Interdiffusion, Crystallography and Mechanical Properties of Nickel Manganese Gallium Alloys

2016

Le Zhou
University of Central Florida

Find similar works at: http://stars.library.ucf.edu/etd

University of Central Florida Libraries http://library.ucf.edu

Part of the Materials Science and Engineering Commons

STARS Citation
http://stars.library.ucf.edu/etd/4916

This Doctoral Dissertation (Open Access) is brought to you for free and open access by STARS. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of STARS. For more information, please contact lee.dotson@ucf.edu.
INTERDIFFUSION, CRYSTALLOGRAPHY AND MECHANICAL PROPERTIES OF NICKEL MANGANESE GALLIUM ALLOYS

by

LE ZHOU
B.S. Beihang University, 2010

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Materials Science and Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

Spring Term
2016

Major Professor: Yongho Sohn
ABSTRACT

NiMnGa Heusler alloys, functioning as either ferromagnetic shape memory alloys or magentocaloric materials, have both practical applications and fundamental research value. The functional properties of NiMnGa alloys are closely related to the martensitic transformation from high temperature austenitic phase to low temperature martensitic phase. Alloys can be used for room temperature or high temperature applications, depending on the martensitic transformation temperature, which is compositional sensitive. The microstructure and crystallography of the martensites can be very complex but are crucial to the optimization of the material performance.

In this study, for the first time, a combinatorial study by combining solid-to-solid diffusion couples and various characterization techniques was carried out to fundamentally investigate the NiMnGa ternary alloys. Phase equilibria, interdiffusion behavior, microstructural and crystallographic development, and mechanical properties in NiMnGa alloys were systematically examined. Selected diffusion couples between pure Ni, Ni_{25}Mn_{75} and four ternary off-stoichiometric NiMnGa alloys (i.e., Ni_{52}Mn_{18}Ga_{30}, Ni_{46}Mn_{30}Ga_{24}, Ni_{52}Mn_{30}Ga_{18}, Ni_{58}Mn_{18}Ga_{24} in atomic percent) were assembled and annealed at 800, 850 and 900 °C for 480, 240 and 120 hours, respectively. The microstructure and concentration profiles of the interdiffusion zone were examined by scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS). Concentration profiles across the interdiffusion zone were further quantified by electron probe micro analysis (EPMA). Detailed microstructure and crystallography of the austenite and martensite were investigated using transmission electron microscopy (TEM). TEM thin foils were prepared by using focused ion beam (FIB) in situ lift
out (INLO) technique, which is able to select desired composition from diffusion couples. The mechanical properties, namely reduced elastic modulus and hardness, as a function of composition were assessed via nanoindentation.

Solubility values obtained for various phases were mostly consistent with the existing isothermal phase diagrams, but the phase boundary of the $\gamma$(Mn) + $\beta$ two-phase region was slightly modified. In addition, equilibrium compositions for the $\gamma$(Ni) and $\alpha'$ phases at 900 °C were also determined for the respective two-phase regions. Both austenitic and martensitic phases were found at room temperature in each diffusion couple with a clear interphase boundary. The compositions at the interfaces corresponded close to valence electron concentration (e/a) of 7.6, but decreased to lower values when Mn concentration increased to more than 35 at. %. Average effective interdiffusion coefficients for the $\beta$ phase over various compositional ranges were determined and reported in the light of temperature-dependence. Ternary interdiffusion coefficients were also determined and examined to assess the ternary diffusional interactions among Ni, Mn and Ga. Ni was observed to interdiffuse the fastest, followed by Mn then Ga. Interdiffusion flux of Ni also has strong influences on the interdiffusion of Mn and Ga with large and negative cross interdiffusion coefficients, $\tilde{D}_{MnNi}^{Ga}$ and $\tilde{D}_{GaNi}^{Ga}$. The $\tilde{D}_{NiNi}^{Ga}$ and $\tilde{D}_{MnMn}^{Ga}$ ternary interdiffusion coefficients exhibited minimum values near 52 at. % Ni concentration.

Extensive TEM analyses have been performed for the study of microstructure and crystallography of austenite and martensite from all diffusion couples. Crystallographic variations in martensitic phase, including non-modulated (NM) martensite, modulated (5M or 7M) martensite, were found in the diffusion couples. The 5M and 7M martensites were only
found near the interface between austenite and martensite, corresponding to compositions with lower e/a ratio. The NM martensites were found mostly away from the interface region, with high e/a ratios. The tetragonality ratio (c/a) for NM martensite generally increases with e/a ratio, but also depended on the composition. All martensitic microstructure consists of twinned variants with different orientations that were documented using electron diffraction. The twinning relationship along with the c/a ratio was correlated to martensitic transformation temperature. In addition, pre-martensitic state has been clearly observed in the cubic austenitic phase region, with distinctive tweed microstructure originating from the local lattice distortions.

Mechanical properties including reduced elastic modulus (E_r) and hardness (H) as a function of composition were measured and analyzed by nanoindentation. A decrease of E_r and H was observed with Mn or Ni substituting Ga, and Ni substituting Mn for the austenitic phase. However, an opposite trend was found for the martensitic phase. The softening of the elastic constants near the vicinity of martensitic transformation contributed to the sharp decrease in E_r and H near the interface region. The measured E_r and H had larger scatter for the martensitic phase than those for the austenitic phase. The scatters observed were attributed to the martensitic variants with different orientations. Contribution from the variation in grain orientation or shape memory effect was determined to be small in this investigation.
ACKNOWLEDGMENTS

I would like to express my deepest gratitude to many people who have been helpful and encouraging during my Ph.D. study in Materials Science and Engineering. I am very grateful for the guidance, generosity, and scholarship provided by my advisor Dr. Yongho Sohn. You teach me how to critically think and do research, and give me the opportunity and freedom to do different kinds of projects. This has been extremely helpful for my Ph.D study. I would also like to thank Dr. Helge Heinrich, who introduced me to TEM that is very important to my research. Many thanks to my other committee members: Dr. Kevin. Coffey, Dr. Linan An, and Dr. Nina Orlovskaya as well, who provide valuable advices to the completion of this dissertation. Deep appreciation also goes to the team members in materials characterization facility. I would also like to thank all my fellow colleagues for your friendship and help.

I also express my gratitude to Mr. Kyu Cho and Dr. Anit Giri at the U.S. Army Research Laboratory (ARL). This work has been made possible by financial support of ARL under the Advanced Materials Design and Innovative Processing Development project. Special thanks also go to Mr. Timothy Delahanty at Pittsburgh Materials Technology, Pittsburgh, Pennsylvania, USA, for preparation of the alloys, and Mr. Thomas Beasley at Florida International University, Miami, Florida, USA, for the assistance with EMPA operation.

Most importantly, I would like to thank my parents, my wife and my daughter for the endless support and patience. I will always love you!
# TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................................................... xi

LIST OF TABLES ............................................................................................................................................... xx

CHAPTER 1: INTRODUCTION ......................................................................................................................... 1

1.1. General Background ............................................................................................................................. 1

1.2. Motivation ............................................................................................................................................... 4

1.3. Objectives ............................................................................................................................................... 6

CHAPTER 2: LITERATURE REVIEW ............................................................................................................ 8

2.1. Martensitic Transformation and Crystal Structure .............................................................................. 8

2.2. Martensitic Twins .................................................................................................................................. 12

2.3. Valence Electron Concentration (e/a) .................................................................................................. 15

2.4. Pre-martensitic Transformation ......................................................................................................... 18

2.5. Mechanical Property ............................................................................................................................ 21

2.6. Magnetocaloric Effect ......................................................................................................................... 23

2.7. Diffusion of NiMnGa Alloys .............................................................................................................. 28

CHAPTER 3: EXPERIMENTAL DETAILS .................................................................................................. 32

3.1. Alloy Preparation ................................................................................................................................. 32

3.2. Diffusion Couple Assembly and Annealing ......................................................................................... 33

3.3. Characterization of Interdiffusion Zone .............................................................................................. 35
3.4. Mechanical Testing by Nanoindentation ................................................................. 37

CHAPTER 4: PHASE EQUILIBRIUM AND INTERDIFFUSION ........................................ 41

4.1. Analytical Framework for Interdiffusion ................................................................. 41

4.2. Phase Equilibrium and Martensitic Transformation .............................................. 43

4.3. Interdiffusion Coefficients ...................................................................................... 56

4.4. Discussion .............................................................................................................. 66

4.4.1. Phase Equilibrium .............................................................................................. 66

4.4.2. Martensitic transformation ............................................................................... 66

4.4.3. Ternary Interdiffusion Interactions .................................................................. 67

4.5. Summary .............................................................................................................. 71

CHAPTER 5: MICROSTRUCTURE AND CRYSTALLOGRAPHY ..................................... 73

5.1. Modulated Martensite ......................................................................................... 74

5.2. Non-modulated Martensitic Phase ...................................................................... 78

5.3. Austenitic Phase ................................................................................................... 82

5.4. Phase Boundary between Austenite and Martensite ........................................... 84

5.5. Discussion ........................................................................................................... 88

5.5.1. c/a vs. e/a ....................................................................................................... 88

5.5.2. Martensitic Microstructure and Crystal Structure ........................................... 92

5.5.3. Austenitic Microstructure ............................................................................... 96
5.6. Summary .......................................................................................................................... 101

CHAPTER 6: MECHANICAL PROPERTY ............................................................................. 103

6.1. Reduced Elastic Modulus and Hardness ................................................................. 103

6.2. Discussion .................................................................................................................... 112

6.2.1. Twin Realignment and Superelasticity ............................................................... 112

6.2.2. Composition .......................................................................................................... 115

6.2.3. Orientation Effect ............................................................................................... 118

6.2.4. Lattice Softening ............................................................................................... 121

6.3. Summary .................................................................................................................... 128

CHAPTER 7: SUMMARY ................................................................................................. 131

APPENDIX A: LIST OF PUBLICATIONS AND PRESENTATIONS ............................... 136

A.1 Publications ............................................................................................................. 137

A.2 Conference Presentations ...................................................................................... 139

APPENDIX B: MICROSTRUCTURE, CRYSTALLOGRAPHY AND MECHANICAL
PROPERTIES OF Ni\textsubscript{2+x}Mn\textsubscript{1−x}G\textsubscript{a} ALLOYS (X = 0.14, 0.16, 0.19, 0.22, and 0.24) AND
Ni\textsubscript{49+x}Mn\textsubscript{36−x}In\textsubscript{15} (X=0, 0.5, 1.0, 1.5 and 2.0) ALLOYS ......................................................... 141

B.1 Experimental Details ............................................................................................. 142

B.2 Microstructure and Crystallography of Ni\textsubscript{2+x}Mn\textsubscript{1−x}Ga Alloys (x = 0.14, 0.16, 0.19, 0.22, and 0.24) ......................................................................................................................... 146
B.3 Microstructure and Crystallography of Ni$_{49+x}$Mn$_{36-x}$In$_{15}$ (x=0, 0.5, 1.0, 1.5 and 2.0) ..... 155

B.4 Reduced Elastic Modulus and Hardness .................................................................................. 162

B.5 Summary .................................................................................................................................. 165

LIST OF REFERENCES ....................................................................................................................... 167
LIST OF FIGURES

Figure 1 Mechanism of (a) magnetic shape memory effect and (b) magnetic superelasticity. ...... 2

Figure 2 Graphical representation of magnetic refrigeration [10]. ........................................... 3

Figure 3 Crystal structure of (a) L2₁ austenitic NiMnGa with space group Fm3m, (b) NM martensite with space group F4/mmm and (c) NM martensite with space group I4/mmm. ....... 10

Figure 4 Crystal structures of 7M and 5M martensites by stacking of \{110\} planes from austenite. ....................................................................................................................................................... 11

Figure 5 A schematic showing the twinning elements. K₁ is the twinning plane, η₁ is the shear direction in K₁, S is the shear plane perpendicular to K₁ and intersects K₁ in η₁, K₂ is the plane which is rotated but undistorted as a result of twinning operation, η₂ is a rotated but undistorted directed common to S and K₂. ...................................................................................................... 13

Figure 6 The martensitic start transformation temperature (Mₛ) as a function of e/a value for NiMnGa alloys [48]. ....................................................................................................................................................... 16

Figure 7 Ternary NiMnGa phase diagram with e/a ratio from 7.4-7.6. The blue triangles, black squares and red circles represent NM, 5M and 7M martensites, respectively......................... 17

Figure 8 Temperature dependence of the phonon anomaly in the (ζ,ζ,0) TA₂ branch for Ni₂MnGa alloy in the cubic parent phase [52].................................................................. 19

Figure 9 Relative changes of the elastic constants \( C_{11}, C_L, C_{44} \) and \( C' \) as a function of temperature [19].................................................................................................................................. 20
Figure 10 Stress–strain curves for compression of a single-variant sample of the (a) 7M Ni$_{48.8}$Mn$_{29.7}$Ga$_{21.5}$, (b) 5M Ni$_{49.2}$Mn$_{29.6}$Ga$_{21.2}$ and (c) NM Ni$_{52.1}$Mn$_{27.3}$Ga$_{20.6}$ alloy along the [100] direction at room temperature [59, 60]. .................................................................................................................. 21

Figure 11 Thermodynamics of magnetocaloric effect. .................................................................................................................. 24

Figure 12 Magnetic entropy change as a function of temperature under different magnetic field for Ni$_{52.6}$Mn$_{23.1}$Ga$_{24.3}$ [73] and for Gd$_{3}$(Si$_{2}$Ge$_{2}$) [8]. .................................................................................................................. 26

Figure 13 Magnetic entropy as a function of temperature for (a) Ni$_{2.19}$Mn$_{0.81}$Ga and (b) Ni$_{2.15}$Mn$_{0.85}$Ga [11]. .................................................................................................................................. 27

Figure 14 Magnetic entropy as a function of temperature for (a) Ni$_{0.5}$Mn$_{0.35}$Sn$_{0.15}$ and (b) Ni$_{0.5}$Mn$_{0.37}$Sn$_{0.13}$ [9]. .................................................................................................................................. 28

Figure 15 Isothermal ternary phase diagram of NiMnGa at temperatures of (a) 800°C, (b) 900°C, (c) 1000°C [48]. .................................................................................................................................. 30

Figure 16 Ternary phase diagram at 900 °C showing the starting alloy compositions.............. 33

Figure 17 A schematic representation of the diffusion couple assembly. ......................... 34

Figure 18 Representative focused ion beam image showing the preparation process of TEM foils. .................................................................................................................................. 37

Figure 19 Schematic of a typical load vs. displacement curve. ........................................ 39

Figure 20 A schematic representation of the nanoindentation test. ............................................. 40

Figure 21 X-ray diffraction patterns of the six starting alloys after homogenization at room temperature. .................................................................................................................................. 44
Figure 22 (a) Backscatter electron micrographs, (b) concentration profiles, and the corresponding (c) interdiffusion fluxes of Ni, Mn and Ga from the diffusion couple Ni vs. Ni$_{52}$Mn$_{18}$Ga$_{30}$ annealed at 900 °C for 120 hours. Capital A represents austenite and M represents martensite. 46

Figure 23 (a) Backscatter electron micrographs, (b) concentration profiles, and the corresponding (c) interdiffusion fluxes of Ni, Mn and Ga from the diffusion couple Ni$_{25}$Mn$_{75}$ vs. Ni$_{46}$Mn$_{30}$Ga$_{24}$ annealed at 900 °C for 120 hours. Capital A represents austenite and M represents martensite. 47

Figure 24 Backscatter electron micrograph for diffusion couples Ni vs. Ni$_{52}$Mn$_{18}$Ga$_{30}$ annealed at 800 °C for 480 hours at (a) low magnification and (b) high magnification. Two small white rectangles in (a) represent the areas for TEM analyses. 48

Figure 25 (a) BF TEM micrograph of the α’-(Ni,Mn)$_3$(Ga,Mn) phase, and the corresponding selected area diffraction patterns from orientation, (b) [111] and (c) [11$ar{2}$]. 49

Figure 26 Isothermal ternary phase diagram at (a) 800 °C, (b) 850 °C and (c) 900 °C for Ni-Mn-Ga system with solubility compositions previously reported and determined from the current study. Data from the current study is given in solid squares while those from others presented by crosses. 51

Figure 27 (a) Backscatter electron micrographs, (b) concentration profiles, and (c) the corresponding interdiffusion fluxes of Ni, Mn and Ga from the diffusion couple, Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni$_{52}$Mn$_{30}$Ga$_{18}$ annealed at 900 °C for 120 hours. Capital A represents austenite and M represents martensite. 52
Figure 28 (a) Backscatter electron micrographs, (b) concentration profiles, and (c) the corresponding interdiffusion fluxes of Ni, Mn and Ga from the diffusion couple, Ni$_{46}$Mn$_{30}$Ga$_{24}$ vs. Ni$_{52}$Mn$_{30}$Ga$_{18}$ annealed at 900 °C for 120 hours. Capital A represents austenite and M represents martensite.

Figure 29 (a) Backscatter electron micrographs, (b) concentration profiles, and (c) the corresponding interdiffusion fluxes of Ni, Mn and Ga from the diffusion couple, Ni$_{46}$Mn$_{30}$Ga$_{24}$ vs. Ni$_{58}$Mn$_{18}$Ga$_{24}$ annealed at 900 °C for 120 hours. Capital A represents austenite and M represents martensite.

Figure 30 Compositions with martensitic transformation near room temperature. Squares, circles and triangles represent compositions obtained from diffusion couples annealed at 800 °C, 850 °C and 900 °C, respectively.

Figure 31 Diffusion paths from diffusion couples annealed at (a) 800 °C, (b) 850 °C and (c) 900 °C plotted on isothermal Ni-Mn-Ga phase diagram.

Figure 32 Temperature dependence of average effective interdiffusion coefficients for Ni, Mn and Ga in the β phase. The average effective interdiffusion coefficients were determined from diffusion couples, (a) Ni vs. Ni$_{52}$Mn$_{18}$Ga$_{30}$, (b) Ni vs. Ni$_{46}$Mn$_{30}$Ga$_{24}$, (c) Ni$_{25}$Mn$_{75}$ vs. Ni$_{52}$Mn$_{18}$Ga$_{30}$ (d) Ni$_{25}$Mn$_{75}$ vs. Ni$_{46}$Mn$_{30}$Ga$_{24}$, and (e) Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni$_{52}$Mn$_{30}$Ga$_{18}$, (f) Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni$_{58}$Mn$_{18}$Ga$_{24}$, (g) Ni$_{46}$Mn$_{30}$Ga$_{24}$ vs. Ni$_{52}$Mn$_{30}$Ga$_{18}$, (h) Ni$_{46}$Mn$_{30}$Ga$_{24}$ vs. Ni$_{58}$Mn$_{18}$Ga$_{24}$.
Figure 33 Main ternary interdiffusion coefficient (a) $D_{GaN}^{Ni}$ and $D_{GaN}^{Mn}$ as a function of Ni or Mn concentration ........................................................................................................................................ 71

Figure 34 (a) Bright field TEM and (b) high resolution TEM micrograph of Ni$_{52.1}$Mn$_{24.8}$Ga$_{23.1}$ from diffusion couple of Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni$_{52}$Mn$_{30}$Ga$_{18}$. Selected area diffraction pattern from (c) one variant from (d) twin boundaries indicating the 5M structure ............................................................................. 75

Figure 35 (a) Bright field TEM and (b) high resolution TEM micrograph of Ni$_{54.9}$Mn$_{17.4}$Ga$_{27.7}$ from diffusion couple of Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni$_{58}$Mn$_{18}$Ga$_{24}$. Selected area diffraction pattern from (c) one variant from (d) twin boundaries indicating the 7M structure ............................................................................. 77

Figure 36 (a) Bright field TEM and (b) selected area diffraction pattern of Ni$_{51.3}$Mn$_{24.5}$Ga$_{24.2}$ from diffusion couple of Ni$_{46}$Mn$_{30}$Ga$_{24}$ vs. Ni$_{58}$Mn$_{18}$Ga$_{24}$ showing the 12M structure. ................. 78

Figure 37 (a) Low magnification and (b) high magnification bright field TEM micrograph of Ni$_{52.0}$Mn$_{26.4}$Ga$_{21.6}$ from diffusion couple of Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni$_{52}$Mn$_{30}$Ga$_{18}$. (c) and (d) are selected area diffraction patterns from two adjacent martensitic variants indicating the NM structure ................................................................................................................. 80

Figure 38 (a) Experimental and (b) simulated selected area diffraction patterns from twin boundaries of two adjacent martensitic variants. (c) A schematic representation of the NM martensitic twin variants ...................................................................................................................................... 82

Figure 39 (a) Bright field TEM and (b) selected area diffraction pattern of Ni$_{50.9}$Mn$_{24.9}$Ga$_{24.2}$ from diffusion couple of Ni$_{46}$Mn$_{30}$Ga$_{24}$ vs. Ni$_{58}$Mn$_{18}$Ga$_{24}$ showing the austenitic structure. (c) Bright field TEM and (d) selected area diffraction pattern of Ni$_{49.6}$Mn$_{29.2}$Ga$_{21.8}$ from diffusion couple of Ni$_{46}$Mn$_{30}$Ga$_{24}$ vs. Ni$_{52}$Mn$_{30}$Ga$_{18}$ showing the austenitic structure ................................................................. 84
Figure 40 (a) Bright field TEM micrograph of Ni$_{54.9}$Mn$_{17.4}$Ga$_{27.7}$ from diffusion couple of Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni$_{58}$Mn$_{18}$Ga$_{24}$. (b) and (c) are selected area diffraction pattern from austenite and the boundary between austenite and 7M, respectively. (d) A simulated diffraction pattern from the boundary. ........................................................................................................................ 86

Figure 41 (a) Bright field TEM micrograph of Ni$_{52.1}$Mn$_{24.8}$Ga$_{23.1}$ from diffusion couple of Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni$_{52}$Mn$_{30}$Ga$_{18}$. (b) and (c) are selected area diffraction patterns from austenite and 5M martensite, respectively. .................................................................................................. 87

Figure 42 (a) Bright field TEM micrograph of Ni$_{55.8}$Mn$_{15.6}$Ga$_{28.6}$ from diffusion couple of Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni annealed at 800 °C for 480 hour. (b) and (c) are selected area diffraction patterns from austenite and NM martensite, respectively. .................................................................................................... 88

Figure 43 Plot of lattice parameter a and c, and tetragonality ratio (c/a) of NM martensite as a function of e/a. Black, blue and red color represent c/a, a and c respectively. Solid symbols are from the current study while hollow symbols are from literature [27, 36, 50, 113-115]. Particularly, solid squares are compositions rich in Mn, which are from diffusion couple of Ni$_{25}$Mn$_{75}$ vs. Ni$_{52}$Mn$_{18}$Ga$_{30}$. .......................................................................................................... 91

Figure 44 A schematic of different but equivalent variants after transformation from cubic austenite to tetragonal or orthorhombic martensite. .......................................................................................................................... 93

Figure 45 Plot of martensitic start temperature (M$_s$) [27, 32, 48, 50] and tetragonal ratio (c/a) for NM martensite as a function of e/a. .......................................................................................................................... 96

Figure 46 (a) low magnification and (b) high magnification BF TEM of the tweed microstructure for Ni$_{54.9}$Mn$_{17.4}$Ga$_{27.7}$ from diffusion couple of Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni$_{58}$Mn$_{18}$Ga$_{24}$. (c) high
resolution TEM micrograph showing the strain contrast and the corresponding fast-Fourier transform. (d) SADP of the sample from $[\bar{1}1\bar{1}]$ orientation................................................................. 99

Figure 47 Three representative nanoindentation curves from austenite (black), martensite (blue) and from near the interface between austenite and martensite (red). ......................................................... 104

Figure 48 Representative (a) secondary electron and corresponding (b) backscatter electron micrograph of the interdiffusion zone near the interface between austenite and martensite showing the nanoindents after nanoindentation tests................................................................. 105

Figure 49 Reduced elastic modulus and hardness for series I diffusion couples......................... 107

Figure 50 Reduced elastic modulus and hardness for series II diffusion couples. ..................... 108

Figure 51 Reduced elastic modulus and hardness for series III diffusion couples.................... 109

Figure 52 Ternary mapping of reduced elastic modulus and hardness for the ternary NiMnGa alloys............................................................................................................................................. 111

Figure 53 Deformation mechanisms for (a) martensite and (b) austenite under a Berkovich indenter. ...................................................................................................................................... 113

Figure 54 The first order derivative of reduced elastic modulus to composition when (a) Mn substitutes Ga when Ni is around 52 at.%, (b) Ni substitutes Ga when Mn is around 18 at.%, (c) Ni substitutes Ga when Mn is around 30 at.%, (d) Ni substitutes Mn when Mn is around 18 at.%. These correspond to series III diffusion couples in Figure 51................................................................. 117

Figure 55 A schematic showing the nanoindentation measurement from the terminal end of the diffusion couples.......................................................................................................................... 119
Figure 56 Reduced elastic modulus and hardness obtained on the terminal end from diffusion
couple of Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni$_{58}$Mn$_{18}$Ga$_{24}$................................................................. 120

Figure 58 Young’s modulus as a function of (a) Bulk modulus (B), (b) C$_{44}$ and (c) C’............. 126

Figure 59 A schematic of change of M$_s$ (red) and E$_s$ or H (blue) across the interdiffusion zone.
..................................................................................................................................................... 128

Figure 60 X-ray diffraction patterns from the Ni$_{2-x}$Mn$_{1-x}$Ga (x=0.14, 0.16, 0.19, 0.22 and 0.24)
alloys at room temperature.......................................................................................................... 147

Figure 61 Lattice parameters, a and c, and tetragonality ratio c/a determined at room temperature
for the Ni$_{2+x}$Mn$_{1-x}$Ga (x=0.14, 0.16, 0.19, 0.22 and 0.24) alloys as a function of c/a ratio....... 148

Figure 62 (a) Bright-field TEM micrograph from the Ni$_{2.14}$Mn$_{0.86}$Ga alloy showing the
martensitic variants. (b) Bright-field TEM micrograph from the twin variants and boundary.
Selected area diffraction patterns of the Ni$_{2.14}$Mn$_{0.86}$Ga alloy from (c) individual martensitic
variant and (d) twin boundary region............................................................................................. 150

Figure 63 High resolution TEM micrographs and corresponding fast Fourier transform patterns
from the Ni$_{2.14}$Mn$_{0.86}$Ga alloy: (a) individual martensitic variant and (b) twin boundary region.
.......................................................................................................................................................... 151

Figure 64 (a) Bright field TEM micrograph of martensitic variants from Ni$_{2.16}$Mn$_{0.84}$Ga alloy and
(b) the corresponding selected area diffraction pattern from [111] orientation. ......................... 152

Figure 65 High resolution TEM micrograph and corresponding fast Fourier transform pattern
from the Ni$_{2.16}$Mn$_{0.84}$Ga alloy. ...................................................................................................... 153

xviii
Figure 66 X-ray diffraction patterns from the Ni$_{49+x}$Mn$_{36-x}$In$_{15}$ (x=0, 0.5, 1.0, 1.5 and 2) alloys at room temperature. ....................................................................................................................... 155

Figure 67 (a) Bright field TEM micrograph and (b) corresponding selected area diffraction pattern from the Ni$_{49}$Mn$_{36}$In$_{15}$ alloy. (c) High resolution TEM micrograph and (d) corresponding inversed fast Fourier transform filtered micrograph for the Ni$_{49}$Mn$_{36}$In$_{15}$ alloy. ......................... 157

Figure 68 (a) Bright field TEM micrograph and (b) corresponding selected area diffraction pattern from the Ni$_{50}$Mn$_{35}$In$_{15}$ alloy. ........................................................................................... 158

Figure 69 (a) Bright field TEM micrograph from the Ni$_{50.5}$Mn$_{34.5}$In$_{15}$ alloy. Selected area diffraction patterns were collected from area (b) 1, (c) 2 and (d) 3................................................................. 159

Figure 70 Bright field TEM micrograph from (a) twin boundary and (b) one martensitic variant in the Ni$_{50.5}$Mn$_{34.5}$In$_{15}$ alloy. High resolution TEM micrograph from (c) twin boundary and (d,e) individual martensitic variant. .................................................................................................................................. 161

Figure 71 Reduced elastic modulus and hardness for the (a) Ni$_{2+x}$Mn$_{1-x}$Ga Alloys (x = 0.14, 0.16, 0.19 and 0.22) and (b) Ni$_{49+x}$Mn$_{36-x}$In$_{15}$ (x=0, 0.5, 1.0, 1.5 and 2) alloys measured by nanoindentation.................................................................................................................................. 163
LIST OF TABLES

Table 1 Typical lattice parameter for the austenitic structure, NM, 5M and 7M martensitic structure in different crystallographic systems. ................................................................. 12

Table 2 Twinning elements for 5M and 7M martensite in NiMnGa alloys [41]. .................. 14

Table 3 Nominal and XEDS-measured alloy compositions for the diffusion couples in atomic percent. ........................................................................................................................................ 32

Table 4 Terminal compositions, in atomic percent, of the diffusion couples, and the temperature and time of diffusion anneal. ........................................................................................................ 35

Table 5 Equilibrium compositions of the γ, α’ and β phases, in atomic percent, determined by EPMA from the diffusion couple series I and II annealed at 800 °C, 850 °C and 900 °C. .......... 49

Table 6 Equilibrium compositions of the γ, α’ and β phases, in atomic percent, determined from the diffusion couples annealed at 800 °C, 850 °C and 900 °C by XEDS. ............................................. 50

Table 7 The Ni-Mn-Ga alloy compositions, in atomic percent, and the corresponding e/a ratio, at the interface between the austenite and martensite determined from the concentration profiles. 56

Table 8 Average effective interdiffusion coefficients and the corresponding activation energy and pre-exponential factor for Ni, Mn and Ga in the β phase determined from series I and II diffusion couples. .......................................................................................................................... 61

Table 9 Average effective interdiffusion coefficients and the corresponding activation energy and pre-exponential factor for Ni, Mn and Ga in the β phase determined from series III diffusion couples. ......................................................................................................................................... 62
Table 10 Ternary interdiffusion coefficients at 800 °C as a function of composition in the β phase determined from the diffusion couples examined in this study............................................... 63

Table 11 Ternary interdiffusion coefficients at 850 °C as a function of composition in the β phase determined from the diffusion couples examined in this study............................................... 64

Table 12 Ternary interdiffusion coefficients at 900 °C as a function of composition in the β phase determined from the diffusion couples examined in this study............................................... 65

Table 13 Compositions from diffusion couples that are investigated by TEM and the corresponding crystal structure and lattice parameters................................................................. 89

Table 14 Experimental or calculated elastic constants and moduli for austenitic NiMnGa alloys. ..................................................................................................................................................... 125

Table 15 Composition of the five Ni-Mn-Ga alloys measured by XEDS in atomic percent with standard deviation in the parenthesis and the corresponding e/a ratio........................................ 144

Table 16 Composition of the five Ni-Mn-In alloys measured by XEDS in atomic percent with standard deviation in the parenthesis and the corresponding e/a ratio........................................ 145

Table 17 Martensitic start (Mₜ), martensitic finish (Mᵣ), austenitic start (Aₜ), austenitic finish (Aᵣ) and Curie temperature (Tₑ) determined by differential scanning calorimetry for the five Ni-Mn-Ga alloys. The reduced elastic modulus (Eₑ) and hardness (H) with standard deviation in the parenthesis were measured by nanoindentation for the alloys................................................... 146

Table 18 Crystal structures and lattice parameters (Å) for the Ni₂₋ₓMn₁₋ₓGa (x=0.14, 0.16, 0.19, 0.22 and 0.24) alloys determined by X-ray diffraction......................................................... 148
Table 19 Martensitic start (M_s), martensitic finish (M_f), austenitic start (A_s), austenitic finish (A_f) and Curie temperature (T_c) determined by differential scanning calorimetry for the five Ni-Mn-In alloys. The reduced elastic modulus (E_r) and hardness (H) with standard deviation in the parenthesis were measured by nanoindentation for the alloys.
CHAPTER 1: INTRODUCTION

1.1. General Background

Ternary NiMnGa alloys, also termed as ferromagnetic shape memory alloys (FSMAs) or magnetocaloric materials (MCM), attracted great interest in recent years due to potential practical applications and for fundamental research values. The alloy exhibits magnetic shape memory effect or magnetic superelasticity when subjected to an applied magnetic field, which makes it suitable for sensors and actuators application. It also shows normal or inverse magnetocaloric effect (MCE), which can potentially replace conventional gas compression cooling technology. In addition to various applications, this alloy provides important scientific values in fundamental understanding of the martensitic phase transformation and martensitic structures.

Shape memory effect and superelasticity come from reversible martensitic transformation based on shear mechanism of diffusionless transformation [1]. Research on shape memory alloys (SMAs) exploded after the discovery of TiNi alloy in 1963 [2]. In 1996, Ullakko et al. reported a magnetic field induced strain of 0.2% in a single crystal Ni$_2$MnGa alloy, which opened up the field of FSMAs [3]. The magnetic field induced shape memory effect or superelasticity have a similar origin and mechanism as those induced by thermal changes or stress field. Figure 1 (a) illustrates the mechanism of magnetic field induced shape memory effect. The magnetization of each magnetic domain within different martensitic variants initially points along the easy axis in order to minimize the energy. When a magnetic field is applied, provided that the magnetic anisotropy is high and the twinning stress between martensitic variants is low, the martensitic
variants may rotate to align their easy axis along the magnetic field direction [4]. The shape memory effect is achieved by heating the sample up above the transformation temperature so that the martensitic variants disappear and the original shape recovers. The mechanism of magnetic superelasticity is also illustrated in Figure 1 (b). This mechanism depends on inducing the martensitic transition under magnetic field rather than twin boundary motion between martensitic variants [4]. Therefore, a large shift in martensitic transformation temperature is required to achieve superelasticity.

![Figure 1 Mechanism of (a) magnetic shape memory effect and (b) magnetic superelasticity.](image)

Magnetic refrigeration is based on magnetocaloric effect, which means an adiabatic temperature change or an isothermal entropy change induced by application or removal of a magnetic field. The original phenomenon was first reported in 1881 by Warburg [5] and later
was utilized to achieve extremely low temperature (e.g. below 0.002 K [6, 7]). The motivation for room temperature magnetic refrigeration was stimulated by the discovery of rare earth based Gd$_2$(Si$_2$Ge$_2$) alloy in 1997, which exhibited a giant magnetocaloric effect [8]. The idea of magnetic cooling is presented in Figure 2. The magnetic material is heated in presence of magnetic field, after which the heat is expelled to surroundings by heat transfer. Then, by removing the magnetic field, the material is cooled below ambient temperature and absorbs heat from the surroundings. Recently, an inverse magnetocaloric effect was also reported where selected materials cool down when magnetized while heat up when demagnetized [9].

![Figure 2 Graphical representation of magnetic refrigeration](image)

Heusler alloys, Ni$_2$MnGa and related off-stoichiometric compounds show both magnetic superelasticity [3] and the magnetocaloric effect [11]. These functional properties are closely related to the martensitic transformation and structure of the materials, which are sensitive to the composition. The alloys undergo both a diffusionless first order phase transformation from high
symmetric austenite to low symmetric martensite, and a second order transition from ferromagnetic state to paramagnetic state. Due to these unique magneto-structural properties, NiMnGa alloys have gained significant interests both practically and scientifically.

1.2. Motivation

Extensive investigations on the magnetic properties and martensitic transformation in Ni-Mn-Ga alloys have been carried out, but with limited focus on the phase equilibria or diffusion kinetics within the alloys. Recently, two-phase shape memory alloys (martensite + $\gamma$) have been developed by increasing the Ni content or alloying a fourth element. The $\gamma$ ($cF4, F\overline{m}3m$) phase is beneficial for ductility and thermal cycling stability of the alloys [12]. Precipitation of cubic Ni$_3$Ga ($cP4, Pm3m$) during thin film deposition with high Ni content has been reported [13]. Accurate information on phase equilibrium of the ternary Ni-Mn-Ga alloys is important for understanding their processing-properties relations and for designing higher order alloys with enhanced properties.

Diffusion-controlled processing techniques are being studied to develop fabrication technologies of shape memory alloys including Ni-Mn-Ga alloys. Ni-Mn-Ga microtubes have been successfully produced through interdiffusion of Mn and Ga into Ni tubes [14]. Thin films of Ni-Mn-Ga have been also obtained via diffusion between three electrochemically deposited Ni/Mn/Ga layers [15]. Therefore, the knowledge of interdiffusion coefficients in the ternary NiMnGa alloy system would help design the process parameter for the fabrication of NiMnGa
alloys. In other research, combinatorial studies of nanoindentation and diffusion couples have proven to be feasible for identifying high temperature shape memory alloys [16].

The advancement of nanoindentation has facilitated the research of mechanical property of materials within small volume. For example, the effect of a ductile second phase on the martensitic phase transformation had been successfully examined in a dual phase CoNiAl shape memory alloy by employing nanoindentation [17]. The elastic modulus and hardness for NiMnAl shape memory alloys over a large compositional range were mapped out by performing nanoindentation over thin film libraries [18]. A combination of indentation and diffusion couple technique was also demonstrated to be promising in selecting shape memory alloy with desired operating temperature [16]. In all cases, nanoindentation has been proved to be useful in the study of property and application of shape memory alloys.

For NiMnGa and other shape memory alloys, the structural softening of the lattice associated with the martensitic transformation has been recognized by measuring some of the elastic constants. As a function of temperature, a softening of some elastic constants has been observed toward the martensitic transformation [19-21]. So far, the measuring of the elastic constants typically employed ultrasonic methods at different temperatures on samples with fixed compositions [19-23]. Yet, the Young’s modulus for NiMnGa has not been systematically studied over a large compositional range so far. Furthermore, measuring the Young’s modulus of alloy with different compositions and thus different martensitic transformation temperature provides an alternate but equivalent way to investigate the structural softening.
1.3. Objectives

In this dissertation, a combinatorial approach to characterize diffusion couples is carried out to fundamentally investigate the ternary NiMnGa alloys. A compositional gradient was generated after high temperature interdiffusion, and continuous change of martensitic transformation temperature was achieved over the different compositions. Experiments were carefully designed so that each diffusion couple has phase boundary between martensite and austenite at room temperature. Through the diffusion couples, the partial isothermal ternary NiMnGa phase diagram was assessed. The interdiffusion behavior was investigated to provide useful data for the fabrication of the alloys. The microstructures of the NiMnGa alloys with different composition were examined through electron microscopy. Different crystal structures associated with different compositions are revealed. The mechanical properties including reduced elastic modulus ($E_r$) and hardness (H) were obtained following nanoindentation measurements. Possible factors that influence the mechanical property were examined and analyzed with respect to composition, crystal structure and martensitic transformation.

Following the objective of this study, this dissertation is divided into three main sections:

CHAPTER 4: Investigations on isothermal NiMnGa phase diagram and ternary interdiffusion coefficients.

CHAPTER 5: Characterization of the microstructure from the interdiffusion zone including details of different crystal structures associated with the martensites at selected compositions.
CHAPTER 6: Assessment of the mechanical properties for the ternary NiMnGa alloys over a large range of composition as determined by nanomechanical testings.

The work in this dissertation provides unique and original contributions to advance the knowledge of NiMnGa alloys.
CHAPTER 2: LITERATURE REVIEW

2.1. Martensitic Transformation and Crystal Structure

Ni$_2$MnGa ternary alloy belongs to Heusler groups of alloys, which undergoes a series of phase transformation or order-disorder transformation from high temperature to low temperature. Upon cooling from liquid phase the alloys solidify in the disordered A$_2$ phase where Ni, Mn and Ga occupy the lattice randomly [24]. Upon further cooling, the A$_2$ phase is partially ordered into the B$_2$ phase, where Ni occupies its own sublattice while Mn and Ga occupy the other sublattice randomly. Further cooling would induce another order-disorder transformation from partially ordered B$_2$ phase to L$_{21}$ phase, where all Ni, Mn and Ga occupy their own sublattices. Martensitic transformation comes from cooling the L$_{21}$ phase to a low temperature, less symmetric martensitic phase. However, for a particular ternary alloy composition, some of the transformation step may be omitted or hard to be detected. For example, differential thermal analysis and neutron diffraction technique shows no clear evidence for the transformation from A$_2$-B$_2$, and indicates that the B$_2$-L$_{21}$ phase transformation occurs very rapidly which makes the B$_2$ phase difficult to be retained by quenching [25].

In general, the martensitic transformation from high temperature austenitic to low temperature martensitic phase is of more interests. The high temperature austenitic has an ordered L$_{21}$ crystal structure with space group $Fm\bar{3}m$. The crystal structure of L$_{21}$ is illustrated in Figure 3(a), which can be interpreted as four face centered cubic (FCC) sub-lattices interpenetrating with each other. There are eight Ni atoms, four Mn and four Ga atoms in each
unit cell, which occupies their own sublattices. The lattice parameter, $a$, of a stoichiometric Ni$_2$MnGa is approximately 5.82 Å, as listed in Table 1.

In the low temperature martensitic state, the crystal structure is complex and varies depending on the alloy composition, processing history and residual stress. Composition is an important factor in determining the crystal structure of the martensitic phase at room temperature [26]. Commonly identified martensitic structures include non-modulated tetragonal martensite (NM), five-layer modulated martensite (5M or 10M) and seven-layered modulated martensite (7M or 14M) [27].

The simplest crystal structure for the martensite is the NM tetragonal structure, in which there are typically two different systems describing the unit cells, as shown in Figure 3(b) and (c). The first is built directly from the cubic axes of austenite, where two axes shrink and the other one elongates. The other one is based on the principal axes of the martensite. The space groups for the two systems are F4/mmm and I4/mmm, respectively. These two systems are only different in the choice of crystallographic axes. The orientation relationship between them is $(001)_F \parallel (001)_I$, $[100]_F \parallel [110]_I$, and the lattice parameter relationship is $a_F = \sqrt{2}a_I$, $c_F = c_I$. Although the second unit cell is crystallographically favored since it has a smaller volume, the first unit cell is usually preferred in describing the strains induced by magnetic field [28]. An example of the lattice parameter for NM martensite is listed in Table 1.
For the modulated martensites, primarily two models have been proposed to describe the crystal structure. The first model describes that the martensite is built up by a periodic shuffling (or modulation) of the $(110) \left[ \bar{1} \bar{1}0 \right]$ system so that every 5th or 7th $(110)$ plane maintains the original position. The displacement of each plane is characterized by the function:

$$\Delta_n = A \sin \left( \frac{2\pi n}{L} \right) + B \sin \left( \frac{4\pi n}{L} \right) + C \sin \left( \frac{6\pi n}{L} \right),$$

where $L$ is modulation period, and $A$, $B$ and $C$ can be adjusted to fit the experimental results [29]. The second model utilizes the model for the long-period martensites of NiAl-type alloys [30], where the basal planes derived from $(110)$ planes of the austenite stacks following the $\left( \bar{5} \bar{2} \right)_2$ or $\left( \bar{3} \bar{2} \right)_2$ sequences (in Zhdanov notation). In this model, the martensitic unit cell has the $a$ and $b$ axes on the basal planes and $c$ axis along the stacking direction as shown in Figure 4. Because of the stacking sequence, this model usually results in a monoclinic unit cell with monoclinic angle $\beta$ higher than $90^\circ$. However, the

![Figure 3](image-url)
monoclinic angle is only slightly deviated from 90°, so it is quite often and appropriate to simplify the 5M or 7M martensitic structure to be a tetragonal or orthorhombic crystal structure [31-33]. Examples of the lattice parameters for 5M and 7M martensite in different crystallographic systems are listed in Table 1.

Figure 4 Crystal structures of 7M and 5M martensites by stacking of \{110\} planes from austenite.

Some attempts have been made in order to distinguish between these two different models [27, 34]. The modulation model is favored for the description of 5M martensites because the \(\beta\) angle very close to 90°, which satisfies the tetragonal unit cell of 5M determined experimentally. However, the argument is invalid if the structure of 5M cannot be determined precisely as tetragonal. For 7M, the \((52)\) stacking model is preferred as high resolution
transmission electron microscopy (HRTEM) results confirmed its nano-twinned nature which is inherent to the stacking model [34].

Table 1 Typical lattice parameter for the austenitic structure, NM, 5M and 7M martensitic structure in different crystallographic systems.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Crystal Structure</th>
<th>Unit Cell</th>
<th>Lattice Parameter (Å)</th>
<th>Monoclinic Angle (°)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₅₀Mn₂₅Ga₂₅[35]</td>
<td>L₂₁</td>
<td>Cubic</td>
<td>5.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni₅₅Mn₁₉.₅Ga₂₅.₅[36]</td>
<td>NM</td>
<td>Tetragonal</td>
<td>5.43, 6.57</td>
<td>1.21</td>
<td></td>
</tr>
<tr>
<td>Ni₅₀Mn₂₈Ga₂₂[37]</td>
<td>5M</td>
<td>Tetragonal</td>
<td>6.17, 5.75</td>
<td>0.93</td>
<td></td>
</tr>
<tr>
<td>Ni₅₂.₈Mn₂₆.₇Ga₂₀.₅[38]</td>
<td>7M</td>
<td>Orthorhombic</td>
<td>6.19, 5.74, 5.48</td>
<td>0.88</td>
<td></td>
</tr>
</tbody>
</table>

2.2. Martensitic Twins

The martensitic transformation from austenite to martensite usually brings about a twinned microstructure. The twinning is typically described by the four twinning elements – K₁, η₁, K₂ and η₂, which are schematically presented in Figure 5. K₁ represents the invariant plane or the twinning plane, which is neither rotated nor distorted during the shear displacement. The lattice points on the upper side of the K₁ plane are displaced along the shear direction η₁ by an amount of u₁ proportional to their distance to K₁ following [39]:

\[ u₁ = sx \]  

where s is the shear magnitude and x is the distance to K₁ plane. The plane S is the shear plane, which contains η₁ and is normal to K₁ plane. K₂ is another undistorted plane during the displacement, and intersects with plane S in η₂ direction.
The four twinning elements can be either rational or irrational, depending on whether they pass though the lattice points. Accordingly, there are typically three different types of twins depending on which twinning elements are rational. If the twinning elements $K_1$ and $\eta_2$ are rational while $K_2$ and $\eta_1$ are irrational, the twins are called type I twins. Vice versa, if $K_2$ and $\eta_1$ are rational while $K_1$ and $\eta_2$ are irrational, this form type II twins. A third case is when all four twinning elements are rational, the twins are called compound twins. For type I twins, the twinning process is equivalent to a rotation by $180^\circ$ about the normal to $K_1$ plane. For type II twins, the two twin crystals are related by a rotation of $180^\circ$ about the $\eta_1$ direction [39].

From a practical point of view, different types of twins can be revealed via TEM characterization. For a type I twin, if the incident electron beam is parallel to the twinning plane,
two sets of diffraction spots from the twins can be obtained. For a type II twin, however, a single diffraction is observed if the incident electron beam is along the $\eta_1$ direction [40].

For NiMnGa alloys, different types of twins have been reported depending on the crystal structure of the martensitic phase. For NM martensite, the type of twin belongs to the compound twin, as all four twinning elements are rational. The twinning element for a NM martensite is identified to be $K_1 = (101)$, $\eta_1 = [10\overline{1}]$, $K_2 = (\overline{1}01)$, $\eta_2 = [101]$. For 5M or 7M martensite, all three types of twins have been observed. Table 2 lists the twinning elements of all three types of twins, for the 5M and 7M martensite. The coordinate system used to determine the twinning elements are based on the monoclinic structure. The rational twinning elements remain the same for different compositions, but the irrational twinning elements may change since the lattice parameters are different with different compositions [37, 40-42].

Table 2 Twinning elements for 5M and 7M martensite in NiMnGa alloys [41].

<table>
<thead>
<tr>
<th>Structure</th>
<th>Twin Type</th>
<th>$K_1$</th>
<th>$\eta_1$</th>
<th>$K_2$</th>
<th>$\eta_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5M</td>
<td>Type I</td>
<td>$(125)$</td>
<td>$[1.721 \overline{1} 0.056]$</td>
<td>$(0.882 \overline{1} 0.589)$</td>
<td>$(\overline{5} \overline{3} \overline{1})$</td>
</tr>
<tr>
<td></td>
<td>Type II</td>
<td>$(0.882 \overline{1} 0.589)$</td>
<td>$[5 \overline{5} 1]$</td>
<td>$(\overline{1}25)$</td>
<td>$[1.719 \overline{1} 0.056]$</td>
</tr>
<tr>
<td></td>
<td>Compound</td>
<td>$(105)$</td>
<td>$[5 \overline{0} 1]$</td>
<td>$(\overline{1}05)$</td>
<td>$[501]$</td>
</tr>
<tr>
<td>7M</td>
<td>Type I</td>
<td>$(1\overline{2}7)$</td>
<td>$[1.038 \overline{1} 0.137]$</td>
<td>$(0.521 \overline{1} 3.350)$</td>
<td>$(77 \overline{1})$</td>
</tr>
<tr>
<td></td>
<td>Type II</td>
<td>$(0.521 \overline{1} 3.350)$</td>
<td>$[771]$</td>
<td>$(1\overline{2}7)$</td>
<td>$[1.038 \overline{1} 0.137]$</td>
</tr>
<tr>
<td></td>
<td>Compound</td>
<td>$(107)$</td>
<td>$[701]$</td>
<td>$(\overline{1}07)$</td>
<td>$[701]$</td>
</tr>
</tbody>
</table>

The formation of different types of twins may influence the microstructure of the martensitic variants. It was reported that two types of interfaces between twinned martensite can
be distinguished for 5M martensite, namely crossing and step type interface [43]. Furthermore, the different interfacial morphologies may influence the twinning stress and thus the mobility of the twin boundary [44-46]. Therefore, the type of twins formed in the NiMnGa alloys has a large impact on their properties.

2.3. Valence Electron Concentration (e/a)

Valence electron concentration (e/a) is defined as the ratio of valence electrons to atoms. For ternary alloys with composition Ni_{100-x-y}Mn_xGa_y, the e/a ratio is calculated as:

\[
e/a = \frac{10 \times (100 - x - y) + 7 \times x + 3 \times y}{100} = 10 - 0.03x - 0.07y
\]

(2)

Therefore, the iso-e/a ratio in a ternary isothermal phase diagram appears as parallel lines.

The e/a ratio has been postulated to govern the properties and the martensitic phase transformation in NiMnGa alloys. For example, the martensitic transformation temperature (T_m) is plotted as a function of e/a ratio, where nearly a linear relationship was found, but with relatively large standard deviation [47, 48]. Figure 6 presents a summarized plot of martensitic start transformation temperature (M_s) as a function of e/a ratio near the Ni_{2}MnGa regions [48]. Regardless of the crystal structure of the transformed martensitic phase, the M_s monotonically increases as e/a ratio increases overall. The scatter is relatively large due to possibly other factors. Furthermore, if one element has a fixed concentration, the T_m increases with an increase of e/a value with much less scatter. That is to say, the T_m increases as the Ni substitutes Mn or Ga, and Mn substitutes Ga, while T_m decreases if the Ga substitutes Ni or Mn, and Mn substitutes Ni [31, 36, 49, 50]. In addition, the boundary condition for different martensitic structures has been
reported to be related to the e/a ratio. A suggested value of 7.71 for e/a ratio separates the NM martensites and the modulated martensites [51].

Figure 6 The martensitic start transformation temperature (M_s) as a function of e/a value for NiMnGa alloys [48].

Figure 7 plots a section of the ternary NiMnGa phase diagram superimposed with some alloy compositions investigated in previous studies whose martensitic transformation is higher than room temperature. The iso-e/a ratio from 7.4 to 7.6 is also plotted as several parallel lines in the phase diagram. The blue triangles, black squares and red circles represent NM, 5M and 7M martensites at room temperature, respectively.
Figure 7 indicates that most alloys studied in literature focus on a compositional range with e/a ratio of 7.4 to 7.8 and near the stoichiometric composition. It appears that NM martensites tend to have an e/a ratio larger than 7.7 while modulated martensites with an e/a ratio smaller than 7.7. In particular, 5M martensites only exist with e/a < 7.7. However, it is also noticed that there are certain compositions that do not quite follow the trend. The experimental error induced when reporting the actual composition has been one important factor that affects the accuracy of the rule. Sometimes only the nominal compositions are documented while sometimes the measured compositions are reported but with different measuring techniques or conditions. It appears that a systematic study will be helpful to elucidate the trend. Nonetheless,
the e/a ratio has provided certain guidance in selecting the alloy compositions despite the fact that it is mostly empirical.

2.4. Pre-martensitic Transformation

Research for NiMnGa alloys has also demonstrated that before the martensitic transformation, there is pre-martensitic transformation and corresponding anomalous behavior in the lattices.

Inelastic neutron scattering has been carried out for near-stoichiometric Ni$_2$MnGa alloy above its $M_s$ to investigate the phonon dispersion curve [52, 53]. A measured phonon dispersion curve for the $(\zeta, \zeta, 0)$ transverse acoustic (TA$_2$) branch as a function of temperature is presented in Figure 8. A striking feature is that the $(\zeta, \zeta, 0)$TA$_2$ branch is strongly temperature dependent and develops to a distinct minimum at around $\zeta_0 = 0.33$ as temperature is lowered toward to the $M_s$. It is noted that other modes, such as TA$_1$ or longitudinal acoustic (LA) branch are only slightly temperature dependent which can be explained by stiffening of the lattice at low temperature [52]. This phonon softening near the martensitic transformation indicates a pre-martensitic transformation due to lattice instability. Since the $(\zeta, \zeta, 0)$TA$_2$ branch corresponds to elastic constant $C' = (C_{11} - C_{12})/2$ in the limit of $\zeta_0 \to 0$, the elastic constants probably would also change as the temperature decreases.
Figure 8 Temperature dependence of the phonon anomaly in the $(\zeta, \zeta, 0)$ TA$_2$ branch for Ni$_2$MnGa alloy in the cubic parent phase [52].

The elastic constants for a cubic phase can be obtained by measuring of the velocity of ultrasonic waves propagated along certain easy crystallographic orientations, such as the [001], [110] and [111] orientation of the cubic austenitic phase. For example, the elastic constants for a near stoichiometric Ni$_2$MnGa alloy are reported to be: $C_{11} = 136 \pm 3$ GPa, $C_{44} = 102 \pm 3$ GPa, $C_L = (C_{11} + C_{12} + 2C_{44})/2 = 222 \pm 9$ GPa, $C' = (C_{11} - C_{12})/2 = 22 \pm 2$ GPa [19]. The elastic constants were also measured as a function of temperature across the martensitic transformation region, which is presented in Figure 9 [19]. Interestingly, the anomalies are again observed that there is a softening for the elastic constants near the transformation temperature. Similar results
have also been reported elsewhere for other compositions [54, 55]. Such a softening prior to the martensitic transformation has also been observed in other alloys that exhibiting martensitic transformation [21], and was also attributed to lattice instabilities associated to the pre-martensitic transformation.

![Graph showing relative changes of elastic constants](image)

Figure 9 Relative changes of the elastic constants $C_{11}$, $C_L$, $C_{44}$ and $C'$ as a function of temperature [19].

The pre-martensitic state has also been observed during the TEM investigation [56-58]. The characteristic microstructure is so called a “tweed” microstructure with striated contrast due to local lattice strains. The electron diffraction patterns also reveal diffused and elongated streaks
around the diffraction spots, but without the change of the cubic symmetry. All these indicate some local atomic displacements due to the shear softening before the martensitic transformation.

2.5. Mechanical Property

Mechanical properties for NiMnGa alloys have been typically examined by stress-strain curves obtained from conventional tensile testings. Figure 10 shows three representative compressive stress-strain curves for three NiMnGa single crystals with different compositions and thus different crystal structures as well. These curves show similar features that a stress plateau shows up when the stress increases to a certain level. The stress plateau indicates the initiation of twin boundary movement, and thus corresponds to the twinning stress. After the completion of the twin boundary movement, the stress continues to rise accompanied with increasing strain. The twinning stress for 7M and 5M martensite is as low as only 2 MPa, while that for the NM martensite is nearly 20 MPa.

![Figure 10 Stress–strain curves for compression of a single-variant sample of the (a) 7M Ni\textsubscript{48.8}Mn\textsubscript{29.7}Ga\textsubscript{21.5}, (b) 5M Ni\textsubscript{49.2}Mn\textsubscript{29.6}Ga\textsubscript{21.2} and (c) NM Ni\textsubscript{52.1}Mn\textsubscript{27.3}Ga\textsubscript{20.6} alloy along the [100] direction at room temperature [59, 60].](image)

Figure 10 Stress–strain curves for compression of a single-variant sample of the (a) 7M Ni\textsubscript{48.8}Mn\textsubscript{29.7}Ga\textsubscript{21.5}, (b) 5M Ni\textsubscript{49.2}Mn\textsubscript{29.6}Ga\textsubscript{21.2} and (c) NM Ni\textsubscript{52.1}Mn\textsubscript{27.3}Ga\textsubscript{20.6} alloy along the [100] direction at room temperature [59, 60].
In addition to the determination of twinning stress, some attempts have been made on the measurements of hardness for NiMnGa alloys by Vickers hardness measurement. The Vickers hardness for bulk NiMnGa alloys around its stoichiometric composition ranges from 270 to 350 Hv [61, 62]. It was also noticed that the hardness seemed to be lower near the stoichiometric composition and increased with deviation from the stoichiometry [61]. The hardness measurement on a series of Fe-modified NiMnGa bulk alloys showed that the Vickers hardness increased when Fe substitutes Mn [62].

The evaluation of the mechanical properties of NiMnGa alloys by micro- or nano-indentation has also been reported before. Because of its small indentation depth, micro- or nano-indentation is very useful to test thin films. The hardness and elastic modulus for Ni$_{43.8}$Mn$_{29.2}$Ga$_{27}$ thin films are up to 5.5 GPa and 155 GPa, but also depended on the film thickness due to substrate effect [63]. Similarly, the hardness and elastic modulus for thin films with composition of Ni$_{55}$Mn$_{24.5}$Ga$_{20.5}$ varies from 4.1 GPa to 4.6 GPa and from 101 GPa to 151 GPa, respectively, which were also thickness dependent [64]. For NiMnGa bulk alloys, the hardness and elastic modulus measured by micro- or nano-indentation are consistent without the influence of substrate. It is reported that for Ni$_{2+x}$Mn$_{1-x}$Ga alloys in the martensitic phase region, the reduced elastic modulus varies from 105 GPa to 120 GPa and increased as Ni substitutes Mn [65]. Similarly, the reduced elastic modulus for Ni$_{50.3}$Mn$_{29.0}$Ga$_{20.1}$ was about 98 GPa [66]. It appears that the hardness and elastic modulus is measured slightly higher in thin films [67], probably due to both substrate effect and residual stress in thin films.
The mechanical properties such as the modulus and hardness of the NiMnGa alloys are important when considering them to be used for actuators. However, there is no systematic study so far concerning the measurement of mechanical properties as a function of composition. This is probably because conventional measurement requires the fabrication many bulk alloys with different compositions, which is very time consuming. Recently, the hardness and the reduced elastic modulus were mapped across a large fraction of the ternary phase diagram for the shape memory alloy – NiMnAl [18]. The method has been termed as high-throughput screening, which carried out nanoindentation across thin-film libraries with a large range of compositions [18, 68]. A similar combinatorial approach that employs both nanoindentation and diffusion couples also successfully mapped out the hardness and elastic modulus map for a ternary Ti-Zr-Ta system [69]. The method is easy and fast to obtain the desired properties of the studied alloys, regardless of the alloy system, and thus can be also applied to NiMnGa alloys.

2.6. Magnetocaloric Effect

Magnetocaloric effect (MCE) is a phenomenon where the magnetic materials heat or cool due to the external magnetic field. The MCE is intrinsic to magnetic materials, and comes from the magnetic entropy change with varying the magnetic field.

The thermodynamics of MCE is illustrated in Figure 11. Initially, at zero or low magnetic field, the magnetic spins are randomly aligned. When magnetic field is applied, the magnetic spins tend to align along the external field, resulting in a decrease of the magnetic entropy. That is to say the magnetic field leads to a decrease in entropy isothermally or $\Delta S_M$. Then, if the magnetic field is removed, the magnetic spins recover their originally random state, and should cause an increase in magnetic entropy. If the material is in adiabatic environment, the lattice
entropy has to drop so that the overall entropy remains the same. This will lead to a decrease in temperature or $\Delta T_{ad}$ in the material. Therefore, by applying and removing magnetic field, cooling of the material can be achieved. By continuing such cycles, low temperature can be obtained.

![Figure 11 Thermodynamics of magnetocaloric effect.](image)

The $\Delta S_M$ and $\Delta T_{ad}$ are two important parameters that quantify the MCE. For a paramagnetic or a ferromagnetic material, the sign is negative for $\Delta S_M$ and positive for $\Delta T_{ad}$, which means the application of magnetic field reduces the magnetic entropy isothermally or heats up the materials adiabatically. These two parameters are related as expressed by the fundamental Maxwell’s equation [70]:

$$
\left( \frac{\partial S(T, H)}{\partial H} \right)_T = \left( \frac{\partial M(T, H)}{\partial T} \right)_H
$$

(3)
where $M$ and $H$ represent the magnetization and magnetic field. Therefore, for an isothermal-isobaric process, the entropy change can be calculated by integration of equation (3):

$$\Delta S_M(T, \Delta H) = \int_{H_1}^{H_2} \left( \frac{\partial M(T, H)}{\partial T} \right)_{H} dH$$

(4)

Additionally, for the reversible adiabatic process, we have the following equation:

$$-TdS_M = dq = CdT$$

(5)

where $C$ is the heat capacity of the materials. Combining equations (4) and (5) we can obtain:

$$\Delta T_{ad}(T, \Delta H) = -\int_{H_1}^{H_2} \left( \frac{T}{C(T, H)} \right)_{H} \left( \frac{\partial M(T, H)}{\partial T} \right)_{H} dH$$

(6)

From equations (4) and (6), a large entropy change can be achieved when the magnetic field change is large or the derivative of magnetization to temperature is large [70]. For a simple paramagnet or ferromagnet, the magnetization decreases as temperature increases, resulting in a negative $\Delta S_M$ and positive $\Delta T_{ad}$. Also, the maximum value of $\Delta S_M$ and $\Delta T_{ad}$ should be at the Curie temperature because the derivative of magnetization to temperature is the largest around Curie temperature.

For those materials that undergo second order or continuous phase transformation, the MCE is limited due to the fact that the magnetization changes gradually across the transition region. However, the MCE can be enhanced if the materials have first order or discontinuous phase transition, as has been observed in Gd$_5$(Si$_2$Ge$_2$) [8]. In addition to ferromagnetic ordering at Curie temperature, this material further transforms to another ferromagnetic structure accompanied by the structural transition from orthorhombic to monoclinic structure. This
structure transition brings a sharp change in the magnetization across the transition temperature region, which leads to a giant MCE. The MCE for Gd$_5$(Si$_2$Ge$_2$) is twice as large as that for pure Gd [8]. Other materials that undergo first order transition also exhibit giant MCE include LaFeSi [71] or MnAs [10] based materials.

Large magnetic entropy change is also observed in NiMnGa alloy at its first order transition [72, 73]. The peak value of the entropy change for Ni$_{52.6}$Mn$_{23.1}$Ga$_{24.3}$ alloy at a magnetic field of 5T reaches 18.0 J/Kg·K [73], which is close to 18.5 J/Kg·K found in Gd$_5$(Si$_2$Ge$_2$) under the same magnetic field, as presented in Figure 12 [8]. This large entropy change should be attributed to the sharp magnetization change due to first order transition from low symmetric martensite to high symmetric austenite.

Figure 12 Magnetic entropy change as a function of temperature under different magnetic field for Ni$_{52.6}$Mn$_{23.1}$Ga$_{24.3}$ [73] and for Gd$_5$(Si$_2$Ge$_2$) [8].
By fine-tuning the composition of NiMnGa alloys, the first order transition could be coincided with the second order transition, and lead to giant MCE. For alloys with the general formula of Ni$_{2-x}$Mn$_{1-x}$Ga, it was found that, when $x=0.19$, the alloy exhibits a coupled first order and second order transition at temperature around 330K [11, 74, 75]. L. Pareti et al. studied the entropy change of Ni$_{2.15}$Mn$_{0.85}$Ga and Ni$_{2.19}$Mn$_{0.81}$Ga with magnetic field from 0 – 1.6T [11]. Results showed that the peak value for Ni$_{2.19}$Mn$_{0.81}$Ga reaches 20 J/Kg·K at 1.6T, while is only 5 J/Kg·K for Ni$_{2.15}$Mn$_{0.85}$Ga as presented in Figure 13. This giant MCE is also connected to the structural transition from paramagnetic austenite to ferromagnetic martensite.

Figure 13 Magnetic entropy as a function of temperature for (a) Ni$_{2.19}$Mn$_{0.81}$Ga and (b) Ni$_{2.15}$Mn$_{0.85}$Ga [11].

Due to the inherent nature of first order transition, MCE becomes complex for some other Heuslar alloys. In one case, an inverse MCE has been observed in NiMnSn alloys [9]. The inverse MCE means the alloy cools under applied magnetic field and heats when the field is removed, or the magnetic entropy change by applying magnetic field is positive. For Ni$_{0.5}$Mn$_{0.35}$Sn$_{0.15}$ and Ni$_{0.5}$Mn$_{0.37}$Sn$_{0.13}$, the magnetic entropy change is positive because the
∂M/∂T is positive across the structure transition when the magnetic field is applied. Figure 14 presents the magnetic entropy change of Ni$_{0.5}$Mn$_{0.35}$Sn$_{0.15}$ and Ni$_{0.5}$Mn$_{0.37}$Sn$_{0.13}$, where the peak values of Ni$_{0.5}$Mn$_{0.37}$Sn$_{0.13}$ reaches 19.5 J/Kg·K when the field is 5T, and is also comparable to that of Gd$_5$(Si$_2$Ge$_2$). Some other alloys also show inverse MCE, including NiMnIn [76] and NiMnSb alloys[77].

Figure 14 Magnetic entropy as a function of temperature for (a) Ni$_{0.5}$Mn$_{0.35}$Sn$_{0.15}$ and (b) Ni$_{0.5}$Mn$_{0.37}$Sn$_{0.13}$ [9].

2.7. Diffusion of NiMnGa Alloys

Diffusion studies on NiMnGa alloys or other similar ternary alloys are rare, and have been primarily aimed at determining the ternary phase diagrams. By combining the results from
diffusion couples or triples and selected equilibrium alloys, phase diagrams of ternary alloys such as NiMnIn \[78\], NiFeGa \[79\], NiCoGa \[80\] have been determined.

NiMnGa ternary phase diagram has also been investigated before \[48, 81\]. Diffusion couples with solid/solid, liquid/solid and gas/solid type and binary phase alloys were annealed and quenched from a temperature range of 800°C to 1000°C, and thus preliminary phase diagrams were obtained, as presented in Figure 15. The phase diagram determined includes a large single β phase region. Also, it dictates the region of two phase (γ-Ni and β) FSMAs where the γ-Ni helps increase the ductility and thermal cycling stability of the NiMnGa alloys \[12\]. Therefore, accurate information on phase equilibrium of the ternary Ni-Mn-Ga alloys is important for understanding their processing-properties relations and for designing higher order alloys with enhanced properties.

However, limited efforts have been attempted to investigate or determine the interdiffusion behavior in NiMnGa alloys. To the authors’ knowledge, only tracer diffusion coefficients of $^{63}$Ni, $^{54}$Mn and $^{67}$Ga in Ni rich Ni$_{53.7}$Mn$_{21.1}$Ga$_{25.2}$ have been reported \[82, 83\]. However, the knowledge of interdiffusion coefficients is helpful to design the process parameter for the fabrication of some delicate NiMnGa alloys, such as tubes \[14\] or thin films \[15\].
In addition to the determination of ternary phase diagram, diffusion experiment is unique in creating a compositional gradient. In NiMnGa alloys, the martensitic transformation temperature is closely related to the composition or valence electron ratio: in the diffusion zone, a gradient composition with different martensitic transition temperatures can co-exist. Thus, an interface created by martensitic transformation at room temperature should be present, which separates the austenite and martensite. This is helpful in determining the compositions with martensitic transformation temperature close to room temperature, which are of practical interests for room temperature refrigeration. Also, martensites with different crystal structures...
may co-exist in the martensitic zone, which would be useful in studying crystallography and transformation mechanisms.
CHAPTER 3: EXPERIMENTAL DETAILS

3.1. Alloy Preparation

Six alloy buttons including pure Ni, Ni$_{25}$Mn$_{75}$ and four ternary off-stoichiometric NiMnGa alloys with nominal compositions of Ni$_{52}$Mn$_{18}$Ga$_{30}$, Ni$_{46}$Mn$_{30}$Ga$_{24}$, Ni$_{52}$Mn$_{30}$Ga$_{18}$ and Ni$_{58}$Mn$_{18}$Ga$_{24}$ (in atomic percent) were melted and remelted five times in an arc furnace under an argon atmosphere to ensure compositional homogeneity. Additional homogenization heat treatment was carried out for the six alloys in quartz capsules filled with argon at 950°C for 168 hours followed by water quenching. All alloys after homogenization were examined by X-ray diffraction and scanning electron microscopy (SEM) equipped with X-ray energy spectroscopy (XEDS) for compositional and microstructural homogeneity. Detailed alloy selection, and both the nominal and measured alloy compositions are reported in Table 3 [84]. These six starting alloys were also marked in the ternary phase diagram, as shown in Figure 16. Alloys were then sectioned into small pieces with a thickness of approximate 3 mm using a low speed diamond saw.

Table 3 Nominal and XEDS-measured alloy compositions for the diffusion couples in atomic percent.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Nominal Composition (at. %)</th>
<th>e/a</th>
<th>EDS-measured Composition (wt. %)</th>
<th>e/a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Mn</td>
<td>Ga</td>
<td>Ni</td>
</tr>
<tr>
<td>1</td>
<td>52</td>
<td>18</td>
<td>30</td>
<td>7.36</td>
</tr>
<tr>
<td>2</td>
<td>45</td>
<td>30</td>
<td>25</td>
<td>7.35</td>
</tr>
<tr>
<td>3</td>
<td>52</td>
<td>30</td>
<td>18</td>
<td>7.84</td>
</tr>
<tr>
<td>4</td>
<td>58</td>
<td>18</td>
<td>24</td>
<td>7.78</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>25</td>
<td>75</td>
<td>0</td>
<td>7.75</td>
</tr>
</tbody>
</table>
Figure 16 Ternary phase diagram at 900 °C showing the starting alloy compositions.

3.2. Diffusion Couple Assembly and Annealing

The surface of each alloy piece was metallographically ground with 600, 800 and 1200 SiC papers to obtain a flat and smooth surface just before diffusion couple assembly. High purity ethanol was used during the grinding process as the lubricant to avoid oxidation. The surfaces of two selected alloys were placed in contact and held tightly by two stainless steel clamping disks to form a jig. Al₂O₃ spacers were placed in between the stainless steel discs and diffusion couples to prevent any possible reaction at high temperature. A schematic representation of the diffusion couple assembly is shown in Figure 17.
The assembled diffusion couples, with a piece of Ta foil (i.e., an oxygen getter) were encapsulated in quartz capsules, which were repeatedly evacuated and purged with argon to reach a vacuum of $10^{-9}$ atm ($10^{-6}$ torr). Finally the capsule was backfilled with UHP argon so that the pressure in the capsule remained slightly higher than 1 atm at high temperature, and sealed.

Diffusion annealing was performed using a Lindberg/Blue™ three-zone tube furnace. Each set of diffusion couples were annealed at 800°C, 850°C and 900°C for 480, 240 and 120 hours, respectively. Eight sets, and thus a total of twenty four diffusion couples, were prepared and annealed in this study as listed in Table 4. These diffusion couples were separated into three series, namely, Ni vs. Ni-Mn-Ga (series I), Ni-Mn vs. Ni-Mn-Ga (series II) and Ni-Mn-Ga vs. Ni-Mn-Ga (series III). After annealing, the quartz capsules were quickly removed from the furnace, dropped into cold water and broken. After quenching, the diffusion couples were
mounted in epoxy and metallographically polished down to 0.25 μm using diamond paste for characterization.

Table 4 Terminal compositions, in atomic percent, of the diffusion couples, and the temperature and time of diffusion anneal.

<table>
<thead>
<tr>
<th>Series</th>
<th>Diffusion Couples</th>
<th>Temperature (°C)</th>
<th>Time (hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Ni vs. Ni$<em>{52}$Mn$</em>{18}$Ga$_{30}$</td>
<td>800</td>
<td>480</td>
</tr>
<tr>
<td></td>
<td></td>
<td>850</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td></td>
<td>900</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>Ni vs. Ni$<em>{46}$Mn$</em>{30}$Ga$_{24}$</td>
<td>800</td>
<td>480</td>
</tr>
<tr>
<td></td>
<td></td>
<td>850</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td></td>
<td>900</td>
<td>120</td>
</tr>
<tr>
<td>II</td>
<td>Ni$<em>{25}$Mn$</em>{75}$ vs. Ni$<em>{52}$Mn$</em>{18}$Ga$_{30}$</td>
<td>800</td>
<td>480</td>
</tr>
<tr>
<td></td>
<td></td>
<td>850</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td></td>
<td>900</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>Ni$<em>{25}$Mn$</em>{75}$ vs. Ni$<em>{46}$Mn$</em>{30}$Ga$_{24}$</td>
<td>800</td>
<td>480</td>
</tr>
<tr>
<td></td>
<td></td>
<td>850</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td></td>
<td>900</td>
<td>120</td>
</tr>
<tr>
<td>III</td>
<td>Ni$<em>{52}$Mn$</em>{18}$Ga$<em>{30}$ vs. Ni$</em>{52}$Mn$<em>{30}$Ga$</em>{18}$</td>
<td>800</td>
<td>480</td>
</tr>
<tr>
<td></td>
<td></td>
<td>850</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td></td>
<td>900</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>Ni$<em>{52}$Mn$</em>{18}$Ga$<em>{30}$ vs. Ni$</em>{58}$Mn$<em>{18}$Ga$</em>{24}$</td>
<td>800</td>
<td>480</td>
</tr>
<tr>
<td></td>
<td></td>
<td>850</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td></td>
<td>900</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>Ni$<em>{46}$Mn$</em>{30}$Ga$<em>{24}$ vs. Ni$</em>{52}$Mn$<em>{30}$Ga$</em>{18}$</td>
<td>800</td>
<td>480</td>
</tr>
<tr>
<td></td>
<td></td>
<td>850</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td></td>
<td>900</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>Ni$<em>{46}$Mn$</em>{30}$Ga$<em>{24}$ vs. Ni$</em>{58}$Mn$<em>{18}$Ga$</em>{24}$</td>
<td>800</td>
<td>480</td>
</tr>
<tr>
<td></td>
<td></td>
<td>850</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td></td>
<td>900</td>
<td>120</td>
</tr>
</tbody>
</table>

3.3. Characterization of Interdiffusion Zone

The microstructure of each diffusion couple was examined by a Zeiss™ Ultra-55 field emission scanning electron microscope (FE-SEM). Concentration profiles across the interdiffusion zone were obtained by both the electron probe micro analyzer (EPMA, JEOL
8900R Superprobe) and X-ray energy dispersive spectroscopy (XEDS) equipped on the FE-SEM. The operation conditions for EPMA were 20 kV of accelerating voltage and 20 nA of probe current, with step size of 10 μm. For the thin intermetallic phase formed in diffusion couple Ni/Ni$_{52}$Mn$_{18}$Ga$_{30}$, a step size of 2 μm was used. Multiple EPMA line scans at different positions of the interdiffusion zones were collected and analyzed for each diffusion couple. The concentration profiles for each diffusion couple was fitted using piecewise cubic smoothing splines for subsequent quantitative analyses.

Detailed microstructure and crystal structure of the phases were investigated by a FEI/Tecnai™ F30 300 kV transmission electron microscope (TEM). In situ lift out (INLO) technique was employed to obtain site-specific TEM thin foils by using a FEI™ TEM200 focused ion beam (FIB). Figure 18 illustrates the preparation process of the TEM foil using FIB. The location of the interested area is first identified through the secondary electron image. After milling two trenches around, the foil is lifted out using a W probe and welded to a Cu TEM grid. Further thinning process is carried out until the foil is less than 100 nm. A low milling current of 10 pA during the final stage of thinning was used to minimize any damages. Cleaning of the TEM foils were carried out using plasma cleaner before loading into TEM to remove any contamination.
3.4. Mechanical Testing by Nanoindentation

Nanoindentation can be used to obtain mechanical properties of materials within small volume, which is appropriate to extract the mechanical property from the diffusion couples. For assessment of the mechanical property through nanoindentation, the Oliver-Pharr method [85, 86] was employed. Figure 19 presents a schematic of a typical load vs. displacement curve from nanoindentation. Hardness (H) and reduced elastic modulus (E_r) can be extracted from the load-displacement curve, according to the following equations:
\[ H = \frac{P_{\text{max}}}{A} \]  

(7)

\[ E_r = \frac{S \sqrt{\pi}}{2 \sqrt{A}} \]  

(8)

where \( P_{\text{max}} \) is the maximum load applied, \( A \) is the contact area and \( S \) is the initial unloading stiffness. \( A \) is the contact area as a function of contact depth \( (h_c) \) which can be determined using the equation:

\[ h_c = h_{\text{max}} - \varepsilon \frac{P_{\text{max}}}{S} \]  

(9)

where \( h_{\text{max}} \) is the maximum indentation depth, \( \varepsilon \) is a constant \((0.75)\) used to account for edge effects including the deflection of the surface at the contact perimeter. For a Berkovich tip, \( A \) can be described by an \( n^{\text{th}} \) \((n = 3 - 6)\) order polynomial in which the coefficients are determined through tip area calibration on a standard fused quartz sample before testing.

The reduced elastic modulus acquired from the indentation test is a composite value influenced by both the elastic properties of the test sample and the indenter, following the equation below:

\[ \frac{1}{E_r} = \left( \frac{1-\nu_i^2}{E_i} \right) + \left( \frac{1-\nu_s^2}{E_s} \right) \]  

(10)

where \( E_i \) and \( \nu_i \) are the Young’s modulus and Poisson’s ratio of the indenter, \( E_s \) and \( \nu_s \) are the Young’s modulus and Poisson’s ratio of the test materials. Therefore, the Young’s modulus of the material can be calculated provided that the Poisson’s ratio is known.
In this study, nanoindentation measurements were carried out using a Hysitron™ TI Premier instrumented quasi-static nano-mechanical tester with a 100 nm diamond Berkovich tip. The Young’s modulus and Poisson’s ratio for the tip is 1140 GPa and 0.07. Load controlled indentation tests were conducted at room temperature using line profile perpendicularly across the interdiffusion zone for each diffusion couple. Each indentation line profile consists of 50 – 150 indents depending on the length of the interdiffusion zone. Three line profiles were carried out for each diffusion couple in order to obtain standard deviations. The separation between each indent was 20 μm both horizontally and vertically, in order to avoid any influence from adjacent and previous indents. A schematic representation of the nanoindentation test for the diffusion
couples is shown in Figure 20. Each indentation measurement consisted of a 5 second loading cycle to a peak load of 5 mN, followed by a 2 second hold segment and then a 10 second unloading cycle. Reduced elastic modulus and hardness values were determined from the load-displacement curves according to the Oliver-Pharr method [85, 86] as discussed before. After the nanoindentation measurement, each diffusion couple was examined by an optical microscope (Olympus LEXT OLS 3000) under polarized light or SEM so as to coordinate the location of each indent.

Figure 20 A schematic representation of the nanoindentation test.
4.1. Analytical Framework for Interdiffusion

In this study, the interdiffusion flux of individual component for each diffusion couple was calculated by [87, 88]:

\[ \bar{J}_i = \frac{C_i^+ - C_i^-}{2t} \left[ Y_i \left[ \int_{x_i}^{x} \frac{1 - Y_i}{V_m} dx + \int_{x_i}^{x} \frac{Y_i}{V_m} dx \right] \right] \quad (i = Ni, Mn, Ga) \]  

where \( \bar{J}_i \) is the interdiffusion flux, \( x \) is the distance, \( C_i^+ \) and \( C_i^- \) represent compositions of component \( i \) at the terminal ends of the diffusion couples, \( V_m \) is the molar volume, and \( Y_i \) is the relative concentration variable defined as \( Y_i = (C_i - C_i^-) / (C_i^+ - C_i^-) \). It is assumed that the variation in molar volume follows Vegard’s law in the \( \gamma \) solid solution regions as:

\[ V_m^\gamma = V_m^{Ni} C_{Ni} + V_m^{Mn} C_{Mn} + V_m^{Ga} C_{Ga} \]  

where \( V_m^\gamma \) is the molar volume of the \( \gamma \) solid solution, \( V_m^{Ni} \), \( V_m^{Mn} \) and \( V_m^{Ga} \) are molar volume of Ni, Mn and Ga which equal to \( 6.6 \times 10^{-6} \), \( 7.3 \times 10^{-6} \) and \( 11.2 \times 10^{-6} \) m\(^3\)/mol, respectively. Variables \( C_{Ni}, C_{Mn} \) and \( C_{Ga} \) are composition given by atomic percent of Ni, Mn and Ga. It is also assumed a constant molar volume in the \( \beta \) phase region as will be validated later.

The average effective interdiffusion coefficient \( \tilde{D}_i^{eff} \), which represents the interdiffusion behavior over a selected compositional range, is also calculated using the equation [89, 90]:

\[ \tilde{D}_i^{eff} = \frac{\int_{x_i}^{x_{1/2}} \bar{J}_i dx}{C_{i_i}^{x_{1/2}} - C_{i_i}^{x_i}} \quad (i = Ni, Mn, Ga) \]
where $x_1$ and $x_2$ represent two different locations, and $C_i^{x_1}$ and $C_i^{x_2}$ is the corresponding composition at these two locations.

For certain independent pairs of diffusion couples, concentration profiles share a common composition (i.e., intersection of diffusion paths plotted on ternary isothermal phase diagram), and the main and cross ternary interdiffusion coefficient at the common composition can be determined since:

$$\tilde{J}_i = -\sum_{j=1}^{n-1} \tilde{D}_{ij} \frac{\partial C_j}{\partial x} \quad (i = 1, 2, ..., n - 1) \quad (14)$$

Eq. (14) can be specifically expressed for the ternary Ni-Mn-Ga system with Ni as the dependent concentration variable:

$$\tilde{J}_{Mn} = -\tilde{D}_{MnMn} \frac{\partial C_{Mn}}{\partial x} - \tilde{D}_{MnGa} \frac{\partial C_{Ga}}{\partial x}$$
$$\tilde{J}_{Ga} = -\tilde{D}_{GaMn} \frac{\partial C_{Mn}}{\partial x} - \tilde{D}_{GaGa} \frac{\partial C_{Ga}}{\partial x}$$
$$\tilde{J}_{Ni} = -(\tilde{J}_{Mn} + \tilde{J}_{Ga}) \quad (15)$$

For the pair of diffusion couple with a common composition, a total of four equations can be set up, so that the four main and cross interdiffusion coefficients can be obtained. In addition, for some diffusion couples, concentration profiles exhibit a relative maximum or minimum, $\frac{\partial C_i}{\partial x} = 0$, and a partial set of main or cross interdiffusion coefficients can be directly determined based on Eq. (15).
4.2. Phase Equilibrium and Martensitic Transformation

Figure 21 presents XRD patterns collected at room temperature from the six terminal alloys after homogenization. XRD patterns for Ni$_{52}$Mn$_{18}$Ga$_{30}$ and Ni$_{46}$Mn$_{30}$Ga$_{24}$ alloys corresponded to the austenitic phase at room temperature and were indexed according to the L2$_1$ crystal structure [31]. The lattice parameters were calculated to be $a = 0.5811$ nm and $a = 0.5836$ nm, respectively, for Ni$_{52}$Mn$_{18}$Ga$_{30}$ and Ni$_{46}$Mn$_{30}$Ga$_{24}$ alloys. XRD patterns from alloys Ni$_{52}$Mn$_{30}$Ga$_{18}$ and Ni$_{58}$Mn$_{18}$Ga$_{24}$ corresponded to the martensitic phase and were indexed according to the crystal structure of non-modulated (NM) tetragonal martensite [27]. The lattice parameters were $a = 0.5395$ nm, $c = 0.6702$ nm and $a = 0.5390$ nm, $c = 0.6646$ nm, respectively, for Ni$_{52}$Mn$_{30}$Ga$_{18}$ and Ni$_{58}$Mn$_{18}$Ga$_{24}$ alloys. No other phases were observed from the XRD patterns, indicating that these four alloys consisted of only the $\beta$ phase at high temperature [48, 81]. Ni and Ni$_{25}$Mn$_{75}$ both had a face centered cubic crystal structure, with lattice parameters of $a = 0.3524$ nm and $a = 0.3684$ nm, respectively, according to the XRD patterns shown in Figure 21.
Figure 21 X-ray diffraction patterns of the six starting alloys after homogenization at room temperature.

Microstructures, concentration profiles and the corresponding interdiffusion flux profiles for diffusion couples Ni vs. Ni_{52}Mn_{18}Ga_{30} and Ni_{25}Mn_{75} vs. Ni_{46}Mn_{30}Ga_{24} annealed at 900 °C for 120 hours are presented in Figure 22 and Figure 23. They represent typical microstructure, concentration profiles and interdiffusion flux profiles from the series I and series II diffusion couples. Diffusion couples that were annealed at 800 °C and 850 °C exhibited similar interdiffusion microstructures and concentration profiles. The interdiffusion zone consisted of γ (either Ni- or Mn-rich) and β phases. Part of the β phase, closer to the Ni and NiMn alloy, transformed to martensite during quenching, as revealed by the lamellar microstructure in Figure 22 and Figure 23. The contrast of the lamellas for the martensitic phases primarily comes from
the orientation difference, not the compositional difference. The rest of β phase remained as austenite, and thus an interface separating austenite and martensite was observed as labeled in Figure 22 and Figure 23.

For the diffusion couple Ni vs. Ni₅₂Mn₁₈Ga₃₀, an intermetallic phase formed between γ(Ni) and β phase during interdiffusion. Representative micrographs highlighting this intermetallic phase are presented in Figure 24 using the couple annealed at 800 °C. To confirm and investigate the phases, TEM characterization was carried out on thin foils that were prepared using FIB-INLO technique. The selected areas for TEM sample prepared by FIB-INLO are illustrated by two solid white rectangles shown in Figure 24(a). The first area was chosen at the interface between the intermetallic phase and martensitic phase. Figure 25(a) shows the bright field (BF) TEM micrograph of the intermetallic phase, and Figure 25(b) and (c) show the corresponding selected area diffraction pattern (SADP) from two different orientations. The SADPs confirmed that the intermetallic phase is α’-(Ni,Mn)₃(Ga,Mn) phase, which has a L₁₂ crystal structure with lattice parameter of a = 3.59Å. The lattice parameter is close to that reported for α’-Ni₃Ga phase [13, 91], despite some dissolved Mn.
Figure 22 (a) Backscatter electron micrographs, (b) concentration profiles, and the corresponding (c) interdiffusion fluxes of Ni, Mn and Ga from the diffusion couple Ni vs. Ni$_{52}$Mn$_{18}$Ga$_{30}$ annealed at 900 °C for 120 hours. Capital A represents austenite and M represents martensite.
Figure 23 (a) Backscatter electron micrographs, (b) concentration profiles, and the corresponding (c) interdiffusion fluxes of Ni, Mn and Ga from the diffusion couple \( \text{Ni}_{25}\text{Mn}_{75} \) vs. \( \text{Ni}_{46}\text{Mn}_{30}\text{Ga}_{24} \) annealed at 900 °C for 120 hours. Capital A represents austenite and M represents martensite.
The equilibrium phase compositions (i.e., solubility limits) determined by EPMA from
diffusion couples annealed at 800 °C, 850 °C and 900 °C are listed in Table 5. Since the
compositions were typically measured by XEDS by other investigators [92], for comparison,
Table 6 also lists the compositions determined by XEDS in this study. Compositions obtained by
EPMA and XEDS agree well. Combining the EPMA data obtained from this study and results
from previous investigations [48, 81, 91], the isothermal ternary phase diagrams at 800°C, 850°C
and 900°C were constructed as illustrated in Figure 26.

Figure 24 Backscatter electron micrograph for diffusion couples Ni vs. Ni$_{52}$Mn$_{18}$Ga$_{30}$ annealed at
800 °C for 480 hours at (a) low magnification and (b) high magnification. Two small white
rectangles in (a) represent the areas for TEM analyses
Figure 25 (a) BF TEM micrograph of the $\alpha'$-(Ni,Mn)$_3$(Ga,Mn) phase, and the corresponding selected area diffraction patterns from orientation, (b) $[11\bar{1}]$ and (c) $[1\bar{1}2]$

Table 5 Equilibrium compositions of the $\gamma$, $\alpha'$ and $\beta$ phases, in atomic percent, determined by EPMA from the diffusion couple series I and II annealed at 800 °C, 850 °C and 900 °C.

<table>
<thead>
<tr>
<th>Diffusion Couples</th>
<th>Temperature (°C)</th>
<th>$\gamma$</th>
<th>$\beta$</th>
<th>$\alpha'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni vs. Ni$<em>{52}$Mn$</em>{18}$Ga$_{30}$</td>
<td>800</td>
<td>72.8</td>
<td>11.1</td>
<td>16.1</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>73.2</td>
<td>11.5</td>
<td>15.3</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>73.0</td>
<td>12.3</td>
<td>14.7</td>
</tr>
<tr>
<td>Ni vs. Ni$<em>{46}$Mn$</em>{30}$Ga$_{24}$</td>
<td>800</td>
<td>66.8</td>
<td>21.9</td>
<td>11.3</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>65.3</td>
<td>21.9</td>
<td>12.8</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>66.4</td>
<td>21.4</td>
<td>12.2</td>
</tr>
<tr>
<td>Ni$<em>{25}$Mn$</em>{75}$ vs. Ni$<em>{52}$Mn$</em>{18}$Ga$_{30}$</td>
<td>800</td>
<td>29.2</td>
<td>62.7</td>
<td>8.1</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>30.1</td>
<td>61.3</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>31.8</td>
<td>58.9</td>
<td>9.3</td>
</tr>
<tr>
<td>Ni$<em>{25}$Mn$</em>{75}$ vs. Ni$<em>{46}$Mn$</em>{30}$Ga$_{24}$</td>
<td>800</td>
<td>28.8</td>
<td>63.1</td>
<td>8.1</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>31.0</td>
<td>58.8</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>31.9</td>
<td>58.9</td>
<td>9.2</td>
</tr>
</tbody>
</table>
Table 6 Equilibrium compositions of the $\gamma$, $\alpha'$ and $\beta$ phases, in atomic percent, determined from the diffusion couples annealed at 800 °C, 850 °C and 900 °C by XEDS.

| Diffusion Couples | Temperature (°C) | $\gamma$ | | | | | | $\beta$ | | | | | | $\alpha'$ | | | | | | | |
|-------------------|-----------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Ni vs. Ni$_{52}$Mn$_{18}$Ga$_{30}$ | 800 | 72.3 | 10.7 | 17.0 | 58.3 | 14.9 | 26.8 | 70.6 | 8.4 | 20.9 | 67.2 | 7.6 | 25.2 | 68.1 | 8.5 | 23.4 |
| Ni vs. Ni$_{46}$Mn$_{30}$Ga$_{24}$ | 800 | 65.1 | 22.9 | 12.0 | 54.5 | 26.2 | 19.3 | - | - | - | - | - | - | - | - | - |
| Ni$_{25}$Mn$_{75}$ vs. Ni$_{52}$Mn$_{18}$Ga$_{30}$ | 800 | 29.3 | 62.2 | 8.5 | 38.0 | 48.9 | 13.1 | - | - | - | - | - | - | - | - | - |
| Ni$_{25}$Mn$_{75}$ vs. Ni$_{46}$Mn$_{30}$Ga$_{24}$ | 800 | 28.6 | 63.3 | 8.1 | 37.8 | 48.1 | 14.1 | - | - | - | - | - | - | - | - | - |

Figure 27, Figure 28 and Figure 29 present the microstructures, concentration profiles and calculated interdiffusion flux profiles, respectively for diffusion couples, Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni$_{52}$Mn$_{30}$Ga$_{18}$, Ni$_{46}$Mn$_{30}$Ga$_{24}$ vs. Ni$_{52}$Mn$_{30}$Ga$_{18}$, Ni$_{46}$Mn$_{30}$Ga$_{24}$ vs. Ni$_{58}$Mn$_{18}$Ga$_{24}$, and, annealed at 900°C for 120 hours. These figures represent typical results from diffusion couple series III. The interdiffusion zones for all diffusion couples show uniform microstructure on the left-hand-side and lamellar microstructure on the other side at room temperature with a clear phase boundary as labeled in Figure 27 through Figure 29. The two distinctive contrasts correspond to the austenitic and martensitic phases, respectively, similar to those observed in series I and series II diffusion couples.
Figure 26 Isothermal ternary phase diagram at (a) 800 °C, (b) 850 °C and (c) 900 °C for Ni-Mn-Ga system with solubility compositions previously reported and determined from the current study. Data from the current study is given in solid squares while those from others presented by crosses.
Figure 27 (a) Backscatter electron micrographs, (b) concentration profiles, and (c) the corresponding interdiffusion fluxes of Ni, Mn and Ga from the diffusion couple, Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni$_{52}$Mn$_{30}$Ga$_{18}$ annealed at 900 °C for 120 hours. Capital A represents austenite and M represents martensite.
Figure 28 (a) Backscatter electron micrographs, (b) concentration profiles, and (c) the corresponding interdiffusion fluxes of Ni, Mn and Ga from the diffusion couple, Ni$_{46}$Mn$_{30}$Ga$_{24}$/Ni$_{52}$Mn$_{30}$Ga$_{18}$ annealed at 900 °C for 120 hours. Capital A represents austenite and M represents martensite.
Figure 29 (a) Backscatter electron micrographs, (b) concentration profiles, and (c) the corresponding interdiffusion fluxes of Ni, Mn and Ga from the diffusion couple, $\text{Ni}_{46}\text{Mn}_{30}\text{Ga}_{24}$ vs. $\text{Ni}_{58}\text{Mn}_{18}\text{Ga}_{24}$ annealed at 900 °C for 120 hours. Capital A represents austenite and M represents martensite.
The compositions at the interface separating austenite and martensite from each diffusion couple was determined from the EPMA concentration profiles, and are listed in Table 7 and plotted on the room-temperature ternary phase diagram as shown in Figure 30. Since all diffusion couples were quenched in water, the presence of austenite in the diffusion couple corresponds to compositions with martensitic transformation temperatures lower than room temperature. On the other hand, the presence of martensite reveals the compositional range with martensite transformation temperatures higher than room temperature. Therefore, the compositions at the interface, listed in Table 7, possess near-room temperature martensitic transformation, suitable for room temperature applications.

Figure 30 Compositions with martensitic transformation near room temperature. Squares, circles and triangles represent compositions obtained from diffusion couples annealed at 800 °C, 850 °C and 900 °C, respectively.
Table 7 The Ni-Mn-Ga alloy compositions, in atomic percent, and the corresponding e/a ratio, at the interface between the austenite and martensite determined from the concentration profiles.

<table>
<thead>
<tr>
<th>Diffusion Couples</th>
<th>Temperature (°C)</th>
<th>Atom Percent (at. %)</th>
<th>e/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni vs. Ni52Mn18Ga30</td>
<td>800</td>
<td>55.8</td>
<td>15.6</td>
</tr>
<tr>
<td>Ni vs. Ni52Mn18Ga30</td>
<td>850</td>
<td>55.9</td>
<td>15.9</td>
</tr>
<tr>
<td>Ni vs. Ni52Mn18Ga30</td>
<td>900</td>
<td>55.5</td>
<td>16.5</td>
</tr>
<tr>
<td>Ni vs. Ni46Mn30Ga24</td>
<td>800</td>
<td>51.2</td>
<td>25.9</td>
</tr>
<tr>
<td>Ni vs. Ni46Mn30Ga24</td>
<td>850</td>
<td>51.6</td>
<td>25.7</td>
</tr>
<tr>
<td>Ni vs. Ni46Mn30Ga24</td>
<td>900</td>
<td>51.4</td>
<td>25.9</td>
</tr>
<tr>
<td>Ni25Mn75 vs. Ni52Mn18Ga30</td>
<td>800</td>
<td>44.3</td>
<td>34.9</td>
</tr>
<tr>
<td>Ni25Mn75 vs. Ni52Mn18Ga30</td>
<td>850</td>
<td>43.8</td>
<td>35.2</td>
</tr>
<tr>
<td>Ni25Mn75 vs. Ni52Mn18Ga30</td>
<td>900</td>
<td>43.9</td>
<td>35.1</td>
</tr>
<tr>
<td>Ni25Mn75 vs. Ni46Mn30Ga24</td>
<td>800</td>
<td>42.2</td>
<td>35.8</td>
</tr>
<tr>
<td>Ni25Mn75 vs. Ni46Mn30Ga24</td>
<td>850</td>
<td>43.3</td>
<td>34.7</td>
</tr>
<tr>
<td>Ni25Mn75 vs. Ni46Mn30Ga24</td>
<td>900</td>
<td>43.7</td>
<td>35.4</td>
</tr>
<tr>
<td>Ni52Mn18Ga30 vs. Ni52Mn30Ga18</td>
<td>800</td>
<td>51.6</td>
<td>25.7</td>
</tr>
<tr>
<td>Ni52Mn18Ga30 vs. Ni52Mn30Ga18</td>
<td>850</td>
<td>52.0</td>
<td>25.1</td>
</tr>
<tr>
<td>Ni52Mn18Ga30 vs. Ni52Mn30Ga18</td>
<td>900</td>
<td>52.0</td>
<td>24.9</td>
</tr>
<tr>
<td>Ni52Mn18Ga30 vs. Ni58Mn18Ga24</td>
<td>800</td>
<td>54.7</td>
<td>17.4</td>
</tr>
<tr>
<td>Ni52Mn18Ga30 vs. Ni58Mn18Ga24</td>
<td>850</td>
<td>55.0</td>
<td>17.5</td>
</tr>
<tr>
<td>Ni52Mn18Ga30 vs. Ni58Mn18Ga24</td>
<td>900</td>
<td>54.9</td>
<td>17.4</td>
</tr>
<tr>
<td>Ni46Mn30Ga24 vs. Ni52Mn30Ga18</td>
<td>800</td>
<td>49.6</td>
<td>29.9</td>
</tr>
<tr>
<td>Ni46Mn30Ga24 vs. Ni52Mn30Ga18</td>
<td>850</td>
<td>49.4</td>
<td>30.4</td>
</tr>
<tr>
<td>Ni46Mn30Ga24 vs. Ni52Mn30Ga18</td>
<td>900</td>
<td>49.4</td>
<td>29.8</td>
</tr>
<tr>
<td>Ni46Mn30Ga24 vs. Ni58Mn18Ga24</td>
<td>800</td>
<td>51.7</td>
<td>24.2</td>
</tr>
<tr>
<td>Ni46Mn30Ga24 vs. Ni58Mn18Ga24</td>
<td>850</td>
<td>51.9</td>
<td>23.5</td>
</tr>
<tr>
<td>Ni46Mn30Ga24 vs. Ni58Mn18Ga24</td>
<td>900</td>
<td>51.3</td>
<td>24.5</td>
</tr>
</tbody>
</table>

4.3. Interdiffusion Coefficients

The molar volumes, based on the lattice parameters determined, were estimated to be $7.38 \times 10^{-6}$, $7.48 \times 10^{-6}$, $7.34 \times 10^{-6}$, $7.26 \times 10^{-6}$, $6.60 \times 10^{-6}$ and $7.52 \times 10^{-6}$ m$^3$/mol, respectively, for the Ni$_{52}$Mn$_{18}$Ga$_{30}$, Ni$_{46}$Mn$_{30}$Ga$_{24}$, Ni$_{52}$Mn$_{30}$Ga$_{18}$, Ni$_{58}$Mn$_{18}$Ga$_{24}$, Ni and Ni$_{25}$Mn$_{75}$ alloys. Meanwhile, the molar volume of (Ni, Mn)$_3$(Mn, Ga) phase is $7.02 \times 10^{-6}$ m$^3$/mol according to the TEM measurement. For the ternary NiMnGa alloys, the volume change for transformation from
austenite to martensite in Ni-Mn-Ga alloys would be very small [4, 93]. Therefore, similar values of molar volumes validate the assumption of constant molar volume for the β phase during interdiffusion, as mentioned in section 3. Furthermore, the order-disorder transformation in Ni$_2$MnGa [94], from L2$_1$ structure to B2 structure occurs at 788 °C, and the transformation temperature decreases as the composition deviates away from the stoichiometric composition [24, 25, 92, 94, 95]. Therefore, the interdiffusion in the β phase examined in this study occurs in the B2 structure at and above 800 °C.

Series III diffusion couples were designed so that each diffusion couple has one component with similar terminal concentrations. For example, the iso-concentration component is Ni for the diffusion couple Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni$_{52}$Mn$_{30}$Ga$_{18}$ shown in Figure 27, Mn for Ni$_{46}$Mn$_{30}$Ga$_{24}$ vs. Ni$_{52}$Mn$_{30}$Ga$_{18}$ shown in Figure 28, and Ga for Ni$_{46}$Mn$_{30}$Ga$_{24}$ vs. Ni$_{58}$Mn$_{18}$Ga$_{24}$ shown in Figure 29. The concentration profiles for the iso-concentration component exhibited relative extrema as a result of interdiffusion flux of the other independent component, frequently observed in ternary systems with significant diffusional interactions [96, 97].

The diffusion paths for all diffusion couples annealed at 800 °C, 850 °C and 900 °C are presented on the isothermal ternary phase diagram in Figure 31. A typical S shape diffusion path is observed for series I and III diffusion couples, while series II diffusion couples exhibit a double-serpentine diffusion path [98, 99].

The average effective interdiffusion coefficients for the three components in β phase from each diffusion couple are reported in Table 8 and Table 9. The values are only calculated for two components from series III diffusion couples, and not for the iso-concentration component, since
Equation (3) does not allow for calculations with negligible compositional differences. The average effective interdiffusion coefficients along with the standard deviations, separately for each diffusion couple, are also plotted as a function of inverse absolute temperature in Figure 32. All exhibit a good Arrhenius temperature-dependence in the compositional range examined in this study. The activation energies and pre-exponential factors of the average effective interdiffusion coefficients were calculated as also reported in Table 8 and Table 9. Overall, the average interdiffusion coefficients determined from series I and II diffusion couples were larger than those from series III diffusion couples. It should be noted that the diffusion paths for series III diffusion couples ranged nearby the stoichiometric composition.

Since the diffusion paths between Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni$_{52}$Mn$_{30}$Ga$_{18}$ and Ni$_{46}$Mn$_{30}$Ga$_{24}$ vs. Ni$_{58}$Mn$_{18}$Ga$_{24}$, and between Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni$_{52}$Mn$_{30}$Ga$_{18}$ and Ni vs. Ni$_{46}$Mn$_{30}$Ga$_{24}$ intersect at a common composition, as shown by Figure 31, the ternary interdiffusion coefficients were calculated for this composition using Equation (5). In addition, ternary interdiffusion coefficients were determined at compositions where the concentration gradient of a component (e.g., relative maximum and minimum in iso-concentration component shown in Figure 27, Figure 28 and Figure 29) is zero. The calculated ternary interdiffusion coefficients and the corresponding compositions are reported in Table 10, Table 11 and Table 12.
Figure 31 Diffusion paths from diffusion couples annealed at (a) 800 °C, (b) 850 °C and (c) 900 °C plotted on isothermal Ni-Mn-Ga phase diagram.
Figure 32 Temperature dependence of average effective interdiffusion coefficients for Ni, Mn and Ga in the β phase. The average effective interdiffusion coefficients were determined from diffusion couples, (a) Ni vs. Ni_{52}Mn_{18}Ga_{30}, (b) Ni vs. Ni_{46}Mn_{30}Ga_{24}, (c) Ni_{25}Mn_{75} vs. Ni_{52}Mn_{18}Ga_{30} (d) Ni_{25}Mn_{75} vs. Ni_{46}Mn_{30}Ga_{24}, and (e) Ni_{52}Mn_{18}Ga_{30} vs. Ni_{52}Mn_{30}Ga_{18}, (f) Ni_{52}Mn_{18}Ga_{30} vs. Ni_{58}Mn_{18}Ga_{24}, (g) Ni_{46}Mn_{30}Ga_{24} vs. Ni_{52}Mn_{30}Ga_{18}, (h) Ni_{46}Mn_{30}Ga_{24} vs. Ni_{58}Mn_{18}Ga_{24}. 
Table 8 Average effective interdiffusion coefficients and the corresponding activation energy and pre-exponential factor for Ni, Mn and Ga in the β phase determined from series I and II diffusion couples.

<table>
<thead>
<tr>
<th>Diffusion couple</th>
<th>Temperature (°C)</th>
<th>( \tilde{D}_{Ni}^{\text{eff}} ) (m²/s)</th>
<th>( \tilde{Q}_{Ni}^{\text{eff}} ) (kJ/mole)</th>
<th>( \tilde{D}_{0,Ni}^{\text{eff}} ) (m²/s)</th>
<th>( \tilde{Q}_{0,Ni}^{\text{eff}} ) (kJ/mole)</th>
<th>( \tilde{D}_{Mn}^{\text{eff}} ) (m²/s)</th>
<th>( \tilde{Q}_{0,Mn}^{\text{eff}} ) (kJ/mole)</th>
<th>( \tilde{D}_{Ga}^{\text{eff}} ) (m²/s)</th>
<th>( \tilde{Q}_{Ga}^{\text{eff}} ) (kJ/mole)</th>
<th>( \tilde{D}_{0,Ga}^{\text{eff}} ) (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni vs. Ni_{52}Mn_{18}Ga_{30}</td>
<td>800</td>
<td>4.34 (0.43) \times 10^{-14}</td>
<td>161.9 (8.2)</td>
<td>4.17 (2.64) \times 10^{-6}</td>
<td>164.6 (7.3)</td>
<td>5.73 (3.17) \times 10^{-6}</td>
<td>159.9 (5.2)</td>
<td>2.35 (2.04) \times 10^{-04}</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>9.90 (0.40) \times 10^{-14}</td>
<td>161.9 (8.2)</td>
<td>4.17 (2.64) \times 10^{-6}</td>
<td>164.6 (7.3)</td>
<td>5.73 (3.17) \times 10^{-6}</td>
<td>159.9 (5.2)</td>
<td>2.35 (2.04) \times 10^{-04}</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>2.03 (0.01) \times 10^{-13}</td>
<td>181.0 (1.3)</td>
<td>1.39 (0.28) \times 10^{-6}</td>
<td>145.5 (4.4)</td>
<td>6.27 (1.69) \times 10^{-5}</td>
<td>204.7 (12.6)</td>
<td>1.01 (0.88) \times 10^{-04}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni vs. Ni_{46}Mn_{30}Ga_{24}</td>
<td>800</td>
<td>2.38 (0.24) \times 10^{-14}</td>
<td>181.0 (1.3)</td>
<td>1.39 (0.28) \times 10^{-6}</td>
<td>145.5 (4.4)</td>
<td>6.27 (1.69) \times 10^{-5}</td>
<td>204.7 (12.6)</td>
<td>1.01 (0.88) \times 10^{-04}</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>6.20 (0.78) \times 10^{-14}</td>
<td>181.0 (1.3)</td>
<td>1.39 (0.28) \times 10^{-6}</td>
<td>145.5 (4.4)</td>
<td>6.27 (1.69) \times 10^{-5}</td>
<td>204.7 (12.6)</td>
<td>1.01 (0.88) \times 10^{-04}</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>1.36 (0.15) \times 10^{-13}</td>
<td>217.9 (1.5)</td>
<td>3.34 (2.94) \times 10^{-3}</td>
<td>179.0 (2.8)</td>
<td>4.35 (1.03) \times 10^{-05}</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni_{25}Mn_{75} vs. Ni_{52}Mn_{18}Ga_{30}</td>
<td>800</td>
<td>1.24 (0.02) \times 10^{-13}</td>
<td>156.3 (0.2)</td>
<td>5.14 (0.06) \times 10^{-6}</td>
<td>217.9 (1.5)</td>
<td>3.34 (2.94) \times 10^{-3}</td>
<td>179.0 (2.8)</td>
<td>4.35 (1.03) \times 10^{-05}</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>2.90 (0.13) \times 10^{-13}</td>
<td>156.3 (0.2)</td>
<td>5.14 (0.06) \times 10^{-6}</td>
<td>217.9 (1.5)</td>
<td>3.34 (2.94) \times 10^{-3}</td>
<td>179.0 (2.8)</td>
<td>4.35 (1.03) \times 10^{-05}</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>5.49 (0.06) \times 10^{-13}</td>
<td>161.1 (5.5)</td>
<td>1.61 (0.72) \times 10^{-6}</td>
<td>183.1 (1.8)</td>
<td>1.51 (0.30) \times 10^{-4}</td>
<td>200.2 (2.6)</td>
<td>7.39 (2.26) \times 10^{-04}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni_{25}Mn_{75} vs. Ni_{46}Mn_{30}Ga_{24}</td>
<td>800</td>
<td>2.49 (0.38) \times 10^{-13}</td>
<td>161.1 (5.5)</td>
<td>1.61 (0.72) \times 10^{-6}</td>
<td>183.1 (1.8)</td>
<td>1.51 (0.30) \times 10^{-4}</td>
<td>200.2 (2.6)</td>
<td>7.39 (2.26) \times 10^{-04}</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>4.49 (0.04) \times 10^{-13}</td>
<td>161.1 (5.5)</td>
<td>1.61 (0.72) \times 10^{-6}</td>
<td>183.1 (1.8)</td>
<td>1.51 (0.30) \times 10^{-4}</td>
<td>200.2 (2.6)</td>
<td>7.39 (2.26) \times 10^{-04}</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>1.16 (0.11) \times 10^{-12}</td>
<td>101 (1.0)</td>
<td>1.01 (0.10) \times 10^{-12}</td>
<td>200.2 (2.6)</td>
<td>7.39 (2.26) \times 10^{-04}</td>
<td>200.2 (2.6)</td>
<td>7.39 (2.26) \times 10^{-04}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 9 Average effective interdiffusion coefficients and the corresponding activation energy and pre-exponential factor for Ni, Mn and Ga in the β phase determined from series III diffusion couples.

<table>
<thead>
<tr>
<th>Diffusion couple</th>
<th>Temperature (°C)</th>
<th>( \tilde{D}_{\text{Ni}}^{\text{eff}} ) (m²/s)</th>
<th>( \tilde{Q}_{\text{Ni}}^{\text{eff}} ) (kJ/mole)</th>
<th>( \tilde{D}_{0,\text{Ni}}^{\text{eff}} ) (m²/s)</th>
<th>( \tilde{Q}_{\text{Mn}}^{\text{eff}} ) (kJ/mole)</th>
<th>( \tilde{D}_{0,\text{Mn}}^{\text{eff}} ) (m²/s)</th>
<th>( \tilde{D}_{\text{Ga}}^{\text{eff}} ) (m²/s)</th>
<th>( \tilde{Q}_{\text{Ga}}^{\text{eff}} ) (kJ/mole)</th>
<th>( \tilde{D}_{0,\text{Ga}}^{\text{eff}} ) (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₅₂Mn₁₈Ga₃₀ vs. Ni₅₂Mn₃₀Ga₁₈</td>
<td>800</td>
<td>---</td>
<td>---</td>
<td>1.81 (0.06) x 10⁻¹⁵</td>
<td>237.2 (5.5)</td>
<td>2.47 (0.03) x 10⁻¹⁵</td>
<td>222.1 (11.4)</td>
<td>2.35 (2.04) x 10⁻¹⁴</td>
<td></td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>---</td>
<td>---</td>
<td>4.89 (0.18) x 10⁻¹⁵</td>
<td>1.76 (0.17) x 10⁻¹⁴</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>---</td>
<td>---</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni₅₂Mn₃₀Ga₃₀ vs. Ni₅₈Mn₁₈Ga₂₄</td>
<td>800</td>
<td>1.85 (0.21) x 10⁻¹⁴</td>
<td>202.8 (3.7)</td>
<td>1.42 (0.40) x 10⁻⁰₄</td>
<td>---</td>
<td>1.07 (0.11) x 10⁻¹⁴</td>
<td>209.6 (3.6)</td>
<td>1.76 (0.48) x 10⁻¹⁴</td>
<td></td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>5.60 (0.20) x 10⁻¹⁴</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>3.30 (0.13) x 10⁻¹⁴</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>1.28 (0.09) x 10⁻¹³</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>7.93 (0.45) x 10⁻¹⁴</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni₄₆Mn₃₀Ga₂₄ vs. Ni₅₂Mn₃₀Ga₁₈</td>
<td>800</td>
<td>2.48 (0.36) x 10⁻¹⁴</td>
<td>158.6 (1.8)</td>
<td>1.29 (0.11) x 10⁻⁰₆</td>
<td>---</td>
<td>6.14 (0.14) x 10⁻¹⁵</td>
<td>175.3 (12.8)</td>
<td>1.96 (1.41) x 10⁻₀⁶</td>
<td></td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>5.47 (0.30) x 10⁻¹⁴</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>1.20 (0.43) x 10⁻¹⁴</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>1.13 (0.14) x 10⁻¹³</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>3.33 (0.56) x 10⁻¹⁴</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni₄₆Mn₃₀Ga₂₄ vs. Ni₅₈Mn₁₈Ga₂₄</td>
<td>800</td>
<td>1.54 (0.11) x 10⁻¹⁴</td>
<td>168.1 (1.2)</td>
<td>2.37 (0.16) x 10⁻⁰₆</td>
<td>1.26 (0.13) x 10⁻¹⁴</td>
<td>171.9 (5.1)</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>3.59 (0.09) x 10⁻¹⁴</td>
<td>---</td>
<td>3.20 (0.12) x 10⁻¹⁴</td>
<td>3.11 (1.33) x 10⁻⁰₆</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>7.67 (0.45) x 10⁻¹⁴</td>
<td>---</td>
<td>6.48 (0.31) x 10⁻¹⁴</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
</tbody>
</table>

62
Table 10 Ternary interdiffusion coefficients at 800 °C as a function of composition in the β phase determined from the diffusion couples examined in this study.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition (atom percent)</th>
<th>Ternary interdiffusion coefficients (x 10⁻¹⁴ m²/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Mn</td>
</tr>
<tr>
<td>Ni₅₂Mn₁₈Ga₃₀ vs. Ni₅₂Mn₃₀Ga₁₈</td>
<td>51.71</td>
<td>23.90</td>
</tr>
<tr>
<td>Ni₅₂Mn₃₀Ga₂₄ vs. Ni₅₂Mn₁₈Ga₃₀ vs. Ni₄₆Mn₃₀Ga₂₄ vs. Ni₅₂Mn₁₈Ga₂₄</td>
<td>51.61</td>
<td>25.66</td>
</tr>
<tr>
<td>Ni₅₂Mn₁₈Ga₃₀ vs. Ni₅₈Mn₁₈Ga₂₄</td>
<td>51.91</td>
<td>20.72</td>
</tr>
<tr>
<td>Ni₅₂Mn₃₀Ga₁₈ vs. Ni₅₂Mn₃₀Ga₃₀</td>
<td>51.62</td>
<td>26.97</td>
</tr>
<tr>
<td>Ni₅₂Mn₃₀Ga₃₀ vs. Ni₅₂Mn₂₆Ga₈</td>
<td>53.19</td>
<td>16.78</td>
</tr>
<tr>
<td>Ni₅₂Mn₃₀Ga₂₄ vs. Ni₅₂Mn₁₈Ga₂₄</td>
<td>56.27</td>
<td>17.88</td>
</tr>
<tr>
<td>Ni₄₆Mn₃₀Ga₂₄ vs. Ni₅₂Mn₁₈Ga₂₄</td>
<td>48.02</td>
<td>27.82</td>
</tr>
<tr>
<td>Ni₅₂Mn₁₈Ga₂₄ vs. Ni₅₂Mn₁₈Ga₂₄</td>
<td>50.39</td>
<td>30.42</td>
</tr>
<tr>
<td>Ni₅₂Mn₁₈Ga₂₄ vs. Ni₅₂Mn₁₈Ga₂₄</td>
<td>50.82</td>
<td>25.02</td>
</tr>
<tr>
<td>Ni₅₂Mn₁₈Ga₂₄ vs. Ni₅₂Mn₁₈Ga₂₄</td>
<td>56.36</td>
<td>18.40</td>
</tr>
</tbody>
</table>
Table 11 Ternary interdiffusion coefficients at 850 °C as a function of composition in the β phase determined from the diffusion couples examined in this study.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition (atom percent)</th>
<th>Ternary interdiffusion coefficients (x 10^{-14} m^2/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni_{52}Mn_{30}Ga_{30} vs. Ni_{52}Mn_{30}Ga_{18} and Ni_{52}Mn_{30}Ga_{24} vs. Ni_{53}Mn_{18}Ga_{24}</td>
<td>Ni Mn Ga</td>
<td>$\dot{D}_M^{Ni}$ $\dot{D}_G^{Ni}$ $\dot{D}_N^{Ni}$ $\dot{D}_M^{Mn}$ $\dot{D}_G^{Mn}$ $\dot{D}_N^{Mn}$ $\dot{D}_M^{Ga}$ $\dot{D}_G^{Ga}$ $\dot{D}_N^{Ga}$</td>
</tr>
<tr>
<td>52.16 23.30 24.54</td>
<td>2.09 1.74 0.36 0.86 1.24 -0.16 -0.36 0.50 2.60</td>
<td>0.16 -1.74 0.34</td>
</tr>
<tr>
<td>Ni_{52}Mn_{30}Ga_{30} vs. Ni_{52}Mn_{30}Ga_{18} and Ni vs. Ni_{52}Mn_{30}Ga_{24}</td>
<td>Ni Mn Ga</td>
<td>$\dot{D}_M^{Ni}$ $\dot{D}_G^{Ni}$ $\dot{D}_N^{Ni}$ $\dot{D}_M^{Mn}$ $\dot{D}_G^{Mn}$ $\dot{D}_N^{Mn}$ $\dot{D}_M^{Ga}$ $\dot{D}_G^{Ga}$ $\dot{D}_N^{Ga}$</td>
</tr>
<tr>
<td>51.95 25.58 22.47</td>
<td>3.07 2.63 1.06 1.63 3.92 -0.14 -0.60 0.57 4.26</td>
<td>0.14 -2.63 0.44</td>
</tr>
<tr>
<td>Ni_{52}Mn_{30}Ga_{30} vs. Ni_{52}Mn_{18}Ga_{24}</td>
<td>Ni Mn Ga</td>
<td>$\dot{D}_M^{Ni}$ $\dot{D}_G^{Ni}$ $\dot{D}_N^{Ni}$ $\dot{D}_M^{Mn}$ $\dot{D}_G^{Mn}$ $\dot{D}_N^{Mn}$ $\dot{D}_M^{Ga}$ $\dot{D}_G^{Ga}$ $\dot{D}_N^{Ga}$</td>
</tr>
<tr>
<td>52.14 20.31 27.56</td>
<td>--- --- --- --- -0.05 --- 0.51 --- 0.05 ---</td>
<td>0.46</td>
</tr>
<tr>
<td>Ni_{52}Mn_{30}Ga_{30} vs. Ni_{52}Mn_{18}Ga_{18}</td>
<td>Ni Mn Ga</td>
<td>$\dot{D}_M^{Ni}$ $\dot{D}_G^{Ni}$ $\dot{D}_N^{Ni}$ $\dot{D}_M^{Mn}$ $\dot{D}_G^{Mn}$ $\dot{D}_N^{Mn}$ $\dot{D}_M^{Ga}$ $\dot{D}_G^{Ga}$ $\dot{D}_N^{Ga}$</td>
</tr>
<tr>
<td>51.94 26.72 21.35</td>
<td>--- --- --- --- -0.07 --- 0.56 --- 0.07 ---</td>
<td>0.49</td>
</tr>
<tr>
<td>Ni_{52}Mn_{30}Ga_{30} vs. Ni_{52}Mn_{18}Ga_{24}</td>
<td>Ni Mn Ga</td>
<td>$\dot{D}_M^{Ni}$ $\dot{D}_G^{Ni}$ $\dot{D}_N^{Ni}$ $\dot{D}_M^{Mn}$ $\dot{D}_G^{Mn}$ $\dot{D}_N^{Mn}$ $\dot{D}_M^{Ga}$ $\dot{D}_G^{Ga}$ $\dot{D}_N^{Ga}$</td>
</tr>
<tr>
<td>53.19 16.93 29.88</td>
<td>--- 2.49 --- 2.79 --- --- --- --- 5.28 --- -2.49 ---</td>
<td>---</td>
</tr>
<tr>
<td>Ni_{52}Mn_{30}Ga_{18} vs. Ni_{52}Mn_{18}Ga_{24}</td>
<td>Ni Mn Ga</td>
<td>$\dot{D}_M^{Ni}$ $\dot{D}_G^{Ni}$ $\dot{D}_N^{Ni}$ $\dot{D}_M^{Mn}$ $\dot{D}_G^{Mn}$ $\dot{D}_N^{Mn}$ $\dot{D}_M^{Ga}$ $\dot{D}_G^{Ga}$ $\dot{D}_N^{Ga}$</td>
</tr>
<tr>
<td>56.49 17.98 25.53</td>
<td>--- 2.70 --- 4.20 --- --- --- --- 6.90 --- -2.70 ---</td>
<td>---</td>
</tr>
<tr>
<td>Ni_{52}Mn_{30}Ga_{24} vs. Ni_{52}Mn_{18}Ga_{18}</td>
<td>Ni Mn Ga</td>
<td>$\dot{D}_M^{Ni}$ $\dot{D}_G^{Ni}$ $\dot{D}_N^{Ni}$ $\dot{D}_M^{Mn}$ $\dot{D}_G^{Mn}$ $\dot{D}_N^{Mn}$ $\dot{D}_M^{Ga}$ $\dot{D}_G^{Ga}$ $\dot{D}_N^{Ga}$</td>
</tr>
<tr>
<td>47.76 27.74 24.50</td>
<td>--- 4.94 --- 1.67 --- --- --- --- 6.61 --- -4.94 ---</td>
<td>---</td>
</tr>
<tr>
<td>Ni_{52}Mn_{30}Ga_{18} vs. Ni_{52}Mn_{18}Ga_{24}</td>
<td>Ni Mn Ga</td>
<td>$\dot{D}_M^{Ni}$ $\dot{D}_G^{Ni}$ $\dot{D}_N^{Ni}$ $\dot{D}_M^{Mn}$ $\dot{D}_G^{Mn}$ $\dot{D}_N^{Mn}$ $\dot{D}_M^{Ga}$ $\dot{D}_G^{Ga}$ $\dot{D}_N^{Ga}$</td>
</tr>
<tr>
<td>49.85 30.56 19.59</td>
<td>--- 3.02 --- 1.50 --- --- --- --- 4.52 --- -3.02 ---</td>
<td>---</td>
</tr>
<tr>
<td>Ni_{52}Mn_{30}Ga_{24} vs. Ni_{52}Mn_{18}Ga_{24}</td>
<td>Ni Mn Ga</td>
<td>$\dot{D}_M^{Ni}$ $\dot{D}_G^{Ni}$ $\dot{D}_N^{Ni}$ $\dot{D}_M^{Mn}$ $\dot{D}_G^{Mn}$ $\dot{D}_N^{Mn}$ $\dot{D}_M^{Ga}$ $\dot{D}_G^{Ga}$ $\dot{D}_N^{Ga}$</td>
</tr>
<tr>
<td>50.04 25.67 24.29</td>
<td>--- 0.33 --- 3.16 --- -0.33 --- --- --- ---</td>
<td>---</td>
</tr>
<tr>
<td>Ni_{52}Mn_{18}Ga_{24} vs. Ni_{52}Mn_{18}Ga_{24}</td>
<td>Ni Mn Ga</td>
<td>$\dot{D}_M^{Ni}$ $\dot{D}_G^{Ni}$ $\dot{D}_N^{Ni}$ $\dot{D}_M^{Mn}$ $\dot{D}_G^{Mn}$ $\dot{D}_N^{Mn}$ $\dot{D}_M^{Ga}$ $\dot{D}_G^{Ga}$ $\dot{D}_N^{Ga}$</td>
</tr>
<tr>
<td>55.11 19.64 25.25</td>
<td>--- 0.60 --- 2.89 --- -0.60 --- --- --- ---</td>
<td>---</td>
</tr>
</tbody>
</table>

64
Table 12 Ternary interdiffusion coefficients at 900 °C as a function of composition in the in the β phase determined from the diffusion couples examined in this study.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition (atom percent)</th>
<th>Ternary interdiffusion coefficients (x 10^{-14} m^2/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni_{52}Mn_{18}Ga_{30} vs. Ni_{52}Mn_{30}Ga_{18} and Ni_{46}Mn_{30}Ga_{24} vs. Ni_{50}Mn_{18}Ga_{24}</td>
<td>Ni</td>
<td>Mn</td>
</tr>
<tr>
<td>51.71</td>
<td>23.90</td>
<td>24.39</td>
</tr>
<tr>
<td>Ni_{52}Mn_{18}Ga_{30} vs. Ni_{58}Mn_{18}Ga_{24} vs. Ni_{46}Mn_{30}Ga_{24}</td>
<td>Ni</td>
<td>Mn</td>
</tr>
<tr>
<td>52.02</td>
<td>25.54</td>
<td>22.44</td>
</tr>
<tr>
<td>Ni_{52}Mn_{18}Ga_{30} vs. Ni_{58}Mn_{18}Ga_{24} and Ni vs. Ni_{46}Mn_{30}Ga_{24}</td>
<td>Ni</td>
<td>Mn</td>
</tr>
<tr>
<td>52.31</td>
<td>20.25</td>
<td>27.44</td>
</tr>
<tr>
<td>Ni_{52}Mn_{18}Ga_{30} vs. Ni_{58}Mn_{30}Ga_{18}</td>
<td>Ni</td>
<td>Mn</td>
</tr>
<tr>
<td>52.00</td>
<td>26.90</td>
<td>21.10</td>
</tr>
<tr>
<td>Ni_{52}Mn_{30}Ga_{30} vs. Ni_{58}Mn_{18}Ga_{24} vs. Ni_{46}Mn_{30}Ga_{24}</td>
<td>Ni</td>
<td>Mn</td>
</tr>
<tr>
<td>53.08</td>
<td>16.79</td>
<td>30.13</td>
</tr>
<tr>
<td>Ni_{52}Mn_{18}Ga_{30} vs. Ni_{58}Mn_{18}Ga_{24}</td>
<td>Ni</td>
<td>Mn</td>
</tr>
<tr>
<td>56.48</td>
<td>17.80</td>
<td>25.72</td>
</tr>
<tr>
<td>Ni_{52}Mn_{30}Ga_{30} vs. Ni_{58}Mn_{18}Ga_{24} vs. Ni_{46}Mn_{30}Ga_{24}</td>
<td>Ni</td>
<td>Mn</td>
</tr>
<tr>
<td>47.93</td>
<td>27.56</td>
<td>24.51</td>
</tr>
<tr>
<td>Ni_{52}Mn_{18}Ga_{30} vs. Ni_{58}Mn_{18}Ga_{24}</td>
<td>Ni</td>
<td>Mn</td>
</tr>
<tr>
<td>Ni_{52}Mn_{18}Ga_{30} vs. Ni_{58}Mn_{18}Ga_{24}</td>
<td>Ni</td>
<td>Mn</td>
</tr>
<tr>
<td>50.46</td>
<td>25.50</td>
<td>24.04</td>
</tr>
<tr>
<td>Ni_{52}Mn_{18}Ga_{30} vs. Ni_{58}Mn_{18}Ga_{24}</td>
<td>Ni</td>
<td>Mn</td>
</tr>
<tr>
<td>55.49</td>
<td>18.96</td>
<td>25.55</td>
</tr>
</tbody>
</table>
4.4. Discussion

4.4.1. Phase Equilibrium

Compositions determined for solubility within phases using diffusion couples were used to verify the accuracy of the phase diagrams. Figure 26(a) shows sections of the re-plotted Ni-Mn-Ga isothermal ternary phase diagram at 800 °C. Solid squares represent data from this diffusion study and crosses represent compositions reported in literatures. By inspecting the phase boundary, the compositions obtained from this diffusion study were very close to the ones presented by Yang et al. [48]. The solubility of Mn in α’ phase in this study was slightly higher than that compiled in the literature. The section of the Ni-Mn-Ga isothermal ternary phase diagram at 900 °C is presented in Figure 26(c). Although most phase boundaries show very close agreement with those reported by Yang et al. [48], the phase boundary of the two-phase, β + γ(Mn) region was observed to be different. It is noted that the data in this study has been confirmed by both EPMA and XEDS as reported in Table 5 and Table 6. By adopting the data from this study, the two-phase, β + γ(Mn) region will have a similar shape to that at 800 °C. Additionally, this study reported the compositional data for the boundary of the γ(Ni) + α’ two-phase region at 900 °C to help complete the phase diagram.

4.4.2. Martensitic transformation

Martensitic transformation temperature (T_m) is important in Ni-Mn-Ga alloys, which is also sensitive to composition. Valence electron concentration (e/a) has been commonly employed for the estimation of T_m, where it is generally believed that T_m increases as e/a increases [31, 50, 100-102]. The T_m is near room temperature when e/a is close to 7.6 [48]. The design of the four starting NiMnGa ternary alloys had two alloys with e/a ratio of 7.4, and the
other two with e/a ratio of 7.8. The XRD patterns shown in Figure 21 indeed indicate that Ni$_{52}$Mn$_{18}$Ga$_{30}$ and Ni$_{46}$Mn$_{30}$Ga$_{24}$ are austenite, while Ni$_{52}$Mn$_{30}$Ga$_{18}$ and Ni$_{58}$Mn$_{18}$Ga$_{24}$ are martensite at room temperature. All diffusion couple experiments are carried out between one alloy with e/a = 7.4 and the other one with e/a > 7.8. Thus, the e/a ratio within the interdiffusion zone is likely to be near 7.6, and have an interface between austenite and martensite at room temperature. The micrographs of the diffusion couples confirm that sharp austenitic/martensitic phase boundary exists within each diffusion couple. In addition, the compositions at the austenitic/martensitic interface were extracted from the EPMA measurement for all diffusion couples, as shown in Figure 30. These compositions are generally very close to the iso-e/a ratio of 7.6. However, when the Mn content increased to more than 35 at. %, compositions at the austenitic/martensitic interface corresponded to the e/a ratio lower than 7.6.

4.4.3. Ternary Interdiffusion Interactions

The interdiffusion behavior in ternary Ni-Mn-Ga system was investigated at 800 °C, 850 °C and 900 °C in this study. As reported in Table 10, Table 11 and Table 12, magnitude of main ternary interdiffusion coefficients, $\tilde{D}_{NiNi}^{Mn}$ is about 3-7 times larger than $\tilde{D}_{GaGa}^{Mn}$, and that of $\tilde{D}_{NiNi}^{Ga}$ is about 4-12 times larger than $\tilde{D}_{MnMn}^{Ga}$ for all three temperatures examined. Also, magnitude of $\tilde{D}_{MnMn}^{Ni}$ coefficients is in general slightly larger than $\tilde{D}_{GaGa}^{Ni}$. Therefore, in the B2 NiMnGa alloys, the Ni interdiffuses significantly faster than Mn or Ga, and Mn interdiffuses slightly faster than Ga.

Diffusional interaction among Ni, Mn and Ga can be understood based on the development of concentration profiles and the corresponding interdiffusion fluxes, and cross
terms in ternary interdiffusion coefficients. In series III diffusion couples with iso-Ni diffusion couples shown in Figure 27, very little interdiffusion flux of Ni was observed. The diffusion couple, $\text{Ni}_{52}\text{Mn}_{18}\text{Ga}_{30}$ vs. $\text{Ni}_{52}\text{Mn}_{30}\text{Ga}_{18}$ behaved like a pseudo-binary diffusion couple. However, for iso-Mn and iso-Ga diffusion couples, appreciable interdiffusion fluxes of Mn and Ga, respectively, are observed as presented in Figure 28 and Figure 29. The $\beta$ phase has a B2 crystal structure above 800 °C. In the B2 structure of Ni-Mn-Ga alloys, the Ni atom occupies the center position of the cube, while Mn and Ga randomly occupy the corner positions [95, 103]. This partially ordered structure may lead to variation in diffusional behavior for Ni, Mn and Ga, observed in series III diffusion couples.

Diffusional interactions among Ni, Mn and Ga can be quantitatively understood by examining the main and cross ternary interdiffusion coefficients. The $\tilde{D}_{\text{MnNi}}^{\text{Ga}}$ cross coefficients are negative and larger in magnitude than the main coefficients $\tilde{D}_{\text{MnMn}}^{\text{Ga}}$. This implies that the interdiffusion flux of Mn is strongly influenced by the interdiffusion flux of Ni. This corresponds well with the experimental observation in Figure 28 where large Mn interdiffusion flux is generated against the Ni interdiffusion flux, despite the initial absence of concentration gradient of Mn in the iso-Mn diffusion couple, $\text{Ni}_{46}\text{Mn}_{30}\text{Ga}_{24}$ vs. $\text{Ni}_{52}\text{Mn}_{30}\text{Ga}_{18}$. Similarly, the $\tilde{D}_{\text{GaNi}}^{\text{Mn}}$ cross coefficients are also negative and appreciable relative to the main coefficients $\tilde{D}_{\text{GaGa}}^{\text{Mn}}$. Figure 29 presents a significant and positive Ga interdiffusion flux against the interdiffusion flux of Ni in iso-Ga diffusion couple, $\text{Ni}_{46}\text{Mn}_{30}\text{Ga}_{24}$ vs. $\text{Ni}_{58}\text{Mn}_{18}\text{Ga}_{24}$. However, the magnitudes of $\tilde{D}_{\text{NiMn}}^{\text{Ga}}$ or $\tilde{D}_{\text{NiGa}}^{\text{Mn}}$ cross coefficients were, respectively, much smaller than that of $\tilde{D}_{\text{NiNi}}^{\text{Ga}}$ and $\tilde{D}_{\text{NiNi}}^{\text{Mn}}$ main coefficients. Therefore, in iso-Ni diffusion couples, interdiffusion flux of Ni is not significant as
shown in Figure 27. However the $\tilde{D}^{\text{Mn}}_{\text{NiGaD}}$ coefficients were negative, while $\tilde{D}^{\text{Ga}}_{\text{NiMn}}$ coefficients were positive.

In all three temperatures investigated, both $\tilde{D}^{\text{Ni}}_{\text{MnGaD}}$ and $\tilde{D}^{\text{Ni}}_{\text{GaMnD}}$ coefficients were positive. Their magnitudes were smaller than the respective main coefficients, $\tilde{D}^{\text{Ni}}_{\text{MnMnD}}$ and $\tilde{D}^{\text{Ni}}_{\text{GaGaD}}$. The $\tilde{D}^{\text{Ni}}_{\text{MnGaD}}$ coefficients were in general larger than $\tilde{D}^{\text{Ni}}_{\text{GaMnD}}$ coefficients. Therefore the determination and examination of ternary interdiffusion coefficients reveal that, in B2 NiMnGa alloys, Ni interdiffuses the fastest, followed by Mn then Ga. Interdiffusion flux of Ni also has strong influences on the interdiffusion of Mn and Ga with large negative cross interdiffusion coefficients, $\tilde{D}^{\text{Ga}}_{\text{MnNiD}}$ and $\tilde{D}^{\text{Mn}}_{\text{GaNiD}}$.

Quantitative trends in ternary interdiffusion coefficients may be related to the partial ordering of the B2 structure and the corresponding diffusion mechanisms [82, 99, 104]: Ni occupies one sublattice, and the other sublattice is interchangeably occupied by Mn and Ga [95, 103]. The magnitude of $\tilde{D}^{\text{Ga}}_{\text{NiNiD}}$ and $\tilde{D}^{\text{Mn}}_{\text{NiNiD}}$ is much larger (e.g., 3 ~ 12 times) than $\tilde{D}^{\text{Ga}}_{\text{NiMn}}$ and $\tilde{D}^{\text{Mn}}_{\text{NiGa}}$, which implies that Ni primarily diffuses via vacancies on its own sublattices rather than via Mn/Ga sublattice to form Ni antisites. However, the magnitude of $\tilde{D}^{\text{Ga}}_{\text{MnMn}}$ and $\tilde{D}^{\text{Mn}}_{\text{GaGa}}$ is comparable to that of $\tilde{D}^{\text{Ga}}_{\text{MnNi}}$ and $\tilde{D}^{\text{Mn}}_{\text{GaNi}}$, which suggests that Mn and Ga diffuses not only through vacancies on their own sublattices, but also through Ni sublattices to form Mn or Ga antisites. In other words, vacancy formation energy for Ni is lower than for Mn and Ga, while formation energy for Mn and Ga antisites is lower than for Ni antisites. The magnitudes of main ternary interdiffusion coefficients, $\tilde{D}^{\text{Ni}}_{\text{MnMn}}$ and $\tilde{D}^{\text{Ni}}_{\text{GaGa}}$, are also similar to the respective cross ternary
interdiffusion coefficients, $\tilde{D}_{\text{NiMnGa}}^{\text{Ni}}$ and $\tilde{D}_{\text{GaMn}}^{\text{Ni}}$, and thus Mn and Ga can interchange with each other during diffusion. Ga is more likely to stay in its own lattice as Mn diffuses slightly faster than Ga as discussed before.

Figure 33 illustrates the magnitude of main ternary interdiffusion coefficients of $\tilde{D}_{\text{NiNi}}^\text{Ga}$ and $\tilde{D}_{\text{MnMn}}^\text{Ga}$ as a function of Ni or Mn concentration, respectively. The magnitude of $\tilde{D}_{\text{NiNi}}^\text{Ga}$ exhibits a minimum around 52 at.% Ni concentration for all three temperatures. A similar trend is observed for $\tilde{D}_{\text{MnMn}}^\text{Ga}$ with a minimum around 23 at.% Mn. This is consistent with the results reported in Table 9, where the average interdiffusion coefficients of the $\beta$ phase determined from series III diffusion couples are reported to be smaller than those determined from series I and series II diffusion couples. For example, at 900 °C, diffusion couple Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni$_{52}$Mn$_{30}$Ga$_{18}$ with a minimum deviation from the near stoichiometric composition in its concentration profiles has a relatively smaller depth of interdiffusion, roughly 900 μm, compared to other couples. Activation energy determined from temperature-dependence of average effective interdiffusion coefficients from this type of diffusion couple is large as reported in Table 8 and Table 9.

It has been reported previously [105-108] that even in binary alloys with B2 structure, minimum interdiffusion occurs at a near stoichiometric composition. For example, in NiAl alloys, the interdiffusion coefficients varied as Ni concentration changed, with a minimum around 51-52 at.% Ni [105-108]. Despite possible experimental errors, the deviation from stoichiometry can be explained by compositional dependent thermodynamic factors and variation in defect structures on either side of the stoichiometric compositions [106, 108].
In this section, phase equilibria, microstructural development and interdiffusion behavior in Ni-Mn-Ga alloys were investigated by examining a series of solid-to-solid diffusion couples. Selected alloys between pure Ni, Ni\textsubscript{25}Mn\textsubscript{75} and four off-stoichiometric Ni-Mn-Ga alloys were coupled and annealed at 800 °C, 850 °C and 900 °C for 480h, 240h and 120h, respectively. The microstructure of the interdiffusion zone consisted of both austenitic and martensitic phase at room temperature for each diffusion couple, which was confirmed by analytical TEM. The compositions determined from the austenite/martensite interface correspond to those with martensitic transformation temperatures near room temperature. This transformation composition corresponded close to iso-e/a ratio of 7.6, but changed toward to lower e/a ratio when the Mn content increased to more than 35 at.%. Average effective interdiffusion coefficients and the corresponding activation energies were determined from each diffusion couple, and indicated
compositional dependence in addition to Arrhenius temperature-dependence. The magnitude of main ternary interdiffusion coefficient exhibited minimum values near 52 at. % Ni concentration. Ni was observed to interdiffuse the fastest, followed by Mn then Ga. Interdiffusion flux of Ni also has strong influences on the interdiffusion of Mn and Ga with large and negative cross interdiffusion coefficients, $\tilde{D}^{Ga}_{MnNi}$ and $\tilde{D}^{Mn}_{GaNi}$. 
CHAPTER 5: MICROSTRUCTURE AND CRYSTALLOGRAPHY

For first time, microstructure and crystallography of austenitic and martensitic phase of NiMnGa alloys were investigated using TEM foils obtained from diffusion couples. As has been observed and discussed in previous chapter, the NiMnGa alloys have a large solubility range according to the phase diagram. Diffusion couple is unique in generating a smooth concentration gradient over a large compositional range in NiMnGa alloys. Therefore, by examining selected compositions from the diffusion couples using TEM, not only certain properties of the NiMnGa alloys can be properly studied, but also some trends can be revealed.

One concern may arise when considering the composition of the TEM foil studied. Due to the unique feature of the diffusion couple, concentration gradient may also exist in the TEM foil. According to all the concentration profiles, the concentration gradient for any element has a maximum value of approximately 0.025 at. %/μm, and in general much less. All TEM foils in this study are about 8-10 μm in length. This means that the concentration difference in a TEM foil is no more than 0.25 at. % and typically much less, even when the TEM foil is cut parallel to the interdiffusion direction. On the other hand, if the TEM foil is prepared perpendicular to the interdiffusion direction, the concentration gradient in a TEM foil would be negligible. Therefore, it is reasonable to assume a negligible compositional difference in a TEM foil in this study. All the compositions reported in this study are based on the fitted EPMA concentration profile. Most TEM foils presented in this chapter are acquired from the couples that are annealed at 900 °C for 120 h, unless specifically stated.
5.1. Modulated Martensite

Several modulated martensites with different modulation periods have been found in the diffusion couples through extensive search by TEM. Figure 34 shows one representative example of the 5M martensite from diffusion couple Ni$_{52}$Mn$_{18}$Ga$_{30}$/Ni$_{52}$Mn$_{30}$Ga$_{18}$. The composition of this TEM foil based on EPMA is about Ni$_{52.1}$Mn$_{24.8}$Ga$_{23.1}$. The bright field TEM micrograph presented in Figure 34(a) reveals the martensitic lamellar microstructure, with a thickness of 50 – 300 nm for different martensitic variants. Some martensitic variants cross over with others. Figure 34(c) and (d) are selected area diffraction patterns (SADP) of [1 1 1] orientation from one of the martensitic variants and from the twin boundaries. Additional four less-intense but sharp diffraction spots were observed between the two fundamental diffraction spots, as marked in Figure 34(c), which verifies that the martensite at this composition has a 5M crystal structure. Moreover, adjacent martensitic variants have twinning relationship, as revealed by a common diffraction spot shared by two variants. The twinning plane is (2 0 2) according to the indexing. In this case, the twinning plane is rational and thus the twin belongs to a type I twin. A high resolution (HRTEM) micrograph is presented in Figure 34(b) and shows the lattice layers of the 5M structure. The thickness ratio between the bright and dark lattice fringes is roughly 3:2, which is consistent with the 5M model mentioned before [27]. Meanwhile, the thickness ratio is not consistent everywhere, which probably caused some diffused streaks in the diffraction pattern in Figure 34(c) and (d).
Figure 34 (a) Bright field TEM and (b) high resolution TEM micrograph of Ni\textsubscript{52.1}Mn\textsubscript{24.8}Ga\textsubscript{23.1} from diffusion couple of Ni\textsubscript{52}Mn\textsubscript{18}Ga\textsubscript{30} vs. Ni\textsubscript{52}Mn\textsubscript{30}Ga\textsubscript{18}. Selected area diffraction pattern from (c) one variant from (d) twin boundaries indicating the 5M structure.

Figure 35 presents a 7M martensite with the composition of Ni\textsubscript{54.9}Mn\textsubscript{17.4}Ga\textsubscript{27.7} from diffusion couple Ni\textsubscript{52}Mn\textsubscript{18}Ga\textsubscript{30} vs. Ni\textsubscript{58}Mn\textsubscript{18}Ga\textsubscript{24}. This specific TEM foil consists of both austenitic and 7M martensitic phase, as shown by the BF TEM micrograph in Figure 35(a), where the two plates with thickness of about 200 – 300 nm are the martensitic variants. The SADPs in Figure 35(c) and (d) are acquired from on single martensitic variant and from the twin
boundary area from [1 \bar{1}] orientation, respectively. Similar to that observed in the 5M structure, extra six sharp diffraction spots were observed between two fundamental spots. Also, the two martensitic variants formed a twinning relationship with the twinning plane of (20\bar{2}), which was revealed by the common diffraction spots in Figure 35(d). Similar to 5M martensite, this is a type I twin as the twinning plane is rational. Figure 35(b) shows a representative HRTEM micrograph from one martensitic variant, which clearly shows the lattice fringes contrast. The thickness ratio between bright and dark fringes is typically about 5:2, but is not uniform everywhere.
Figure 35 (a) Bright field TEM and (b) high resolution TEM micrograph of Ni_{54.9}Mn_{17.4}Ga_{27.7} from diffusion couple of Ni_{52}Mn_{18}Ga_{30} vs. Ni_{58}Mn_{18}Ga_{24}. Selected area diffraction pattern from (c) one variant from (d) twin boundaries indicating the 7M structure.

In addition to the 5M and 7M martensites that are most commonly observed in bulk alloys, martensites with other modulated periods have also been found in the diffusion couples. Figure 36 presents the BF TEM micrograph and corresponding SADP of a 12M martensite from Ni_{51.3}Mn_{24.5}Ga_{24.2} acquired from diffusion couple Ni_{46}Mn_{30}Ga_{24} vs. Ni_{58}Mn_{18}Ga_{24}. The thickness of the martensitic variants is typically less than 500 nm. Additional eleven superlattice
diffraction spots were observed between two fundamental diffraction spots, indicating a 12M martensitic crystal structure. Although the 12M martensite has not been commonly found in bulk alloys, high resolution TEM studies have found 12M martensite coexisting with other modulated martensites and revealed a \((7\bar{5})\) stacking sequence \([34, 109]\).

Figure 36 (a) Bright field TEM and (b) selected area diffraction pattern of Ni\(_{51.3}\)Mn\(_{24.5}\)Ga\(_{24.2}\) from diffusion couple of Ni\(_{46}\)Mn\(_{30}\)Ga\(_{24}\) vs. Ni\(_{58}\)Mn\(_{18}\)Ga\(_{24}\) showing the 12M structure.

5.2. Non-modulated Martensitic Phase

Other than modulated martensitic phases, many non-modulated (NM) martensites have been found in all diffusion couples via extensive TEM. Figure 37(a) presents a typical BF TEM micrograph of the NM martensite for Ni\(_{52.0}\)Mn\(_{26.4}\)Ga\(_{21.6}\) obtained from diffusion couple of Ni\(_{52}\)Mn\(_{18}\)Ga\(_{30}\) vs. Ni\(_{52}\)Mn\(_{30}\)Ga\(_{18}\). These martensitic variants formed self-accommodated microstructure with various thicknesses ranging from 300 nm to a few microns. Within each variant, there are other sets of martensitic variants with straight boundary as shown in Figure 37(b). In Figure 37(a), however, the contrast within each martensitic variant was complicated
due to the overlapping of inclined twin boundary [110]. This is because, in a general BF mode, the twin boundary is not parallel to the incident electron beam. Such a “twins within twins” microstructure has been reported before, and was usually described as hierarchical structures [111]. There were different names for the hierarchical twins in literature. In this dissertation, the thick variant is designated as primary twin variant, while the thin variant within the primary variant is named as secondary twin variant. Figure 37(b) shows that these secondary twin variants also had different thicknesses, but only in the range of a few tens of nanometers. The SADPs from two different individual martensitic variant are presented in Figure 37(c) and (d) from [1 1 1] orientation. Both show a twinned diffraction pattern that share a common diffraction spot (20 2). These secondary twins belong to compound twin group with a coherent twinning boundary. The orientation relationship can be represented as \([1 \bar{1} 1] \parallel [\bar{1} 1 \bar{1}], (20 \bar{2}) \parallel (20 \bar{2}).\)
Figure 37 (a) Low magnification and (b) high magnification bright field TEM micrograph of Ni$_{52.0}$Mn$_{26.4}$Ga$_{21.6}$ from diffusion couple of Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni$_{52}$Mn$_{30}$Ga$_{18}$. (c) and (d) are selected area diffraction patterns from two adjacent martensitic variants indicating the NM structure.

Figure 38(a) presents the SADP from the boundary area between the two primary variants. A simulated diffraction pattern is also presented in Figure 38(d), which superimposes both the SADPs from each variant that were shown in Figure 37(c) and (d), in order to help reveal the twinning relationship across the primary martensitic variants. A schematic
representation of the martensitic variants is shown in Figure 38(c). The internal twins are designated as V1, V2, V3 and V4, respectively. As discussed above, the secondary variants pair (i.e., V1 and V2 pair, V3 and V4 pair) within each primary variants form strict compound twins. However, the variant across the primary twin boundary is much complicated. There is a misorientation angle ($\alpha$) of about 3.5° between the $\{022\}$ plane for V1 and the $\{022\}$ plane for V3. Therefore, the boundary between the two primary variants did not follow the twinning relationship, even though it is typically termed as twin boundary. The two primary variants are related by a twin operation plus a small rotation [112]. This may also cause some distortion among the primary boundary area shown by the dark contrast near the boundary area in Figure 37(a). Thus, the primary twin boundary is incoherent in this case.

It has just been recently found that the misorientation angle is closely related to the twinning fraction, $\lambda$ [113]. $\lambda$ is defined as the volume fraction of the thinner secondary variant in a primary variant, and thus the value is always less than 0.5. As the value of the $\lambda$ decreases from 0.5 to 0.1, the $\alpha$ decreases from about 6° to near zero degree [113]. The $\lambda$ is determined to be roughly 0.35 from Figure 37(b) in the present case, by measuring the fraction of the white contrast. The $\alpha$ of 3.5° is consistent with that reported in the literature [113]. When the $\lambda$ approaches zero, the thin secondary variant nearly vanishes and consequently the thick primary variant will form strict twin relationship.
5.3. Austenitic Phase

A few TEM studies have been also carried out on the austenitic phase in the diffusion couples, where the austenitic phase is located near the phase boundary between austenite and martensite. Although the $M_s$ is not available, it is presumed that the $M_s$ is slightly lower than room temperature for those austenites that were very close to the phase boundary. Figure 39(a)
presents the BF TEM micrograph and corresponding SADP for Ni_{50.9}Mn_{24.9}Ga_{24.2} from the diffusion couple of Ni_{46}Mn_{30}Ga_{24} vs. Ni_{58}Mn_{18}Ga_{24}. Although the austenite is a single phase and suppose to have a uniform microstructure, the BF TEM micrograph showed a lot of striations with black and white contrast, as shown in Figure 39(a). The corresponding SADP from [010] orientation also shows diffused streaks along the \langle 101 \rangle direction around each diffraction spots in Figure 39(b). The average spacing among striations is roughly 18 nm. Figure 39(c) and (d) shows another austenitic phase that is also located near the phase boundary, but from a different diffusion couple. The composition is Ni_{49.0}Mn_{29.2}Ga_{21.8} from diffusion couple of Ni_{46}Mn_{30}Ga_{24} vs. Ni_{52}Mn_{30}Ga_{18}. Similarly, the microstructure exhibited striations crossing with each other with different contrast. The corresponding SADP from [101] orientation also shows diffused streaks around each diffraction spot due to those striated feature of the austenite. This microstructural feature in the austenite has been observed before, and is referred to as tweed microstructure, which is typically found due to the pre-martensitic transformation.
5.4. Phase Boundary between Austenite and Martensite

A phase boundary between austenite and martensite forms in each diffusion couple after quenching to room temperature. Figure 40(a) shows the BF TEM micrograph of such a phase boundary between austenite and 7M martensite for Ni$_{54.9}$Mn$_{17.4}$Ga$_{27.7}$ from the diffusion couple of Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni$_{58}$Mn$_{18}$Ga$_{24}$. This is the same TEM foil as that shown in Figure 35. At this
interface, the 7M martensitic laths nucleate and grow within the austenite. Those near-transformed austenitic phase forms domain microstructure with different tweed contrast within different domains. The SADP from one of the domains from $[\bar{1}\bar{1}]$ orientation is presented in Figure 40(b), with extra diffused diffraction spots along the 110 direction. The diffused maxima is located approximately 1/7 position between the two primary diffraction spots. Such tweed microstructure and diffused SADP has been also observed in other austenitic phase as shown in Figure 39. The SADP from the phase boundary between the austenite and 7M martensite is presented in Figure 40(c), along with a simulated pattern in Figure 40(d) to help reveal the orientation relationship. It appears that one common diffraction spot (202) is shared by both phases, and indicates that the invariant plane during the martensitic phase transformation is (202) plane.
Figure 40 (a) Bright field TEM micrograph of Ni_{54.9}Mn_{17.4}Ga_{27.7} from diffusion couple of Ni_{52}Mn_{18}Ga_{30} vs. Ni_{58}Mn_{18}Ga_{24}. (b) and (c) are selected area diffraction pattern from austenite and the boundary between austenite and 7M, respectively. (d) A simulated diffraction pattern from the boundary.

Figure 41(a) presents another BF TEM micrograph of the interface for Ni_{52.1}Mn_{24.8}Ga_{23.1} from the diffusion couple of Ni_{52}Mn_{18}Ga_{30} vs. Ni_{52}Mn_{30}Ga_{18}. The corresponding SADPs from the austenite and 5M martensite are presented in Figure 41(b) and (c), respectively, from the [010] orientation. Just like those austenitic phase presented before, diffused diffraction spots are
observed in Figure 41(b) with maxima located approximately 1/5 between the primary diffraction spots along the $\langle 202 \rangle$ direction. The 5M martensite consisted of twinned variants with thickness varying from 100 – 500 nm. The SADP in Figure 41(c) revealed the twinning pattern with the twinning plane of $\langle 202 \rangle$. The extra diffraction spots directly indicating the 5M crystal structure were not shown from this orientation.

Figure 41 (a) Bright field TEM micrograph of Ni$_{52.1}$Mn$_{24.8}$Ga$_{23.1}$ from diffusion couple of Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni$_{52}$Mn$_{30}$Ga$_{18}$. (b) and (c) are selected area diffraction patterns from austenite and 5M martensite, respectively.

A third kind of interface between austenite and NM martensite was found in the diffusion couples. Figure 42(a) presents the BF TEM micrograph of Ni$_{55.8}$Mn$_{15.6}$Ga$_{28.6}$ from the diffusion couple of Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni that was annealed at 800 °C for 480 hour. Tweed microstructure is observed in the austenitic phase corresponded to the smearing of the diffraction spots along the $\langle 202 \rangle$ direction as shown in Figure 42(b). However, this diffraction pattern exhibited diffused lines only without diffraction maxima. The NM martensite consisted of twinning variants, in the
thickness range of micron scale, with the twinning plane of $(202)$ as revealed in Figure 42(c). However, the extra diffraction spots are observed around each fundamental spot that were not exactly located along the $\langle202\rangle$ direction.

Figure 42 (a) Bright field TEM micrograph of Ni$_{55.8}$Mn$_{15.6}$Ga$_{28.6}$ from diffusion couple of Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni annealed at 800 °C for 480 hour. (b) and (c) are selected area diffraction patterns from austenite and NM martensite, respectively.

5.5. Discussion

5.5.1. c/a vs. e/a

Extensive TEM characterization has been carried out to investigate the microstructure and crystal structure of the NiMnGa alloys, as presented above. A summary of the compositions that have been examined and related crystallographic information such as e/a ratio, crystal structure, lattice parameter and tetragonality ratio (c/a) is listed in Table 13.
Table 13 Compositions from diffusion couples that are investigated by TEM and the corresponding crystal structure and lattice parameters.

<table>
<thead>
<tr>
<th>Diffusion couple</th>
<th>EPMA Composition (at. %)</th>
<th>e/a</th>
<th>Crystal structure</th>
<th>Lattice Parameters (Å)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Mn</td>
<td>Ga</td>
<td></td>
<td>a</td>
</tr>
<tr>
<td>Ni$<em>{52}$Mn$</em>{18}$Ga$_{30}$ vs. Ni</td>
<td>59.3</td>
<td>14.3</td>
<td>26.4</td>
<td>7.723</td>
<td>NM</td>
</tr>
<tr>
<td></td>
<td>57.8</td>
<td>14.8</td>
<td>27.4</td>
<td>7.637</td>
<td>NM</td>
</tr>
<tr>
<td></td>
<td>55.8</td>
<td>15.6</td>
<td>28.6</td>
<td>7.529</td>
<td>A</td>
</tr>
<tr>
<td>Ni$<em>{52}$Mn$</em>{18}$Ga$<em>{30}$ vs. Ni$</em>{25}$Mn$_{75}$</td>
<td>38.7</td>
<td>48.1</td>
<td>13.2</td>
<td>7.631</td>
<td>NM</td>
</tr>
<tr>
<td></td>
<td>40.7</td>
<td>43.5</td>
<td>15.8</td>
<td>7.587</td>
<td>NM</td>
</tr>
<tr>
<td></td>
<td>43.8</td>
<td>35.1</td>
<td>21.1</td>
<td>7.474</td>
<td>A</td>
</tr>
<tr>
<td>Ni$<em>{46}$Mn$</em>{30}$Ga$_{24}$ vs. Ni</td>
<td>51.4</td>
<td>25.9</td>
<td>22.7</td>
<td>7.633</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>51.8</td>
<td>24.9</td>
<td>23.1</td>
<td>7.700</td>
<td>5M</td>
</tr>
<tr>
<td>Ni$<em>{52}$Mn$</em>{18}$Ga$<em>{30}$ vs. Ni$</em>{52}$Mn$<em>{30}$Ga$</em>{18}$</td>
<td>51.9</td>
<td>17.6</td>
<td>30.5</td>
<td>7.336</td>
<td>A</td>
</tr>
<tr>
<td>Ni$<em>{52}$Mn$</em>{30}$Ga$<em>{18}$ vs. Ni$</em>{52}$Mn$<em>{30}$Ga$</em>{18}$</td>
<td>52.1</td>
<td>24.8</td>
<td>23.1</td>
<td>7.638</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>52.0</td>
<td>26.4</td>
<td>21.6</td>
<td>7.696</td>
<td>5M</td>
</tr>
<tr>
<td>Ni$<em>{52}$Mn$</em>{18}$Ga$<em>{30}$ vs. Ni$</em>{58}$Mn$<em>{18}$Ga$</em>{24}$</td>
<td>52.0</td>
<td>27.3</td>
<td>20.7</td>
<td>7.733</td>
<td>NM</td>
</tr>
<tr>
<td>Ni$<em>{52}$Mn$</em>{18}$Ga$<em>{30}$ vs. Ni$</em>{58}$Mn$<em>{18}$Ga$</em>{24}$</td>
<td>54.9</td>
<td>17.4</td>
<td>27.7</td>
<td>7.540</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>55.9</td>
<td>17.7</td>
<td>26.4</td>
<td>7.620</td>
<td>NM</td>
</tr>
<tr>
<td>Ni$<em>{56}$Mn$</em>{30}$Ga$<em>{18}$ vs. Ni$</em>{52}$Mn$<em>{30}$Ga$</em>{18}$</td>
<td>56.8</td>
<td>17.9</td>
<td>25.4</td>
<td>7.689</td>
<td>NM</td>
</tr>
<tr>
<td>Ni$<em>{46}$Mn$</em>{30}$Ga$<em>{24}$ vs. Ni$</em>{52}$Mn$<em>{30}$Ga$</em>{18}$</td>
<td>49.0</td>
<td>29.2</td>
<td>21.7</td>
<td>7.602</td>
<td>A</td>
</tr>
<tr>
<td>Ni$<em>{46}$Mn$</em>{30}$Ga$<em>{24}$ vs. Ni$</em>{52}$Mn$<em>{30}$Ga$</em>{18}$</td>
<td>49.4</td>
<td>29.8</td>
<td>20.8</td>
<td>7.648</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>49.9</td>
<td>30.2</td>
<td>21.9</td>
<td>7.704</td>
<td>NM</td>
</tr>
<tr>
<td>Ni$<em>{50}$Mn$</em>{30}$Ga$<em>{18}$ vs. Ni$</em>{58}$Mn$<em>{18}$Ga$</em>{24}$</td>
<td>50.6</td>
<td>30.3</td>
<td>19.1</td>
<td>7.755</td>
<td>NM</td>
</tr>
<tr>
<td>Ni$<em>{50}$Mn$</em>{30}$Ga$<em>{18}$ vs. Ni$</em>{58}$Mn$<em>{18}$Ga$</em>{24}$</td>
<td>50.9</td>
<td>24.9</td>
<td>24.2</td>
<td>7.560</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>53.0</td>
<td>22.2</td>
<td>24.8</td>
<td>7.598</td>
<td>NM</td>
</tr>
<tr>
<td>Ni$<em>{55}$Mn$</em>{18}$Ga$<em>{24}$ vs. Ni$</em>{58}$Mn$<em>{18}$Ga$</em>{24}$</td>
<td>55.5</td>
<td>18.9</td>
<td>25.6</td>
<td>7.642</td>
<td>NM</td>
</tr>
</tbody>
</table>
Figure 43 plots the lattice parameter and c/a for the NM martensites both from current study and from literature [27, 36, 50, 114-116] as a function of e/a ratio. Results from this study matched close to those from the literature. Generally, the lattice parameter a decreases and c increases with an increase of e/a ratio, which results in an increase of c/a with increasing e/a ratio. However, two different trends are observed from Figure 43: one marked with squares and the other marked with circles. Those marked with squares have slightly higher c/a ratio from 1.22 to 1.31. These three compositions are from diffusion couple of Ni$_{25}$Mn$_{75}$ vs. Ni$_{52}$Mn$_{18}$Ga$_{30}$, with compositions away from the Ni$_2$MnGa regions due to higher Mn content (35 – 48 at.%). Those marked with circles have compositions with Mn content less than 30 at.%, which are closer to the stoichiometric Ni$_2$MnGa composition.
Figure 43 Plot of lattice parameter $a$ and $c$, and tetragonality ratio ($c/a$) of NM martensite as a function of $e/a$. Black, blue and red color represent $c/a$, $a$ and $c$ respectively. Solid symbols are from the current study while hollow symbols are from literature [27, 36, 50, 114-116]. Particularly, solid squares are compositions rich in Mn, which are from diffusion couple of $\text{Ni}_{25}\text{Mn}_{75}$ vs. $\text{Ni}_{52}\text{Mn}_{18}\text{Ga}_{30}$.

On the other hand, the $c/a$ ratio for the 5M martensite is generally about 0.94, as listed in Table 13. For the 7M martensite, the $c/a$ ratio is about 0.90. These values are in agreement with those reported previously [26]. The $c/a$ ratio is critical in estimating the magnetic field induced strain (MFIS) caused by twin boundary motion. A theoretical maximum twinning strain $\varepsilon_0$ can be calculated based on the following equation by considering the lattice parameter:
\[
\varepsilon_0 = \left| \frac{c}{a} - 1 \right|
\]

Accordingly, the maximum MFIS is about 6% for 5M martensite [117] and 10% for 7M martensite [59], both of which have been achieved experimentally. However, despite the possible larger maximum MFIS of around 20% for a NM martensite, no observation of large MFIS has been reported for NiMnGa alloys with the NM martensite. This is attributed to a much larger twinning stress (\(\tau_{\text{twin}}\)) of about 6–20 MPa for the NM martensite [118-120]. As a comparison, the \(\tau_{\text{twin}}\) for a modulated martensite is generally less than 2 MPa [45, 59, 121]. The different microstructure and crystallography between modulated and NM martensites contribute to the different twinning stress.

### 5.5.2. Martensitic Microstructure and Crystal Structure

Microstructural features for the NM and modulated martensitic phase can be obtained according to the extensive TEM characterization in this study. Upon cooling from high temperature cubic phase, a self-accommodated microstructure consisting of different variants were formed in order to minimize the transformation strain. For martensites with a tetragonal structure, there were three possible variants, as shown in Figure 44. For a martensite with an orthorhombic structure, there are six possible variants after transformation. These variants are inherently equivalent, and only differ in the way of axis orientation.
With the martensitic transformation proceeding, there would be an interface between austenite and martensite which is the habit plane. The fixed lattice parameter of the cubic austenitic phase places restrictions on the transformation front, so that the formation of martensite with only one variant is not favored due to high strain energy caused by lattice mismatch. However, the energy can be reduced by forming martensites with long axis and short axis alternating along the habit plane (101) [122]. Twin boundary is formed to connect these different variants since it exhibits lower interface energy [122].

Twinning has been observed in all martensites. For modulated martensites, Figure 34, Figure 35 and Figure 36 showed that the primary martensitic variants formed with different orientations. In fact, with each primary variant, the atomic layers itself for a modulated martensites also formed nano-secondary twins as have been verified by HRTEM work [34, 109,
For NM martensite, Figure 37 and Figure 42 presented that the microstructure also consists of primary martensitic variants within which there were secondary twins. Such a twinned microstructure helps to minimize the transformation strain energy both parallel and perpendicular to the habit plane [122]. In brief, the general feature for a martensite in NiMnGa alloy consisted of hierarchical twinned microstructure.

On the other hand, there were microstructural differences between the NM and modulated martensites. In modulated martensites, the secondary twins had a width of a few atomic layers, and the primary twins had a width of a few hundred nanometers, as shown in Figure 34, Figure 35, Figure 36, Figure 40 and Figure 41. For the NM martensites, the width for the secondary twins was approximately 10-40 nanometers, and that for the primary twins was in the micrometer scales, as shown in Figure 37 and Figure 42. Clearly, the thickness of the twins in modulated martensites is thinner than that in the NM martensites. This corresponds to a higher number of twinned variants and twin boundaries in the modulated structure. Some previous research also reports similar findings that the 7M martensite had thinner lamellas compared to the NM martensite in a polycrystalline NiMnGa alloy [36, 42, 124]. Thus it is plausible that the twin boundary energy for the modulated martensite is lower than that for the NM martensite [42, 124]. During martensitic transformation, more twin boundaries can form in modulated martensite so as to further minimize the transformation strain at the habit plane.

Lower temperature may favor the formation of modulated martensites because of its lower twin boundary energy. This may also account for why the $M_s$ for transformation from austenite to modulated martensite is lower than that for transformation from austenite to NM
martensite. In this study, modulated martensite is only found near the interface area of the diffusion couple, meaning that the $M_s$ is near room temperature. On the other hand, NM martensite is always found when the composition is always away from the interface area with higher e/a ratio, as summarized in Table 13. Also in the bulk alloys investigated so far, the $M_s$ for a modulated martensite is typically close to or less than room temperature.

The $M_s$ for the NM martensite can be correlated to the c/a ratio as well. Figure 45 plots both the c/a ratio and $M_s$ for NM martensite only as a function of e/a ratio. The c/a ratio is obtained from this study and literature, while the $M_s$ is extracted from literature. Figure 45 shows that the c/a ratio generally increases when the e/a ratio increases, and the NM martensite tends to form with high $M_s$. As discussed in section 5.5.1, with increasing e/a ratio, the lattice parameter $a_T$ decreases and $c_T$ increases for the NM martensite, while the lattice parameter $a_A$ for the austenite does not change significantly. This means that the difference of lattice parameter $|a_A - a_T|$ and $|c_T - a_A|$ is increasing. According to the discussion above, a large difference of the lattice parameter is not favorable for the martensitic transformation. Therefore, an increase of the transformation temperature is necessary to facilitate the transformation.
5.5.3. Austenitic Microstructure

The microstructure of austenitic phase was also investigated in this study, mostly at locations near the austenite/martensite interface within the diffusion couple. Although the $M_s$ is not obtainable for these compositions, it is estimated that the $M_s$ is slightly lower than room temperature in most cases. The austenite exhibited tweed microstructure with striation features along different directions. This microstructure is typically associated to the pre-martensitic transformation [56-58], which is a precursor phenomenon as the temperature approaches the $M_s$. The formation of tweed microstructure can start as early as more than 100 K above the $M_s$ temperature in some cases [125]. In addition to NiMnGa alloys, the tweed microstructure has been also observed in other alloys that exhibiting martensitic transformation, including NiAl [126], NiTi, Fe-Pd [125, 127] and other Heusler alloys [128].
The characteristic feature of the tweed microstructure is a distinct contrast between striations along different directions. The spacing among striations for the austenitic NiMnGa alloys studied in this study was approximately 10 – 20 nm. For comparison, the average spacing for the tweed striations for a Fe-Pd alloy was reported to be 16 nm [125]. Because of these striations, it would be expected to see a reciprocal lattice spacing of roughly 0.05 – 0.1 nm near the fundamental diffraction spots in the SADP. In reality, such spacing is too short to be observed practically in a SADP, and is most likely hidden within the fundamental diffraction spots.

However, there are indeed extra diffused diffraction spots other than those fundamental ones, which have been observed for the austenitic phase as shown in Figure 39 and Figure 41. By measuring the reciprocal lattice spacing between the diffused and the fundamental diffraction spots, a typical value of around 0.7 – 0.8 nm was obtained. This corresponds to a much shorter lattice spacing in real space of only about 1.2 – 1.4 nm. Therefore, there are probably more features with the striations of the tweed microstructure.

A tweed microstructure from the composition Ni_{54.9}Mn_{17.4}Ga_{27.7} from the diffusion couple of Ni_{52}Mn_{18}Ga_{30} vs. Ni_{58}Mn_{18}Ga_{24} is presented in Figure 46. The general microstructure based on the low magnification BF TEM micrograph showed similar striated features with a spacing of about 15 nm. However, high magnification BF TEM micrograph in Figure 46(b) showed further contrast within each tweed striation. The spacing among these finer striations was only about 1 – 2 nm, corresponding to a reciprocal spacing of 0.5 – 1 nm. These finer striations with various thicknesses caused the diffuse scattering, as indicated by the arrows in the SADP.
from $[1\bar{1}1]$ orientation shown in Figure 46(d). Figure 46(c) presents a HRTEM micrograph from the same area, which clearly showed striated contrast due to strain effect in the sample. In this field of view, the striations extended in the same direction, which caused the spots to diffuse along only one direction in the corresponding fast-Fourier transform. However, the SADP taken from a larger area has diffused spots along all possible $\langle 202 \rangle$ direction, indicating that the striation could occur in different directions.
Figure 46 (a) low magnification and (b) high magnification BF TEM of the tweed microstructure for Ni_{54.9}Mn_{17.4}Ga_{27.7} from diffusion couple of Ni_{52}Mn_{18}Ga_{30} vs. Ni_{58}Mn_{18}Ga_{24}. (c) high resolution TEM micrograph showing the strain contrast and the corresponding fast-Fourier transform. (d) SADP of the sample from $[\bar{1}11]$ orientation.

The SADP of the austenitic phase appeared similar to the SADP of a modulated martensitic phase from $[\bar{1}11]$ orientation, as presented in Figure 34(c) and Figure 35(c). In spite of the more symmetric cubic crystal structure, the diffused diffraction spots are only located near the fundamental diffraction spots for the austenitic phase. However, some hints from the
modulated martensitic structure may help understand the tweed pattern of the austenitic phase. As mentioned before, the modulated structure has been established by the periodic stacking of the \( (202) \) plane along the \( \langle 202 \rangle \) direction from the austenitic phase, which caused extra diffraction spots between the fundamental spots. As an analogy to the austenitic phase, the extra diffused diffraction spots strongly suggest the existence of some atomic displacements during the pre-martensitic transformation [56, 125]. The displacement of atoms from their equilibrium position causes lattice strains in the alloy, which is the origin of the tweed microstructure. Given that the striated contrast is parallel to the \( (202) \) plane, and the diffused diffraction spots are along the \( \langle 202 \rangle \) direction, the displacement vectors can be represented as:

\[
R = q\{202\}/\langle 220 \rangle
\]  

(17)

Where \( R \) is the atomic displacement and \( q \) is the fraction of the distance between the two consecutive atomic layers [125]. Since the austenitic phase has a cubic symmetry, there are several but equivalent ways of atomic displacement in the alloy. This is represented as different contrast direction and may form domain like microstructure in the austenitic phase, as shown in Figure 35. As martensitic transformation is a first order transition, which occurs through nucleation and growth process, these domains in the pre-martensitic state probably serve as the nucleation site. During transformation, they will grow to martensitic variants with different orientations.
5.6. Summary

In this section, detailed microstructure and crystallography of martensite and austenite with various compositions from the diffusion couples were examined through TEM. Modulated martensites, including 7M and 5M martensites, have been identified in the diffusion couples. The modulated martensites were only found near the phase boundary between austenite and martensite, indicating $M_s$ is near or slightly higher than room temperature. The microstructure was similar for 7M and 5M martensite, which consists of twinned variants with thickness ranging from 100 to 500 nm. The crystal structure for 7M is orthorhombic and for 5M is tetragonal, but both are slightly monoclinal distorted.

NM martensites, with tetragonal crystal structure, were frequently identified in the diffusion couples. The microstructure generally consisted of two sets of martensitic variants: primary martensitic variants with thickness in the range from 500 nm to a few microns and secondary martensitic variants with thickness on a few tens of nanometers. The secondary martensitic variants formed strict twinning relationship with straight twin interface. The relationship between two primary martensitic variants was not simply twinning relationship, which resulted in an incoherent interface. A general increase of $c/a$ ratio along with the increase of $T_m$ has been correlated with the increase of $e/a$ ratio. A higher $c/a$ ratio may cause larger lattice mismatch between austenite and martensite during the martensitic transformation, which would be responsible for a higher $M_s$.

The austenitic phase investigated from the diffusion couples typically showed pre-martensitic microstructure. Striated features were observed by TEM, which was caused by the
local lattice distortion before martensitic transformation. Diffused scattering along the $\langle 101 \rangle$ direction was frequently observed in the electron diffraction pattern for the cubic austenitic phase. This indicates that the lattice shear is along the $\langle 101 \rangle$ direction. By examining the interface between austenite and martensite, it would be expected that the diffused scattering would eventually evolve to sharp diffraction spots after the completion of the martensitic transformation.
CHAPTER 6: MECHANICAL PROPERTY

For the first time, the elastic and plastic properties (i.e. reduced elastic modulus and hardness) for the NiMnGa alloys as a function of compositions were determined through analysis of the load-displacement profiles by the Oliver-Pharr method. This is achieved by combining the diffusion couple experiments and nanoindentation technique. As discussed before, the diffusion couples in this study generated a smooth concentration gradient, which covered a large range of compositions in the $\beta$ phase region. Since nanoindentation technique measures the mechanical properties at small volume, a one to one relationship can be established between mechanical property and composition. In the following section, only results measured from diffusion couples annealed at 900 °C are reported.

6.1. Reduced Elastic Modulus and Hardness

Three representative nanoindentation load-displacement curves from one of the diffusion couples are presented in Figure 47, for austenite, martensite and near the austenite/martensite phase boundary. In all cases, both loading and unloading curves are smooth without any pop in. The unloading curve is characterized by a large remnant deformation. The maximum indentation depth is typically less than 250 nm, which is very small compared to the length of interdiffusion zone. Therefore, it is appropriate to assume a constant composition within each indentation volume. The maximum indentation depth was typically larger near the austenite/martensite phase boundary than that for the austenite or martensite.
Figure 47 Three representative nanoindentation curves from austenite (black), martensite (blue) and from near the interface between austenite and martensite (red).

Figure 48(a) presents the secondary electron micrograph of the indentation linear profiles across the interdiffusion zone after the indentation tests have been performed. As described in the experimental section, three line profiles with separation of 20 μm both horizontally and vertically were carried out across the interdiffusion zone, as shown in Figure 48(a). The triangular shaped indents left on the clean polished surface are from the pyramidal Berkovich tip. The backscatter electron micrograph shown in Figure 48(b) facilitated the positioning of the indents so that the position of the indents can be correlated to the composition. However, the positioning of the indents for all diffusion couples is completed with the help of an optical microscope, because of its convenience.
Figure 48 Representative (a) secondary electron and corresponding (b) backscatter electron micrograph of the interdiffusion zone near the interface between austenite and martensite showing the nanoindents after nanoindentation tests.

The $E_r$ and $H$ obtained from nanoindentation line profile across the interdiffusion zone, superimposed with the corresponding concentration profile, are plotted in Figure 49, Figure 50 and Figure 51 for series I, series II and series III diffusion couples, respectively. In these plots, the green diamonds and yellow solid lines represent the average value of raw $E_r$ or $H$ and smoothed value. Black solid, blue dotted and red dashed represent the fitted concentration of Ni, Mn and Ga, respectively. The vertical black dashed line indicates the interface between austenite and martensite. Based on Figure 49, the $E_r$ for pure Ni obtained from this study is roughly 180 GPa. According to equation (10), by taking 1140 GPa and 0.07 as the Young’s modulus and Poison’s ratio of the diamond indenter and 0.31 as the Poison’s ratio of pure Ni, the Young’s modulus of the Ni in this study is calculated to be about 200 GPa. This is very close to Young’s modulus of bulk Ni reported before [129, 130], and verifies that the nanoindentation data in this study is accurate.
The primary focus will be on the evaluation of $E_r$ and $H$ as a function of NiMnGa compositions that are located within the $\beta$ phase. No attempt was made to convert the $E_r$ to the Young’s modulus since the Poission’s ratio for NiMnGa alloys at different compositions is not available. However, if it is assumed that the Poission’s ratio remains relatively unchanged as a function of composition varied with diffusion couples.

Figure 49 presents the $E_r$ and $H$ for series I diffusion couples, which are multiphase diffusion couple with one terminal end being Ni, as also evidenced from the diffusion paths in Figure 31. The $E_r$ and $H$ varied from 85 GPa to 135 GPa, and from 4 GPa to 6 GPa, respectively, within the compositional range in these diffusion couples. For the austenitic phase, both $E_r$ and $H$ monotonically decreased as the composition gets closer to the austenite/martensite interface composition. Similarly, for the martensitic phase, both $E_r$ and $H$ decreased as the composition approached the phase boundary area. The same trend was observed for both diffusion couples, despite the fact that the compositions are very different.
Figure 49 Reduced elastic modulus and hardness for series I diffusion couples.

Figure 50 presents the $E_r$ and $H$ for series II diffusion couples which are also multiphase diffusion couple but with one terminal end being Ni$_{25}$Mn$_{75}$. Part of the compositions for the ternary NiMnGa alloys within these two diffusion couples are Mn rich. The $E_r$ and $H$ vary from about 90 GPa to 125 GPa and from 4.5 GPa to 5.5 GPa, respectively. Similar to that observed in series I diffusion couples, $E_r$ and $H$ decrease in both austenitic and martensitic phase when the composition gets near the phase boundary.
Figure 50 Reduced elastic modulus and hardness for series II diffusion couples.

Figure 51 presents the $E_r$ and $H$ for series III diffusion couples, which are single-phase diffusion couples with only the $\beta$ phase. The $E_r$ and $H$ for these compositions varied from about 85 GPa to 125 GPa and from 4 GPa to 5.5 GPa, respectively. A V-shaped curve for $E_r$ and $H$ as a function of composition was observed for these diffusion couples despite their different diffusion paths, similar to the trend observed in series I and series II diffusion couples. One stunning observation from the measurement of $E_r$ and $H$ is that a minimum value always existed near the phase boundary between austenite and martensite in spite of differences in composition.
Figure 51 Reduced elastic modulus and hardness for series III diffusion couples.
Another characteristic feature observed for all nanoindentation curves was that the scatter of $E_r$ is generally larger for the martensitic phase than that for the austenitic phase, as revealed by larger standard deviations shown in Figure 49, Figure 50 and Figure 51. The standard deviation for the austenitic phase was typically less than 5% of the corresponding $E_r$, while the standard deviation for the martensitic phase ranged from 5% to 15% of the corresponding $E_r$. A similar trend is observed when comparing the $H$ for martensitic and austenitic phase.

The large range of compositions generated by the diffusion couples has allowed an effective evaluation of $E_r$ and $H$ for the NiMnGa alloys. Figure 52 presents the $E_r$ and $H$ as a function of compositions in the ternary isotherm by combining the nanoindentation and composition data. The iso-\(e/a\) ratio lines from 7.2 to 8.0 are also plotted to help visualize the trend. It is interesting that the contour of the $E_r$ or $H$ lies near parallel to iso-\(e/a\) ratio lines, despite some fluctuation. The trend is not preserved when the Mn content is relatively high, i.e. higher than 35 at. %. The minimum value for $E_r$ was roughly 90 GPa, which occurs around compositions with \(e/a\) ratio close to about 7.6. The $E_r$ varied roughly from 85 GPa to 140 GPa for the martensitic phase, while from 85 GPa to 110 GPa for the austenitic phase over the compositional range studied. On the other hand, the $H$ varied approximately from 3.5 GPa to 5.5 GPa for both the martensitic and austenitic phase.

There are limited data regarding to the modulus and hardness of NiMnGa alloys measured by nanoindentation. Our previous research for Ni\(_{2+x}\)Mn\(_{1-x}\)Ga (x=0.14, 0.16, 0.19, 0.22, 0.22) alloys with martensitic phase showed that the reduced elastic modulus varied from 105 GPa to 120 GPa as x increases [65]. Similarly, the reduced elastic modulus for Ni\(_{50.9}\)Mn\(_{29.0}\)Ga\(_{20.1}\)
reported to be about 98 GPa [66]. These values are very close to that measured through diffusion couples at similar compositions.

Figure 52 Ternary mapping of reduced elastic modulus and hardness for the ternary NiMnGa alloys.
6.2. Discussion

6.2.1. Twin Realignment and Superelasticity

Although many studies have reported the $E_r$ and $H$ value for different kinds of shape memory alloys using nanoindentation technique, it is argued that the data may be influenced by other factors. The concern comes from the strain component under a high stress. The stress during the nanoindentation process may cause twin realignment for the martensite or induce austenitic-martensitic phase transformation for the austenite, which may generate additional strains and thus affect the calculated absolute values of $E_r$ or $H$.

For the measurement of the martensitic region, there may be twin realignment during the loading process. As has shown in Figure 10, the lowest stress required for the twin movement for NiMnGa is in the range of a few tens of MPa or even less, depending on the composition and crystal structure [59, 60]. Such a twinning stress is much lower than that generated beneath a sharp Berkovich tip (on the order of several GPa [131]). Therefore, the displacement of the loading curve probably contains the contribution from strain caused from twin movement. Moreover, it is known that such twin movement is not recoverable simply by removing the stress.

A different situation needs to be considered for the measurement of austenitic region, where the stress under the Berkovich tip may induce the martensitic transformation. This has been known as the superelasticity effect, similar to the magnetic superelasticity effect. In this case, a stress induced strain may arise during the indentation process. This process is recoverable when the stress is removed.

The two different situations are schematically illustrated in Figure 53. The Berkovich is a sharp tip, and the stress generated is in the order of several GPa, and even higher underneath the
tip [131]. Such a high stress exceeds the yielding point of the NiMnGa alloy [132], and thus a large portion under the tip would be plastically deformed. This portion is not recoverable, and would remain as remnant displacements as shown in Figure 47. Far away from the tip though, the stress is relatively small and the deformation is mostly elastic. The elastic deformation would be recovered when the stress is removed. In between the two zones where the stress is lower than the yielding point, there would be a mixed region of deformation mechanism from elastic deformation and twin realignment or martensitic transformation.

Figure 53 Deformation mechanisms for (a) martensite and (b) austenite under a Berkovich indenter.

Many investigations have been carried out to understand the shape memory effect and the superelasticity under nanoindentation measurement, especially for NiTi alloys [133-137]. Generally, it is believed that under the complex stress condition caused by nanoindentation, the shape memory effect or superelasticity indeed occur. The effect is more pronounced when the indenter is spherical as the stress is more uniform or when the indentation depth is low.
Therefore, for the $E_r$ and $H$ reported for the NiMnGa alloys in this study, the shape memory effect or superelasticity may influence the value. Because of the extra strain generated either by twin realignment or by martensitic transformation, the projected area becomes larger. According to equation (7) and (8), the calculated $E_r$ and $H$ may be lower if more such extra strain is involved.

For the martensitic phase in all diffusion couples, the twinning stress would be potentially lower near the interface area due to modulated structure or lower c/a ratio. As a result, the region involving strains due to twin realignment would be larger when measurement is performed near the interface area. It is thus more likely to underestimated $E_r$ or $H$ near the interface area, which is in agreement with the experimental results as shown before.

For the austenite phase in all diffusion couples, the situation depends on if the applied stress was able to induce martensitic transformation or not. The stress induced martensitic transformation is typically analyzed according to Clausius-Clapeyron relationship:

$$\frac{d\sigma}{dT} = -\frac{\Delta S}{\varepsilon} = -\frac{\Delta H}{\varepsilon T}$$

(18)

where $\sigma$ is the uniaxial applied stress, $\varepsilon$ is the transformation strain, $\Delta S$ is the entropy of transformation per unit volume, $\Delta H$ is the enthalpy of transformation per unit volume and $T$ is temperature [1]. Accordingly, a higher stress is required to induce martensitic transformation if the temperature is higher, which has been experimentally verified [132, 138]. Considering the austenitic phase in the diffusion couples, as has shown in previous chapter, the martensitic transformation temperature becomes higher as it approaches the interface area. This is equivalent
to that the difference between martensitic transformation temperature and room temperature is smaller. Therefore, the required stress to potentially induce martensitic transformation is smaller near the interface area. As a result, the region involving strains due to martensitic transformation is larger, and $E_r$ and $H$ are more likely to be underestimated near the interface area. This is also in agreement with the $E_r$ and $H$ curves shown in section 6.1.

However, in this study, it is postulated that the absolute values affected because of the deformation strain from twin realignment or superelasticity effect are very small. The Berkovich is a sharp tip and the stress generated is in the order of several GPa or even higher underneath the tip [131]. Such a high stress is much larger than the yielding stress for NiMnGa alloy, which is reported to be 200 – 350 MPa [132]. Therefore, a large portion of the NiMnGa alloys beneath the indenter undergoes plastic deformation, while the portion of NiMnGa alloys undergoes twin realignment or martensitic transformation is small. This is also reflected in the load-displacement curves shown in Figure 47, where no pop-ins were observed for both loading or unloading curves and large amount of remnant deformation remains.

6.2.2. Composition

Composition is obviously the most important factor that affects the mechanical property of the NiMnGa alloys, since the modulus is closely related to the bonding strength of the atoms. Since the series III diffusion couples were designed that there is an iso-composition element, it becomes easy to investigate the effect on mechanical properties when one element substitutes the other one in a sublattice. Figure 54 presents the first order derivative of reduced elastic modulus to composition when one element substitutes another element, while keeping the third element relative constant. These numbers were calculated based the series III diffusion couples as shown
in Figure 51. For example, in Figure 54(a), the Y axis means the change in reduced elastic modulus when one atomic percent of Mn substitutes Ga, at the corresponding Mn composition shown in X axis while Ni is nearly constant at 52 at.%. A negative value means a decreasing trend while a positive number means an increasing trend.

For the austenitic phase, a decrease in the $E_r$ can be achieved by Mn or Ni substituting Ga, and Ni substituting Mn. With one percent of Mn substituting Ga, the change of $E_r$ is up to -10 GPa. With one percent of Ni substituting Ga, the change of $E_r$ is up to -40 GPa. With one percent of Ni substituting Mn, the change of $E_r$ is up to -6 GPa. But this change is nonlinear, and becomes very large when the composition approaches the interface between martensite and austenite.

For the martensitic phase, on the other hand, an opposite trend is revealed. An increase in the $E_r$ is achieved by Mn or Ni substituting Ga, and Ni substituting Mn. With one percent of Mn substituting Ga, the change of $E_r$ is up to 15 GPa. With one percent of Ni substituting Ga, the change of $E_r$ is up to 34 GPa. With one percent of Ni substituting Mn, the change of $E_r$ is up to 15 GPa. The effect of composition change on the $E_r$ also becomes larger as it approaches the interface area.
Figure 54 The first order derivative of reduced elastic modulus to composition when (a) Mn substitutes Ga when Ni is around 52 at.%, (b) Ni substitutes Ga when Mn is around 18 at.%, (c) Ni substitutes Ga when Mn is around 30 at.%, (d) Ni substitutes Mn when Mn is around 18 at.%. These correspond to series III diffusion couples in Figure 51.

The different trends observed for austenite and martensite may be attributed to the different crystal structures. As described in previous sections, the austenite has a cubic L2₁ crystal structure, while the crystal structure of martensite is tetragonal or orthorhombic. However, composition does not appear to be the only factor that influences the trend observed in Figure 54 where a significant change was observed always near the interface between austenite and martensite.
6.2.3. Orientation Effect

The Young’s modulus is dependent on the grain orientation for an anisotropic material. For austenitic NiMnGa alloy, despite its cubic crystal structure, the anisotropic factor is large near the transformation region, and has been reported to be nearly 10. For martensitic NiMnGa alloy, it would be expected that the anisotropic factor is even higher because of its less symmetric crystal structure. Two different types of contributions – from grain orientation and from martensitic variant orientation were taken into considering to examine the scatter in the measured $E_r$ and $H$.

In order to examine the effect of grain orientation on the scatter of $E_r$ and $H$, additional nanoindentation measurements were carried out on the terminal end of selected diffusion couples. Figure 55(a) schematically presents how the measurements were conducted. The line profile is perpendicular to the interdiffusion direction so that the compositions along the line were similar. The indentation set up remained the same as reported in section 3.4, but the space between individual indent was 200 $\mu$m so that a total of 20 measurements should cover a large area with different grains. Although the grain size was not obtainable for the diffusion couples, it was estimated to be close to the millimeter scale or larger based on some SEM micrographs and previous work [36].
Each value of $E_r$ and $H$ measured from the terminal end of diffusion couple Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni$_{58}$Mn$_{18}$Ga$_{24}$ is presented in Figure 56. The average $E_r$ along with the standard deviation was $112.3 \pm 3.8$ GPa and $131.6 \pm 14.3$ GPa for the austenite and martensite, respectively. The average $H$ along with the standard deviation was $4.76 \pm 0.10$ and $4.76 \pm 0.31$ for the austenite and martensite, respectively. The average values are close to those reported in Figure 51(c) and (d).
Figure 56 Reduced elastic modulus and hardness obtained on the terminal end from diffusion couple of Ni$_{52}$Mn$_{18}$Ga$_{30}$ vs. Ni$_{58}$Mn$_{18}$Ga$_{24}$.

For the austenitic phase, the standard deviation was less than 5% of the average value of $E_r$ or $H$. This indicates that the grain orientation only has small contribution to the scatter of the measured $E_r$ or $H$ in this study, despite the fact that the austenitic NiMnGa is known to be anisotropic. The reasons for why the grain orientation contribution is small in this study are not clear yet, but it is possible that the grain orientation difference is small among those grains or the indentation depth is large enough.

For the martensitic phase, on the other hand, the scatter was clearly higher and the standard deviation was about 10% of the average value of $E_r$ or $H$. This is consistent with the results shown in section 6.1. For the martensitic phase, the crystal structure can be different – NM or modulated 5M or 7M structure depending on the compositions as discussed in previous chapters. The tetragonal or monoclinic crystal structure, along with larger anisotropy compared to the cubic structure for the austenite, mostly likely caused the large scatter. Furthermore, all martensitic phases consist of plate like variants with different orientations, as shown in section
5.2. Additionally, the width of those martensitic variants was typically less than a few microns. Since the measurements have chances to randomly indent on any variant or on the interface between twin variants, a large scatter can arise. Similar observations have been reported before where different values were obtained for different variants in a 7M NiMnGa alloy [33].

6.2.4. Lattice Softening

Since all the $E_r$ and $H$ vs. composition curves shown in section 6.1 exhibited a minimum value near the interface between austenite and martensite, where the martensitic transformation occurs around room temperature, it is reasonable to postulate that the martensitic transformation may also influence the measured $E_r$ or $H$.

Indeed, a decrease of Young’s modulus has been observed in another well-known shape memory alloy – NiTi alloy. Through a resonance technique, the elastic moduli for near stoichiometric NiTi were determined at various temperatures across the transformation temperature [139]. Both Young’s modulus and shear modulus exhibited a minimum value near the transformation temperature, and rose rapidly above and below this temperature [139]. Minimum Young’s modulus near transformation temperature has been further confirmed in recent studies for three slightly off-stoichiometric sputter-deposited NiTi films and NiTi polycrystals [20, 21, 140]. The elastic constants of longitudinal mode $C_L = (C_{11}+C_{12}+2C_{44})/2$ and the transverse mode $C' = (C_{11}-C_{12})/2$ and $C_{44}$ for a single crystal NiTi has also been reported to show a minimum value near the transformation temperature [20]. The softening of the elastic
constants observed in NiTi alloys has been attributed to the lattice instabilities associated with the pre-martensitic transformation [21].

It is possible that the pre-martensitic transformation near the interface region affects the mechanical properties of the NiMnGa. So far, there have been investigations that measured the elastic constants of the NiMnGa alloys near the vicinity of the martensitic transformation region using ultrasonic method. However, a complete study of $E_r$ and $H$ is first reported in this study, as a function of composition. Some hints can be obtained by relating the elastic constants and the measured $E_r$.

The elastic constants can be converted to the measured $E_r$ from nanoindentation. For polycrystals, the isotropic elastic moduli can be determined from individual grains through an averaging process according to the Voigt-Reuss-Hill (VRH) average method [141]. The Voigt average assumes that the local strain is equal to the mean strain, which defines the upper limit of the elastic moduli. For a cubic phase, the bulk modulus $(B)$ and shear modulus $(G)$ can be calculated according to the following equation:

$$B_r = \frac{C_{11} + 2C_{12}}{3}$$

$$G_r = \frac{C_{11} - C_{12} + 3C_{44}}{5} = \frac{2C' + 3C_{44}}{5}$$

On the other hand, the Reuss average assumes that the local stress is equal to the mean stress, which provides a lower limit of the elastic moduli. Accordingly, the $B$ and $G$ can be calculated for cubic crystals:
The conversion between the stiffness and compliance has been applied for the above equation for a cubic structure, where the conversion is:

\[
B_r = \frac{C_{11} + 2C_{12}}{3} \tag{21}
\]

\[
G_r = \frac{5}{4(S_{11} - S_{12}) + 3S_{44}} = \frac{5}{\frac{2}{C'} + \frac{3}{C_{44}}} \tag{22}
\]

The VRH average takes the average of the Voigt and Reuss average, which best represents the B and G of the polycrystals [141]. Therefore, the VRH average of B and G can be written as:

\[
S_{11} = \frac{C_{11} + C_{12}}{(C_{11} - C_{12})(C_{11} + 2C_{12})} \tag{23}
\]

\[
S_{12} = \frac{-C_{12}}{(C_{11} - C_{12})(C_{11} + 2C_{12})} \tag{24}
\]

\[
S_{44} = \frac{1}{C_{44}} \tag{25}
\]

Furthermore, the isotropic Young’s modulus can be obtained from B and G through the well-known relationship:
Based on equation (26), (27) and (28), a change in the elastic constant will result in a change in the Young’s modulus. According to previous measurements on the single crystal elastic constant for NiMnGa alloys as a function of temperature, the change in $C_{11}$ and $C_{12}$ is relatively small across the martensitic transformation zone [19]. That means the change in B is also small. However, there is a sharp decrease for both $C'$ and $C_{44}$ as the temperature approaches $M_s$, which results in a decrease in G based on equation (27). As a result, the E should decrease because B remains relatively constant while G decreases.

Table 14 presents some elastic constants and modulus for austenitic NiMnGa alloys extracted from various sources. If only elastic constants are measured, the elastic moduli will be calculated according to equation (26), (27) and (28). For Ni$_2$MnGa alloy, the E ranges from 100 to 130 GPa. This is in agreement with the measured value from nanoindentation in this study. The $E_r$ for Ni$_2$MnGa according to Figure 52 in this study is roughly 105 – 110 GPa, which results in E of about 99 – 104 GPa, if Poison’s ratio is assumed to be 0.38. Moreover, despite some discrepancies for absolute values, E clearly decreases as the temperature gets close to the martensitic transformation due to the decrease in $C'$ and $C_{44}$.

\[
E = \frac{9B}{1+3\frac{B}{G}} \quad (28)
\]
Table 14 Experimental or calculated elastic constants and moduli for austenitic NiMnGa alloys.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Method</th>
<th>$C_{11}$ (GPa)</th>
<th>$C_{12}$ (GPa)</th>
<th>$C_{44}$ (GPa)</th>
<th>$C'$ (GPa)</th>
<th>B (GPa)</th>
<th>G (GPa)</th>
<th>E (GPa)</th>
<th>ν</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_2$MnGa[142]</td>
<td>Calculated</td>
<td>163</td>
<td>152</td>
<td>107</td>
<td>5.5</td>
<td>155.7</td>
<td>39.6</td>
<td>109</td>
<td>0.38</td>
</tr>
<tr>
<td>Ni$_2$MnGa[143]</td>
<td>Calculated</td>
<td>173</td>
<td>141.6</td>
<td>99.4</td>
<td>15.9</td>
<td>152.1</td>
<td>48.8</td>
<td>132.3</td>
<td>0.35</td>
</tr>
<tr>
<td>Ni$_2$MnGa[144]</td>
<td>Calculated</td>
<td>168</td>
<td>152.2</td>
<td>107</td>
<td>7.9</td>
<td>157.5</td>
<td>42.6</td>
<td>117.2</td>
<td>0.38</td>
</tr>
<tr>
<td>Ni$_2$MnGa[145]</td>
<td>Experimental</td>
<td>142</td>
<td>134</td>
<td>104</td>
<td>4</td>
<td>137</td>
<td>36.7</td>
<td>101.1</td>
<td>0.37</td>
</tr>
<tr>
<td>Ni$_2$MnGa[146]</td>
<td>Experimental</td>
<td>152</td>
<td>143</td>
<td>103</td>
<td>4.5</td>
<td>146</td>
<td>37.1</td>
<td>103</td>
<td>0.38</td>
</tr>
<tr>
<td>Ni$_2$MnGa[146]</td>
<td>Experimental</td>
<td>~265K</td>
<td>151</td>
<td>145</td>
<td>101</td>
<td>3</td>
<td>147</td>
<td>34.5</td>
<td>96</td>
</tr>
<tr>
<td>Ni$_2$MnGa[19]</td>
<td>Experimental</td>
<td>~230K</td>
<td>136</td>
<td>100</td>
<td>102</td>
<td>18</td>
<td>112</td>
<td>52</td>
<td>135</td>
</tr>
<tr>
<td>Ni$_2$MnGa[147]</td>
<td>Experimental</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>107.9</td>
</tr>
</tbody>
</table>

In order to better analyze the influence of B, C$_{44}$ and C' on the E, plots of B, C$_{44}$ or C' vs. E were presented in Figure 57, by varying one variable but keeping the other two constant. The values were chosen based on experimental and calculated data reported before as listed in Table 14. Figure 57(a) indicated that the E is insensitive to the variation of B, even with a large change in B. This means that E is also insensitive to C$_{11}$ and C$_{12}$, according to equation (26). However, decreases in C$_{44}$ and C' caused a large decrease in E, as illustrated by large slopes in Figure 57(c) and (d). Particularly in the E vs. C' curve, the smallest E when C' approaches zero, is in the range of 76 – 92 GPa, depending on the value of C$_{44}$ and B. Recalling from the E$_r$ measured from diffusion couples via nanoindentation in section 6.1, the minimum E$_r$ is in the range of 82 – 95 GPa depending on the composition. By taking Poison’s ratio as 0.38 according to Table 14, the E is calculated to be 76 – 89 GPa. This agrees well with the predicted value from Figure 57(c).
Figure 57 Young’s modulus as a function of (a) Bulk modulus (B), (b) $C_{44}$ and (c) $C’$.

The above analyses primarily focused on the austenitic phase, with a cubic crystal structure. For the martensitic phase with either tetragonal or orthorhombic crystal structure, similar analyses can be carried out but require more elastic constants. Full matrix of the elastic constants has not been experimental measured so far. Although elastic constants matrix for NM tetragonal Ni$_2$MnGa was reported by first principles calculation [144], it is noticed that it may
not represent true value since NM tetragonal Ni$_2$MnGa does not exist at room temperature. However, some extended experiments by measuring $C'$ and $C_{44}$ to lower temperature have observed that both values start to increase after the martensitic transformation [19]. Therefore, it is reasonable to speculate that similar trend may hold true for martensitic phase that the $E$ may increase as temperature decreases from $M_s$, because of an increase in these shear related elastic constants.

As has been observed in section 6.1, the nanoindentation curves for all diffusion couples exhibit a depression toward the interface region between austenite and martensite. This can be attributed to the lower of elastic moduli as the temperature approaches the $M_s$. In previous measurements for elastic constants, experiments are carried out by fixing the alloy composition and by varying the temperature across the transition region. However, in diffusion couple experiments, the temperature is fixed at room temperature, while the compositions smoothly vary across the interdiffusion zone. According to discussion in previous chapters, the $M_s$ temperature across the interdiffusion zone also changed as a function of composition or e/a ratio. It generally follows that the $M_s$ increased from the austenitic terminal end to the martensitic terminal end. This is schematically illustrated in Figure 58, which shows that the temperature gap between $M_s$ and room temperature becomes smaller from the austenite region to near the interface region. This means that the martensitic transformation is about to occur near the interface, or pre-martensitic transformation has already occurred. As a matter of fact, this TEM investigation has demonstrated that, indeed, there is a pre-martensitic transformation characterized by tweed microstructure and diffused diffraction pattern. Accordingly, the elastic constants are more likely softened near the interface region, which would contribute to the depression of the $E_r$ or $H$ curve.
On the other side of the interface, the temperature gap between $M_s$ and room temperature starts to increase, and the transformation would be more complete. The elastic constants should stiffen after the transformation, which results in the increase in $E_r$ or $H$.

![Figure 58 A schematic of change of $M_s$ (red) and $E_r$ or $H$ (blue) across the interdiffusion zone.](image)

6.3. Summary

For first time, the elastic and plastic properties of the ternary NiMnGa alloys as a function of compositions were determined through analysis of the load-displacement curves of nanoindentation by the Oliver-Pharr method. The data obtained from the diffusion couples was comparable from those experimental and calculated data from literature.

For all diffusion couples, an asymmetric V-shaped curve was observed for the measured $E_r$ and $H$, despite that the diffusion paths were different. The location of the minimum
corresponded to the phase boundary between austenite and martensite. Opposite trends of \( E_r \) and \( H \) as a function of compositions were observed for austenite and martensite. With Mn or Ni substituting Ga, and Ni substituting Mn, the \( E_r \) and \( H \) decrease for the austenite but increase for the martensite.

In addition to the compositional effect, lattice softening associated with the pre-martensitic transformation also contributes to the V-shaped curve. By examining the Young’s modulus using the Voigt-Reuss-Hill average model, it was found that the softening of the elastic constants \( C’ \) and \( C_{44} \) would decrease the Young’s modulus. Since the pre-martensitic transformation was verified near the phase boundary according to the TEM investigation, it was expected that the \( C’ \) and \( C_{44} \) was lower near this region. This would result in a lower Young’s modulus near the phase boundary area.

Besides the elastic and plastic deformation during the indentation, twin realignment in the martensite and stress induced martensitic transformation in the austenite may cause additional strain. This may result in a lower measured \( E_r \) and \( H \) by nanoindentation. It was qualitatively argued that this effect was more pronounced near the phase boundary region, which was consistent with the observed V-shaped curve. However, the contribution from twin realignment or stress induced martensitic transformation may be negligible, since the measured values agreed well with experimental and calculated data in literature.

It was also found that the scatter of the \( E_r \) and \( H \) for the martensite was much larger than that for the austenite. This is due to that the martensite consists of many variants with different
orientations. On the other hand, the grain orientation has little effect on the scatter, as confirmed by the experiments.
CHAPTER 7: SUMMARY

Ni-Mn-Ga alloys have various functional properties and have the potential to be used in different applications. The martensitic transformation is the key reason that brings Ni-Mn-Ga alloys different kinds of properties. A better understanding of the martensitic transformation, and related microstructure and crystallography of the austenite and martensite, is crucial to improve the performance and discover new alloys. In this study, a combinatorial study using diffusion couples was carried out, aiming at comprehensively investigating the properties and advancing the development of Ni-Mn-Ga alloys.

Solid to solid diffusion couples were fabricated by assembling two selected alloys from a total of six alloys: Ni, Ni_{25}Mn_{75}, Ni_{52}Mn_{18}Ga_{30}, Ni_{46}Mn_{30}Ga_{24}, Ni_{52}Mn_{30}Ga_{18} and Ni_{58}Mn_{18}Ga_{24} (in atomic percent). These diffusion couples were annealed at 800 °C, 850 °C and 900 °C for 480 hour, 240 hour and 120 hour, respectively. The resultant interdiffusion zones were subjected to electron microscopy analyses for compositional, kinetic and structural knowledge. Nanoindentation testing was also performed across the interdiffusion zone to determine the mechanical properties as a function of compositions.

Phase equilibria and interdiffusion behavior were analyzed by examining the microstructural development and concentration profiles. The interdiffusion zone for each diffusion couple consisted of both austenitic and martensitic phase with distinct microstructural features at room temperature. Certain diffusion couples also contained γ(Ni) and γ(Mn) solid solution, and α-(Ni,Mn)_{3}(Ga,Mn) intermetallic. Compositions obtained from these phase boundaries provide additional information to examine the accuracy and modify the ternary phase
diagram. The compositions determined from the austenite/martensite phase boundary represent compositions with martensitic transformation temperatures near room temperature. These compositions corresponded close to iso-e/a ratio of 7.6, but changed toward to lower e/a ratio with Mn content increased to more than 35 at.%. Interdiffusion coefficients were quantitatively calculated from concentration profiles. Average effective interdiffusion coefficients and the corresponding activation energies indicated compositional dependence in addition to Arrhenius temperature-dependence. The magnitude of main ternary interdiffusion coefficient exhibited minimum values near 52 at.% Ni concentration. Ni was observed to interdiffuse the fastest, followed by Mn then Ga. Interdiffusion flux of Ni also has strong influences on the interdiffusion of Mn and Ga with large and negative cross interdiffusion coefficients, $\tilde{D}_{MnNi}$ and $\tilde{D}_{GaNi}$.

Extensive TEM analyses have been carried out to investigate the microstructure and crystallography of martensite and austenite with various compositions from the diffusion couples. Modulated martensites, including 7M and 5M martensites that have been commonly identified in bulk alloys, were found in the diffusion couples. The microstructure was similar for 7M and 5M martensite, which consists of twinned variants with thickness ranging from 100 to 500 nm. The crystal structure for 7M is orthorhombic and for 5M is tetragonal, but both are slightly monoclincally distorted. In addition, NM martensites with tetragonal crystal structure, were frequently identified in the diffusion couples. The microstructure for NM martensite generally consisted of two sets of martensitic variants: primary martensitic variants with thickness in the range from 500 nm to a few microns and secondary martensitic variants with thickness on a few tens of nanometers. The secondary martensitic variants formed strict twinning relationship with straight twin interface. However, the relationship between two primary martensitic variants was
not simply twinning relationship, which resulted in an incoherent interface. The modulated martensites were only found near the phase boundary between austenite and martensite, indicating $M_s$ is near or slightly higher than room temperature. However, NM martensites were typically found away from the phase boundary region, indicating $M_s$ is higher than room temperature. In addition, by combining literature data and experimental data from this study, a general increase of $c/a$ ratio along with the increase of $T_m$ has been correlated with the increase of $e/a$ ratio. A higher $c/a$ ratio may cause larger lattice mismatch between austenite and martensite during the martensitic transformation, which would be responsible for a higher $M_s$.

In addition, the austenitic phase investigated from the diffusion couples typically showed pre-martensitic feature. Characteristic tweed microstructure consisted of striated contrasts were observed by TEM, which was caused by the local lattice distortion before martensitic transformation. Diffused scattering in the electron diffraction pattern along the $\langle 101 \rangle$ direction was frequently observed for the cubic austenitic phase. This indicates that the lattice shear is along the $\langle 101 \rangle$ direction. Despite the possible lattice distortion, the crystal structure remained to be cubic. By examining the interface between austenite and martensite, it would be expected that the diffused scattering would eventually evolve to sharp diffraction spots after the completion of the martensitic transformation.

The reduced elastic modulus and hardness for NiMnGa alloys as a function of compositions were extracted from the diffusion couples. The analyses were performed through the load-displacement curves of nanoindentation using the Oliver-Pharr method. The data reported in this study was in close agreement with those experimental and calculated data from
literature. Asymmetric V-shaped curves were observed for the measured $E_r$ and $H$ across the interdiffusion zone, despite that the diffusion paths were different. A minimum value was always identified near the phase boundary between austenite and martensite. Opposite trends of $E_r$ and $H$ as a function of compositions were observed for austenite and martensite. With Mn or Ni substituting Ga, and Ni substituting Mn, the $E_r$ and $H$ decrease for the austenite but increase for the martensite.

Lattice softening associated with the pre-martensitic transformation also contributed to the V-shaped curve for $E_r$ and $H$. According to the Voigt-Reuss-Hill average model, Young’s modulus is dependent on elastic constants. For Ni-Mn-Ga alloys, it was found that the softening of the elastic constants $C'$ and $C_{44}$ would decrease the Young’s modulus. Previous research has shown that the elastic constants soften continuously towards the martensitic transformation due to lattice softening. In this study, the phase boundary vicinity represented regions where martensitic transformation just occurred or nearly occurred. It would be expected that the $C'$ and $C_{44}$ was lower near this region, which would result in a lower Young’s modulus near the phase boundary area.

Additional strains may be caused by twin realignment in the martensite and stress induced martensitic transformation in the austenite. This may result in a lower measured $E_r$ and $H$ by nanoindentation. Qualitatively analyses showed that these effects were more pronounced near the phase boundary region, which was consistent with the observed V-shaped curve. However, the contribution from twin realignment or stress induced martensitic transformation may be negligible, since the measured values agreed well with experimental and calculated data.
in literature. It was also found that the scatter of the $E_r$ and $H$ for the martensite was much larger than that for the austenite. This is because that the martensite consists of many variants with different orientations. On the other hand, the grain orientation has little influence on the scatter, as confirmed by the experiments.
APPENDIX A: LIST OF PUBLICATIONS AND PRESENTATIONS
A.1 Publications


5. **Le Zhou**, Anit Giri, Kyu Cho, Yongho Sohn, “Martensitic transformation and mechanical properties of Ni$_{49+x}$Mn$_{36-x}$In$_{15}$ (x=0, 0.5, 1.0, 1.5 and 2) alloys”, *Materials Science and Engineering A*, vol. 646, pp. 57-65, 2015.


11. **Le Zhou**, Anit Giri, Kyu Cho, Helge Heinrich, Yongho Sohn, “Microstructural and crystallographic characterization of Ni$_{2-x}$Mn$_{1-x}$Ga Alloys (x = 0.14, 0.16, 0.19, 0.22, and 0.24) by transmission electron microscopy”, *Metallurgical and Materials Transactions E*, vol. 1 (3), pp. 239-246, 2014.


A.2 Conference Presentations


6. Le Zhou (Presenter), Anit Giri, Kyu Cho, Yongho Sohn, “Microstructural and crystallographic characterization of Ni_{49+x}Mn_{36-x}In_{15} alloys (x=0, 0.5, 1, 1.5 and 2.0)”, 144th TMS Annual Meeting & Exposition, Orlando, FL, March 15-19, 2015.


CA, August 6-9, 2014.


APPENDIX B: MICROSTRUCTURE, CRYSTALLOGRAPHY AND MECHANICAL PROPERTIES OF $\text{Ni}_{2+X}\text{Mn}_{1-X}\text{Ga}$ ALLOYS ($X = 0.14, 0.16, 0.19, 0.22, \text{ AND } 0.24$) AND $\text{Ni}_{49+X}\text{Mn}_{36-X}\text{In}_{15}$ ($X = 0, 0.5, 1.0, 1.5 \text{ AND } 2.0$) ALLOYS
B.1 Experimental Details

In addition to the investigation of NiMnGa alloys using diffusion couples, bulk NiMnGa and NiMnIn alloys have also been examined to study the microstructure, crystallography and mechanical properties. This section summarized the important results. Detailed results can be found in the published papers [36, 65, 148].

Polycrystalline Ni$_{2+x}$Mn$_{1-x}$Ga alloys with nominal compositions of x=0.14, 0.16, 0.19, 0.22 and 0.24 were triple arc melted in argon atmosphere, followed by homogenization at 1000°C for 72h under high vacuum (10$^{-6}$ Torr). Differential scanning calorimetry (TA Instruments™ Q2000 DSC) with a heating/cooling rate of 10 K/min was carried out for all alloys to identify the martensitic transformation temperature. The Curie temperature ($T_c$) was also determined from the magnetization versus temperature plot, and confirmed based on the inflection point of the DSC curves. The Curie temperatures of two alloys (Ni$_{2+x}$Mn$_{1-x}$Ga, where x = 0.14 and 0.16) were verified to coincide with the data obtained from the magnetization versus temperature plots.

For each alloy, specimens with approximate size of 5 mm × 5 mm × 3 mm were sectioned, and ground to 1200-grit SiC-paper to smoothen the surface. The specimens were then subjected to conventional X-ray diffraction (XRD, Rigaku D-Max B Diffractometer) with Cu K$_α$ radiation to determine the crystal structures and lattice parameters. The specimens were then mounted in epoxy and metallographically polished down to 0.25 μm, followed by chemical etching with Marble’s Reagent to reveal the martensitic microstructure. Initial microstructural observation was carried out by using optical microscopy (Olympus™ LEXT OLS-3000). The actual compositions of the five alloys were examined by X-ray energy dispersive spectroscopy
(XEDS) equipped on a Zeiss™ Ultra 55 field emission scanning electron microscope (FE-SEM). For the XEDS analysis, 20 random measurements were performed on each sample so as to obtain the average value with standard deviation.

In addition, polycrystalline Ni$_{49+x}$Mn$_{36-x}$In$_{15}$ with nominal compositions of $x=0$, 0.5, 1.0, 1.5 and 2, were triple arc melted in an argon atmosphere, followed by homogenization at 850°C for 72h under a vacuum ($10^{-6}$ Torr). For convenience, the five alloys are designated as InA – InE with increasing $x$ value, as listed in Table 15.

A small portion of the alloys were sectioned and ground into powders. The powders were sealed in quartz tubes and pumped into high vacuum, followed by annealing at 550°C for 6h to remove any residual stress induced by mechanical grinding. The powders were then subjected to XRD, with Cu K$_{α}$ radiation to determine the crystal structures. Differential scanning calorimetry (DSC Perkin-Elmer Pyris 1 DSC) with a heating/cooling rate of 10 K/min was carried out for all alloys to identify the martensitic transformation temperature. Samples with weight about 20 mg were cut from the center of the alloy for the DSC measurement. The Curie temperature was also identified based on the inflection point from the DSC curves. Specimens with an approximate size of 5 mm × 5 mm × 3 mm were also sectioned and mounted in epoxy, followed by metallographic preparation using diamond paste down to 0.25 μm finish. Microstructural observation was carried out by using a Zeiss™ Ultra 55 FE-SEM. The actual compositions of the five alloys were quantified by XEDS equipped on the FE-SEM. For the XEDS analysis, 20 random measurements were performed on each sample to determine the average values and standard deviations, as reported in Table 16.
Transmission electron microscopy (FEI™ Tecnai F30 TEM) and scanning TEM equipped with high angle annular dark field (HAADF) detector, operating with accelerating voltage of 300 kV was employed to examine the details of microstructure and crystallography at room temperature. All the TEM foils were prepared via focused ion beam (FIB-FEI™ 200 TEM) in-situ lift-out (INLO) technique, which is capable of selecting site-specific areas. For each alloy, up to four TEM foils were prepared by INLO-FIB for statistically-confident TEM observations.

Nanoindentation measurements were carried out using a Hysitron TI Premier instrumented quasi-static nano-mechanical tester with a 100 nm diamond Berkovich tip. Each indentation profile consisted of a 5 second loading cycle to a peak load of 5 mN, followed by a 2 second hold segment, and then 10 second unloading cycle. For each alloy, a total of 45 indents were performed over the polished alloy surface, consisting of a square array of 3 × 3 indents over five random areas. The separation between each indent was 20 μm both horizontally and vertically, in order to avoid any influence from adjacent indents. Reduced elastic modulus (E_r) and hardness (H) values were determined from the load-displacement curves according to the Oliver-Pharr method.

Table 15 Composition of the five Ni-Mn-Ga alloys measured by XEDS in atomic percent with standard deviation in the parenthesis and the corresponding e/a ratio.

<table>
<thead>
<tr>
<th>Nominal Composition</th>
<th>Designation</th>
<th>Ni</th>
<th>Mn</th>
<th>Ga</th>
<th>e/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{2.14}$Mn$</em>{0.86}$Ga</td>
<td>GaA</td>
<td>52.9 (0.46)</td>
<td>21.5 (0.31)</td>
<td>25.6 (0.48)</td>
<td>7.564</td>
</tr>
<tr>
<td>Ni$<em>{2.16}$Mn$</em>{0.84}$Ga</td>
<td>GaB</td>
<td>53.0 (0.42)</td>
<td>21.1 (0.19)</td>
<td>25.9 (0.47)</td>
<td>7.555</td>
</tr>
<tr>
<td>Ni$<em>{2.19}$Mn$</em>{0.81}$Ga</td>
<td>GaC</td>
<td>53.6 (0.50)</td>
<td>20.4 (0.21)</td>
<td>26.0 (0.45)</td>
<td>7.568</td>
</tr>
<tr>
<td>Ni$<em>{2.22}$Mn$</em>{0.78}$Ga</td>
<td>GaD</td>
<td>54.2 (0.39)</td>
<td>19.9 (0.26)</td>
<td>25.9 (0.44)</td>
<td>7.592</td>
</tr>
<tr>
<td>Ni$<em>{2.24}$Mn$</em>{0.76}$Ga</td>
<td>GaE</td>
<td>54.7 (0.22)</td>
<td>19.5 (0.19)</td>
<td>25.8 (0.27)</td>
<td>7.605</td>
</tr>
</tbody>
</table>
Table 16 Composition of the five Ni-Mn-In alloys measured by XEDS in atomic percent with standard deviation in the parenthesis and the corresponding e/a ratio.

<table>
<thead>
<tr>
<th>Nominal Composition</th>
<th>Designation</th>
<th>Ni</th>
<th>Mn</th>
<th>In</th>
<th>e/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni49Mn36In15</td>
<td>InA</td>
<td>48.1</td>
<td>36.5</td>
<td>15.4</td>
<td>7.826</td>
</tr>
<tr>
<td>Ni49.5Mn35.5In15</td>
<td>InB</td>
<td>48.6</td>
<td>35.9</td>
<td>15.5</td>
<td>7.839</td>
</tr>
<tr>
<td>Ni50Mn35In15</td>
<td>InC</td>
<td>49.5</td>
<td>35.0</td>
<td>15.5</td>
<td>7.865</td>
</tr>
<tr>
<td>Ni50.5Mn34.5In15</td>
<td>InD</td>
<td>50.4</td>
<td>34.4</td>
<td>15.2</td>
<td>7.902</td>
</tr>
<tr>
<td>Ni51Mn34In15</td>
<td>InE</td>
<td>49.8</td>
<td>34.8</td>
<td>15.5</td>
<td>7.874</td>
</tr>
</tbody>
</table>
B.2 Microstructure and Crystallography of Ni$_{2+x}$Mn$_{1-x}$Ga Alloys ($x = 0.14, 0.16, 0.19, 0.22,$ and $0.24$)

Martensite start ($M_s$) and finish ($M_f$), and austenite start ($A_s$) and finish ($A_f$) temperatures were determined from DSC measurement as listed in Table 17. Table 17 also lists the Curie temperature measured from magnetization curves [149]. Martensitic transformation temperature ($T_m$) defined as $T_m = 1/2 (M_s + M_f)$ and austenitic transformation temperature ($T_a$) defined as $T_a = 1/2 (A_s + A_f)$ are also reported in Table 17. All specimens are observed to have a temperature hysteresis ($\Delta T = T_a - T_m$) between the forward and reverse martensitic transformations. These transformation temperature increased as the Ni-content increased in the Ni$_{2+x}$Mn$_{1-x}$Ga ($x=0.14, 0.16, 0.19, 0.22$ and $0.24$) alloys, with the Ni$_{2.14}$Mn$_{0.86}$Ga ($x=0.14$) alloy having the $T_m$ closest to the room temperature. Moreover, $\Delta T$ for the Ni$_{2.14}$Mn$_{0.86}$Ga ($x=0.14$) alloy is only 5K, while that for other alloys is approximately 10K. The $T_c$ also slightly increased as the Ni-content (or $x$) increased. The Ni$_{2.16}$Mn$_{0.84}$Ga ($x=0.16$) alloy had the structural transformation and magnetic transition temperatures to be nearly identical [149].

Table 17 Martensitic start ($M_s$), martensitic finish ($M_f$), austenite start ($A_s$), austenite finish ($A_f$) and Curie temperature ($T_c$) determined by differential scanning calorimetry for the five Ni-Mn-Ga alloys. The reduced elastic modulus ($E_r$) and hardness ($H$) with standard deviation in the parenthesis were measured by nanoindentation for the alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$M_s$/$^\circ$C</th>
<th>$M_f$/$^\circ$C</th>
<th>$T_m$/$^\circ$C</th>
<th>$A_s$/$^\circ$C</th>
<th>$A_f$/$^\circ$C</th>
<th>$T_a$/$^\circ$C</th>
<th>$T_c$/$^\circ$C</th>
<th>$E_r$/GPa</th>
<th>$H$/GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaA</td>
<td>40</td>
<td>35</td>
<td>37.5</td>
<td>40</td>
<td>45</td>
<td>42.5</td>
<td>62</td>
<td>105.9 (8.6)</td>
<td>5.63 (0.42)</td>
</tr>
<tr>
<td>GaB</td>
<td>63</td>
<td>51</td>
<td>57</td>
<td>62</td>
<td>74</td>
<td>68</td>
<td>66</td>
<td>113.9 (7.0)</td>
<td>6.14 (0.39)</td>
</tr>
<tr>
<td>GaC</td>
<td>77</td>
<td>66</td>
<td>71.5</td>
<td>76</td>
<td>87</td>
<td>81.5</td>
<td>85</td>
<td>118.5 (9.1)</td>
<td>6.05 (0.41)</td>
</tr>
<tr>
<td>GaD</td>
<td>155</td>
<td>127</td>
<td>141</td>
<td>138</td>
<td>162</td>
<td>150</td>
<td>102</td>
<td>122.1 (6.5)</td>
<td>5.46 (0.33)</td>
</tr>
<tr>
<td>GaE</td>
<td>158</td>
<td>146</td>
<td>152</td>
<td>158</td>
<td>172</td>
<td>165</td>
<td>99</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

Figure 59 presents the XRD patterns of all alloys at room temperature. The Ni$_{2+x}$Mn$_{1-x}$Ga alloys with $x = 0.16, 0.19, 0.22$ and $0.24$ show similar XRD patterns, which can be indexed
according to the NM tetragonal structure. The indexing of these patterns is based on the same crystallographic axes as of the parent austenitic phase, so that the tetragonality ratio c/a is larger than 1. The lattice parameters of a and c, as well as c/a ratio, calculated for these alloys are listed in Table 18, and plotted in Figure 60 to clarify the changes in lattice parameters with the c/a ratio. As the c/a ratio increases (i.e., substitution of Ni for Mn), lattice parameters a slightly decreases and c increases. Therefore, the tetragonality ratio, c/a also increases as the c/a ratio increases, which is consistent with the results from the diffusion couples.

![X-ray diffraction patterns](image.png)

Figure 59 X-ray diffraction patterns from the Ni$_{2+x}$Mn$_{1-x}$Ga (x=0.14, 0.16, 0.19, 0.22 and 0.24) alloys at room temperature.

The XRD pattern for the Ni$_{2.14}$Mn$_{0.86}$Ga alloy with x = 0.14 is clearly different from other alloys as shown in Figure 59. The diffraction pattern is indexed according to a monoclinic unit...
cell, which indicates that the martensite in this alloy has a modulated 7M crystal structure. Table 18 listed the lattice parameter for Ni$_{2.14}$Mn$_{0.86}$Ga (x=0.14) alloy based on the 7M crystal structure.

Table 18 Crystal structures and lattice parameters (Å) for the Ni$_{2+x}$Mn$_{1-x}$Ga (x=0.14, 0.16, 0.19, 0.22 and 0.24) alloys determined by X-ray diffraction.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Crystal Structure</th>
<th>Space Group</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>β (°)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaA</td>
<td>7M Monoclinic</td>
<td>P2/m</td>
<td>4.217</td>
<td>5.421</td>
<td>29.521</td>
<td>92.98</td>
<td></td>
</tr>
<tr>
<td>GaB</td>
<td>NM Tetragonal</td>
<td>Fmmm</td>
<td>5.477</td>
<td>6.492</td>
<td>1.185</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GaC</td>
<td>NM Tetragonal</td>
<td>Fmmm</td>
<td>5.462</td>
<td>6.512</td>
<td>1.192</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GaD</td>
<td>NM Tetragonal</td>
<td>Fmmm</td>
<td>5.434</td>
<td>6.573</td>
<td>1.209</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GaE</td>
<td>NM Tetragonal</td>
<td>Fmmm</td>
<td>5.442</td>
<td>6.593</td>
<td>1.212</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 60 Lattice parameters, a and c, and tetragonality ratio c/a determined at room temperature for the Ni$_{2+x}$Mn$_{1-x}$Ga (x=0.14, 0.16, 0.19, 0.22 and 0.24) alloys as a function of e/a ratio.
Figure 61(a) and (b) present typical low and high magnification BF TEM micrographs of martensitic variants from the Ni$_{2.14}$Mn$_{0.86}$Ga (x=0.14) alloy. Selected area diffraction patterns (SADP) from a single martensitic variant and from the interface between two adjacent variants are presented in Figure 61(c) and (d), respectively. The thickness of the primary martensitic variants in this alloy varied from 100nm to 300nm, which is very thin and consistent with approximate observation from optical microscopy. Figure 61(b) also shows layered contrast with intervals of only a few nanometers, and indicates that the structure is modulated. Also shown in Figure 61(b) is a dark contrast at the interface between adjacent two primary variants, indicating that the boundary may be distorted. The SADP from the martensitic variant in Figure 61(c) shows six superlattice diffraction spots between the fundamental diffraction spots. Thus, the presence of modulated 7M martensite is confirmed for the Ni$_{2.14}$Mn$_{0.86}$Ga (x=0.14) alloy. From the SADPs, the lattice parameter is determined to be $a = 4.24\text{Å}$, $b=5.44\text{Å}$, $c=29.44\text{Å}$ and $\beta=93.2^\circ$ for this monoclinic structure; this is quite close to that determined by XRD. The SADP with [210] zone axis from the boundary region indicates that two adjacent variants are twinned, where the twinning plane is $(\overline{1}2\overline{7})$. 
Figure 61 (a) Bright-field TEM micrograph from the Ni$_{2.14}$Mn$_{0.86}$Ga alloy showing the martensitic variants. (b) Bright-field TEM micrograph from the twin variants and boundary. Selected area diffraction patterns of the Ni$_{2.14}$Mn$_{0.86}$Ga alloy from (c) individual martensitic variant and (d) twin boundary region.

High resolution TEM (HRTEM) micrographs from a single martensitic variant and from the twin boundary region were examined via fast Fourier transform (FFT) as presented in Figure 62. The thin-layered microstructure, consisting of only several atomic layers, is the modulated 7M structure. In NiMnGa alloys, a perfect 7M martensite typically has a (52)$_2$ stacking sequence, which forms secondary nano twins within the primary twin variants. However, the diffused spots in FFT indicate that the layered structure is locally imperfect, or some stacking
faults might have been generated during the martensitic transformation. Figure 62(b) also shows the HRTEM micrograph from the boundary between two primary martensitic variants. This twin boundary appears to be not perfectly flat, with some distortion within a thickness range of a few atomic layers. This implies that the primary twin boundary is not coherent. Fast Fourier transformation from the boundary region shows that the two variants have basically the same 7M crystal structure, as also seen from the SADP in Figure 61(d).

Figure 62 High resolution TEM micrographs and corresponding fast Fourier transform patterns from the Ni$_{2.14}$Mn$_{0.86}$Ga alloy: (a) individual martensitic variant and (b) twin boundary region.

TEM investigation from Ni$_{2+x}$Mn$_{1-x}$Ga alloys with $x = 0.16$, 0.19, 0.22 and 0.24 showed similar microstructure and crystal structure, but very different from the Ni$_{2.14}$Mn$_{0.86}$Ga ($x = 0.14$) alloy. Figure 63(a) presents a typical BF TEM micrograph taken from the Ni$_{2.16}$Mn$_{0.84}$Ga ($x = 0.16$) alloy. The width of the primary martensitic variants for these samples is typically in the range of micrometers, and thicker than that for the Ni$_{2.14}$Mn$_{0.86}$Ga ($x = 0.14$) alloy. In Figure 63(b), the SADP with the orientation of $[111]$ indicates that the adjacent martensitic variants are
twinned, with the twinning plane of \( \{20\bar{2}\} \). However, the dark contrast seen in Figure 63(a) at the interface between adjacent primary variants indicates that the twin boundary is also distorted.

Figure 63 (a) Bright field TEM micrograph of martensitic variants from Ni\(_{2.16}\)Mn\(_{0.84}\)Ga alloy and (b) the corresponding selected area diffraction pattern from \([111]\) orientation.

Figure 63(a) also reveals that, within each primary martensitic variant, thinner secondary twin variants with straight boundaries exist. Figure 64 demonstrates by HR-TEM, taken from the orientation of \([111]\), that the thickness of these secondary twins varies from 10 nm to 20 nm, and lead to some diffuse scattering in the corresponding FFT. The FFT also shows a similar pattern to the SADP taken from the twin boundary area at the orientation of \([111]\). Therefore, these secondary nano-twins in NM martensites have the same orientation relationship as in the primary twins, where the twinning plane is the same, \( \{20\bar{2}\} \), as highlighted in Figure 64.
Both NM and 7M martensites formed hierarchical twins – secondary twins within the primary twins. Secondary twins form at the habit plane so as to minimize the lattice elastic strain energy during the austenite-to-martensite transformation. For both NM and 7M martensites, the coherency of the primary twin boundary was lost, corresponding to higher boundary energy for the primary twin variants. The primary twin variants with different alignment with respect to the secondary twins were also observed in this study, despite their higher boundary energy. Formation of the primary twin variants can help reduce the strains perpendicular to the habit plane during phase transformation [122]. There are microstructural differences between 7M and NM martensites. In 7M martensites, the secondary twins have a width of a few atomic layers,
and the primary twins have a width of a few hundred nanometers, as seen in Figure 61 and Figure 62, respectively. For the NM martensites, the width for the secondary twins is about 10-20 nanometers and that for the primary twins is in the micrometer scales, as shown in Figure 63 and Figure 64, respectively. Clearly, the thickness of the twins in 7M martensites is thinner than that in the NM martensites, and correspond a higher number of twin boundaries. This study is consistent with that observed from the diffusion couples.
B.3 Microstructure and Crystallography of Ni$_{49+x}$Mn$_{36-x}$In$_{15}$ ($x=0, 0.5, 1.0, 1.5$ and $2.0$)

XRD patterns collected at room temperature from the five NiMnIn alloy powders are presented in Figure 65. Two distinct patterns are observed. For the InA alloy, the XRD pattern was indexed according to the L2$_1$ crystal structure, corresponding to the austenite phase for Heusler alloys. For alloys, InB, InC, InD, and InE, the XRD patterns are similar, especially in the two-theta range from 40 to 50°, where the main peaks of the martensitic phase are located. These patterns are indexed according to the monoclinic 7M crystal structure of martensite. The crystal structure for each phase was also validated by TEM, as will be shown later.

![X-ray diffraction patterns](image)

Figure 65 X-ray diffraction patterns from the Ni$_{49+x}$Mn$_{36-x}$In$_{15}$ ($x=0, 0.5, 1.0, 1.5$ and $2.0$) alloys at room temperature.

The martensitic start ($M_s$), martensitic finish ($M_f$), austenitic start ($A_s$) and austenitic finish ($A_f$) temperatures were determined from the DSC curves and are reported in Table 19. The
Curie temperature ($T_c$) was also extracted based on the inflection point in the DSC curve. It should be noted that for InA, the martensitic transformation temperature, $T_m$, was too low to be properly measured by the instrument and could not be determined. According to DSC data, it is confirmed that InA alloy is austenitic at room temperature and InC, D and E alloys are martensitic. However, both austenite and martensite might co-exist at room temperature for InB alloy because its $M_f$ is slightly lower than room temperature. The $T_c$ for InC and InE may contain a large uncertainty due to overlap with $T_m$. Although $T_c$ does not vary much among the different alloys, $T_m$ is very sensitive to e/a ratio. $T_m$ is clearly observed to increase when the e/a ratio increases (or as Ni substitutes Mn), which is similar to that observed in NiMnGa alloys. In this study, the $T_m$ for InA can be estimated to be approximately 12°C assuming $T_m$ is linearly dependent on e/a ratio. Therefore, the InA alloy remained as austenite after cooling to room temperature.

Table 19 Martensitic start ($M_s$), martensitic finish ($M_f$), austenitic start ($A_s$), austenitic finish ($A_f$) and Curie temperature ($T_c$) determined by differential scanning calorimetry for the five Ni-Mn-In alloys. The reduced elastic modulus ($E_r$) and hardness (H) with standard deviation in the parenthesis were measured by nanoindentation for the alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$M_s / ^\circ C$</th>
<th>$M_f / ^\circ C$</th>
<th>$T_m / ^\circ C$</th>
<th>$A_s / ^\circ C$</th>
<th>$A_f / ^\circ C$</th>
<th>$T_c / ^\circ C$</th>
<th>$E_r / \text{GPa}$</th>
<th>$H / \text{GPa}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>InA</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>44</td>
<td>80.2 (3.6)</td>
<td>4.61 (0.12)</td>
</tr>
<tr>
<td>InB</td>
<td>26.7</td>
<td>18.1</td>
<td>22.4</td>
<td>26.4</td>
<td>36.6</td>
<td>31.5</td>
<td>96.7 (8.7)</td>
<td>5.67 (0.61)</td>
</tr>
<tr>
<td>InC</td>
<td>45.5</td>
<td>35.6</td>
<td>40.6</td>
<td>46.3</td>
<td>57.2</td>
<td>51.8</td>
<td>101.9 (8.2)</td>
<td>5.40 (0.64)</td>
</tr>
<tr>
<td>InD</td>
<td>73.2</td>
<td>62.5</td>
<td>67.9</td>
<td>71.9</td>
<td>83.5</td>
<td>77.7</td>
<td>109.9 (8.0)</td>
<td>5.84 (0.50)</td>
</tr>
<tr>
<td>InE</td>
<td>48.0</td>
<td>39.3</td>
<td>43.7</td>
<td>46.7</td>
<td>56.0</td>
<td>51.4</td>
<td>107.1 (11.6)</td>
<td>5.20 (0.78)</td>
</tr>
</tbody>
</table>

Detailed microstructure and crystallography for the five NiMnIn alloys were examined by TEM. Figure 66(a) and (b) present a BF TEM micrograph for the InA alloy and the corresponding selected area electron diffraction pattern (SADP) from the [010] orientation.
These results confirm that the InA alloy has a L2₁ crystal structure at room temperature. A representative HRTEM micrograph and the inversed fast Fourier transform filtered image from the InA alloy are shown in Figure 66(c) and (d). A tweed microstructure was observed as shown in the HRTEM image, which indicated the occurrence of pre-martensitic transformation and is similar to that in NiMnGa alloys. This would be responsible for the smearing in the SADP shown in Figure 66(b), as revealed by the diffused scattering along the \( \langle 202 \rangle \) direction.

Figure 66 (a) Bright field TEM micrograph and (b) corresponding selected area diffraction pattern from the Ni₄₉Mn₃₆In₁₅ alloy. (c) High resolution TEM micrograph and (d) corresponding inversed fast Fourier transform filtered micrograph for the Ni₄₉Mn₃₆In₁₅ alloy.
Extensive TEM investigations have also been carried out for InB, InC, InD and InE alloys. They exhibited similar microstructures and 7M monoclinic crystal structure according to TEM. Figure 67(a) presents a typical BF TEM micrograph of the martensitic microstructure from InC alloy. The martensitic variants are plate- or spear-shaped, with thicknesses varying from 100 nm to 1 μm. SADP with [010] orientation from one of the martensitic variants is presented in Figure 67(b). Six superlattice diffraction spots are identified between the primary fundamental diffraction spots, corresponding to the 7M monoclinic structure. Generally a perfect 7M martensitic crystal follows a \((\frac{52}{2})_2\) stacking sequence. However, some diffused lines are observed in the SADP along the [0014] direction, and suggest that there are distortion and/or stacking faults in the martensitic structure.

Figure 67 (a) Bright field TEM micrograph and (b) corresponding selected area diffraction pattern from the Ni_{50}Mn_{35}In_{15} alloy.
A representative BF TEM micrograph from the InD alloy is presented in Figure 68(a). The martensitic plates have thickness range of 50 to 200 nm. To investigate the orientation relationship between adjacent martensitic variants, a series of SADPs were taken from the twin boundary area as marked by white circles in Figure 68(a) and are presented in Figure 68(b) through (d). A few different orientation relationships between martensitic variants A, B, C and D are obtained based on these SADPs: \( \{ \overline{1}27 \} A \parallel \{ \overline{1}27 \} B \), \( [0\overline{7}2] A \parallel [0\overline{7}2] B \), \( \{ \overline{1}27 \} B \parallel \{ \overline{1}27 \} C \), \( [0\overline{7}2] B \parallel [\overline{5}1\overline{0}] C \), and \( \{ \overline{1}27 \} C \parallel \{ \overline{1}27 \} D \), \( [\overline{5}1\overline{0}] C \parallel [0\overline{7}2] D \).

Figure 68 (a) Bright field TEM micrograph from the Ni\(_{50.5}\)Mn\(_{34.5}\)In\(_{15}\) alloy. Selected area diffraction patterns were collected from area (b) 1, (c) 2 and (d) 3.
The details of the 7M martensite have also been investigated through high magnification BF and high resolution TEM (HRTEM), as shown in Figure 69. Figure 69(a) and (c) are acquired from the twin boundary region between the two 7M martensite variants with different orientations. Figure 69(b) presents the BF micrograph from the $[2\bar{1}0]$ orientation, where the modulation period can be observed: the modulation period is hidden when the orientation is $[0\bar{7}2]$, as shown in the HR TEM in Figure 69(e). The thickness ratio between the dark and light fringes is approximately 5:2, and generally follows the $(5\bar{2})$ stacking sequence. However, a different stacking sequence was also observed, as marked in Figure 69(b), which turned out to be $(25552)$. Different stacking orders may be responsible for the diffused streaks in the diffraction patterns observed.
Figure 69 Bright field TEM micrograph from (a) twin boundary and (b) one martensitic variant in the Ni$_{50.5}$Mn$_{34.5}$In$_{15}$ alloy. High resolution TEM micrograph from (c) twin boundary and (d,e) individual martensitic variant.
B.4 Reduced Elastic Modulus and Hardness

The average reduced elastic modulus \( (E_r) \) and hardness \( (H) \) along with standard deviations, measured via nanoindentation for the NiMnGa and NiMnIn alloys, are reported in Table 17 and Table 19. The plots of \( E_r \) and \( H \) as a function of e/a ratio for NiMnGa and NiMnIn alloys are presented in Figure 70. Figure 70(a) shows the \( E_r \) for \( \text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga} \) alloys varied from 105 to 123 GPa, and increased with increasing e/a ratio. It should be noted that the four \( \text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga} \) alloys are all martensitic at room temperature: \( \text{Ni}_{2.14}\text{Mn}_{0.86}\text{Ga} \) had a 7M martensitic structure while the other three alloys were NM martensite. On the other hand, the variation of \( H \) as a function of e/a ratio is relatively small without clear trend. These values measured from bulk alloys agree well with those measured from diffusion couples, as reported in section 6.1.

In addition, Figure 70(b) shows that the \( E_r \) for the austenitic \( \text{InA} \) alloy is only about 80 GPa, which is much lower than those for the martensitic \( \text{InB}, \text{InC}, \text{InD} \) and \( \text{InE} \) alloys. Similarly, the \( H \) for the \( \text{InA} \) alloy is about 4.6 GPa, much lower than the martensitic alloys. However, unlike the reduced elastic modulus for the martensite, the hardness values for the martensitic alloys vary from 5.2 to 5.8 GPa, without much correlation to the alloy composition. Large standard deviations were observed for \( \text{InB} \) through \( \text{InE} \) alloys consisting of martensitic phase. The observations for the NiMnIn alloys are similar to the NiMnGa alloys.

As discussed in previous chapter, composition may not be the only factor that affects the \( E_r \) and \( H \). The pre-martensitic transformation, accompanied with phonon and elastic softening, may have contributed to the low values measured for austenitic \( \text{InA} \) alloy. Indeed, the TEM investigation, as shown in Figure 66, confirmed the characteristic feature of pre-martensitic...
transformation. Since the $T_m$ for InA alloy is estimated at 12 °C which is just slightly lower than room temperature, it is reasonable that the pre-martensitic transformation occurs.

Figure 70 Reduced elastic modulus and hardness for the (a) $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ Alloys ($x = 0.14, 0.16, 0.19$ and $0.22$) and (b) $\text{Ni}_{49+x}\text{Mn}_{36-x}\text{In}_{15}$ ($x=0, 0.5, 1.0, 1.5$ and $2$) alloys measured by nanoindentation.

Moreover, the standard deviations of $E_r$ and $H$ for the martensitic phase are much larger than that for the austenitic phase for $\text{Ni}_{49+x}\text{Mn}_{36-x}\text{In}_{15}$ alloys as presented in Figure 70(b). Despite the absence of austenitic phase in the $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ alloys, the scatter of the $E_r$ and $H$ values for
the martensite is large. This observation again is consistent with that reported from diffusion couples. Extensive TEM analyses have revealed that there are many variants with different orientations in the martensites. As discussed before, in shape memory alloys, there are three orientation variants if the austenitic phase transforms to tetragonal martensite or six orientation variants if the austenitic phase transforms to orthorhombic martensite. In addition, the Heusler alloys are strongly anisotropic materials. Therefore, the larger scatter of the reduced elastic modulus for the martensites can be attributed to the orientation differences among different martensitic variants.
B.5 Summary

A series of Ni\textsubscript{2+x}Mn\textsubscript{1-x}Ga (x=0.14, 0.16, 0.19, 0.22 and 0.24) polycrystalline alloys were prepared and characterized for microstructural and crystallographic analyses. Martensitic transformation temperatures were found to increase with an increase of e/a ratio, and Ni\textsubscript{2.16}Mn\textsubscript{0.84}Ga alloy had the closest transition temperature to the room temperature. While modulated 7M martensites were observed in Ni\textsubscript{2.14}Mn\textsubscript{0.86}Ga alloy, only the NM martensites were found in all other alloys at room temperature. The lattice parameters for the NM martensites were determined by XRD and the c/a ratio was found to increase with an increase in e/a. Both NM and 7M martensites consisted of twin variants with different orientations. The thickness of the variants in 7M martensites was smaller than that for NM martensites. For NM martensites, the primary twin variant thickness was in the micrometer scale, and each variant consisted of very fine secondary twin variants with a thickness of few tens of nanometer. For 7M martensites, the primary twin variant thickness was in the nanometer scale, and the variant consisted of very fine structure that has only a few atomic layers corresponding to the structural modulation.

Five polycrystalline Ni\textsubscript{49+x}Mn\textsubscript{36-x}In\textsubscript{15} (x=0, 0.5, 1.0, 1.5 and 2) alloys were prepared and characterized by DSC, XRD, TEM and nanoindentation to examine the martensitic transformation and mechanical properties. The martensitic transformation temperature increased as the e/a ratio increased. However, the Curie temperature was found to be independent on the composition. The austenitic phase was observed for the Ni\textsubscript{49}Mn\textsubscript{36}In\textsubscript{15} alloy at room temperature, while 7M martensites were observed for other alloys. These martensites formed twin microstructure with different orientation for the martensitic variants. For the martensitic phase, the reduced elastic modulus increased from 96 to 110 GPa with an increase in the e/a ratio from
7.84 to 7.90. However, hardness was almost independent on the composition. The reduced elastic modulus and hardness for the austenitic Ni\textsubscript{49}Mn\textsubscript{36}In\textsubscript{15} alloy was much lower than the martensitic alloys. The large scatter in the reduced elastic modulus and hardness values observed for the martensitic alloys may be attributed to the orientation difference among martensitic variants. Nanoindentation measurements on Ni\textsubscript{2+\textit{x}}Mn\textsubscript{1-\textit{x}}Ga (\textit{x}=0.14, 0.16, 0.19 and 0.22) alloys showed similar results: the reduced elastic modulus for martensitic phase increased from 105 to 123 GPa as the e/a ratio increased from 7.56 to 7.63.
LIST OF REFERENCES


32 N. Lanska, O. Soderberg, A. Sozinov, Y. Ge, K. Ullakko, and V. Lindroos, Composition and temperature dependence of the crystal structure of Ni-Mn-Ga alloys, *Journal of Applied Physics*, 95, 8074-8078, 2004


36 L. Zhou, A. Giri, K. Cho, H. Heinrich, B. S. Majumdar, and Y. Sohn, Microstructural and Crystallographic Characterization of Ni$_{2+x}$Mn$_{1-x}$Ga Alloys (x= 0.14, 0.16, 0.19, 0.22, and 0.24) by Transmission Electron Microscopy, *Metallurgical and Materials Transactions E*, 1, 239-246, 2014


55 P. Zhao, L. Dai, J. Cullen, and M. Wuttig, Magnetic and elastic properties of Ni$_{49.0}$Mn$_{23.5}$Ga$_{27.5}$ premartensite, *Metallurgical and Materials Transactions A*, 38, 745-751, 2007


L. Zhou, A. Mehta, A. Giri, K. Cho, and Y. Sohn, Martensitic transformation and mechanical properties of Ni_{49+x}Mn_{36–x}In_{15} (x= 0, 0.5, 1.0, 1.5 and 2.0) alloys, *Materials Science and Engineering: A*, **646**, 57-65, 2015


A. Fujita, S. Fujieda, Y. Hasegawa, and K. Fukamichi, Itinerant-electron metamagnetic transition and large magnetocaloric effects in La (Fe_{x}Si_{1-x})_{13} compounds and their hydrides, *Physical Review B*, **67**, 104416, 2003


F.-x. Hu, B.-g. Shen, J.-r. Sun, and G.-h. Wu, Large magnetic entropy change in a Heusler alloy Ni_{52.8}Mn_{23.1}Ga_{24.5} single crystal, *Physical Review B*, **64**, 132412, 2001


171
86 W. C. Oliver and G. M. Pharr, Measurement of hardness and elastic modulus by instrumented indentation: Advances in understanding and refinements to methodology, *Journal of materials research*, 19, 3-20, 2004
B. Ingale, R. Gopalan, M. Rajasekhar, and S. Ram, Studies on ordering temperature and martensite stabilization in Ni\textsubscript{55}Mn\textsubscript{20−x}Ga\textsubscript{25+x} alloys, *Journal of Alloys and Compounds*, **475**, 276-280, 2009


N. Lanska, O. Soderberg, A. Sozinov, Y. Ge, K. Ullakko, and V. Lindroos, Composition and temperature dependence of the crystal structure of Ni–Mn–Ga alloys, *Journal of Applied Physics*, **95**, 8074-8078, 2004


L. Zhou, A. Giri, K. Cho, H. Heinrich, B. S. Majumdar, and Y. Sohn, Microstructural and Crystallographic Characterization of Ni\textsubscript{2+x}Mn\textsubscript{1−x}Ga Alloys (x= 0.14, 0.16, 0.19, 0.22, and 0.24) by Transmission Electron Microscopy, *Metallurgical and Materials Transactions E*, 1-8, 2014


111 P. Müllner and A. H. King, Deformation of hierarchically twinned martensite, Acta Materialia, 58, 5242-5261, 2010
113 S. Ouyang, Y. Yang, M. Han, Z. Xia, B. Huang, X. Luo, G. Zhao, and W. Zhang, Twin relationships between nanotwins inside A–C type variant pair in Ni–Mn–Ga alloy, Acta Materialia, 84, 484-496, 2015
115 Y. Li, Y. Xin, C. Jiang, and H. Xu, Shape memory effect of grain refined Ni_{54}Mn_{25}Ga_{21} alloy with high transformation temperature, Scripta materialia, 51, 849-852, 2004
116 Y. Ma, C. Jiang, Y. Li, H. Xu, C. Wang, and X. Liu, Study of Ni_{50+x}Mn_{25}Ga_{25-x} (x= 2–11) as high-temperature shape-memory alloys, Acta Materialia, 55, 1533-1541, 2007
118 O. Söderberg, L. Straka, V. Novák, O. Heczko, S.-P. Hannula, and V. Lindroos, Tensile/compressive behaviour of non-layered tetragonal Ni_{52.8}Mn_{25.7}Ga_{21.5}alloy, Materials Science and Engineering: A, 386, 27-33, 2004
120 V. Chernenko, M. Chmielus, and P. Mullner, Large magnetic-field-induced strains in Ni-Mn-Ga nonmodulated martensite, Applied Physics Letters, 95, 104103, 2009
133 W. Ni, Y.-T. Cheng, and D. S. Grummon, Microscopic shape memory and superelastic effects under complex loading conditions, *Surface and Coatings Technology*, 177, 512-517, 2004

175


