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Novel In Situ Study of Magnetocaloric Heusler Alloy

Roozbeh Nikkhah Moshai
rnikk001@fiu.edu

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

NOVEL *IN SITU* STUDY OF MAGNETOCALORIC HEUSLER ALLOY

A dissertation submitted in partial fulfillment of the

requirements for the degree of

DOCTOR OF PHILOSOPHY

in

MATERIALS SCIENCE AND ENGINEERING

by

Roozbeh Nikkhah-Moshaie

2016

To: Interim Dean Ranu Jung
College of Engineering and Computing

This dissertation, written by Roozbeh Nikkhah-Moshaie and entitled Novel *In Situ* Study of Magnetocaloric Heusler Alloy, having been approved in respect to style and intellectual content, is referred to you for judgment. We have read this dissertation and recommend that it be approved.

Surendra K. Saxena

Jin He

Gerard Bourne

W. Kinzy Jones, Co-Major Professor

Benjamin Boesl, Co-Major Professor

Date of Defense: July 8, 2016

The dissertation of Roozbeh Nikkhah-Moshaie is approved.

Interim Dean Ranu Jung
College of Engineering and Computing

Andrés G. Gil
Vice President for Research and Economic Development
and Dean of the University Graduate School

Florida International University, 2016

DEDICATION

I dedicate this dissertation to my father who passed away, my mother, brother, and sister, who have always inspired me.

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ABSTRACT OF THE DISSERTATION
NOVEL *IN SITU* STUDY OF THE MAGNETOCALORIC HEUSLER ALLOY

by

Roozbeh Nikkhah-Moshaie

Florida International University, 2016

Miami, Florida

Professor Benjamin Boesl, Co-Major Professor

Professor Kinzy Jones, Co-Major Professor

The objective of this research was to develop a novel technique for mechanical treatment to manipulate the microstructure of Nickel-Manganese-Gallium Heusler alloys to increase anisotropy, which can lead to higher magnetocaloric properties. $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ intermetallics have the potential to be employed in magnetic refrigeration devices including residential refrigerators, heat pumps, and air conditioning. Solid-state magnetic refrigeration systems are smaller, quieter, and reduce energy consumption by 20% compared to existing conventional vapor-cycle refrigeration devices which rely on harmful hydro-fluorocarbon gases and pump millions of tons of greenhouse gases into the atmosphere. The magnetic refrigeration market is predicted to reach US\$ 315.7 Million by 2022.

Magnetic refrigeration systems can also be used in electronic systems and the space industry. The current state-of-the-art magnetic refrigeration systems use expensive rare earth elements including Gadolinium (Gd). The need to replace Gd and other rare earth elements with cheaper and more available elements led to other alloys including Ni-Mn-Ga. By understanding the processing-microstructure-property relationship of Ni-Mn-Ga alloy, it is possible to manipulate the microstructure in order to obtain higher refrigeration

capacity. It is a promising alternative to rare earth elements and improves national security by minimizing foreign dependence on the import of rare earth metals.

This novel *in situ* study establishes that twin boundaries can be manipulated in a polycrystalline

Ni-Mn-Ga alloy. This results in a change in magnetocrystalline anisotropy, which leads to a higher magnetic cooling power. Mechanical loading in a preferred direction, traditionally referred to as a training process, was able to move the twin boundaries, and the combination of focused ion beam imaging linked specific movement with mechanical loading. This technique, *in situ* monitoring process, can be utilized to devise training procedures for future iterations of magnetocaloric and shape memory alloys.

TABLE OF CONTENTS

CHAPTER	PAGE
1. Motivation	1
Literature Review	3
Magnetocaloric Phenomenon	3
Fabrication Methods of Ni-Mn-Ga Alloys	5
Structural Study of Ni-Mn-Ga Alloys	6
Magnetocaloric Properties	7
Twin Boundaries, Anisotropy and Entropy Change	9
Magnetocaloric Effect of Ni-Mn-Ga Alloys	11
Overlap of the Magnetic Transition and Structural Transformation	12
Effect of Thermal Cycling.....	12
Effect of Isobaric Thermal Cycling	13
Effect of High Pressure in Magnetocaloric Properties of Ni-Mn-Ga.....	14
References	23
2. Hypothesis	27
Research outline	29
Alloy Synthesis	28
Homogenization	29
Structural and Microstructural Characterization.....	30
Magnetic Measurements	30
<i>In Situ</i> Mechanical Experiments Inside FIB	30
<i>In Situ</i> Thermomechanical Experiments Under an Optical Microscope.....	31
<i>In Situ</i> High-Pressure X-ray Diffraction	31
Mechanical Alloying and Spark Plasma Sintering (SPS)	32
References	34
3. Experimental	34
Materials	34
Alloy Synthesis	34
Encapsulation and Homogenization	34
Heat Treatment	37
Wire-EDM	37
Diamond Anvil Cell (DAC).....	37
Spark Plasma Sintering (SPS)	37
Ball Milling.....	39
Uniaxial Press	39
Metallographic Sample Preparation.....	39
Vibratory Polishing Machine to Prepare Samples For EBSD	39
Instrumental Characterization	40
Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) ..	39
X-ray Diffraction (XRD)	39
Magnetic Measurements	41
High-Pressure Synchrotron X-ray Diffraction.....	41
<i>In Situ</i> Mechanical Treatment Inside FIB	41
<i>In Situ</i> Thermomechanical Treatment.....	43
EBSD Experiments Inside FIB	43

Transmission Electron Microscopy (TEM)	43
References	45
4. Results and Discussion	46
Structure and Chemical Composition of Alloys.....	46
Magnetic Measurements	49
Microstructural Analysis	57
<i>In Situ</i> Mechanical Loading And Imaging Inside FIB	60
<i>In Situ</i> Thermomechanical Treatment.....	62
<i>In Situ</i> High-Pressure X-ray Diffraction	65
Mechanical Alloying and Spark Plasma Sintering (SPS)	71
References	79
5. Conclusion	82
6. Recommendations for Future Work	84
<i>In Situ</i> Mechanical Treatment Inside FIB equipped with EBSD	84
<i>In Situ</i> Thermomechanical Treatment Inside FIB	84
<i>In Situ</i> Thermomechanical Treatment Inside FIB equipped with EBSD	84
High-Pressure and High-Temperature Synchrotron X- ray Diffraction	84
VITA.....	85

LIST OF TABLES

TABLE	PAGE
Table 1.1. e/a ratio, T_m , and TC of $Ni_{2+x}Mn_{1-x}Ga$ alloys.....	7
Table 3.1. Specifications of materials used for alloy synthesis.....	35
Table 3.2. JCPDS card No. for different compositions.....	40
Table 4.1. Chemical composition of alloys based on EDS.....	46
Table 4.2 Calculated moments on the atoms of Ni_2MnGa and the overall moments.....	68
Table 4.3. The interatomic distance between four Mn and their nearest neighbors.....	69

LIST OF FIGURES

FIGURE	PAGE
Figure 1.1. GE's magnetocaloric refrigeration demo in 2014.....	3
Figure 1.2. The four stages of a magnetic refrigeration cycle.....	4
Figure 1.3. Austenite and martensite structures of Ni_2MnGa	10
Figure 1.4. Thermodynamic relation between thermal, elastic and magnetic variables..	11
Figure 1.5. Magnetic entropy change, ΔS_m , as a function of temperature.....	12
Figure 1.6. Magnetic entropy change of $\text{Ni}_{54.3}\text{Mn}_{20.1}\text{Ga}_{25.6}$	13
Figure 1.7. Magnetic entropy change vs. temperature for $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$	14
Figure 1.8. Magnetic isotherms at $P=0$ and $P=8$ kbar.....	15
Figure 1.9. Temperature dependence of the magnetic entropy change.....	16
Figure 1.10. Isothermal magnetization curves for $\text{Ni}_{50-x}\text{Mn}_{37+x}\text{Sn}_1$ at different pressures...	17
Figure 1.11. Thermomagnetic curves for $\text{Ni}_{50-x}\text{Mn}_{37+x}\text{Sn}_{13}$ at different pressures.....	18
Figure 1.12. Temperature dependence of the magnetic entropy for $\text{Ni}_{50-x}\text{Mn}_{37+x}\text{Sn}_{13}$	19
Figure 1.13. Barocaloric effect as a function of temperature.....	20
Figure 1.14. Magnetic entropy change in Ni_2MnGa and $\text{Ni}_{1.85}\text{Mn}_{1.15}\text{Ga}$	21
Figure 1.15. High-pressure synchrotron X-ray diffraction patterns of Ni_2MnGa	22
Figure 2.1. A schematic EBSD mapping showing macro and micro twin boundaries.....	28
Figure 2.2. A schematic of the SEM Tester 1000.....	31
Figure 2.3. A schematic of a diamond anvil cell.....	32
Figure 2.4. Thermal Technologies 10-4 Spark Plasma Sintering Furnace.....	33
Figure 3.1. Arc Melting Furnace (Colorado School of Mines)	36
Figure 3.2. Custom-made vacuum setup for encapsulation	36
Figure 3.3. Simulated temperature profile	42
Figure 3.4. Thermomechanical setup for in situ study	43

Figure 3.5. <i>In situ</i> thermomechanical treatment setup under the optical microscope.....	44
Figure 4.1. XRD Patterns of samples 1, 2, and 3.....	48
Figure 4.2. Magnetization versus temperature, $M(T)$ in $H = 100$ Oe.....	50
Figure 4.3. M-H curve for sample 1.....	51
Figure 4.4. Magnetization versus temperature, $M(T)$ at different H	51
Figure 4.5. Magnetic entropy change of sample 1 in a 20 KOe applied filed.....	52
Figure 4.6. Magnetic entropy change of sample 1 in a 50 KOe applied filed.....	53
Figure 4.7. Susceptibility vs.temperature.....	55
Figure 4.8. Susceptibility vs. magnetic field strength	56
Figure 4.9. TEM image after 20 minutes grinding.....	57
Figure 4.10. Optical micrograph of sample 3 without etching.....	58
Figure 4.11. TEM micrograph showing nanomodulations.....	59
Figure 4.12. EBSD imaging of sample 3.....	60
Figure 4.13. Ion channeling contrast image in FIB during <i>in situ</i> mechanical loading....	61
Figure 4.14. Optical images during theromicehnical treatement.....	64
Figure 4.15. Synchrotron powder X-ray diffraction patterns.....	70
Figure 4.16. Secondary electron image of the ball milled powder after 60 h.....	72
Figure 4.17. SEM image of the as-SPS sample.....	73
Figure 4.18. SEM images of the as-SPS sample afte annealing.....	74
Figure 4.19. XRD pattern of the ball milled powder after 60h.....	75
Figure 4.20. XRD pattern of the as-SPS sample.....	76
Figure 4.21. XRD pattern of the as-SPS sample after annealing.....	77
Figure 4.22. XRD pattern of the conventionally sintered sample.....	78

1. Motivation

The objective of this research was to investigate the structure and microstructure of an intermetallic heusler alloy in order to achieve higher anisotropy and magnetocaloric properties. Heusler alloys (A_2BC) have the unique property in which changes in temperature occur upon the application of an external magnetic field, enabling their use in many technologies, specifically refrigeration. Solid-state magnetic refrigeration can be applied in cooling devices like residential refrigerators, air conditioners in the automotive industry, and spot cooling in the electronics and space industries [1,2]. Currently, near room temperature technology for magnetic refrigeration requires the use of expensive rare earth elements including Gadolinium (Gd) [3,4]. Nickel-Manganese-Gallium (Ni-Mn-Ga), a Heusler alloy, is much cheaper than Gd alloys. In the last decade, significant scientific research have been carried out on these intermetallics, especially related to the refrigeration capacity, but there is a significant lack of understanding regarding the processing-microstructure-property relationship of this alloy.

Refrigeration and air conditioning consume a huge amount of electricity in the world. Existing technology consists of compressed gas refrigeration systems, which pumps millions of tons of greenhouse gases into the atmosphere. A solid-state Ni-Mn-Ga magnetocaloric based device has the potential for lower energy consumption while eliminating the reliance on gases that have a harmful impact on the atmosphere and the ozone layer. In addition, magnetic refrigeration can result in 20-30% greater efficiency than the existing refrigeration technology in the market. General Electric, GE, predicted that it could reduce energy consumption by 20% while having a quieter and greener refrigeration system [5].

As an example of the potential benefit of this technology, on 05/12/2013 on NASA Expedition 35 at the International Space Station, two astronauts were required to

perform a 5-hour and 30-minute space walk to repair a pump controller that was leaking ammonia coolant [6]. Maintaining pressurized coolant in a vacuum environment is very challenging and requires the use of significant resources and multiple backup systems. Magnetic refrigeration has the potential to streamline the entire cooling process and eliminate the use of dangerous compressed gasses. The future of the development of the technology is reliant on an improvement in the intermetallic alloys themselves.

In the USA, General Electric, Oak Ridge National Lab., Ames National Lab., and National Institute of Standards and Technology, NIST, have been involved in research on solid-state magnetic refrigeration systems. The U.S. Department of Energy has funded projects to develop the next generation of magnetocaloric materials. It is still in the early stages of research, but the hope is that new magnetic materials will further improve the competitiveness of solid-state refrigeration systems. In 2014, GE demonstrated a prototype of a magnetic refrigerator and announced that they will bring it to market by 2020 [7]. The demo is shown in Figure 1.1.

In India, China, France, Germany, Spain, and Japan, significant research funding have been focusing on magnetic refrigeration technologies. Cooltech Applications, founded in 2003 in France with 32 employees and four investors, is the first company in the world to industrialize and commercialize a magnetic refrigeration product. They made the first prototype in 2008, and spent 35 MEuro on R&D and industrialization projects.

Figure 1.1 GE's magnetocaloric refrigeration demo in 2014 [7].

The magnetic refrigeration market is predicted to reach US\$ 315.7 Million by 2022, which includes products (refrigeration, air conditioning, heat pumps) and applications (domestic, commercial, transportation & industrial) [8]. The key players in the market are Cooltech Applications (France), Astronautics Corporation America, General Electric, Whirlpool Corporation (U.S.), and Camfridge Ltd (U.K.).

Literature Review

Magnetocaloric Phenomenon

Magnetic refrigeration derived from magnetocaloric materials with high refrigeration capacity at low magnetic fields is a promising alternative to conventional compressed gas technologies. In Figure 1.2, the working mechanism of the magnetocaloric effect is illustrated. When an external magnetic field is applied, the magnetic moments inside the

material will be aligned in the direction of the magnetic field, increasing the temperature of the material (Figure 1.2a). The heat can be taken away by a heat sink (Figure 1.2b). Then, the thermal contact with the heat sink is broken so that the system is insulated (called adiabatic). The magnetic field is removed to allow a decrease in temperature of the material (Figure 1.2c). This can be used to cool down an adjacent system/material (Figure 1.2d). Finally, the magnetocaloric material temperature will return to its normal operating temperature, and the cycle repeats.

Figure 1.2. The four stages of a magnetic refrigeration cycle. The stages include (a) adiabatic (or insulated) magnetization, (b) remove heat, (c) adiabatic demagnetization, and (d) cool refrigerator contents [4].

In Figure 1.2a, the magnetization occurs adiabatically, so the drop in magnetic entropy is balanced by an increase in lattice entropy (vibration of atoms in the lattice), leading to an increase in the temperature of the sample. In Figure 1.2c, the adiabatic demagnetization causes an increase in the magnetic entropy of the sample and, in turn,

a decrease in its lattice entropy and temperature. For wide-spread implementation of this technology, the following four tasks should be considered: (1) the initial operating temperature should be near room temperature, (2) the applied magnetic field should be provided by a permanent magnet (for economic and safety reasons), (3) the entropy change should be as high as possible to increase the MCE, and (4) hysteresis during cyclic magnetization and de-magnetization should be minimal.

In relations to factor (1) & (3), Ni-Mn-Ga alloys exhibit both a structural transformation and a magnetic transition, resulting in a large magnetocaloric effect (MCE) near room temperature. In order to achieve enhanced efficiency or high refrigeration capacity, the entropy change should be as high as possible. To reach this goal, both the structural and the magnetic transition temperature should co-occur, resulting in increased entropy change due to both the magnetic transition (occurring at the Curie temperature) and the crystalline anisotropy change (due to structural transformation). Significant research has been conducted in Heusler alloys to understand the MCE and to tune the composition for co-occurrence of transition temperatures to near room temperature [2,4, 9,10]. What is lacking is a systematic, detailed study on microstructural effects on MCE.

Fabrication Methods of Ni-Mn-Ga Alloys

Arc-melting is the most commonly used method in the preparation of polycrystalline Ni-Mn-Ga alloys. It is simple and yields a homogenized sample. However, recently other methods including mechanical alloying and Spark Plasma Sintering (SPS) have also been utilized to synthesize polycrystalline Ni-Mn-Ga alloys [11,12,13]. Researchers have also been looking for new phases, different mechanical properties, changes in transformation temperatures and behaviors, and possible metastable structures. Tian et al. reported that samples made by SPS of ball-milled powders of an arc-melted alloy shows a similar martensitic transition to that of arc melted samples [11]. This processing

technique does result in a smaller grain size of sintered samples, and therefore the material shows lower martensitic transformation temperatures compared to conventional bulk alloys. In addition, the ductility of the sintered Ni-Mn-Ga alloy is higher than that of arc-melted alloys. In fact, the fracture strain in this sintered sample is 27%, a significant improvement over an 8% failure strain for arc-melted samples. One detriment of this process is that the magnetic field induced strain in the sintered sample is low due to the presence of more amount of grain boundaries, resulting from small grains.

Patrick et al. investigated Ni-Mn-Ga fabricated by SPS using the spark erosion method in cryogenic liquid argon and nitrogen [12]. SEM studies revealed that the morphology of particles depends on the cryogenic liquid and differs from spherical solid to hollow balls, which affect the sintered product and resulting magnetic properties.

Structural Study of Ni-Mn-Ga Alloys

Ni-Mn-Ga intermetallics have both magnetic shape memory and magnetocaloric properties [14]. Based on the chemical composition, $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ alloys can be paramagnetic or ferromagnetic at room temperature with a martensite and/or austenite structure. Martensitic structural transformation temperature (T_m) and magnetic transition temperature, i.e. Curie temperature (T_c) are strongly dependent on chemical composition [15]. Several studies reported that e/a (electron concentration of the outer shell to atom ratio) tunes T_m and T_c [16,17]. Different compositions of off-stoichiometric $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ alloys result in various T_m and T_c (see Table 1) [18,19]. Higher magnetic entropy change was reported when T_m and T_c come close together when e/a is around 7.7. It has been proposed that for co-occurrence of transitions, e/a should be approximately 7.7 [20, 21].

TABLE 1.1 e/a ratio, T_m, and T_c of Ni₂+xMn_{1-x}Ga alloys [20]

Nominal Composition	Composition by ICP-OES	e/a	T _m (K)	T _c (K)
Ni _{2.16} Mn _{0.84} Ga	Ni _{2.136} Mn _{0.798} Ga	7.612	260	328
Ni _{2.18} Mn _{0.82} Ga	Ni _{2.151} Mn _{0.771} Ga	7.625	262	319
Ni _{2.2} Mn _{0.82} Ga	Ni _{2.191} Mn _{0.732} Ga	7.656	328	320
Ni _{2.22} Mn _{0.78} Ga	Ni _{2.208} Mn _{0.737} Ga	7.665	288	305
Ni _{2.24} Mn _{0.76} Ga	Ni _{2.219} Mn _{0.689} Ga	7.680	324	324
Ni _{2.26} Mn _{0.74} Ga	Ni _{2.282} Mn _{0.633} Ga	7.727	445	325

It can be concluded from Table 1 that the Ni_{2.24}Mn_{0.76}Ga alloy with e/a=7.680 gives the same T_m and T_c at 324 K. In a separate study by Banic et al., it was reported that for Ni_{2.20}Mn_{0.80}Ga, e/a=7.650, T_m and T_c are around 334 K [16].

Magnetocaloric Properties

Two important parameters in the characterization of magnetocaloric materials are the adiabatic temperature change, ΔT_{ad} , and the magnetic entropy change, ΔS_M . ΔT_{ad} is the temperature change of the material when adiabatically magnetized and demagnetized. As previously stated, these two properties are related; changes in the magnetic entropy are balanced in the material by changes in lattice entropy causing a release of heat, defined by ΔT_{ad} . This change in the temperature relates to the magnitude of magnetization (order of magnetic moments) of the material. As a result, materials with large ΔS_M would give higher ΔT_{ad} .

ΔS_M and ΔT_{ad} are affected by the change in magnetization versus temperature $(\partial M/\partial T)_H$ and the specific heat capacity (C_p) of the material. ΔT_{ad} and ΔS_M can be calculated by the Maxwell relation:

$$\Delta T_{ad} = -\mu_0 \int_0^{H_{max}} \frac{T}{c_p} \left(\frac{\partial M}{\partial T} \right)_H dH \quad (1)$$

$$\Delta S_m = \mu_0 \int_0^{H_{max}} \left(\frac{\partial M}{\partial T} \right)_H dH \quad (2)$$

Here, μ_0 is the permeability of free space and H_{max} is the maximum applied magnetic field.

The magnitude of heat transferred between cold and hot reservoirs is the refrigerant capacity, RC:

$$RC(H) = \int_{T_{cold}}^{T_{hot}} \Delta S_M(T, H) dT \quad (3)$$

The magnetocaloric effect or refrigeration capacity is referred to as the area under the entropy change vs. temperature curve [4, 15, 24]. According to equations 2 and 3, in order to maximize MCE we should have high H_{max} , high $(\partial M/\partial T)_H$, and low C_p . For economic and safety reasons, magnetocaloric materials are required to operate under a moderate magnetic field, and C_p cannot be manipulated for a chosen alloy. This leaves only $(\partial M/\partial T)_H$; previous findings indicate that by changing the composition in $Ni_{2+x}Mn_{1-x}Ga$, co-occurrence of the structural and magnetic transitions near room temperature occur, leading to a higher entropy change and, as a result, an increased MCE [15, 17]. As stated earlier, it was proposed that for co-occurrence of transitions, e/a should be approximately 7.7 [22, 23]. While the co-occurrence of structural and magnetic transitions was a major achievement, further increase in $(\partial M/\partial T)_H$ is desired for commercial implementation. As such, it can then be concluded that a large MCE occurs at a temperature where $(\partial M/\partial T)_H$ is high, i.e. a sharp, discontinuous change in magnetization vs. temperature curve. In other words, the transition is preferred to be of the first order. In Ni-Mn-Ga alloys, there is a structural phase transition from martensitic to austenite, which is a first order transition. It has been reported that by modifying the chemical composition it is possible to bring the temperature of the magnetic transition

(Curie temperature, T_c) near the structural transition temperature (T_m) [20]. By decreasing T_c , the magnitude of the discontinuity of the M-T curve increases, resulting in higher ΔS_M . One possible avenue to increase MCE in this alloy is to increase magnetocrystalline anisotropy by motion of twin boundaries. In Ni-Mn-Ga alloys for shape memory applications, it was shown that mechanical stress and the magnetic field can reorient martensite variants by this motion [25,26].

Twin Boundaries, Anisotropy and Entropy Change

In Ni-Mn-Ga alloys, there are two types of anisotropies: the magnetocrystalline anisotropy and magnetoelastic anisotropy, which are related to the crystal structure and the applied/residual stress of material, respectively.

Magnetocrystalline anisotropy is independent of grain size and shape, and can be analyzed by measuring magnetization vs. field (M-H) curves along different crystallographic orientations. In fact, the magnetization reaches saturation in different applied magnetic fields in different crystal directions.

Magnetoelastic anisotropy is a result of the strain. During magnetization, crystals experience strain, and in turn, a change in dimension. This is called the magnetostriction effect. The inverse of this relationship is also true; applied strain can lead to a change in a magnetization, which is called the Villari effect. External stress can help create a preferred (easy) direction of magnetization [27].

Further investigation is required to define the relationship among MCE and the microstructure, martensitic transformation & crystal anisotropy. When $T_m < T_c$, upon applying a magnetic field or during heating, a low temperature, low symmetry ferromagnetic (FM) martensite phase transforms to a high temperature FM austenite phase with a cubic structure at T_m . When the temperature increases to the Curie temperature, the FM austenite phase transforms to the paramagnetic (PM) austenite

phase. As a result, upon applying the magnetic field the FM phase will transform to the PM phase, resulting in an enhancement of the MCE due to a higher increase in magnetic entropy change. As shown in Figure 1.3, along with the non-modulated tetragonal martensite phase there are least two other reported modulated structures, 5-layered modulated (5M) tetragonal and 7M orthorhombic/monoclinic with different strain levels [14].

Figure 1.3. Austenite and martensite structures of Ni_2MnGa . The atoms are: Light grey: Ni, white: Mn, black: Ga. (a) The $L2_1$ structure showing also the relationship with the tetragonal unit cell, which is also shown in part (b). (c) The tetragonal unit cell viewed from the top and (d) the 5 M and (e) 7 M modulated structures obtained by shearing the tetragonal cell [14].

As shown in Figure 1.4, there is a thermodynamic relationship between thermal, elastic, and magnetic variables in Ni-Mn-Ga intermetallic alloys [14]. We hypothesize that by

exploiting the mechanical and thermal properties, microstructure anisotropy will increase, leading to a higher entropy change.

Figure 1.4. Thermodynamic relation between thermal, elastic and magnetic variables. Magnetic shape-memory properties arise from the cross magnetic–elastic variable response. Magnetocaloric and elastocaloric properties arise, respectively, from the interplay between thermal and magnetic and thermal and elastic variables [14].

Magnetocaloric Effect of Ni-Mn-Ga Alloys

For the first time in 2000, Hu et al. reported MCE in Ni–Mn–Ga alloys, for an applied field below and above 1 T, based on a martensitic transformation and a magnetic transition near 197 and 290 K, respectively [28,29]. In 2003, Pareti et al. investigated the magnetic properties of $\text{Ni}_{2.15}\text{Mn}_{0.85}\text{Ga}$ and $\text{Ni}_{2.19}\text{Mn}_{0.81}\text{Ga}$. In the latter, the martensitic structural transformation and the magnetic transition occur simultaneously. With a magnetic field between 0 to 1.6 T, the magnetic entropy change was 20 J/kg K around 362 K, while

ΔS_M was 5 J/kg K around 310 K when only the structural transition occurs (Figure 1.5) [15].

Figure 1.5. Magnetic entropy change, ΔS_m , as a function of the temperature. The magnetic field varies between 0 to 1.6 T, for: (a) $\text{Ni}_{2.15}\text{Mn}_{0.85}\text{Ga}$ and (b) $\text{Ni}_{2.19}\text{Mn}_{0.81}\text{Ga}$ [15].

Overlap of the Magnetic Transition and Structural Transformation

Among the investigations focused on changing the composition to yield higher entropy change near room temperature at low magnetic field, in 2011 Zhang et al. reported a maximum entropy change of -1.4 J/kgK at 355 K at 5 kOe (0.5 T) of a $\text{Ni}_{51}\text{Mn}_{29}\text{Ga}_{20}$ thin film with $e/a = 7.7$ and a thickness of 250 nm [17]. This entropy change is 35% larger than that of a Gd thin film -0.91 J/kg K at 284 K- with a thickness of 40 nm at 6.2 kOe [18]. It is still low, but it shows a potential in spot cooling applications including micro-scale refrigerant devices at low magnetic fields. Khan et al. reported an overlap of magnetic transition and structural transformation at 350 K, which yielded a magnetic entropy change of -66.2 J/kgK in an applied field of 50 kOe in $\text{Ni}_{0.19}\text{Mn}_{1.89}\text{Ga}$ [19].

Effect of Thermal Cycling

In 2012, Booth and Majetich reported the effect of repeated thermal cycling on the MCE in $\text{Ni}_{54.3}\text{Mn}_{20.1}\text{Ga}_{25.6}$ [30]. As seen in Figure 1.6, the magnetic entropy change is higher at -10.9 J/kg K and -9.4 J/kg K in an applied field of 20 kOe for post-thermally cycled samples during heating and cooling, respectively. The transition temperatures occur at

about 340K in heating and 331K in cooling. Although the magnetic entropy change increased, the peak width decreased, and in turn, the area under the curve, i.e. refrigeration capacity, remained almost constant. Nonetheless, this is an important result, as it shows there is a significant influence of magnetic properties as a function of thermal history.

Figure 1.6. Magnetic entropy change of $\text{Ni}_{54.3}\text{Mn}_{20.1}\text{Ga}_{25.6}$ as a function of temperature. The entropy change calculated from heating and cooling isotherms, before and after 37 thermal cycles through the martensitic transformation measured in a 20 kOe applied field [30].

Effect of Isobaric Thermal Cycling

In 2013, Giri et al. reported that thermal cycling under compressive stress can enhance the magnetic entropy change [31]. The samples were thermally cycled 8 times between 293K and 373K under a compressive stress of 20MPa. The results indicate that the magnetic entropy change increased as much as 79% for sample $\text{Ni}_{2.16}\text{Mn}_{0.84}\text{Ga}$ as shown in Figure 1.7.

Figure 1.7. Magnetic entropy change vs. temperature for $\text{Ni}_{2+x} \text{Mn}_{1-x} \text{Ga}$. The magnetic field change is 7 T [31].

It is important to note that both the peaks width and height increased with thermomechanical treatment. Also important to note is that Giri et al. did not report any information related to the crystallographic texture as a function of thermomechanical treatment.

Effect of High Pressure in Magnetocaloric Properties of Ni-Mn-Ga

A main challenge in fabrication of a reliable magnetocaloric device is reducing the thermal and magnetic hysteresis losses. Magnetic transition at T_c is a thermodynamically second-order transition which take place continuously, while structural transformation at T_m is a first order transition which occurs abruptly. The thermal hysteresis emanates from the first-order structural transition, i.e martensitic phase transformation around T_m . This means that the structural transformation does not occur at the same temperature during cooling and heating. In other words, the heating and the cooling sections of the magnetization curve, M-H, are separated by the hysteresis. In addition, the thermal hysteresis causes that the entropy change curves, in ΔS_m vs T plot, take place at different temperatures during cooling and heating. The magnetic hysteresis is also a problem in materials with first-order transition [4].

It was reported that by applying extreme pressure it is possible to almost eliminate the magnetic hysteresis in $\text{Ni}_{2.208}\text{Mn}_{0.737}\text{Ga}$ as can be seen in Figure 1.8 [20]. By applying hydrostatic pressure from $P=0$ to 8 kbar, martensitic transformation temperature (T_m) and Curie temperature (T_c) increased by dM_s/dP of 0.6 K/kbar and dT_c/dP of 0.46 K/kbar, respectively, while the magnetic entropy change dropped slightly from 96 J/KgK to 86 for $\text{Ni}_{2.208}\text{Mn}_{0.737}\text{Ga}$ (see Figure 1.9). In addition, the temperature of the entropy change peak increased about 6 K from 291 K at $P=0$ to 297 K at $P=8$ kbar, respectively, as shown in Figure 1.9. There was a large magnetic hysteresis in M-H curve at $P=0$, which disappeared at $P=8$ Kbar. However, they did not report any phase transformation and structural change in the alloy.

Figure 1.8. Magnetic isotherms at $P=0$ and $P=8$ kbar. The temperature ranges from 279 to 303 K (a) and from 287 to 292 K (b at $P=0$ kbar and from 290 to 320 K (a) and from 295 to 300 K (b) at $P=8$ kbar [20].

Figure 1.9 Temperature dependence of the isothermal magnetic entropy change [20].

Pressure also could be used to tune the martensitic transformation temperature, Curie temperature, and magnetic properties of magnetocaloric materials. In a separate research, hydrostatic pressure ($P=0$ to 12 kbar) was applied to investigate martensitic transformation and magnetocaloric properties in $\text{Ni}_{50-x}\text{Mn}_{37+x}\text{Sn}_{13}$ Heusler alloy [32]. For $x=2$, there was about a 3.1 K/kbar and 0.3 K/kbar change of the martensitic transition and Curie temperature with pressure, respectively. The results from M-T curve of this alloy indicates that the hydrostatic pressure did not affect the thermal hysteresis. Figure 1.10 shows the isothermal magnetization curves, M-H, which indicate that the magnetization decreases with an increase in pressure.

Figure 1.10. Isothermal magnetization curves for $\text{Ni}_{50-x}\text{Mn}_{37+x}\text{Sn}_{13}$ at different pressures [32].

Figure 1.11 shows magnetization vs. temperature at different pressures in an applied field of 50 kOe. This clearly shows the changes in the magnetization values with pressure in the low temperature phase, martensite, and high temperature phase, austenite. For instance, magnetization of austenite decreased 20 emu/g at a pressure of 8 kbar in $\text{Ni}_{50-x}\text{Mn}_{37+x}\text{Sn}_{13}$ alloy with $x=2$.

Figure 1.11. Thermomagnetic curves for $\text{Ni}_{50-x}\text{Mn}_{37+x}\text{Sn}_{13}$ at different pressures [32].

Magnetic entropy change vs. temperature plots, at different pressures, are given in Figure 1.12, which indicates an increase in temperature and a decrease in entropy as the pressure increases. At ambient pressure, the entropy change was 34 J/kgK, while it decreased to 22.5 J/kgK at $P = 8$ kbar in $\text{Ni}_{50-x}\text{Mn}_{37+x}\text{Sn}_{13}$ with $x=3$.

Figure 1.12. Temperature dependence of the magnetic entropy for $\text{Ni}_{50-x}\text{Mn}_{37+x}\text{Sn}_{13}$ [32].

Mañosa et al. reported caloric effect only by applying high pressure- barocaloric effect- in order to tune the martensitic transformation temperature and Curie temperature [33]. Maximum entropy change of 24.4 J/kgK was obtained under a hydrostatic pressure of 2.6 kbar in $\text{Ni}_{49.26}\text{Mn}_{36.08}\text{In}_{14.66}$. The temperature dependence of the entropy change attained by hydrostatic pressure are shown in Figure 1.13.

Figure 1.13. Barocaloric effect as a function of temperature [33].

In a separate study, the entropy change decreased from 19.2 to 6.04 J/kgK while pressure increased from 0 to 9.69 kbar in Ni_2MnGa . In off-stoichiometric $\text{Ni}_{1.85}\text{Mn}_{1.15}\text{Ga}$, the entropy change decreased from 8.9 to 1.27 J/kgK, while pressure increased from 0 to 7.4 kbar as can be seen in Figure 1.14 [34]. High pressure causes a decrease in the magnetization difference between the martensite and austenite phases. This results in a decrease in the magnetic entropy change [32]. All results show that high pressure caused a decrease in the magnetic entropy change.

Figure 1.14. Magnetic entropy change in Ni_2MnGa and $\text{Ni}_{1.85}\text{Mn}_{1.15}\text{Ga}$ [34].

Higher pressure was also applied to investigate the structural change in Heusler alloys. High-pressure synchrotron X-ray diffraction was carried out on Ni_2MnGa at different pressures of 7.3 to 30.6 GPa [35]. The results exhibited no phase transformation (see Figure 1.15). The reason could be that they started from a very high pressure, 7.3 GPa. Structural transformations could occur in lower pressures. There is a lack of structural study to correlate the changes in magnetic properties, due to high-pressure, to structural and phase transformations.

Figure 1.15. High-pressure synchrotron X-ray diffraction patterns of Ni_2MnGa . The unit is GPa [35].

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2. Hypothesis

The goal of this research is to investigate the following hypothesis:

Hypothesis: *The combination of thermomechanical treatment and in situ imaging can result in controlled twin boundary movement in Ni₂MnGa intermetallics, resulting in higher magnetocrystalline anisotropy and increased refrigeration capacity.*

In this research, synthesis and characterization of the single phase martensitic alloy at room temperature was completed. By taking advantage of the magnetic shape memory/magnetostrictive nature of Ni-Mn-Ga alloy, the study of the microstructure under stress and pressure was completed. It was determined that prior heat treatment and mechanical history could play a key role in the response of this material in a magnetic field by affecting the twin boundaries and reorientation of martensitic variants.

In Figure 2.1, a schematic EBSD mapping of macro and micro twin boundaries is exhibited. The Figure 2.1 represents the possible alignment of twin boundaries in a polycrystalline sample. By applying compression, region A shrinks to the left, and region B expands at the expense of region A. This can be explained by the fact that region B has the shorter lattice parameter c (z -axis) along the compression direction. This “training process” has been applied in the past on Ni-Mn-Ga single crystals and polycrystalline alloys to increase the shape memory effect and can be completed by applying a magnetic field or compressive stress along different preferred directions [1, 2]. A successful training process in single crystals can result in single variant twin

boundaries, i.e. more texture. Motion of twin boundaries will result in anisotropy enhancement.

Figure 2.1. A schematic EBSD mapping showing macro and micro twin boundaries: before and after compressive stress.

Three different *in situ* techniques were completed to analyze the four major factors influencing the performance of magnetocaloric materials defined in the previous section. First, the development of a novel *in situ* mechanical loading inside a focused ion beam microscope was completed to correlate the external mechanical loading to twin boundaries movement. Second, *in situ* thermomechanical treatment under an optical microscope was completed to investigate the addition of variations in temperature on the microstructure. Finally, *in situ* high pressure synchrotron X-ray diffraction experiments were completed to study the influence of high pressures on the structural transformation. In addition, we attempted to synthesize the Ni-Mn-Ga alloy via spark plasma sintering method from starting materials, for the first time, to understand the phase evolution during sintering and annealing.

Research outline

The plan to test the validity of hypothesis consists of eight stages:

1. Alloy Synthesis
2. Homogenization
3. Structural and Microstructural Characterization
4. Magnetic Measurements
5. *In Situ* Mechanical Experiments Inside FIB
6. *In Situ* Thermomechanical Experiments under an Optical Microscope
7. *In Situ* High-Pressure X-ray Diffraction
8. Mechanical Alloying and Spark Plasma Sintering (SPS)

These steps are briefly described below.

Alloy Synthesis

An arc melting furnace under argon atmosphere was used to prepare $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ ingots with $x = 0$ to 0.26 , using Ni, Mn, and Ga precursors with the purity of 99.99%. The hearth of the furnace was water-cooled copper, which allowed for directional solidification to favor columnar grain growth. Each sample was mechanically pressed, and one time melting and three times remelting process was completed to ensure all materials are mixed and melted.

Homogenization

Two homogenization procedures were used to study the influence of atmosphere on output composition. One portion of the samples were sealed in quartz ampoules filled with argon and homogenized at 1000°C for 3 days. Another portion were homogenized in vacuum. At the end of the homogenization process, samples were quenched in iced water.

Structural and Microstructural Characterization

The chemical composition of each alloy was determined using energy dispersive x-ray spectroscopy (EDS). Samples were subjected to grinding by mortar and pestle, and the structure was verified using an X-ray diffractometer (XRD). A Transmission electron microscope (TEM) was used to investigate the samples. Electron backscatter investigation was carried out in a focused ion beam (FIB) microscope equipped with electron backscatter detector (EBSD).

Magnetic Measurements

To determine Curie temperature, T_c , magnetization versus temperature, $M(T)$, was measured at magnetic field strength, H , of 100 Oe. Magnetization versus magnetic field strength, $M(H)$, was also measured at four different temperatures of 300, 325, 350, and 375K. Magnetization versus temperature, $M(T)$, were also measured at 100, 10,000, 20,000, and 50,000 Oe to give required data to calculate magnetic entropy change.

***In Situ* Mechanical Experiments Inside FIB**

A micro-load frame (SEM Tester 1000 from MTI Instruments) was used to mechanically load the samples to modify the microstructure within the chamber of a JEOL 4500 dual beam FIB; a schematic of the stage is shown in Figure 2.2. The effect of mechanical loading on the microstructural behavior of the martensite phase was studied.

Stage Specifications**Load Capacity**

4450N

Load Cell Accuracy $\pm 0.2\%$ **Max. Crosshead Travel**

28.5mm

Linear Scale Accuracy

20 mm

Loading TypesTension, Compression,
Bending, Fatigue

Figure. 2.2. A schematic of the SEM Tester 1000.

***In Situ* Thermomechanical Experiments Under an Optical Microscope**

Thermomechanical treatment was carried out by a lab-made compression setup with electrical resistance heating elements mounted inside the compression blocks. The microstructure was studied *in situ* under an optical microscope.

***In Situ* High-Pressure X-ray Diffraction**

Arc melted samples were homogenized in the furnace, and then ground by mortar and pestle. The resultant powder was annealed at 500°C for 12 h, in an argon atmosphere in a sealed quartz tube, to release the strain induced during grinding. A diamond anvil cell (DAC) with culet size of 1000 μm was used. A schematic of a DAC is shown in Figure 2.3. The force is applied to the sample placed between the small tips of the diamonds and the metallic gasket [3]. Silicone oil was used as a pressure transmitting medium in order to create quasi-hydrostatic conditions. The sample was subjected to pressure from 0.25 to 2.2 GPa in the DAC in a synchrotron facility. High pressure synchrotron X-ray diffraction experiments were carried out at Argonne National Lab and UC Berkeley National Lab.

Figure 2.3. A schematic of a diamond anvil cell [3].

Mechanical Alloying and Spark Plasma Sintering (SPS)

Mechanical alloying was carried out in a planetary ball mill in a tungsten carbide coated vial with tungsten carbide balls with diameter of 5 mm. A Spark plasma sintering furnace, SPS 10-4 Advanced Technology (see Figure 2.4), was used to sinter ball milled sample at 875°C and 50 MPa for 8 minutes and with 100°C/min heating rate in a graphite mold. As-sps bulk specimen had a diameter of 20 mm and height of 3 mm, and was made of 8 g of powder. In addition, bulk specimens were also prepared by uniaxial press of milled sample at room temperature. Both as-SPS and uniaxially pressed sample were annealed at 1000°C for 18 h in vacuum.

Figure 2.4. Thermal Technologies 10-4 Spark Plasma Sintering Furnace.

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3. Experimental

Materials

High purity metals in the form of chips, powders, and rods were used for alloy synthesis in this study. The list and specifications of these metals are shown in Table 3.1.

Table 3.1. Specifications of materials used for alloy synthesis

Metal	Specification as provided by vendor	Vendor
Mn	Chips, 99.99%	Crescent Chemicals
Mn	Powder, 99.99%	Aldrich
Ni	Powder, 99.99%	Aldrich
Ga	99.99%	Aldrich
Ni	Rod, 99.99%	Aldrich

Alloy Synthesis

At the beginning, three different alloys with three compositions of $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ with $x = 0$ to 0.26 were prepared by arc melting. Samples were sealed in quartz ampoules filled with argon and homogenized at 1000°C for 3 days. Some samples were also homogenized in vacuum. At the end of the homogenization process, samples were quenched in iced water. Arc melting furnaces is shown Figure 3.1.

Encapsulation and Homogenization

Sample 1 was homogenized at 1000°C for 3 days in vacuum. Samples 2 and 3 were sealed in quartz ampoules filled with argon and homogenized at the same temperature for the same time. Foils of zirconium (99.8% pure, Alfa Aesar) were placed inside the quartz tubes to act as a sacrifice to absorb the oxygen impurities in argon. For homogenization, the samples were heated to 1000°C at a heating rate of 10°C/min and kept at that temperature for 72 hours, then cooled in the furnace to 300°C. At the end of

the homogenization process, all samples were quenched in iced water. The custom-made setup for vacuum and argon purging used for encapsulation is shown in Figure 3.2.

(a)

(b)

Figure 3.1. Arc Melting Furnace (Colorado School of Mines).

Figure 3.2. Custom-made vacuum setup for encapsulation.

Heat Treatment

A box furnace and a tube furnace, were used to carry out homogenization of encapsulated as-cast ingots, annealing the encapsulated milled samples, and annealing/sintering of as-SPS sample/ green pellet.

Wire-EDM

Test specimens with the dimension of 3 mm x 3 mm x 3 mm were machined from the arc-melted ingots using a wire electrical discharge machine (Wire-EDM) in order for performing *in situ* mechanical and thermomechanical experiments, respectively. The Wire-EDM was also used to cut thin slices of sample in order for magnetic measurements.

Diamond Anvil Cell (DAC)

A diamond anvil cell (DAC) with culet size of 1000 μ m was used. Silicone oil was used as a pressure transmitting medium in order to create quasi-hydrostatic conditions. A small amount of the sample was loaded into the hole in the DAC stainless steel gasket preindented to a thickness of 100 μ m, along with a small ruby chip at the center of the sample. The sample pressures were calibrated and monitored using the ruby (R1) fluorescence method [1]. The sample was subjected to pressure from 0.25 to 2.2 GPa in the DAC in the synchrotron facility.

Spark Plasma Sintering (SPS)

Spark plasma sintering (SPS) is a promising technique for sintering of oxide, ceramic, and powders. Due to simultaneous application of pressure, electrical current, and rapid heating rate, SPS offers better densification of particles at a temperature lower than that of conventional sintering methods. At the same time, due to shorter sintering time, SPS retains the powder size and structure, limiting grain growth and thus, results in improved mechanical properties. Three different driving forces work simultaneously during spark

plasma sintering. They are the (1) rapid heating rate, (2) presence of electric field, and (3) application of pressure. The heat is generated by resistive or Joule heating in the case of SPS. Extremely high heating rate in SPS causes highly non-uniform temperature distribution. Such localized heating helps in accelerated thermal diffusion at particle surface, local melting within inter-particle contact areas, and also creates thermal stresses which enable dislocation creep. Thus, spark plasma sintering by-passes the initial stage of surface diffusion, as in case of conventional sintering process, and achieves accelerated densification by early activation of consolidation diffusion mechanisms, including grain boundary and lattice diffusion and power-law dislocation creep. Apart from aiding in Joule heating, the electric field also helps in mass transport by increasing point defects and decreasing the activation energy for migration of defects. The electric field has also been reported to produce plasma by inter-particle discharging that generates a cleaning effect on particles surface, resulting into enhanced sintering. Application of pressure in SPS helps in particle rearrangement, destruction of agglomerates and better surface contact between particles. Further, application of pressure generates stress on the particle surface in contact, which results in the lowering of chemical potential of diffusing and thus easy diffusion at lower temperatures. In some cases, application of pressure can cause some amount of plastic deformation that aids the densification [2-4].

The Ni, Mn, and Ga precursors with the purity of 99.99% were weighed based on the ratios of previous studies defined in the previous section in $\text{Ni}_{2.16}\text{Mn}_{0.84}\text{Ga}$ alloy and mixed for 60 h in a planetary ball mill. The obtained precursor after milling was sintered by the SPS technique at 875°C and 50 MPa for 8 minutes and with 100°C/min heating rate in a graphite mold. The consolidated bulk (as-SPS) specimens had a diameter of 20 mm and height of 3 mm, and was made of 8 g of powder. In addition, bulk specimens

were also prepared by uniaxial press at room temperature. Both as-SPS and uniaxially pressed sample were annealed at 1000°C for 18h in vacuum.

Ball Milling

A planetary ball mill was used to mill the mixture of starting material. The vial was coated by tungsten carbide, and balls were made of tungsten carbide with diameter of 5 mm.

Uniaxial Press

A uniaxial press was used to prepare green pellets for arc melting furnace. In addition, it was used to press milled-starting materials for sintering.

Metallographic Sample Preparation

For microstructural studies, samples were mechanically ground with 120, 240, 400, and 600 SiC papers. Samples were then polished by slurry of alumina particles of 1, 0.3, and 0.05 μm . After polishing, some samples were etched in Nital solution (5 vol.% Nitric acid in Ethanol) in order to reveal grain boundaries under an optical microscope.

Vibratory Polishing Machine to Prepare Samples for EBSD

A Buehler VibroMet 2 polisher as a vibratory polishing machine was used to prepare samples for conducting EBSD experiments at Colorado School of Mines.

Instrumental Characterization

Scanning Electron Microscopy (SEM) and Dispersive Spectroscopy (EDS)

A JEOL JSM-6330F Field Emission Scanning Electron Microscopy (FEG-SEM) equipped with Energy Dispersive Spectroscopy (EDS) was used to study the microstructure and chemical composition of the samples. Accelerating voltages of 20 and 25 kV were used.

X-ray Diffraction (XRD)

X-ray diffraction experiments were carried out by a Bruker GADD/D8 X-ray system with Apex smart CCD detector with $\lambda=0.71073 \text{ \AA}$ of Mo-K α as a rotating anode. By comparing the JCPDS cards and observed peaks, the phases present in each sample were determined. ICDD PDF+ 2015 database from the International Center for Diffraction Data was used. The Match 3.1.1 software was used to correlate peaks and database. In Table 3.2, the JCPDS cards which were used as a reference for the analysis, are given.

Table 3.2. JCPDS No. for different compositions

Chemical formula	JCPDS No.	Structure
Ni	01-077-9326	Cubic
Mn- α	00-032-0637	Cubic
Ga	00-005-0601	Orthorhombic
Ni ₂ MnGa	00-050-1518	Cubic
Ni ₂ MnGa	01-074-8832	Tetragonal
Ni _{2.88} Mn _{0.16} Ga _{0.96}	04-013-9295	Cubic
Ni ₂ MnGa	05-001-0330	Orthorhombic
Ni ₂ MnGa	04-016-3020	Tetragonal
Ni _{2.16} Mn _{0.84} Ga	04-008-1270	Tetragonal
MnO	00-007-0230	Cubic

Magnetic Measurements

Magnetic measurements were performed at National High Magnetic Field Lab in Tallahassee, FL. A Vibrating Sample Magnetometer, VSM, was used to perform $M(T)$ at $H=100$ Oe, $M(H)$ at different temperatures, and $M(T)$ at different magnetic fields.

High Pressure Synchrotron X-ray Diffraction

High pressure synchrotron X-ray diffraction experiments were carried out at Argonne National Lab and UC Berkeley National Lab. The arc melted and then homogenized sample ground by mortar and pestle. The resultant powder was annealed at 500°C for 12 h in an argon atmosphere in a sealed quartz tube to release the strain induced during grinding. X-ray diffraction pattern was collected using X-rays of wavelength of $0.4132 \text{ \AA}$ on the heat treated sample at ambient pressure. The sample was subjected to pressure from 0.25 to 2.2 GPa in the DAC in synchrotron facility. Powder X-ray diffraction patterns were collected using X-rays of wavelength of $0.4959 \text{ \AA}$ at the mentioned pressures. At the end, X-ray diffraction pattern was collected using X-rays of wavelength of $0.4132 \text{ \AA}$ on the released sample at ambient pressure. The exposure times varied between 60 and 300 s. The recorded 2D diffraction images were integrated with FIT2D45 [5].

***In Situ* Mechannical Treatment inside FIB**

A JEOL JIB-4500 dual beam focused ion beam (FIB) equipped with micro-load frame (SEM Tester 1000 from MTI Instruments) was used to perform the *in situ* mechanical testing. A liquid Galium Ion beam was used to image the microstructure while the sample was loaded over time. A microload frame (SEM Tester 1000 from MTI Instruments) is used to mechanically treat the samples to modify the microstructure within the chamber of the JEOL dual beam FIB.

***In Situ* Thermomechanical Treatment**

A lab-made *in situ* thermomechanical setup under an optical microscope was built. We used compressed air and a cylinder to apply compression. The maximum compressive stress which the setup could apply on the sample was calculated about 14.4 MPa. Aluminum machined and prepared blocks were fabricated for the compression setup. Each block had two holes, one for the electrical resistance heating element and another for cooling water circulation. The temperature profile of the blocks was simulated by COMSOL 4.0 (see Figure 3.3). Final design was modified to reach higher temperature.

Figure 3.3 Simulated temperature profile.

A k-type thermocouple was attached to the top of the sample to monitor the temperature. The setup was mounted under an optical microscope to allow for an *in situ* study of the

influence of thermomechanical loading on the microstructure. Figure 3.4 and 3.5 show both the thermomechanical design and setup and the complete test setup.

Figure 3.4. Thermomechanical setup for *in situ* study.

Figure 3.5 *In situ* thermomechanical treatment set-up under the optical microscope.

EBSD Experiments Inside FIB

A FEI Helios Nanolab 600i FIB equipped with electron backscatter detector (EBSD) was employed to study macro twin and micro twins at Colorado School of Mines.

Transmission Electron Microscopy (TEM)

Powder preparation was performed to conduct TEM on powders. The JEOL 4500 Focused Ion Beam was used to prepare TEM samples, using the sample lift-out method [6,7]. TEM experiments were completed using a FEI CM-200 operating at 200 kV.

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4. Results and Discussion

Structure and Chemical Composition of Alloys

Sample 1 was homogenized at 1000°C for 3 days in vacuum. Results showed a loss in Mn of 4.3 at% during homogenization in vacuum. Samples 2 and 3, homogenized in quartz ampoules filled with argon, did not show any measurable change in composition. Table 4.1 shows EDS results of the samples after homogenization.

Table 4.1. Chemical composition of alloys based on EDS

Sample no.	Composition based on EDS results	Atomic Percent (%)		
		Mn	Ni	Ga
1	Ni _{2.26} Mn _{0.65} Ga	16.67	57.82	25.51
2	Ni _{1.94} Mn _{0.77} Ga	20.80	52.30	26.90
3	Ni _{2.13} Mn _{0.82} Ga	20.86	53.89	25.25

Changes in structure in ground and ball milled samples were monitored using XRD, and results are shown in Figure 4.1. Sample 1 (Ni_{2.26}Mn_{0.65}Ga) was subjected to 5 minutes grinding by mortar and pestle and 30 minutes of vibrational ball milling. XRD peaks in Figure 4.1 correspond to tetragonal martensite with lattice parameters of $a=3.832$ and $c=6.628$ Å. It was observed that ball milling induced a phase transformation to a cubic structure with $a=3.648$ Å. The obtained lattice parameter is not close to the well-known lattice parameter of austenite structure which is 5.825 Å. So far, two reports confirm the austenite structure with similar lattice parameter as a result of phase transformation induced by milling. Our results correlated well with a study by Tian et al., who also reported a FCC structure with $a=3.665$ Å for Ni_{2.29}Mn_{1.31}Ga resulting from vibration ball milling for 4 h [1]. In addition, Wang et al. reported similar lattice parameter of 3.675 Å in Ni₂MnGa as a result of milling [2]. Similar phase transformation from tetragonal (lower

symmetry structure) to cubic (higher symmetry structure) was reported in the ball milled ZrO_2 , which can be ascribed to structural distortion due to the ball milling [3].

XRD patterns collected on sample 2 ($\text{Ni}_{1.94}\text{Mn}_{0.77}\text{Ga}$) after 5, 10, and 15 minutes grinding indicate that after 5 and 10 minutes grinding, sample 2 consisted of two phases including cubic ($a=5.804 \text{ \AA}$) and tetragonal ($a=3.905$ and $c=6.466 \text{ \AA}$). Co-existence of austenite and martensite was also reported by Banik et al [4]. The lattice parameter of cubic structure in sample 2 is different from austenite phase in sample 1, which results in different indexing of XRD pattern, accordingly. Increasing milling time to 15 minutes smoothed the XRD pattern, indicating introduced atomic disorder. In fact, a majority of the peaks faded away after 15 min milling, and the individual peaks cannot be distinguished, which means the sample did not maintain its crystallinity. The reason for this change in XRD pattern is structural distortion and atomic disorder due to defects generated by milling. These results match those of the literature, i.e. an increase in the grinding time induced atomic disorder [2,5,6].

Sample 3 ($\text{Ni}_{2.13}\text{Mn}_{0.82}\text{Ga}$) was single phase tetragonal martensite. XRD patterns of this sample after 20, 40, and 60 minutes grinding did not show a measurable change in phase, and increase in grinding time only broadened the peaks due to reduction in particle size, and induced stress. Lattice parameters of this tetragonal structure are $a=3.863$ and $c=6.536 \text{ \AA}$.

Figure 4.1. XRD Patterns of samples 1, 2, and 3.

Magnetic Measurements

Magnetic measurements were performed on three samples cut by wire EDM with the thickness of 0.127 mm with the mass of 4.13, 16, and 12.06 mg for sample 1, 2, and 3, respectively. Figure 4.2 exhibits magnetization vs. temperature data, $M(T)$, in $H = 100$ Oe for the three samples. The important thing to note is that it clearly shows Curie temperature, T_C . Normally, magnetic transition will be much broader in larger fields, as is typical for a ferromagnet. T_C was measured 371, 376, and 378K for samples 1, 2, and 3, respectively. Relatively lower T_C in sample 1 could be attributed to higher Ni and lower Mn content.

Figure 4.3 demonstrates magnetization vs. magnetic field strength, $M(H)$, at four different temperatures 300, 325, 350, and 375K for sample 1. With an increase in temperature, the magnetic moment (magnetization) decreases as expected, showing a reasonable evolution from the ordered state to the paramagnetic state. Figure 4.4 also shows magnetization versus temperature, $M(T)$ at 100, 10,000, 20,000, and 50,000 Oe. These data were used to calculate the entropy change versus temperature by the Maxwell relation. In fact, the isotherms were used to calculate the entropy change using numerical integration of the Maxwell relation through the following equation:

$$\Delta S_m = \mu_0 \int_0^{H_{max}} \left(\frac{\partial M}{\partial T} \right)_H dH \quad (1)$$

Temperature dependence of magnetic entropy change at 20 and 50 kOe are presented in Figures 4.5 and 4.6, respectively. The magnetic entropy change at $T_c=371$ K is -1.11 and -2.53 J/kg K at 20 and 50 kOe, respectively. This entropy change is a result of the magnetic transition at Curie temperature. These values are lower than that of Pareti et al., -4.9 J/kg K, of $Ni_{2.15}Mn_{0.85}Ga$ at 16 kOe [7]. Low amount of Mn could be one of the reasons for this considerably low entropy change.

Figure 4.2. Magnetization versus temperature, $M(T)$ in $H = 100 \text{ Oe}$.

Figure 4.3. M-H curve for sample 1.

Figure 4.4. Magnetization versus temperature, M(T) at different H.

Figure 4.5. Magnetic entropy change of sample 1 in a 20 kOe applied field.

Figure 4.6. Magnetic entropy change of sample 1 in a 50 kOe applied field.

There is also a peak at $T=323$ K in each of the Figures 4.5 and 4.6, which seems to be the temperature of the martensitic transformation. The magnetic entropy change at $T_m=323$ K is -0.48 and -1.46 J/kg K at applied field of 20 and 50 kOe, respectively. It can be seen that there is no overlap between martensitic transformation, at $T_m=323$ K, and magnetic transition, at $T_c=371$ K, in the entropy change vs. temperature curve. In other words, there was no co-occurrence of martensitic transformation and magnetic transition in $\text{Ni}_{2.26}\text{Mn}_{0.65}\text{Ga}$, which is the reason for the low magnetic entropy change. When $T_m < T_c$, upon heating the ferromagnetic martensite phase transforms to the ferromagnetic austenite phase at T_m . Then, the ferromagnetic austenite phase transforms to the paramagnetic austenite phase at T_c .

According to XRD results, sample 1 is composed of a martensite phase with a tetragonal structure, which transformed to an austenite phase with a cubic structure after 30 minutes ball milling. In other words, sample 1 was unstable, and could not maintain its crystal structure during milling, compared to sample 3. Magnetic field stabilizes the phase with higher magnetization, the ferromagnetic austenite phase in case of Ni-Mn-Ga, resulting in a decrease in the martensitic transformation temperature, T_m . It can be implied that during magnetization of sample 1, martensite easily transformed to austenite, i.e. structural transformation occurred at lower temperature.

Sample 1 was chosen for further analysis because it had lower $T_c=371$ K compared to sample 2 and 3, which is far from 315 or 335 K compared to the literature [28]. Based on the results and literature, another sample was made with an Ni content between sample 1 and 3 to determine if T_c decreases. Sample 4 was fabricated by arc melting and then homogenized. A slice of it with a thickness of 0.165 mm and a mass of 20.11 mg was prepared by Wire-EDM for magnetic measurements. Figure 4.7 shows the susceptibility versus temperature. Susceptibility, $\chi = M/H$, is the ratio of magnetization to magnetic

field. It is a measure of how magnetizable a substance can become in the presence of a magnetic field. As exhibited in Figure 4.7, T_c is 360 K, which is 10 K lower than sample 1. In Figure 4.8, susceptibility versus magnetic field strength, $\chi(H)$, is exhibited at four different temperatures 300, 325, 350, and 375K. With an increase in temperature, the magnetization decreased as expected. This result indicates that further investigations should be conducted to optimize Ni and Mn to have a lower T_c near room temperature. One possible reason that we could not achieve lower T_c is that we performed homogenization in argon atmosphere rather than vacuum. Based on our findings, in three days homogenization at 1000°C in vacuum, Mn evaporates which causes a decrease in magnetization, M , and Curie temperature, T_c .

Figure 4.7. Susceptibility vs. temperature.

Figure 4.8. Susceptibility vs. magnetic field strength.

Microstructural Analysis

A TEM micrograph of sample 3 after 20 minutes grinding is shown in Figure 4.9. The lattice parameters determined by electron diffraction pattern are $a=3.9254$, $c=6.4455$ Å, which are close to the previously mentioned X-ray diffraction results.

Figure 4.9. TEM image after 20 minutes grinding.

The optical microscopy image in Figure 4.10 shows visible macrotwins in different areas. Spear and wedge-like morphologies can easily be seen within the martensitic phase. Similar microstructure was reported by Matsuda et al. and Zhou et al. [8, 9].

Figure 4.10. Optical micrograph of sample 3 without etching. It shows macrotwins along with wedge and spear morphologies (indicated by arrows).

A TEM image of the sample 3, prepared by *in situ* FIB lift out, also shows nanomodulations with an average width of 23 nm and spacing of 28 nm, as exhibited in Figure 4.11. Similar martensitic modulations was reported earlier [10,11]. Figure 4.12a shows a superimposed EBSD inverse pole figure map with a SEM image using a secondary electron detector. Martensite variants and grain boundaries are visible. Microtwins within variants can be seen in the secondary electron image in Figure 4.12b. Since sample 2 showed phase stability as a function of applied stress, additional analysis was conducted on this sample to further investigate the relationship between microstructure and applied load. Previous research showed that a training process, i.e. reorienting the twin boundaries within martensite variants using external loading, in

single crystal, and polycrystalline NiMnGa alloys can result in a single variant twin boundaries. It can be performed by applying a magnetic field or compressive stress along different directions [12,13]. Gaitzsch et al. reported up to 8% strain in a polycrystalline Ni-Mn-Ga shape memory alloy only by mechanical training [13]. There is another report supporting this claim in polycrystalline NiMnGa shape memory alloys, monitored with EBSD before and after compression up to 30 MPa. The EBSD results confirmed the motion of twin boundaries towards being preferentially aligned parallel to the compression direction [14].

Figure 4.11 TEM micrograph showing nanomodulations.

Figure 4.12. EBSD imaging of sample 3. It shows a) EBSD inverse pole figure map overlaid onto secondary electron image b) secondary electron image. Figure (b) is an inset of Figure (a).

***In Situ* Mechanical Loading and Imaging Inside FIB**

FIB imaging was used to monitor the microstructure during compression tests for two reasons: increased contrast due to the ion channeling mechanism and reduced scan time compared to EBSD. Figure 4.13 shows the progression of the microstructure by FIB imaging of two specimens from sample 3.

Figure 4.13. Ion channeling contrast image in FIB during *in situ* mechanical loading. It includes: a) nominally parallel to twin boundaries (the marker in the upper left remains static for all three images), b) nominally orthogonal to twin boundaries

Uniaxial compression was applied in two directions with respect to directional solidification: nominally parallel to the twin boundaries and nominally perpendicular. As can be seen in Figure 4.13a, there is a gradual change in the angle from 18.2° to 13.0° with respect to vertical. This change in the angle was not observed when the sample was loaded nominally perpendicular to twin boundaries as shown in Figure 4.13b. The reason might be that in Figure 4.13a, martensite variants with indicated twin boundaries have shorter lattice parameter c (z -axis) along the compression direction. As a result, they can be moved easier than twin boundaries in Figure 4.13b [14,15].

***In Situ* Thermomechanical Treatment**

The sample was heated up to 180°C . Then, the pressure was applied, and the sample was cooled by water circulation via the two compression blocks. The microstructure was *in situ* monitored during heating and compression-cooling under an optical microscope connected to a screen. Figure 4.14 shows the twin boundaries on sample 1 from room temperature to 120°C . The microstructure did not change after compression and cooling. In Figure 4.14a, the faint twin structures can be observed. The twinings became significantly more pronounced topographically when temperature increased. This kind of the pronounced twin structure was reported due to heating [16]. The twin boundaries did not disappear as the temperature increased, meaning that the phase transformation from martensite to austenite did not occur due to heat dissipation.

In addition, the maximum compressive stress on the sample was about 14.4 MPa which is lower than the required stress, 30 MPa, to move twin boundaries in a Ni_2MnGa polycrystalline alloy.

30 μm

(a)

30 μm

(b)

30 μm

(c)

(c)

(d)

(e)

Figure 4.14. Optical images during thermomechanical treatment. The temperature ranges from a) room temperature, b) 45, c) 60, d) 80, e) 110, and f) 120 °C.

***In Situ* High-Pressure X-ray Diffraction**

There is one record in the literature on structural study of Ni-Mn-Ga alloy at high pressure by synchrotron X-ray diffraction [17]. Magnetic properties of Heusler alloys strongly depend on the Mn-Mn atomic distance and magnetic exchange interactions. If applied pressure changes the the Mn-Mn distance, magnetocaloric properties will be changed accordingly. On the other hand, the decrease in the Mn-Mn atomic distance may result in antiferromagnetic exchange interactions, which may affect the total magnetic moment [18].

In addition, there is one report which confirms high pressure eliminated the magnetic hysteresis as a hurdle towards commercialization of magnetocaloric Ni-Mn-Ga [19]. All changes in magnetic properties by pressure have structural reasons. Considering the above-mentioned items and the fact that in the industry applying high pressure is not very desirable when it exceeds 10 kbar (1GPa), we hypothesize that similar structural changes at ambient pressure could occur. It could occur using chemical pressure via doping by desired elements, which generates equivalent strain in the structure. This process is called: tuning of the structure by chemical pressure [20]. If the structure, after pressure release, returns to the initial structure at ambient pressure -reversible process- doping could help to maintain the high-pressure structure at the ambient pressure. On the other hand, if after pressure release, the structure does not return to its initial state, phase transformation is irreversible, which is more favorable since it does not require doping. In other words, high-pressure phase is quenchable.

Arc melted and then homogenized sample 3, $\text{Ni}_{2.13}\text{Mn}_{0.82}\text{Ga}$, ground by mortar and pestle. The resultant powder was annealed at 500°C for 12 h in an argon atmosphere to release the strain induced during grinding. Because two different wavelengths of X-rays were used to conduct the XRD experiments in synchrotron facility on samples under

pressure and at ambient pressure, in order to have a comparison and monitor phase evolution and change, unlike the other XRD patterns presented in this dissertation based on 2θ , the synchrotron XRD patterns are presented based on d-spacing. Figure 4.15a demonstrate the diffraction pattern of the sample before applying pressure, which includes tetragonal martensite as a major phase. Its peaks match with the peaks of $\text{Ni}_{2.16}\text{Mn}_{0.84}\text{Ga}$ (JCPDS No. 04-008-1270).

In Figure 4.16b, the XRD pattern of the sample under pressure of 0.25 GPa is exhibited. It can be seen that significant structural change happened compared to Figure 4.16a. In addition, it is obvious that under pressure of 0.25 GPa a considerable background evolved in XRD pattern presented in Figure 4.16b. Ni-Mn-Ga intermetallics consist of four allotropic modifications including cubic, tetragonal, orthorhombic, and monoclinic structures. Applying pressure can result in a structural symmetry change or a total structural change. When pressure increased from 0 to 0.25 GPa a phase transformation from tetragonal towards orthorhombic/monoclinic occurs. The highest intensity peak clearly split into two peaks and the rest of the peaks almost vanished.

Figure 4.16c illustrates the XRD pattern of the sample under pressure of 0.52 GPa. Increasing pressure caused a change in XRD peaks compared to the peaks at the pressure of 0.25 GPa. In Figure 4.16c, the background is less, compared to Figure 4.16b. From Figure 4.16d it can be concluded that the transformation is favored when the pressure increased from 0.52 to 1.50 GPa. In Figure 4.16e, the XRD pattern of the sample under pressure of 2.20 GPa is given. It can be observed that phase transformation is still going on with an increase of pressure from 1.50 to 2.20 GPa.

Considering the behavior of XRD patterns, it can be observed that a gradual structural transformation is occurring from ambient pressure to 2.2 GPa. Unfortunately, the XRD patterns do not have enough quality to be indexed. Further synchrotron XRD

experiments are required at different pressures to achieve more data to be able to index the peaks. Figure 4.16f shows the XRD pattern of the sample after pressure release. It is a different structure from Figure 4.16e which is the sample under a pressure of 2.20 GPa. It is also very different from Figure 4.16a which is the heat treated sample before undergoing pressure. This means that phase transformation at high pressure is irreversible in the sample.

Orthorhombic and monoclinic structures in Ni-Mn-Ga alloys are stable phases at low temperatures [21]. It is important to note that higher pressure could favor structures which are stable at lower temperatures. The coefficient of thermal expansion at a constant pressure is defined as below:

$$\alpha = 1/V(\delta V / \delta T)_P \sim 10^{-5} - 10^{-6} /K \quad (1)$$

Where, V is the volume, T is the temperature, and P is the pressure. A 1% volume change can occur if temperature changes 1000 K.

The isothermal compressibility at a constant temperature is defined as below:

$$\beta = 1/V(\delta V / \delta P)_T \sim 10^{-1} - 10^{-3} /GPa \quad (2)$$

It can be said that 1% volume change can occur if pressure of 1 GPa applies.

Applying a pressure of 1 GPa is more convenient than changing the temperature as 1000 K. This is the reason why applying high pressure is a better approach to manipulate the structure compared to cooling/heating.

Based on XRD patterns, we believe that high pressure caused a phase transformation from a tetragonal towards an orthorhombic/monoclinic structure. The magnetic moment of Mn and the overall magnetic moment are different in an austenitic Ni₂MnGa with cubic structure, a martensitic Ni₂MnGa with tetragonal structure, and a martensitic Ni₂MnGa with orthorhombic/monoclinic structure. The martensite phase with orthorhombic structure, 7M, has the same symmetry of the *Pnnm*, the 58th space group symmetry in

the International Tables for Crystallography [22,23]. Table 4.2 gives the magnetic moments of Mn and the total magnetic moment in different structures of Ni₂MnGa based on the *ab initio* calculations [24,25].

Table 4.2. Calculated magnetic moments on the atoms of Ni₂MnGa and the overall moments

Structure, Phase	Space group	Mn	Ni	Ga	Overall moment
		μ _B	μ _B	μ _B	(per formula unit) μ _B
<i>L2₁</i> , Cubic, Austenite	<i>Fm3̄m</i>	3.25	0.32	0.07	3.87 [24]
<i>L1₀</i> , Tetragonal, Martensite	<i>P4/mmm</i>				4.14 [25]
7M, Orthorhombic, Martensite	<i>Pnnm</i>	3.08	0.33	-0.07	3.26 [24]
		2.89	0.35	-0.07	
		2.41	0.39	-0.07	
		2.31	0.33	-0.06	

As Table 4.2 shows, there are four different moments for Mn in the orthorhombic structure, which is due to the different interatomic distances between Mn and its first neighbor. Tanaka et al. determined the mentioned interatomic distances in 7M structure, which are presented in Table 4.3 [24]. However, in the cubic Ni₂MnGa, there is only one interatomic distance between Mn and Ni, 0.25 nm.

As a fact, the lattice constant of the orthorhombic structure is also different from cubic and tetragonal structures. It is also reported that based on the local densities of states, DOS, the peaks of Mn are low and broadened, which matches to the behavior of those of nearest neighbors (Ni). In addition, based on DOS calculations, the four kinds of Mn

and their nearest neighbors have peaks at the same energy value. This means that the densities of states of Mn and Ni hybridize strongly. The hybridization enhances when the interatomic distances between Mn and Ni decrease, and DOS band broaden accordingly [24].

Table 4.3. The interatomic distance between four Mn and their nearest neighbors [24]

	Mn1	Mn2	Mn3	Mn4
Nearest neighbor	Ni1	Ni2	Ni3	Ni4
Distance (nm)	0.24	0.22	0.20	0.20
(theoretical)				

Applying pressure favors phase transformation from tetragonal to orthorhombic/monoclinic structure which has different interatomic distances of Mn-Ni. In other words, the pressure could be translated to a change in interatomic distances, leading to a change in magnetic properties at room temperature or above.

Mandal et al. reported that at $P=8$ kbar the large magnetic hysteresis almost disappeared in the $\text{Ni}_{2.21}\text{Mn}_{0.74}\text{Ga}$ alloy which was a mixture of martensite and cubic austenite at ambient pressure [19]. The pressure of 8 kbar is equivalent to 0.8 GPa. In our study, this pressure is between 0.5 and 1.5 GPa – Figures 4.15 c and d. The phase transformation and structural change occurred between 0.5 and 1.5 GPa could be the reason for the significant decrease in the magnetic hysteresis. Further investigations including high-pressure synchrotron XRD are required to obtain XRD patterns with higher quality to determine the lattice parameter and interatomic distances.

Figure 4.15. Synchrotron powder X-ray diffraction patterns. The samples are: (a) heat treated, (b) under pressure of 0.25 GPa, (c) 0.52 GPa, (d) 1.50 GPa, (e) 2.20 GPa, and (f) after pressure release.

Mechanical Alloying and Spark Plasma Sintering (SPS)

The mechanical alloying method was used to investigate the possibility to obtain a single phase $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$. SPS is a fast sintering method, which is expected to yield higher density as well as materials with enhanced properties and probably new phases which cannot be achieved by conventional pressing and sintering techniques.

According to my knowledge, there is no report in the literature, which synthesized Ni-Mn-Ga intermetallics by SPS or conventional sintering directly from the starting materials. There are several studies that reported SPS of groundsamples after preparation by arc melting [26,27, 28]. What is new in this work is trying to see if we can reach the off-stoichiometric $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ directly from the starting materials by SPS and without arc melting. We also compared the phase formation and evolution through the SPS method and the conventional pressing and sintering route.

The starting materials were milled in a planetary ball milling for 60 h in a tungsten carbide coated vial with tungsten carbide balls. Figure 4.16 shows the SEM image of the ball milled sample after 60 h. The image exhibits particles ranging from 1 to 10 μm .

Figure 4.16. Secondary electron image of the ball milled powder after 60h.

In Figure 4.17, a SEM image of the cross-section of a sintered particle in the as-SPS sample is given. The sintered layers can be seen, which is not observed in the as-SPS sample after annealing (Figure 4.18). The layered structure could be due to higher pressure during SPS compared to uniaxial press. The as-SPS sample has many porosities which can be seen in Figure 4.17.

Figure 4.17. SEM image of the as-SPS sample.

(a)

(b)

Figure 4.18. SEM images of the sample after SPS and annealing.

As given in Figure 4.19, the XRD pattern exhibits that the sample after 60 h ball milling includes Ni, Mn, and $\text{Ni}_{2.88}\text{Mn}_{0.16}\text{Ga}_{0.96}$. The XRD peaks of Ni and $\text{Ni}_{2.88}\text{Mn}_{0.16}\text{Ga}_{0.96}$ (JCPDS No. 04-013-9295) at 19.87, 22.84, 325.54, and 38.69°, are superimposed which is the reason for the wide peak width at these angles. The peak at 16° belongs to (111) crystallographic plane of MnO (JCPDS No. 00-007-0230). The highest intensity peak, 200, of MnO occurred at 18.6°, which contributed to the highest peak. There is no Ga after milling within the XRD accuracy.

Figure 4.19. XRD pattern of the ball milled powder after 60 h.

The XRD pattern of the as-SPS is exhibited in Figure 4.20. Based on the XRD results, there is no Mn and Ga in the as-SPS sample. Ni, Ni₂MnGa, MnO, and Ni_{2.88}Mn_{0.16}Ga_{0.96} are the existent phases. The Ni₂MnGa (JCPDS No. 05-001-0330) has the orthorhombic structure.

Figure 4.20. XRD pattern of the as-SPS sample.

Figure 4.21 shows the XRD pattern of the as-SPS sample after annealing at 1000°C for 18h in vacuum. This sample is comprised of tetragonal Ni₂MnGa (JCPDS No. 04-016-3020) and Ni_{2.88}Mn_{0.16}Ga_{0.96}. It is difficult to say whether or not Ni still remained in the sample. The intensity of the peaks, 002, 202, 123, marked by red color in Figure 4.21, belonged to orthorhombic Ni₂MnGa, diminished, compared to Figure 4.20.

Figure 4.21. XRD pattern of the as-SPS sample after annealing.

Finally, Figure 4.22 shows the XRD pattern of the uniaxially pressed sample and then sintered at 1000°C for 18h in vacuum. The sample consists of tetragonal Ni_2MnGa (JCPDS No. 04-016-3020) and $\text{Ni}_{2.88}\text{Mn}_{0.16}\text{Ga}_{0.96}$.

Figure 4.22. XRD pattern of the conventionally sintered sample.

The oxidation of Mn occurred in the ball milling process which was carried out in air. Ball milling was performed in 60 minutes periods with a 15-minute interval. The results indicate that:

1. High-energy ball milling for 60 h was not enough to form the final composition of $\text{Ni}_{2.16}\text{Mn}_{0.84}\text{Ga}$, but it was enough to mix and form $\text{Ni}_{2.88}\text{Mn}_{0.16}\text{Ga}_{0.96}$.
2. The Ni_2MnGa formation was favored in both SPS and conventionally sintered samples over the off-stoichiometric $\text{Ni}_{2.16}\text{Mn}_{0.84}\text{Ga}$.
3. The formation of single phase Ni_2MnGa requires more time and diffusion among constituents. Higher sintering temperature, increasing the time of sintering, and adding sintering aids may help the formation of a single phase Ni_2MnGa [29].

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5. Conclusion

The objective of this research was to develop a novel *in situ* mechanical treatment process on Ni-Mn-Ga Heusler alloy to manipulate the microstructure to increase anisotropy, which can lead to higher magnetocaloric properties. The first goal was to achieve a single phase martensite in order for *in situ* mechanical loading process. The twin boundary behavior under a compressive stress was studied by real time monitoring inside a focused ion beam microscope. Twin boundary movement depends on the direction of the compressive stress, and they tend to be aligned to yield maximum possible strain under compression.

$\text{Ni}_{2.13}\text{Mn}_{0.82}\text{Ga}$ yielded a single phase tetragonal martensite based on X-ray diffraction patterns. In sample 1 ($\text{Ni}_{2.26}\text{Mn}_{0.65}\text{Ga}$) with lower Curie temperature, the magnetic entropy change at $T_c=371$ K was calculated -1.11 and -2.53 J/kg K at 20 and 50 kOe, respectively. This entropy change was the result of the magnetic transition at Curie temperature. The magnetic entropy change at $T_m=323$ K was calculated -0.48 and -1.46 J/kg K at applied field of 20 and 50 kOe, respectively, which originated from martensitic structural transformation. There was no overlap between martensitic transformation, at $T_m=323$ K, and magnetic transition at $T_c=371$ K.

Uniaxial compression was applied in two directions with respect to directional solidification: nominally parallel to the twin boundaries and nominally perpendicular. There was a gradual change in the angle from 18.2° to 13.0° with respect to vertical. This change in the angle was not observed when the sample was loaded nominally perpendicular to twin boundaries. *In situ* thermomechanical treatment under optical microscope implied that the compressive stress was not enough to move twin boundaries. Although the twin structure was pronounced due to heating.

High-pressure synchrotron XRD results showed that a phase transformation from a tetragonal towards an orthorhombic/monoclinic structure from $P=0$ to $P= 2.2$ GPa occurred. XRD pattern analysis of the as-SPS sample indicated that the formation of Ni_2MnGa was favored over the off-stoichiometric $\text{Ni}_{2.16}\text{Mn}_{0.84}\text{Ga}$. The formation of single phase Ni_2MnGa requires more time and diffusion.

Our novel *in situ* study establishes that twin boundaries can be manipulated in a polycrystalline Ni-Mn-Ga alloy. This means a change in magnetocrystalline anisotropy, which leads to higher magnetic cooling power. This results in a change in magnetocrystalline anisotropy, which leads to a higher magnetic cooling power. Mechanical loading in a preferred direction, traditionally referred to as a training process, was able to move the twin boundaries, and the combination of focused ion beam imaging linked specific movement with mechanical loading. This technique, *in situ* monitoring process, can be utilized to devise training procedures for future iterations of magnetocaloric and shape memory alloys.

However, more *in situ* study is required to investigate the behavior of twin boundary under stress and heat. A list of suggestions for future research on this area is summarized in the next section.

6. Recommendations for Future Work

Suggestions for future work can be categorized as below:

***In Situ* Mechanical Treatment Inside FIB equipped with EBSD**

This can give an opportunity to monitor twin boundary movement while EBSD pattern changes during the *in situ* mechanical loading. It needs an adjustment inside FIB chamber to have both micro-load frame and EBSD detector.

***In Situ* Thermomechanical Treatment Inside FIB**

Heating the sample will result in phase transformation from martensite to austenite. During cooling, the reverse transformation occurs while the compressive stress is applying. It would be an *in situ* study which covers both austenite and martensite phases.

***In Situ* Thermomechanical Treatment Inside FIB equipped with EBSD**

If adjustment inside the FIB allows, EBSD pattern can be detected in real time during phase transformation and applying compressive stress. It completes the above-mentioned study with the proof of EBSD mapping.

High-Pressure and High-Temperature Synchrotron X-ray Diffraction

More high-pressure and high-temperature synchrotron X-ray diffraction experiments are required to answer the questions which aroused from the first series of the high-pressure synchrotron XRD patterns. The phase transformation and structural evolution are required to be studied along with *ab initio* calculations and magnetic measurements in order to minimize the magnetic hysteresis which is a hurdle for commercialization.

VITA

ROOZBEH NIKKHAH-MOSHAIE

1996-2000, Materials Engineering, B.Sc., University of Tehran, Tehran, Iran

2000-2003, Materials Engineering, M.Sc., University of Tehran, Tehran, Iran

2011-2016, Materials Science and Engineering, Ph.D., Florida International
University, Miami, Florida

DEA Fellowship Award, University Graduate School, Florida International University, 2015

Student Travel Award by National High Magnetic Field Lab (NHMFL, MagLab) to attend summer school, Tallahassee, Florida, 2014.

Student Travel Award by University of Illinois at Chicago to attend Summer Institute on Sustainability and Energy (SISE), Chicago, Illinois, 2014.

Student Travel Award by American Physical Society to attend APS Workshop on Energy, Denver, Colorado, 2014.

Reviewer of Nanomedicine, Impact Factor: 5.41, Publisher: Future Science Group

Reviewer of Materials Sciences and Applications, Impact Factor: 0.99, Publisher: Scientific Research

Member of IEEE (Magnetics Society), Royal Microscopy Society, Materials Research Society (MRS), and American Physical Society (APS)

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