

For the experiments performed with the composite samples, the instrument was partly redesigned [Publication IV]. During the redesign, a linear guide was added to the bottom grip to facilitate the testing of larger samples and a movable magnetic circuit, made using permanents magnets, perpendicular to the sample was added to the instrument. For the measurement, thin pieces with dimensions of 0.6 mm x 2.5 mm x 15 mm were cut from the composite samples so that the long dimension was parallel with the particle chains and thin pieces of paper were wrapped around the center of the samples to stop buckling during measurement [Publication IV].

Figure 11. Laboratory built HF-DMA testing instrument [Publication IV].
2.6.3 Dynamic mechanical analysis

The damping properties were studied directly with the TA Q800 DMA at frequencies of 1, 5, 10, 50 and 100 Hz in single cantilever mode at a stress of 1 MPa [Publication IV]. For the reference samples, steel hybrid composite and pure Hysol 9455 samples were prepared and tested in single cantilever mode with the stress of 1 MPa and 2 MPa respectively. A magnetic circuit made from Fe$_{54.1}$Co$_{45.9}$ struts and permanent magnets was built for the instrument, so that samples could be studied with and without the applied magnetic field of 0.3 T [Publication IV]. During measurements, the magnetic field circuit was attached between the stationary clamps (Fig. 12) so that the field was perpendicular to the bending [Publication IV]. The DMA was used to measure both Ni-Mn-Ga polymer hybrid composite samples [Publication IV] and the Ni-Mn-Ga metal matrix composites [Publication I].

There are multiple different testing fixtures and sample orientations that can be used in DMA testing [103]. In the single cantilever mode, the sample is attached to a stationary clamp and the movable clamp is vibrated at the required frequency and stress (Fig. 12) [103]. This introduces a shearing component to the distortion and during bending the tensile stress increases towards the surface on the bending side of the sample, while there is a zero-stress region at the neutral axis e.g. the center of sample and a gradually increasing compressive stress on the opposite side of the sample [103]. For the hybrid composite samples the calculated peak stress on the surface of the sample was 6.6 ± 0.5 MPa with a peak uniaxial stress of 1 MPa, while for the reference steel hybrid composite the peak stress was 2.5 ± 0.02 MPa [Publication IV].

Figure 12. Schematic presentation of typical DMA single cantilever experimental setup [103].
3. Results and discussion

3.1 Properties of the gas atomized powder

The heat-treatment process for gas atomized Ni-Mn-Ga was developed based on the heat-treatment results in Publication II using ATO1 and ATO2 powders. Due to the different atomization parameters [82] and sieving, the average particle size was different for each atomization batch [Publications II, IV]. For ATO1 the average particle size was 24.4 μm, while for ATO2 it was 15.2 μm and 28.3 μm for ATO3 (Fig. 13) [Publications II, IV]. The resulting particle size distributions for ATO1 and ATO2 were narrow (Fig. 13), as is expected from the gas atomization process [82], however higher atomization pressure widens the particle size distribution slightly. The higher atomization pressure in ATO2 and ATO3 powders resulted in larger amount of finer particles, however after sieving, ATO3 had larger average particle size than ATO1 or ATO2 [Publications II, IV].

![Particle size distribution of ATO1 and ATO2](image)

**Figure 13.** Particle size distribution of ATO1 and ATO2 [Publication II].

The results from chemical composition analysis for ATO1, ATO 2 and ATO3 can be seen in Table 2 before and after heat-treatment [Publications II, IV]. The heat-treatment of ATO1 and ATO2 was done at 800 °C in evacuated quartz ampoules, while the heat-treatment of ATO3 was done using the developed salt as
separation method [112] at 700°C in argon gas flow in the fluidized bed furnace. This process is described in detail in Chapter 2.1. As there is minimal change in the average chemical composition before and after the heat-treatment procedure, specifically in the manganese content of the ATO3 powder (Table 2), the developed heat-treatment procedure for the gas atomized Ni-Mn-Ga powder [112] can be deemed successful [115, Publication IV]. On the other hand, the heat-treatment in evacuated quartz ampoules, as indicated by the change in manganese content of ATO1, led to slight manganese evaporation (Table 2). However, the main advantage in the developed heat-treatment procedure was that, with the salt as a space holder, the particles did not start sintering during the annealing process [112, 115], which did happen with ATO1 and ATO2 powders [Publication II], i.e., ATO1 powder started to sinter between 750-1000°C and ATO2 already at 600°C [Publication II]. As compared to milled Ni-Mn-Ga powder the gas atomized powder started to sinter at a lower temperature [122]. It is likely that the lower sintering temperature is related to enhanced packing and small particle size achieved by the gas atomization method. As ATO1 had larger particles than ATO2 powder during the heat-treatment experiments [Publication II] it is thus expected to require also higher temperatures for densification as observed. The e/a ratios in the Table 2, were calculated using the Formula 2 [46].

<table>
<thead>
<tr>
<th>Pre-alloy</th>
<th>As-atomized</th>
<th>Heat-treated</th>
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<tbody>
<tr>
<td>Ni [%]</td>
<td>Mn [%]</td>
<td>Ga [%]</td>
</tr>
<tr>
<td>ATO1</td>
<td>49.0</td>
<td>26.5</td>
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<tr>
<td>ATO2</td>
<td>49.6</td>
<td>29.2</td>
</tr>
<tr>
<td>ATO3</td>
<td>49.2</td>
<td>29.7</td>
</tr>
</tbody>
</table>

The grain size of the as-atomized powders was measured to be $1.7\pm0.2\ \mu m$ [Publications II, IV]. Heat-treatment at 700°C for 24 hours in evacuated crystal ampoules increased the grain size fivefold in both ATO1 and ATO2 alloys [Publication I]. In the developed heat-treatment process a similar effect was found, however, the increase in grain size was tenfold from the $1.7\ \mu m$ to average $17.9\pm8.5\ \mu m$ for ATO3 [Publication IV]. As the average grain sizes of the atomized powders after the heat-treatment are close to the average particle sizes, the goal of the annealing process was achieved. The particles comprised on average, of 1-4 grains per particle, depending on the particle size as can be seen in Figure 14 [Publications II, IV]. One of the main problems with the optical microscope measurements was that the attachment of Ni-Mn-Ga particles with the Epofix epoxy was not good. Thus, during the grinding and polishing process, some of the smallest particles below the average particle size were pulled loose [Publica-
Results and discussion

However, it is still possible to see that particles below the average particle size consist of 1-2 grains, while larger particles consist of 3-5 grains per particle [Publications II, IV].

![Optical microscope images](image)

Figure 14. Optical microscope images of heat-treated gas atomized powder: (a) ATO1 and (a) ATO2 at 20x magnification and (c) ATO3 at 50x magnification [Publications II, IV].

The saturation magnetization values of the as-atomized powders were low due to the inhomogeneous chemical composition and nonuniform lattice strains, which led to the formation of structures comprised of a mixture of disordered and ordered cubic phases [81]. However, annealing, even at relatively low temperatures (Figure 15) increased the magnetization of the powder close to the previously reported reference saturation values [Publication III]. In ATO1 the saturation magnetization was 65 emu/g (Fig.15a), while for ATO2 it was 61 emu/g (Fig.15b) and for ATO3 47 emu/g (Fig.15c). If the magnetization curves
in Figure 15a and 15b are compared, it can be noted that there is a small difference between the minimum annealing temperatures required for achieving the highest saturation magnetization. With ATO1 the saturation is reached at 750 °C while with ATO2 annealing at 700°C was sufficient [Publication II]. It is notable that these temperatures are close to the temperature typically associated with the ordering temperature range of 520-720°C [72, 73]. Similarly, there is a small difference in the saturation magnetic field, as ATO1 reaches magnetic saturation at applied field of 0.3 T while for ATO2 and ATO3 the saturation magnetization is reached between applied field of 0.6 T and 0.8 T. These differences can be attributed to the different chemical compositions and to the polycrystalline structure of the powder that is comprised of multiple variants [Publications II, IV]. As the powder particles have multiple variants, if the magnetization curves are compared to those found in literature [123, 124], it can be seen that the magnetization curves of ATO2 and ATO3 (Fig. 15a and b) are a mixture of hard and easy axis magnetization behaviors.
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The phase transformation temperatures were studied using low-field ac susceptibility measuring system. When the as-atomized powder was measured, no clear phase transformations could be observed in any of the powders using the low field ac susceptibility measuring system, which is likely due to a very broad phase transformation temperature range due to the mixture of ordered and disordered phases [81]. However, after annealing, all the atomized powders showed clear reversible transformation from low-temperature martensite phase to high temperature austenite phase (Fig 16) [Publications II, IV]. The phase transformation temperatures shown on the graph are the averages of start and finishing temperatures of the phase transformation calculated using Formula 3. ATO1 (Fig.16a) is austenite at room temperature, while ATO2 (Fig.16b) and ATO3 (Fig.16c) are martensitic at room temperature [Publications II, IV]. Additionally, in ATO2 and ATO3 the measurements revealed a two-step reverse phase transformation that appeared during the heating of the powder [Publication IV]. The measured average phase transformation and Curie temperatures are in good agreement with the temperatures predicted using the e/a-ratio [46].
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Figure 16. Low-field ac magnetic susceptibility measurements results and average phase transformation temperatures of (a) ATO1, (b) ATO2 and (c) ATO3 powders heat-treated at 700°C [Publications II, IV].

When the crystal structure was studied using the XRD, all the as-atomized powders showed a cubic structure. After the heat-treatment L2₁ crystal structure was clearly visible with ATO3 showing higher order than ATO2. As the phase transformation temperature of ATO1 was below room temperature (Fig.15a), the structure was still cubic after annealing (Fig.16a). While ATO2 (Fig.16b) and ATO3 (Fig.16c) had a five-layered modulated martensite structure after anneal-
ing. The change in the crystal structure after annealing (Table 3) can be attributed to removal of internal stresses and homogenization of the structure [81].

Table 3. Crystal structure after annealing [Publications II, IV].

<table>
<thead>
<tr>
<th></th>
<th>As-atomized</th>
<th>Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a$ [Å]</td>
<td>$b$ [Å]</td>
</tr>
<tr>
<td>ATO1</td>
<td>5.83</td>
<td>5.83</td>
</tr>
<tr>
<td>ATO2</td>
<td>5.84</td>
<td>5.84</td>
</tr>
<tr>
<td>ATO3</td>
<td>5.84</td>
<td>5.84</td>
</tr>
</tbody>
</table>
Results and Discussion

Figure 17. XRD spectra of as-atomized (black) and annealed (red) (a) ATO1, (b) ATO2 and (c) ATO3 [Publications II, IV].

3.2 Properties of Ni-Mn-Ga composite structures

Three different type of composites were studied in this Thesis. Two of the composites were manufactured using pulsed electric current sintering [Publications I, III], while the third structure was a cast epoxy composite [Publication IV]. Even though the first two structures were manufactured using spark plasma sintering the microstructure properties of the composites are quite different. The
double dispersion composites were almost fully dense [Publication I], while the second type of composite structures were highly porous MSM materials, which can be regarded as an MSM-pore composite [Publication III]. The porous structures and epoxy composites use the heat-treated and gas atomized powder [Publication II] and both show pronounced MFIS [Publications III, IV].

### 3.2.1 Double dispersion Ni-Mn-Ga/WC-Co composites

The characterization of the double dispersion Ni-Mn-Ga/WC-Co compacts began with the XRD analysis (Fig. 18) [Publication I]. The results showed that in Compact 1 the martensite had a non-modulated structure, while in Compact 2 the structure was five-layered modulated. When the XRD peak intensities were compared, it was found that the amount of metallic phase had decreased during consolidation with Compact 1, while the ratios remained in Compact 2 [Publication I].

![XRD patterns](image)

**Figure 18.** XRD patterns (Cu-Kα), of the composites showing the indexed peaks related to the martensite type and the WC [Publication I].

Compositional analysis done with the EDX attached to SEM revealed that both compacts contained WC-Co particles in Ni-Mn-Ga matrix [Publication I]. The WC-Co particles had mostly kept their original structure, although some Co was alloyed into the Ni-Mn-Ga matrix in both compacts. Due to this alloying, the composition of both Composites 1 and 2 changed throughout the composites in the interphase region between the Ni-Mn-Ga matrix and WC-Co. To study this change EDX linescans were performed in Compact 1 (Fig. 19a) starting from the Ni-Mn-Ga matrix into the WC-Co particle and in Compact 2 starting from the WC-Co particle into the Ni-Mn-Ga matrix (Fig. 19b) [Publication I]. In both cases, it can be seen that the cobalt, had diffused through the interphase region.
into the Ni-Mn-Ga matrix. This can be observed in Figure 19, as the cobalt concentration stays stable throughout the interphase region even while the tungsten concentration drops in the interphase region [Publication I]. The SEM analysis was also used to calculate the volume phase fractions of the two phases. Based on the SEM analysis, Composite 1 consists of 90 vol-% of the WC-Co and 10 vol-% of NM Ni-Mn-Ga, while Composite 2 consists 82 vol-% 10M Ni-Mn-Ga and 18 vol-% of WC-Co. The Composite 1 had saturation magnetization of 10 emu/g while Composite 2 had 53.1 emu/g and when these measured values are compared to the reference values of NM and 10M structures, respectively 52 emu/g [54] and 64 emu/g [54,125], the ratio of magnetization is 19.2% for Composite 1 and 83 % for Composite 2. These magnetization ratios agree well with the volume fractions calculated from the SEM images [Publication I]. The difference in the volume fractions calculated with SEM and magnetization can be explained because of cobalt, which has been shown to lower the magnetization of Ni-Mn-Ga when it replaces nickel atoms in the lattice.

The average phase transformation temperature of the composites was studied using the DSC. For Composite 1 (Fig.20a) the average martensite transfor-
formation temperature ($T_M$) was 180 °C, while the average austenite transformation temperature ($T_A$) was 190°C and for Composite 2 (Fig. 20b) the temperatures were respectively 40°C and 51°C [Publication I]. In the magnetic moment vs. temperature measurements, no clear Curie temperature was found for Composite 1, likely due to high WC-Co content of the composite, while for Composite 2 the measured Curie temperature was 112°C. The relative density was analyzed using the Archimedes method. Even though the goal was to manufacture fully dense composites, the relative density of Composite 1 was only 84%, and that of Composite 2 was 92% [Publication I].

Figure 20. DSC curve measured for (a) Composite 1 and for (b) Composite 2. Two machine induced spikes can be seen in the Composite 2 DSC figure marked with circles, which are equipment related and not due to phase changes. The cooling and heating directions and phase transformation temperatures are marked with arrows [Publication I].

The room temperature DMA measurements show that the $\tan \delta$ i.e., the vibration damping capability, of both composites increased with increasing strain (Fig. 21a). The highest measured $\tan \delta$ was found with Composite 2 at over 0.03 (Fig. 21b). Based on the DMA experiments, which show that the $\tan \delta$ is strain dependent, it can be concluded that the dominating damping mechanism in the composite structures is likely energy dissipation due to twin boundary reorientation [Publication I]. However, if the measured $\tan \delta$ of the composites is compared to 10M martensite [4], the damping capability of these composites is still
lower, which can be explained by the higher stiffness of the composites due to WC-Co addition [Publication I].

![Graph showing strain and stress dependency of tan δ in Composite 1 and Composite 2.](image)

**Figure 21.** (a) Measured peak-to-peak strain and stress dependency of tan δ in Composite 1 and Composite 2 at 26°C and at frequency of 1 Hz and (b) DMA results of Composite 1 and Composite 2 [Publication I].

During cavitation erosion testing, Composite 1 experienced massive mass and volume loss, while Composite 2 endured the full cavitation time with minimal mass and volume loss (Fig. 22) [Publication I]. As previous cavitation experiments have shown [69], NM martensite should have higher cavitation erosion resistance than that of 5M martensite. The large difference in the composites cavitation resistance can likely be attributed to large difference in the relative density [126], which has likely led to cavitation bubble formation inside the pores of the material. When the cavitated surfaces were later inspected using SEM, it was found that the Ni-Mn-Ga-Co between the WC-Co particles had disappeared as the composite structure had ruptured along the interphase region.
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(Fig. 22b). Obviously, as the cavitation bubbles collapsed inside the pores of the composite they generated a so called three dimensional pressure wave inside the material that led to rupturing, when typically cavitation affects the material only in two dimensions compressing the material that creates smooth fractures (Fig. 22c) [Publication I].

Figure 22. (a) Cavitation results of Composite 1, Composite 2 and reference Steel 304, (b) a 200x BSE image of Composite 1 after 1.5 h cavitation and (c) a 200x BSE image of Composite 2 after 55 h of cavitation [Publication I].

When the cumulative mass loss of Composite 2 is compared to the reference 304 steel and to the values found in literature for 5M [119], NM [119] and WC-Co [126] it is clear that the Composite 2’s cavitation resistance is higher (Fig. 23). The cavitation resistance of a material is dependent on multiple material properties that promote the binding of the vibrational energy to the structure [119, 127–130] and on the hardness of the material [126]. In shape memory alloys, the most common methods that can bind the vibrational energy are: the formation of stress induced martensite, twinning of martensite, the movement of twin boundaries and the rearrangement of the twin variants [119, 127–130]. Thus, pronounced cavitation erosion resistance of the tested composites is likely due to the combination of increased hardness and wear resistance, due to WC-
Co particles, and the dissipation of vibration energy due to the movement of twin boundaries. Similar results have been obtained from the cavitation erosion tests conducted on the NiTi shape memory alloys [127, 129], where the cavitation erosion resistance was due to formation of stress induced martensite, and from WC-Co cermets [126], where the cavitation resistance was due to the high microhardness and density of the material. A composite structure that can combine these two beneficial effects, namely the hardness and binding of vibrational energy to twin boundary movement, could be suitable for applications where pronounced cavitation erosion is required. However, some more work is required for increasing the relative density and for finding the optimal volume fraction for the two different components.

Figure 23. Cumulative volume loss of Composite 2 during cavitation erosion compared to reference measurement using 304 Steel and values found in literature for NM [119] and 10M martensite [119] and WC-Co [126] [Publication I].

### 3.2.2 Porous pulsed electric current sintered structures

The grain size of the porous spark plasma sintered samples were studied using optical microscope after the sintering and again after the heat-treatment [Publication III, Table 1]. The measured grain sizes after sintering and after heat-treatment are shown in Table 4. The original grain size of the as-atomized powder was 1.6 ±0.2 μm, the sintering process increased the grain size six-fold and annealing further doubled the grain size (Table 2) [Publication III]. As such, the combined effect of sintering and following heat-treatment was comparable to the developed heat-treatment process [112, 115]. During optical microscopy of the sintered and heat-treated samples (Fig.13), twins could be observed in the polished and etched grains (Fig. 24a-b).

Table 4. Measured grain sizes and porosities of the sintered samples after sintering and heat-treatment [Publication III].
Heat-treatment led to the formation of a firm porous structure comprised of larger particle nodes that are connected by thin struts [Publication III]. The measured porosities are shown in Table 4. After the salt removal, it could be observed that larger pores and higher porosity existed on the surface layer of each sample (Fig.24c). This uneven porosity distribution is likely due to segregation of the lighter, but larger, salt particles from the heavier ATO2 particles that occurred when the spark plasma sintering mold was being filled [Publication III]. The segregation of salt and Ni-Mn-Ga powders can also explain the larger difference in the measured porosities. However, this porosity gradient was not observed in the samples that were cut from the center of the sintered samples as shown in the schematic (Fig. 9). Additionally, when the porosity was studied in relation to the compression in the sintering process, it was found that pores that were parallel to the compression had even rectangular shape, while the pores that were perpendicular to the compression were irregularly shaped [Publication III].
The spark plasma sintering process combined with annealing in evacuated quartz ampoules led to a small change in the chemical composition (Table 5). This change in the chemical composition is notable as the heat-treatment procedure was the same as the powder heat-treatment that was reported in Publication II, where the compositional change was much smaller (Table 2). The only difference in the heat-treatments [Publication II, III] is in the sample arrangement. In the powder heat-treatment experiments [Publication II] each ampoule was packed densely with the powder to maximize the amount of material for characterization, while during the heat-treatment of the porous samples each ampoule contained only one highly porous sample as salt had been removed prior to heat-treatment because the salt would have melted at 1000°C [Publication III]. Thus, the higher manganese evaporation can be explained by the increased open porosity around and inside the sample, which led to increased manganese evaporation [Publication III]. This change in composition led to higher phase transformation temperatures compared to the those measured for ATO2 powder annealed at 1000°C \( (T_M=35°C, T_A=42°C) \). The magnetization measurements of the samples showed that the samples had increased magnetization, average 72 emu/g, in comparison to the magnetization of the annealed powder (Fig.15b), however, this was expected as the samples were solid and had larger grain size [Publication III].

Table 5. Chemical composition and average starting and finishing phase transformation temperatures of samples after sintering and heat-treatment [Publication III].

<table>
<thead>
<tr>
<th></th>
<th>Ni [at%]</th>
<th>Mn [at%]</th>
<th>Ga [at%]</th>
<th>TM [°C]</th>
<th>TA [°C]</th>
<th>TC [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPS 1</td>
<td>50.5 ± 0.1</td>
<td>27.2 ± 0.1</td>
<td>22.3 ± 0.1</td>
<td>34.7 ± 0.5</td>
<td>44.2 ± 0.5</td>
<td>97.5 ± 0.5</td>
</tr>
<tr>
<td>SPS 2</td>
<td>51.0 ± 0.1</td>
<td>26.2 ± 0.1</td>
<td>22.7 ± 0.1</td>
<td>37.7 ± 0.5</td>
<td>46.2 ± 0.5</td>
<td>97.2 ± 0.5</td>
</tr>
<tr>
<td>SPS 3</td>
<td>50.5 ± 0.1</td>
<td>27.4 ± 0.2</td>
<td>22.1 ± 0.1</td>
<td>43.3 ± 0.5</td>
<td>50.6 ± 0.5</td>
<td>97.1 ± 0.5</td>
</tr>
<tr>
<td>SPS 4</td>
<td>50.2 ± 0.1</td>
<td>27.8 ± 0.1</td>
<td>22.0 ± 0.1</td>
<td>43.8 ± 0.5</td>
<td>52.8 ± 0.5</td>
<td>97.8 ± 0.5</td>
</tr>
<tr>
<td>SPS 5</td>
<td>50.2 ± 0.2</td>
<td>27.7 ± 0.5</td>
<td>22.1 ± 0.6</td>
<td>37.3 ± 0.5</td>
<td>44.3 ± 0.5</td>
<td>99.5 ± 0.5</td>
</tr>
</tbody>
</table>
The magnetic-field-induced strain measurements of spark plasma sintered samples are presented as peak-to-peak MFIS, when the magnetic field is rotated 420° around the sample, and the measured values are from the xy-area of the sample that was perpendicular to the compression (Fig. 9). The results (Fig. 25 a and c) are based the values reported in Publication III performed at Aalto University. As the measuring set-up at Aalto University consisted just of a camera focused, the samples were remeasured using the dedicated OMMD equipment at Boise State University and these values are presented in Figures 25 b and d. The differences in these two measurement results can be accounted to following reasons. Firstly, as in the measurement setup at Aalto University the camera did not rotate with samples, it is possible that the focal point moved during the measurements. Secondly, as the analyzed images were still images taken from the video of the measurement, the quality of the images was not as high as desired. These factors increase the error during the optical analysis of the images. To account for these factors, the measurements in Aalto were repeated twice for each sample and during each measurement, samples were rotated 10 times. The reported values have thus been calculated from five peak-to-peak MFIS pairs to minimize the error. Lastly, the systematic error of the measurement was analyzed by measuring the calibration dimension of each sample 25 times. This calculation gave each measurement an average error of ±0.04 mm [Publication III]. In the Boise State University OMMD measuring setup, samples were fixed to the sample holder using double-sided tape, which can restrict MFIS. Thus, it is logical that the measured MFIS of the samples are smaller in the Boise results, especially at the higher porosities since higher porosity means that there are less struts that are straining. However, as the camera rotates along with the samples and, instead of lower quality video, takes normal images at set rotation angles, the error during image analysis is smaller. Despite these differences, the MFIS measurements (Fig. 25) are comparable and the values are clearly higher than the shape change due to magnetostriction, -0.0055% [18, 131] in polycrystalline Ni-Mn-Ga and the MFIS of polycrystalline Ni-Mn-Ga [13]. Factors that can affect MFIS are the texture [13], porosity [12], grain size [12] and chemical composition [57], which affect the crystal structure of the Ni-Mn-Ga. Thus, the pronounced MFIS found in the SPS samples is likely a result of the reduced grain boundary constraints, which facilitate twin boundary movement [Publication III]. When the results are compared between the SPS samples in the Aalto University measurements, the MFIS increase can be associated with increasing porosity, however, based on the Boise State University results, the highest MFIS can be found at porosity between 80-82 % and grain size between 24 to 24.5 μm. Even though there is a large difference in the MFIS at low and high porosities and in the small and large grains sizes in the two different measuring setups, the values at porosities of 80-90% and grain sizes of 24-24.5 μm are highly consistent and reliable. In general, when porous structures are used in applications, where higher stress is needed the lower porosity is better. However, if only high MFIS is required, and care is taken to minimize restriction in the design as well as possible, then the higher porosity is a better.
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Results and discussion

3.2.3 Ni-Mn-Ga/epoxy composites

In the epoxy composites, the filling ratio was based on the tensile tests (Fig. 26) that were performed on composites with different filling ratios of gas atomized Ni-Mn-Ga. Previous research has shown that the mechanical properties of polymer composites are sensitive to the filling ratio of Ni-Mn-Ga powder and at higher filling ratios the composites start to become brittle as there is not enough polymer to bind the particles together [23, 29, 30]. Similar effect can be seen in the composite tensile tests as the ultimate tensile strength (UTS) of the composite increases rapidly between 20-35 vol-% Ni-Mn-Ga powder filling ratio. However, when the composite Ni-Mn-Ga filling ratio is increased over 35 vol-%, the measured UTS drops and the composite becomes prone to cracking, which can be seen as the decreasing tensile strain at break. For twin boundary movement to occur, the magnetic and/or mechanical stress needs to overcome the twinning stress of the material, which depends on the crystal structure and other forces such as grain boundary constraints. Previous research [54, 63] has shown that for 5M single crystals the twinning stress is between 0.5-4 MPa (Table 1), with the best single crystals having a twinning stress of 1 MPa. As the heat-
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treated powder has between 1-4 grains on each particle, the twinning stress of the powder is likely higher than in single crystals. Thus, a composite filling ratio between 25 vol-% and 35 vol-% was chosen as the higher UTS of the composites would mean that experiments could be performed using higher stresses without risking sample breakage. The glass transition temperature ($T_g$) of the epoxy was 18.2°C and was measured using DSC. When the gas atomized particles are mixed with the epoxy, the $T_g$ of the composites increases slightly as the particles affect the crosslinking during curing [24]. To reach the highest vibration damping capability with Ni-Mn-Ga composite structures, vibration should be performed close to or at the glass transition temperature, where the tan $\delta$ of the polymer matrix reaches its peak-value. Similar peak-value can be observed in Ni-Mn-Ga near the average phase transformation temperatures. As such, it is synergistically beneficial if these phase transformation temperatures and the matrix glass transition temperature are close to each other [19, 24, 26–28]. This should be possible as previous long term cycling experiments with Ni-Mn-Ga – epoxy composites showed that at 300 Hz the sample temperature increased only 2°C [121].

![Figure 26. Effect of composite filling ratio on the ultimate tensile strength and tensile strain at break (not published before).](image)

The chaining of the gas atomized powder during composite manufacturing using the magnetic field was studied (Fig. 27). It was found [114, 115], that after the powder was mixed with the epoxy, an applied magnetic field of 0.2 T was enough to settle the powder particles into chains in the epoxy (Fig. 27a). The chains formed along the magnetic field lines [114, 115]. The particle chains were evenly spaced along the length and width of the sample. However, in the depth direction the distribution of particles was not as even as some of the particle
chains formed at an angle [Publication IV]. The chains were formed from differently sized particles (Fig. 27b), however, smaller particles mostly filled the gaps between the larger particles (Fig. 27c).}

![Image of optical microscope images](image)

**Figure 27.** Optical microscope images of magnetically oriented particle chains in the epoxy composites at (a) 2.5x magnification, (b) 50x magnification showing single chain and (c) 50x magnification showing a chain with smaller particles next to larger particles [114, 115].

The optical magneto mechanical measuring system at the Boise State University was used to measure the peak-to-peak MFIS of the composite samples. The results indicate that as the magnetic field is rotated around the composite sample, the composite changes its shape. This is to be expected as previous research has shown MFIS in ordered Ni-Mn-Ga particle composites [19]. Moreover, the measured MFIS (Fig. 28) is larger than the MFIS previously reported for Ni-Mn-Ga composites [18, 19]. The gas atomized chains were oriented along the length (y) of the sample and when the field was perpendicular to the chains the length increased. The measured MFIS was noticeable in all the studied filling ratios. However, at highest filling ratio of 35 vol-%, the measured MFIS was over 1.5
times the MFIS with 20 vol-% filling ratio. Compared to the porous spark plasma sintered structures (Fig.25) [Publication III], the measured MFIS of the composite structures is smaller. However, this can be due to the epoxy matrix, which acts like a spring constraining the MFIS, and also due to the orientation of particles, as only the easy axis of magnetization can be oriented with the magnetic field leaving the other two axes to orient randomly. When the field is rotated around the samples, it is unlikely that $\Sigma$MFIS generated by the particle chains is as high as the $\Sigma$MFIS generated by the almost bamboo grained porous structure consisting of larger nodes and thin struts.

![Figure 28](image_url)

**Figure 28.** Measured peak-to-peak MFIS of the composite samples as the field is rotated perpendicular to the width (x) and length (y) of the sample, measured using the Boise State University OMMD [not published before].

When the damping properties of the composites were analyzed using the TA Q800 DMA, it was found that the filling ratio has a large effect on the damping properties and the magnetic field response (Fig. 29). With the lowest filling ratio (Fig.29a), the magnetic field has practically no effect on the composite. However, when the filling ratio is increased (Fig. 29b and c) the applied magnetic field has a pronounced effect on damping capabilities. Similar effect of filling ratio has been found before [19, 27] and composites with filling ratio between 30-40 vol-% have displayed enhanced damping capabilities [28]. The measured $\tan \delta$ values are comparable to the values reported before [23, 24, 36] for Ni-Mn-Ga composites, even though the pure Hysol 9455 (Publication IV Fig 3d) has lower $\tan \delta$ than the polyurethane [36] or the previously used epoxy [23]. It is noticeable that the measured $\tan \delta$ values of the 35 vol-% (Fig. 29c) are quite high compared to previous research [19, 27] even though the particles have been
organized into chains. Previous experiments have shown that the highest damping capabilities in Ni-Mn-Ga/polymer composites are usually associated with disordered composite structures [19], which have more particle-matrix interfaces than the ordered structures. If the measured tan δ values of the composite (Fig 29c) are compared to the damping in just the polymer matrix [Publication IV Fig 3d] and to the reference steel powder composite [Publication IV, Fig. 3e], the increased damping capability of the Ni-Mn-Ga composites is clear. When the vibration frequency increases, tan δ decreases in all of the reference materials with or without applied magnetic field, while with the Ni-Mn-Ga composite the tan δ increases as the vibration energy has to overcome the magnetostress created by the magnetic field to move the twin structure. As both the loss and storage moduli also increase with the application of the magnetic field, it is likely that the stiffening effect is due to suppressed twin boundary movement in the filler particles [Publication IV]. If the measured room temperature tan δ at 1 Hz in the 35 vol-% (Fig.29c) (peak tan δ of 0.8) is compared to the tan δ of Ni-Mn-Ga/WC-Co Composite 2 DMA results (Fig.21a) (peak tan δ of 0.04), the damping capability of the Ni-Mn-Ga/epoxy composite is 20 times higher. However, the decreased damping of Ni-Mn-Ga-Co/WC-Co compared to Ni-Mn-Ga/epoxy composites is likely due to higher stiffness of the Ni-Mn-Ga/WC-Co composite.
Figure 29. DMA measurement results (TA Q800) performed at room temperature. Strain (%) and \(\tan \delta\) with and without field of Ni-Mn-Ga/Hysol 9455-epoxy hybrid composites: (a) filling ratio of 25 vol-%, (b) filling ratio of 30 vol-%, (c) filling ratio of 35 vol-% [Publication IV].

The measurements obtained from the laboratory-built HF-DMA [Publication IV, Fig. 4a-c] performed at room temperature are consistent, even if not exactly comparable, with the DMA measurement results, as the strain of the composite decreases with the application of the magnetic field. Similar to the DMA results, the stiffening effect is more pronounced in the composite with the increased filling ratio [Publication IV, Fig. 4c]. The differences in the DMA and HF-DMA experiments can be attributed to three different factors: the different stress
fields in the experiments, the difference in sample sizes and the viscoelastic nature of the epoxy matrix [Publication IV]. In the single cantilever experiments, one side of the sample has an increasing tensile stress region, while the opposite side has an increasing compressive stress region and at the center of the sample there is a zero stress region [103]. While in the HF-DMA experiments, the macroscopic uniaxial stress is uniformly either tensile or compressive in the whole sample. Sample size affects the results since the inter-chain distance cannot be precisely controlled when the particle chains are oriented through the large sample using the magnetic field [Publication IV]. Thus, when smaller samples are cut from the larger composites, there may be variation in the amount of particle chains. Lastly, due to the viscoelastic nature, it is possible that the smaller stress used in the HF-DMA experiment is not transmitted to the particles fully. However, the effect the particles have on the damping due to change in the composite stiffness is still clearly visible in both DMA and HF-DMA experiments with higher filling ratios.
4. Conclusions

In the present thesis, the processing parameters for the production of magnetically active gas atomized Ni-Mn-Ga powder were developed. The obtained powder was used to manufacture two different Ni-Mn-Ga structures: a highly porous spark plasma sintered structure and a cast Ni-Mn-Ga/epoxy composite. In addition to these two structures, a third composite structure was manufactured from milled Ni-Mn-Ga single crystal – WC-Co recycled powder. Following conclusions can be made from the presented results:

- Double dispersion Ni-Mn-Ga/WC-Co composite structures could dissipate vibrational energy. The pronounced damping is suggested to be due to the dissipation of vibrational energy by twin boundary motion as the tan δ is seen to be clearly strain dependent. Such a composite structure, that can combine high hardness and the binding of vibrational energy to twin boundary movement, could be suitable for applications where pronounced cavitation erosion is required. However, a small volume fraction of Ni-Mn-Ga in one of the composites led to higher porosity and lower performance in cavitation measurements. Therefore, similar to polymer composites, it appears that a minimum filling ratio of Ni-Mn-Ga powder is required to produce an active metal composite. It is proposed that Ni-Mn-Ga can be used to enhance properties in rigid metal matrix composite structures as, even though high ΣMFIS is unlikely, the Ni-Mn-Ga matrix can still bind the vibrational energy to twin boundary movement.

- The heat-treatment process developed during the Thesis and used to heat-treat the gas atomized powder is found suitable for the manufacturing of magnetically active large grained Ni-Mn-Ga particles with minimal compositional changes, based on the annealing experiments in Publication II and the following composite structure properties in Publications III and IV. The produced powder is highly spherical and the narrow particle size distribution can be controlled by adjusting the gas atomization parameters. The proposed heat-treatment homogenizes the structure and relieves stresses created during the fast cooling in the atomization process. This can be observed by the increased magnetization, which is comparable to previously measured magnetization values for single crystals with L2_1 order. The produced powder’s phase transformation temperatures after heat-treatment are also in good agreement.
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with single crystal values at the same chemical composition. Additionally, as the produced powder is highly spherical, it is suitable for powder metallurgical manufacturing processes and for polymer composites.

- Porous structures produced using spark plasma sintering of the manufactured powder and sodium chloride as a removable space holder material were shown to have pronounced MFIS. This is likely due to the reduced grain boundary constraints as the high porosity led to a structure that was formed from thin large grained struts connected through larger nodes. Twins were observed in the large grains of the struts and in the nodes during optical microscopy and the spark plasma sintering process led to the formation of texture in the samples. After heat-treatment, the manufactured structures were rigid and due to the large and interconnected porosity, samples could be filled with polymer.

- Finally, it was shown that Ni-Mn-Ga/Hysol 9455 epoxy composite structures have pronounced vibration damping properties that increased with Ni-Mn-Ga filling ratio and could be controlled using magnetic field. The structures also had pronounced MFIS comparable to previously manufactured Ni-Mn-Ga hybrid polymer composite structures found in literature, however as expected the MFIS was smaller than with the porous spark plasma sintered samples. Magnetic orientation of the Ni-Mn-Ga particles led to the formation of particle chains along the composite structure, comprised of larger particles and smaller particles that filled the holes between the larger particles. The damping properties of the composite are noticeable and the measured tan δ is higher than with previously reported composite structures, even though pronounced damping has previously been associated mostly with disorganized Ni-Mn-Ga/polymer composites. The stiffness of the composites could also be controlled magnetically, thus the composite could be used as an adjustable damping element.

- Based on the experiments and results reported in this Thesis and Publications II-IV, the gas atomization and the following heat-treatment procedure make it possible to manufacture large volumes of compositionally homogenous and active MSM powder. The produced powder can then be used to manufacture magnetically active composite structures that can be used for either actuation or vibration damping. However, further research is required to achieve controllable inter-chain distance of the oriented composites since the active properties of the composites depend on the amount of working Ni-Mn-Ga chains in the composite matrix. Additionally, an epoxy matrix with higher UTS could be investigated as the larger stresses could be used in testing and in applications.

Based on the results obtained, an interesting future direction for the gas atomized Ni-Mn-Ga powder research could be to use the powder in selective laser sintering and manufacturing magnetically active 3D elements. Previous experiments, performed with mechanically milled Ni-Mn-Ga, have proved that the material can be manufactured into 3D structures. However, the randomly
shaped particles have proved difficult to 3D print due to particle flow problems. As the gas atomized particles presented in this Thesis are spherical and have a narrow particle size distribution, the powder should be extremely suitable for additive manufacturing methods such as selective laser melting. Additionally, since the additive manufacturing processes typically require large amounts of powder, the gas atomization, which can produce powder from a few kilograms to several tons, is a suitable powder production method.
References


Conclusions


Conclusions


