ABSTRACT

This research focuses on exploring the influence of Zr additions in Ni-rich Nitinol alloys on the phase stability, transformation temperatures, and thermomechanical behavior using various microanalysis techniques. The dissertation is divided into three major bodies of work: (1) The microstructural and thermo-mechanical characterization of a 50.3Ni-32.2Ti-17.5Zr (at.%) Zr alloy; (2) The characterization and mechanical behavior of 50.3Ni-48.7Ti-1Zr and 50.3Ni-48.7Ti-1Hf alloys to determine how dilute additions alter the phases, transformation temperatures, and thermo-mechanical properties; and (3) The microstructural evolution and transformation behavior comparison of microstructure and transformation temperature for 50.3Ni-(49.7-X)Ti-XZr alloys, where X is 1, 7, or 17.5% Zr aged at either 400°C and 550°C.

The major findings of this work include the following: (1) In the dilute limit of 1% Zr, at 400°C aging, a spherical precipitate, denoted as the S-phase, was observed. This is the first report of this phase. Further aging resulted in the secondary precipitation event of the H-phase. Increasing the aging temperature to 550°C, resulted in no evident precipitation of the S- and H-phase precipitates suggestive this temperature is above the solvus boundary for these compositions. (2) For the 7% and 17.5% Zr alloys, aging at 400°C and 550°C resulted in the precipitation of the H-phase. For the lower temperature anneal, this phase required annealing up to 300 hours of aging to be observed for the 17.5% Zr alloy. Upon increasing the aging temperature, the H-phase precipitation was present in both alloys. The transformation behavior and thermo-mechanical properties are linked to the precipitation behavior.
DEDICATION

I would like to dedicate this dissertation to my family, my fiancé, close friends, and mentors who have played a role in helping me achieve this accomplishment. I greatly appreciate all of the support throughout my entire educational journey. Thank you for everything.
LIST OF ABBREVIATIONS AND SYMBOLS

APT  Atom Probe Tomography
at. % Atomic Percent
BF   Bright Field
DSC  Digital Scanning Calorimetry
FIB  Focused Ion Beam
IVAS Integrated Visualization and Analysis Software
LEAP Local Electrode Atom Probe
NASA National Aeronautics and Space Administration
NiTi Nickel Titanium
NiTiAu Nickel Titanium Gold
NiTiHf Nickel Titanium Hafnium
NiTiPd Nickel Titanium Palladium
NiTiPt Nickel Titanium Platinum
NiTiZr Nickel Titanium Zirconium
SAD  Selected Area Diffraction
SMA  Shape Memory Alloys
TEM Transmission Electron Microscopy
ACKNOWLEDGMENTS

At this time I would like to thank all of those who helped contribute to the success of this research project. First, I would like to thank my advisor Dr. Gregory B. Thompson, the chairman of this dissertation, for helping to guide this research project. I would also like to thank him for always making time to discuss research results, edit papers, or share his knowledge on microscopy and materials science. I am also appreciative of all the members of my committee, Dr. Viola Acoff, Dr. Othmane Benafan, Dr. Amber Genau, and Dr. Mark Weaver for their input and guidance. I would like to thank Dr. Ronald Noebe for providing the multiple samples used in this research and Glen Bigelow and Dr. Othmane Benafan for conducting the shape memory behavior testing reported in this dissertation. Dr. Benafan has also been a mentor through my NASA fellowship and I would like to offer additional thanks to him for all of the great discussions and research input.

I would also like to thank several former and current colleagues. Drs. Monica Kapoor, Florian Vogel, and Chad Hornbuckle for discussions on research and for atom probe training and expertise. Of course, all current and former members of the Thompson Research group for providing an enjoyable environment during my graduate school experience. I would also like to thank Johnny Goodwin, Rob Holler, and Rich Martens from the Central Analytical Facility at the University of Alabama for many hours of training and assistance on the various tools.
## CONTENTS

ABSTRACT ................................................................................................ ii

DEDICATION ........................................................................................... iii

LIST OF ABBREVIATIONS AND SYMBOLS ........................................ iv

ACKNOWLEDGMENTS ........................................................................... v

LIST OF TABLES .................................................................................... vii

LIST OF FIGURES ................................................................................... ix

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

CHAPTER 2 EXPERIMENTAL DETAILS .............................................27

CHAPTER 3 INFLUENCE OF PRECIPITATE COMPOSITION, SIZE, AND SPACING ON THE MARTENSITIC TRANSFORMATION AND FUNCTIONAL BEHAVIOR OF A 50.3Ni-32.2Ti-17.5Zr (at.%) SHAPE MEMORY ALLOY .................34

CHAPTER 4 INFLUENCE OF DILUTE ZIRCONIUM AND HAFNIUM TERNARY ADDITIONS ON PRECIPITATION SHAPE MEMORY PROPERTIES IN 50.3Ni-48.7Ti-1 Zr OR Hf (at.%) ............62

CHAPTER 5 THE INFLUENCE OF ZIRCONIUM ON MICROSTRUCTURE AND TRANSFORMATION TEMPERATURES IN NICKEL-TITANIUM BASED SHAPE MEMORY ALLOYS .........................................................................................100

CHAPTER 6 FUTURE WORK AND CONCLUSIONS .......................140

APPENDIX A .........................................................................................149
LIST OF TABLES

3.1 Approximate $A_f$ and $M_s$ transformation temperatures for various aging times in relation to the hardness value…………………………................43

3.2 Size and inter-precipitate spacing of the H-phase precipitates in 50.3Ni-32.2Ti-17.5Zr alloy aged at 550°C, as measured from TEM results. The error in size and inter-precipitate spacing is the standard deviation of the distribution………………………………………………...........44

3.3 The Average composition (at.%) of the H-phase precipitates in 50.3Ni-32.2Ti-17.5Zr alloy aged at 550°C as measured by atom probe Tomography with the proxigram concentration profile method [39]. The Error for each concentration was calculated using standard deviation…………..47

3.4 Number density of the H-phase precipitates in 50.3Ni-32.2Ti-17.5Zr aged at 550°C as measured by atom probe tomography. The error in number density is based on counting and statistics……………………………………...........50

4.1 The Approximate transformation temperatures for a 50.3Ni-48.7Ti-1Zr (at.%) alloy at various aging times……………………………………………………....72

4.2 The Approximate transformation temperatures for a 50.3Ni-48.7Ti-1Zr (at.%) alloy at various aging times……………………………………………………....73

4.3 Average precipitate and matrix compositions for the S-phase precipitates are various aging times for 1 at % Zr at 400°C……………………………………....80

4.4 The calculated volume fractions and average precipitate diameter of the S-phase precipitates at various aging times for 1 at. % Zr at 400°C……...……....81

4.5 Average precipitate and matrix compositions for the S-phase precipitates are various aging times for 1 at % Zr at 400°C……………………………………....85

5.1 Measured transformation temperatures for [0Zr-400C] and [0Zr-550C]. A single dash indicates that a transformation path response of that type did not occur for the alloy/aging time tested……………………………………...114

5.2 Measured transformation temperatures for [1%Zr/400°C] and 17.5%Zr/400°C]. The transformation temperatures for [7%Zr/400°C] are not included in the table because there was no transformation response detected in the tested
range of -90 to 300°C. A single dash indicates that a transformation path response did not occur for the alloy/aging time tested.................................117

5.3 Measured transformation temperatures for the [1Zr-550C], [7Zr-550C], and [17.5Zr-550C] series after aging for different times. A single dash indicates there was no transformation response for that condition. A double dash indicates that the transformation behavior data was not collected for that aged condition. Temperatures are reported in °C…………………….……..118

5.4 Average precipitate sizes after various aging treatments of Ni_{50.3}Ti_{49.7-x}Zr_x (with x = 1, 7 and 17.5) alloys as determined by TEM. A single dash indicates there was no TEM data acquired for that sample. A double dash depicts there were no precipitates present in that condition. The H-phase is designated H-(l) for the major axis and the minor axis is designated H-(w). For the [7Zr-400C-100h] sample, the precipitates have spherical morphology and the measurement represents the diameter………………………...…...123

5.5 Average inter-precipitate spacing after various aging treatments of Ni_{50.3}Ti_{49.7-x}Zr_x (with x = 1, 7 and 17.5) alloys as determined by TEM. A single dash indicates there was not TEM data gathered for that alloy. A double dash means there were no precipitates present in the microstructure. The inter-precipitate spacing was calculated between precipitates regardless of the precipitate type of its neighbor………………………………………………123

5.6 Average matrix and H-phase precipitates compositions for [7Zr-400C-300hr] and [17.5Zr-400C-300h]. The composition values are average values and correspond to the datasets shown in Figure 5.5 (a and b) respectively…………………………………………………………125

5.7 Average matrix and H-phase precipitates compositions for [7Zr-550C-100hr] and [17.5 Zr-550C-100h]. These compositions correspond to the reconstructions shown in Figure 5.8……………………………………….…..133
LIST OF FIGURES

1.1  Schematic depicting the change in strain as a function of stress and temperature as an alloy is heated and cooled through an entire transformation cycle [1]……………………………………………………………6

1.2  Schematic illustration the different transformation paths generally seen in NiTi alloys [2]……………………………………………………………………7

1.3  Schematic of the three different martensitic transformation paths available in a NiTi shape memory alloy, where the top images are free energy, F, plotted against temperature. Images taken from reference [2]. The bottom images represent DSC scans that result from Case 1 and Case 2 transformations….9

1.4  The NiTi binary phase diagram [53] with an addition showing the phase equilibrium between the B2 and Ti3Ni4 phases [54]………………………………12

1.5  Plot illustrating the effect of increasing Ni (at. %) content on Ms temperature…..14

1.6  Effect of Pt/Hf/Zr/Au/Pd content on the transformation temperatures of various SMA alloys adapted from [6]………………………………………………15

1.7  (a)Schematic of the orthorhombic 192 atom unit cell of the H-phase and (b) TEM BF image showing the morphology of the H-phase [25]………………….18

1.8  Ni-Ti-Zr ternary phase diagram generated from Thermocalc ® at (a)400°C and (b)550°C………………………………………………………………………19

2.1  An example of an indexed mass spectrum showing ZrH and Zr2+………………31

2.2  Morphology guide from ref [4] illustrating how to measure precipitates from various morphologies……………………………………………………………32

3.1  Evolution of Vickers hardness as a function of aging time for 50.3Ni-32.2Ti-17.5Zr (at. %) alloy aged at 550°C…………………………………………………42

3.2  DSC curves of 50.3Ni-32.2Ti-17.5Zr (at. %) alloy aged at 550°C for various times…………………………………………………………………………………43
3.3 (a-d) A series of TEM bright field (BF), STEM-HAADF, and selected area
diffraction (SAD) patterns for (a) solution annealed, (b) 4 hours, (c-d) 72 hours
aging tie at 550°C.................................................................45

3.4 (a) 3D reconstructed atom map of the H-phase precipitate delineated with a
13.66 at. % Zr isoconcentration surface, and (b) corresponding proximity
histogram of the H-phase precipitates. The alloy 50.3Ni-32.2Ti-17.5Zr
was aged for 100 hrs at 550°C....................................................47

3.5 A 3D plot correlating the relationship between transformation temperature,
interprecipitate spacing, and Ni-content in the matrix for various aging times.....51

3.6 A series of constant-load thermal cycling test results for the Ni-32.2Ti-17.5Zr
alloy under (a-b) compressive and (c-d) tensile loading for the (a,c) 4 hour
and (b,d) 100 hour aged conditions..............................................52

3.7 Comparison of load-biased shape memory properties for the 50.3Ni-32.2Ti-
17.5Zr 4 hours aged condition vs. 100 hours aged condition: (a) actuation
strain as a function of applied stress, and (b) residual strain as a function
of applied stress............................................................................54

3.8 (a) Load-biased at 0MPa (strain-temperature response) showing the Af
temperatures and how the Af + 20°C were chosen. (b) Isothermal stress-strain
behavior including the unloading response for sample 72 hours to
investigate the superelastic behavior of that alloy at Af + 20°C . . . . . . . . ....55

4.1 Evolution of Vickers hardness as a function of aging time at 400°C for
(a) 50.3Ni- 48.7Ti-1Zr (at. %) alloy, and (b) 50.3Ni-48.7Ti-1Hf..................70

4.2 DSC curves of (a) 50.3Ni-48.7Ti-1Zr (at. %) and (b) 50.3Ni-48.7Ti-1Hf (at. %)
alloys aged at 400°C for various times..........................................71

4.3 A series of TEM bright field and selected area diffraction (SAD) patterns for
50.3Ni-48.7Ti-1Zr (at. %) at various aging times at 400°C. Each set is a
diffraction patterns taken from [100] and [111] zone axes and a micrograph
representing microstructure for (a-c) solution annealed condition, (d-f) 10 hrs,
(g-i) 24 hrs, (j-l) 100 hrs. The H-phase is indicated by the arrows on the
diffraction patterns........................................................................74

4.4 Bright field image and diffraction patterns taken at 100°C, indicating that
secondary reflections are not the S-phase for (a) 10 hours and the H-phase
for (b) 100 hours.................................................................75

4.5 (a-b) Diffraction images and schematic patterns from Coughlin [41] illustrating
diffuse scattering associated with the H' phase, and (c-d) diffraction images
from this work illustrating no diffuse scattering..........................77
4.6 (a-b). Bright field image of 100 hours sample showing lattice fringes to measure d-spacings, and (c) corresponding reflection on [100] diffraction pattern……………………………………………………………………78

4.7 Atom probe reconstructions for (a)1 hour, (b)10 hours, (c) 24 hours, and (d) 100 hours aging time at 400°C …………………………………………………………………………………79

4.8 STEM-HAADF image showing S-phase and H-phase precipitates at 100 hours aging at 400°C …………………………………………………………………………………81

4.9 a-l). A series of bright field and selected area diffraction (SAD) patterns for 50.3Ni- 48.7Ti-1Hf (at. %) at various aging times at 400°C. The diffraction patterns are taken from [100] and [111] zone axes for (a-b) solution annealed condition, (d-e) 24 hrs of aging, (g-h) 48hrs of aging, and (j-k) 120 hours of aging. In (e), the Ni4Ti3 are shown in the circles while the R-phase is denoted by the arrows. Figure 4.7(g-h) and (j-k) has H-phase present in both zone axes, indicated by the arrows. The corresponding bright fields are shown for solution annealed (c), 24 hours (f), 48 hours (i), and 120 hours (l). The phases present are labeled and indicated by the arrow on the micrograph………………………………………………………….….83

4.10 Atom probe reconstruction of 1% Hf specimen (a) after 24 hours of aging with Ni4Ti3 precipitates delineated with a 45.01 at.% isoconcentration Ti surface, and (b) after 120 hours of aging with both S-phase and H-phase precipitates present, with each phase delineated by a 52.82 at. % isoconcentration Ni surface…………………………………………………………….……….………85

4.11 (a-b). The tension (a) and compressive (b) constant force thermal cycling strain temperature curves for the 50.3Ni-48.7-1Zr (at. %) after 10 hours of aging ........88

4.12 (a-d). Strain (%) vs Temperature graph for the 50.3Ni-48.7Ti-1Hf (at.%) alloy in tension (a, c) and compression (b,d) at 24 hours aging time (a-b) and 48 hours aging time (c-d) under various loads …………………………………..91

4.13 (a-b). Summary plots showing (a) Actuation strain (%) vs Applied stress (MPa), and (b) Residual strain (%) vs. Applied stress for 1%Zr at 10 hours, 1%Hf at 24 hours, and 1%Hf at 48 hours …………………………………….93

5.1 Vickers Hardness (VHN) as a function of aging time for 0% Zr, 1%Zr, 7%Zr, and 17.5%Zr at 400°C (a-d) and 550°C (e-h). Hardening curves (b) and (h) have been re-plotted from references [26] and [25] respectively………………110

5.2 DSC curves for 0% Zr, 1%Zr, 7%Zr, and 17.5%Zr at 400°C (a-d) and 550°C (e-h). The arrow in the DSC curves indicated direction of increasing thermal cycles. DSC curves (b) and (h) have been previously reported in references [26] and [25]………………………………………………………….111
5.3 SAD and BF-TEM depicting the microstructural evolution of \( \text{Ni}_{50.3}\text{Ti}_{49.7-x}\text{Zr}_x \) alloys for (a) \( x = 1 \), (b) \( x = 7 \) and (c) \( x = 17.5 \) after aging at \( 400 \text{ °C} \) for 100 h. Compositions in at.%.................................................................120

5.4 SAD and BF-TEM depicting the microstructural evolution of \( \text{Ni}_{50.3}\text{Ti}_{49.7-x}\text{Zr}_x \) alloys for (a) \( x = 7 \), and (b) \( x = 17.5 \) after aging at \( 400 \text{ °C} \) for 300 h. Compositions in at.%.................................................................122

5.5 APT reconstruction of (a) \( \text{Ni}_{50.3}\text{Ti}_{42.7}\text{Zr}_7 \) delineated using a 6.57 at.% Zr isoconcentration surface, and a (b) \( \text{Ni}_{50.3}\text{Ti}_{42.7}\text{Zr}_{17.5} \) delineated by a 14.57 at.% Zr isoconcentration surface. Both of these samples were aged at \( 400\text{ °C} \) for 300 h.................................................................125

5.6 Microstructural evolution of (a) \( \text{Ni}_{50.3}\text{Ti}_{48.7}\text{Zr}_1 \) (at.%), (b) \( \text{Ni}_{50.3}\text{Ti}_{42.7}\text{Zr}_7 \) (at.%), and (c) \( \text{Ni}_{50.3}\text{Ti}_{32.2}\text{Zr}_{17.5} \) (at. %) as a function of ternary addition amount at \( 550\text{ °C} \) after 24 hours of aging..............128

5.7 Microstructural evolution of (a) \( \text{Ni}_{50.3}\text{Ti}_{48.7}\text{Zr}_1 \) (at.%), (b) \( \text{Ni}_{50.3}\text{Ti}_{42.7}\text{Zr}_7 \) (at.%), and (c) \( \text{Ni}_{50.3}\text{Ti}_{32.2}\text{Zr}_{17.5} \) (at. %) as a function of ternary addition amount at \( 550\text{ °C} \) after 100 h of aging.................................................................130

5.8 Atom probe reconstruction of (a) \( \text{Ni}_{50.3}\text{Ti}_{42.7}\text{Zr}_7 \), and (b) \( \text{Ni}_{50.3}\text{Ti}_{32.2}\text{Zr}_{17.5} \) at \( 550\text{ °C} \) after 100 h aging.................................................................132

6.1 Schematic of experimental results plotted on a Ni-Ti-Zr phase diagram generated at \( 550\text{ °C} \).................................................................141

6.2 Schematic of experimental results plotted on a Ni-Ti-Zr phase diagram generated at \( 400\text{ °C} \).................................................................142

A.1 Vickers hardness curves as a function of aging time for (a) 6.5%Zr, (b) 7%Zr-1%Cr, and (c) 7.5%Zr at \( 400\text{ °C} \). All of these alloys achieved a peak hardness value after 24 hours aging time.................................................................148

A.2 Vickers hardness curves as a function of aging time for (a) 6.5%Zr, (b) 7%Zr-1%Cr, and (c) 7.5%Zr at \( 550\text{ °C} \). These alloys achieved a peak hardness much faster than at \( 400\text{ °C} \).................................................................148

A.3 DSC curves for (a) 6.5%Zr, (b) 7%Zr-1%Cr, and (c) 7.5% Zr at \( 400\text{ °C} \). There was no transformation response detected for any of the alloys in the tested range.................................................................149

A.4 DSC curves (a) 6.5% Zr, (b) 7%Zr-1%Cr, and (c) 7.5% Zr at \( 550\text{ °C} \). For alloys (a) and (b), there was a transformation at 24 hours; however, with an increase in Zr content (alloy c) a transformation does not occur until 100 hours. It is interesting to note that all transformation pathways are B2-B19’ with the exception of alloy (b) where at 24 hours of aging on the heating cycle it is starting to form a doublet peak and upon aging at 100 hours has a symmetric
R-phase transformation pathway

149
CHAPTER 1
INTRODUCTION

1.1 Motivation

The shape memory effect (SME) is a phenomenon whereby a material undergoes a reversible phase change when heated and cooled through a transformation cycle [1]. This transformation is reversible and the original shape, even against an opposing load, is recovered. This shape memory effect was discovered in the NiTi system in the 1960s and is commonly referred to as Nitinol (pronounced ‘night-in-all’) [2]. This name represents the elemental species – Ni and Ti – and the place of its original discovery – the Naval Ordinance Laboratory. Since its discovery, this type of alloy has been used in various engineering applications. The use of NiTi and Nitinol will be used interchangeably through the dissertation. Some of the most successful applications being in the medical field for cardiovascular stents, braces, and eyeglasses [3]. In addition, shape memory alloys (SMAs) are ideal materials that can perform work against an applied load and act as a solid-state actuator. This has led to great interest in utilizing the NiTi system as solid-state actuators. Compared to conventional hydraulic actuators, SMAs offer similar torque (per volume/weight) and are frictionless with less maintenance requirements [1–3]. In addition, the total part count and weight of a shape memory actuator is less than a conventional actuator design making them beneficial for aerospace and related transportation vehicle based applications, where weight savings are essential [6], [7]. Beyond these applications, shape memory
alloys have applications in small motors and fasteners in automobiles; and safety valve actuators for down-hole oil and gas drilling for energy exploration [3]–[5],[8], [9].

This work has focused on research in support of National Aeronautics and Space Administration (NASA) technology advancement program. In 2010, NASA developed a set of fourteen Technology Roadmaps to lead the development of space technologies [10]. These different technology roadmaps are further broken down into sub-categories. This research aims to help achieve the objectives from the materials, structures, mechanical systems, and manufacturing technology roadmap with an emphasis on flexible materials systems. The focus of flexible material systems is the identification of flexible systems that enable the assembly of expandable structures from a small volume to a larger volume through the combined use of rigid linkages and joints with soft thin shells or membranes [10]. The challenges that NASA faces with the technology development of these materials is to offer a material that has an increased volume, lower mass solution than rigid metal or composite structures through a reliance on the ability to minimize weight and stowed volume without sacrificing operational functionality and reliability [10].

Two major issues in bringing Nitinol to fruition as an actuator include, first, the ability to have a greater capacity to tune the transformation range for a given application and, second, maintaining dimensional stability under repeated cycles. Binary Nitinol has a transformation range approximately between -100°C to 100°C, with a dramatic drop in the transformation temperature with slight changes in the Ni-rich stoichiometries. Consequently, Ni-rich Nitinol alloys have largely been ignored because of their low transformation temperatures. Conversely, the modest high temperatures would also poise some limitations in turbomachinery where elevated temperature exposure could be larger than the transformation temperature. The latter factor, dimensionality, refers to the accumulation of retained strain upon cycling through the
transformation. This strain can then lead to changes in part dimensions and a loss of necessary tolerances. Though the equiatomic and Ti-rich Nitinol compositions have a higher transformation temperature than the Ni-rich binary compositions, but they are much more sensitive to these dimensional instabilities.

It has been shown that by adding a third element NiTi system such as Au [11], Pt [12], Pd [13], Hf [14], or Zr [15], [16] can have a dramatic increase in the transformation temperature. These increases have been associated with the precipitation of new phases which appear to have a compositional effect and/or an intrinsic mechanical strain effect (created by the precipitates) in the microstructure in regulating transformation temperature. These increases, even in Ni-rich Nitinol alloys, have been nearly 200% for certain ternary alloys while retaining excellent dimensional stability [17]. Though these increases have placed Ni-rich Nitinol alloys with transformation temperatures of approximately 100 to 200°C, which is still limited to high temperature applications, the ability to tune the transformation while retaining the dimensional stability has generated significant interest in understanding how ternary additions facilitate these properties. Of the ternary additions, the cost associated with alloying with the precious metals Pd, Pt, or Au is commercially prohibitive for any practical applications. Consequently, investigations in to lower cost ternary elements, such as Hf and Zr have emerged as alternative candidates for shape memory applications.

This research has primarily investigated Zr additions to the Ni-rich NiTi system for the following reasons. As previously discussed, using Zr and Hf ternary is substantially less expensive than the precious metal alternatives. However, Zr provides two more advantages than Hf. It too is less expensive, and weight savings. When comparing a Ni-Ti-20Zr to a Ni-Ti-20Hf (at.%), the Zr based alloy is approximately 20% lighter. [18], [19]. Both Zr and Hf, as is Ti, are a transition group
IVB metal providing the opportunity to site substitute the ternary for Ti which could provide a tuning of the stress state (which regulates the martensitic transformation temperature [20]). Interestingly, most of the group IVB transition metal additive work has been in Hf [14], [21]–[24] with fewer papers on Zr [25], [26] Of all these works, they have addressed macro-alloying levels between 15-20% leaving critical gaps in understanding the phase stability and shape memory properties at lower concentrations.

This research has investigated three different ranges of Zr additions to the NiTi system, i.e. 1%, 7%, and 17.5% at a fixed 50.3Ni content. The amount of Zr added to the Ni-rich NiTi alloys depends on the type of actuator (transformation temperature) application targeted. The first part of this dissertation focuses on the microstructural and thermo-mechanical characterization of a 50.3Ni-32.2Ti-17.5Zr alloy to optimize the alloy in terms of transformation behavior and dimensional stability. To date, most research has focused on additions ranging from 15 at. % to 20 at. % and this provides a good basis for comparison of the new data found here to the current literature. In particular, the work conducted has provided the precipitate composition via atom probe for the first time as well as its thermo-mechanical behavior. In particulate to shape memory based actuator applications, providing the shape memory response under loading is necessary to truly ascertain if the alloy is a candidate for such applications. After investigating this higher ternary addition amount (17.5%), a comparison to the dilute 1% study was done to provide the data between the two extremes in terms of Zr concentrations. Prior to the work reported in this dissertation, little information has been published on dilute ternary additions. Hornbuckle et al. [21] investigated a very Ni-rich (54 at. %) NiTi alloy with very dilute Hf additions between 1-4 at. % and noted that H-phase precipitation occurred. This H-phase was similarly reported in Ni-Ti-Hf alloys but at Hf concentrations between 15-20% [25]. An outstanding question would be if that
was a result found in the very Ni-rich composition of Nitinol and/or would be present in slightly enriched Ni concentrations and if such precipitation in the dilute limits is solely for Hf addition. This work then addresses a slight rich composition as well as a comparison to the use of Zr. To ensure a direct comparison, the work here characterized a complimentary 1%Hf alloy to the 1%Zr alloy. Finally, the dissertation addresses the midrange sample.

Sandu [27]–[29] reported the effects of aging on the martensitic transformation and mechanical behavior of a Ni-rich (52Ni-42Ti-6Zr (at.%)) shape memory alloy. However, the precipitate crystal structure still needed to be explored. The goal for the work presented in this dissertation was to determine if similar precipitation occurs at this lower concentration of Ni (50.3 at. %). It was also investigated how dilute amounts of Zr regulated shape memory properties. Using the information collected from all three of these various ranges, a collective study of Zr additions from 17.5% to 1% will be explored at various temperatures to determine the microstructural evolution and transformation behavior as a function of ternary addition amount.

The dissertation is organized in the University of Alabama’s allowed ‘paper-style dissertation.’ The remainder of Chapter 1 will concise of a literature review of the fundamentals of the shape memory effect and prior literature on the additions of Hf and Zr to the Nitinol system. Chapter 2 will include all relevant experimental background information, including the data analysis techniques. Chapter 3 will be the paper style format for the 17.5% Zr paper followed by Chapter 4 being the 1%Zr paper and Chapter 5 being the collective comparison paper at various aging conditions for a binary Nitinol to a 17.5% Zr alloy. Chapter 6 is the conclusion and future direction chapter from the information learned. Finally, an appendix is added that contains a data base of DSC and age hardening behavior for 6.5% and 7.5% Zr additions, which provides a complement data set to those presented in Chapter 5 for future investigations.
1.2 Shape Memory Effect and Transformation Phases

The shape memory effect (SME) is a term that is used to describe a material that is able to undergo a reversible crystal structure change when heated and cooled through a temperature. This is shown in Figure 1.1.

![Figure 1.1. Schematic depicting the change in strain as a function of stress and temperature as an alloy is heated and cooled through an entire transformation cycle [1].](image)

Through this series of events, any deformation experienced due to the change in crystal structure is reversible, which allows for the original shape to be recovered. The low temperature transformation phase is referred to as martensite and the high temperature transformed phase known as austenite [2], [4], [30], [31]. Martensite formation occurs by a diffusionless transformation that occurs in solids, and is generally governed by a shearing mechanism that allows for cooperative movement of atoms near the speed of sound. When undergoing this phase transformation between martensite and austenite, the deformation that accompanies it is predominately occurring via (de)twinning. As the temperature is reduced, the ordered, lower entropy structure becomes preferred and the relatively high entropy cubic austenite structure (B2 NiTi) causes an energy change [30]. As the austenite is cooled, instabilities (such as lattice
softening) help facilitate this break down into the martensite phase [31]. As reported by Otsuka [32], Nitinol based alloys offer three possible martensite candidates: the R-phase, B19, and B19’. Each of these three martensite candidates has their own unique crystal structure as well as parameters pertaining to their formation. Two of these candidates (R and B19) are generally occurring as possible alternative pathways to the final form of martensite. Figure 1.2 illustrates the transformation paths that are generally seen in NiTi based alloys.

Figure 1.2. Schematic illustration the different transformation paths generally seen in NiTi alloys [2].

The B19’ phase, the final form of martensite most commonly seen, has a monoclinic crystal structure [33], [34] and a P21/m space group [35]. The B19’ phase occurs in all NiTi based alloys and can be achieved by either the B2 austenite phase transforming directly to B19’ or by the two additional pathways leading to B19’ by way of the B19 phase or the R-phase. The B19 phase has an orthorhombic crystal structure [36], [37] and has a Pmmb space group [38]. This martensite variant has been reported to be in the Ni-Ti-Cu alloys where the B2 austenite phase will first transform to B19 and then to B19’ [32]. The B19 phase has also been identified to be the final form of martensite in ternary NiTiX (X= Au, Pt, Pd, Hf, and Zr) with macroadditions (>20 at. % for Hf and Zr) of the ternary elements [32]. The B19’ phase has the highest transformation strain of all the variants (~10%) and B19 has the next highest (~8%). The other martensite variant and the second alternative pathway leading to B19’ is the R-phase. The R-phase was originally thought to have a rhombohedral crystal structure [39], [40] (hence the name R-phase), but was found
actually be trigonal and belonging to either the P-3 or P3 space group [41]–[47]. The R-phase has the maximum recoverable strain (~1%) during transformation as compared to the monoclinic B19’ phase transformation (~10%) [30]. The fatigue life of the R-phase is also reported to be very good when compared to the B19’ phase [48]. The R-phase formation and the subsequent formation of the B19’ phase is believed to be attributed to the presence of defects such as dislocations, precipitates, and impurity elements in the binary element [32]. In NiTi based shape memory alloys, the R-phase can be achieved by suppressing the martensitic transformation by five different means: (1) Increasing the Ni content, (2) Aging at lower temperatures between 300°C and 500°C after solution treatment to form Ni₄Ti₃ precipitates [49], (3) Annealing below the recrystallization temperature immediately after cold-working [49], (4) Adding a third element, and (5) Thermal cycling.

Though all three phases could exist, the transformation path is determined by which of these phases is the most stable. These different transformation paths are divided into 3 categories, as shown in Figure 1.3 (a-c) [2]. Case 1 and Case 2 transformations paths will be described more in-depth here as they are relevant to the work presented in this dissertation. In the first case, the monoclinic B19’ phase is the most stable; therefore, the other martensite phases do not appear below the B2 to B19’ transformation temperature [31]. Since the transformation path is for a single phase transformation or step (B2 to B19’), a single transformation peak is measured in a differential scanning calorimetry (DSC) heating scan, where exothermic and endothermic heat associated with a phase transformation is measured as a function of temperature. A case 1 DSC transformation behavior is displayed in Figure 1.3(d) using experimental data.

If there is a temperature at which the R-phase is thermodynamically favored over B19’, the R-phase will first form. Upon cooling, the B2 parent phase first transforms into the R-phase (Step
1) and then is followed by a subsequent lower temperature transformation from the R-phase to B19’ (Step 2). This second step is to lower the free energy. These two different martensitic phases yield two transformation peaks during the heating cycle in the DSC curves, as shown in Figure 1.3(d). There are two different types of B2-R-B19’ transformation behaviors, an asymmetric R-phase transformation, and a symmetric R-phase transformation. The asymmetric R-phase is the more common transformational route. It occurs when, upon heating, a Case 1 (B2-B19’) transformation occurs resulting in one peak present in the heating cycle of a DSC curve. During the cooling cycle, the B19’ phase will first transform to the R-phase (Step 1) and then to the B2 phase (Step 2). This results in two peaks present in the cooling cycle of the DSC curve. For a symmetric transformation, there will be a two-step transformation path (B2-R-B19’) during both the heating and cooling cycles. An experimental example of a symmetric R-phase transformation DSC curve is shown in Figure 1.3(d).

Figure 1.3. (a-c) Schematic of the three different martensitic transformation paths available in a NiTi shape memory alloy, where the top images are free energy, F, plotted against temperature. Images taken from reference [2].

Figure 1.3. (d) Exothermic Heat Flow (J/g)
These transformations can also be directly regulate by the type of precipitates within the shape memory matrix. These secondary phases, otherwise known as precipitates, influence the transformation behavior by both a chemical and mechanical effect. The chemical effect, which was briefly mentioned earlier, occurs when the precipitates absorb Ni—which biases the matrix to be enriched in Ti [50] and alters the elastic constants. The ‘compositional effect’ will then be a function of precipitate type (its composition and solubility range for each of its species). The mechanical effect pertains to influence of stress fields that are present around precipitates. These stress fields act as obstacles to the transformation requiring further under cooling for the transformation to occur [51]. The transformation will occur once the driving force of under-cooling reaches the required level. This phenomenon has been shown to be controlled by the size and inter-particle spacing of these precipitates. Evirgen [51] was among the first to introduce the concept of this mechanism. When the inter-particle spacing is smaller than or comparable to the critical martensite nuclei size, the martensitic transformation is suppressed even in the presence of a Ti-rich matrix [51]. This result then suggests that compositional effects (chemical effect) dominate only after the critical martensite nuclei size is attained. The stress fields around the precipitates can also help raise the transformation temperature if the stress field is sufficiently large and properly oriented, allowing for martensite nucleation [24], [52]. Thus, developing control of precipitate types within the shape memory alloy essential materials engineering means to regulate transformation temperature through its compositional and chemical contributions.

1.3 Nitinol Shape Memory Alloys

Though several different alloys exhibit the shape memory effect, dissertation will focus on the Nitinol compositions, as it provided the basis for materials of study. As briefly discussed above NiTi alloys, as known as Nitinol, are the most common SMAs but are limited in applications by
either a low transformation temperature, generally between -100°C to 100°C, or dimensional instabilities. The binary phase diagram for Ni-Ti is shown in Figure 1.4. Since we are most concerned with composition at and near the equiatomic compositions, the precipitates formed here are reviewed. On the Ti-rich side, the Ti$_2$Ni precipitate forms within the B2 matrix phase. This precipitate has a cF96 Space group and often is observed as a large globular precipitates within the matrix, and readily forms directly to this phase upon precipitation. In contrast, the Ni-rich compositions are very sensitive to a sequence of metastable precipitate phases. Though Ni$_3$Ti, hP16 space group, is the thermodynamic stabilized phase, it is often proceeded by either a Ni$_4$Ti$_3$ (R3) and/or Ni$_3$Ti$_2$ precipitates, dependent upon aging conditions [21]. Of these precipitates, the Ni$_4$Ti$_3$ phase is most sensitive in regulated the shape memory transformation. It forms as lenticular shaped morphology in the matrix which creates a variety of strain within the matrix that regulates the shape memory properties [21]. However, after long term aging the precipitates are widely spaced (high inter-particle spacing) and they will not directly affect the martensitic transformations. Upon quenching from the B2 phase field, Ni$_4$Ti$_3$ readily precipitates within microseconds [21]. A recent paper by Hornbuckle et al.[21] provides a good review on the phase, microstructure and decomposition behavior of these precipitates and the reader is directed to that paper for further details.
Figure 1.4. The NiTi binary phase diagram [53] with an addition showing the phase equilibrium between the B2 and Ti$_3$Ni$_4$ phases [54].

With the basics of NiTi physical metallurgy reviewed, attention is turned to the shape memory properties. Much of the early research in Nitinol focused on varying the composition to determine the transformation temperature and functional behavior. The results of this prior research indicated that Ti-rich and equiatomic compositions have higher transformation temperatures than the Ni-rich compositions, Figure 1.5 [55]–[59].

In general, the Ti-rich alloys have a constant transformation temperature of ~60°C until they reach the equiatomic composition. The exact reasoning why Ti-rich alloys having a higher transformation temperature is still being researched; however, after examining a binary NiTi phase diagram in the 50 atomic percent region, some believe it is due to the lack of solubility on the Ti-rich side where it has a nearly vertical solvus line. This behavior makes it impossible to create a Ti-rich NiTi solid solution. Though the transformation temperature is higher for these equiatomic
and Ti-rich Nitinol alloys, they suffer from poorer mechanical performance with an increase in temperature than their Ni-rich counterparts [60]. Recall, the two key factors for an alloy to be a viable option for a high temperature actuator is to have a high transformation temperature and exhibit excellent dimensional stability.

To achieve these objectives, research moved towards the use of ternary alloy additions to the Ti-rich Nitinol alloys (and later to the Ni-rich alloys). By adding a third element to the alloy, it was hypothesized to facilitate a secondary precipitation event (besides Ti2Ni, as seen in the Ti-rich compositions) that would improve the alloys mechanical performance while still maintaining a high transformation temperature associated with Ti-rich alloys. Some of the most common elements used as ternary alloying additions in Nitinol are Pd, Pt, Zr, Hf, and Au. It is believed that Pd and/or Pt would site substitute for Ni due to similar electron configuration in their outer shell. The same principle was used to hypothesize for Hf and/or Zr, with its site substitution for Ti. Though some form of solid solubility could be expected, these additions were found to also precipitate a series of new types of precipitates which had an effect on the martensitic pathway with the functional behavior altered by varying amounts of the same ternary addition and/or its processing route [32].

For NiTiAu alloys, Wu and Wayman confirmed two types of martensite phases. For lower Au concentrations of 5 and 10 at.% in a Ti50Ni50-XAuX alloy, B19’. At higher Au concentrations between 40 to 50 at.%, B19 was present. In the Ni-Ti-Pd alloys, with <10% (at.%) Pd, the martensitic transformation was found to be a two-step transformation upon cooling from B2 to B19’ by way of the R-phase [61]. This type of transformation behavior was previously introduced as Case 2 in section 1.2. Once the ternary amount is increased to greater than 10%, B19, rather than B19’, was found to be stabilized [61]. For Ni-Ti-Pt alloys containing <10% (at.%) Pt, the
martensitic transformation is reported as a one-step transformation from B2 to B19’. Ni-Ti-Pd alloys, with increasing Pt content the B2 will transform to B19 [62]. Ni-Ti-Hf and Ni-Ti-Zr also revealed a similar trend as with the Pd or Pt addition. When the Zr or Hf addition are <20% at.%, these alloys have been shown to exhibit a one-stage transformation from B2 to B19’ or a two-stage transformation behavior from B2 to R-phase to B19’ [22], [26]. When the alloy addition is > 20%, a B2 to B19 transformation will occur [32]. In more recent years, examination of the Ni-rich alloys has emerged. As shown in Figure 1.5 these alloys were largely ignored because of their below room temperature transformation temperatures making them impractical for several engineering applications in turbomachinery uses. [51]

![Plot illustrating the effect of increasing Ni (at. %) content on Ms temperature.](image)

**Figure 1.5.** Plot illustrating the effect of increasing Ni (at. %) content on Ms temperature.

Based on the success of significant increases in the transformation temperature with a ternary alloy additions with the Ti-rich Nitinol alloys, efforts were done to determine if synergetic effects could occur in these compositions as well.
Figure 1.6 Effect of Pt/Hf/Zr/Au/Pd content on the transformation temperatures of various SMA alloys adapted from [6].

Shown in Figure 1.6, with ever increasing ternary alloy compositions, the martensite transformation temperature (Ms) increases in a near linear trend. For example, once the Hf and Zr alloy additions was greater than 10 at. %, a transformation temperature $>100^\circ$C could be achieved. It was found with a 30 at. % Hf addition that the transformation temperature could reach $\sim500^\circ$C, and a 25 at. % addition of Zr could reach a transformation temperature of $\sim350^\circ$C as reported by Hsiech [16]. These transformation temperatures then place the alloy as a candidate for a high-temperature actuator applications. Since the costs of these ternary additions (Zr or Hf) are much lower than the precious metals, these additions appear to be a viable ternary addition. Though the transformation temperature increased, the prior issues previously noted in terms of the thermo-mechanical performance remained. The transformation behavior’s thermal stability and recovery, an increase in the thermal hysteresis, and poor dimensional stability during thermal cycling were noted in all of the alloys [15], [16], [63], [64]. These drawbacks could not be improved due to the lack of altering of the microstructure.
1.4 Ni-rich alloys with ternary alloys and their properties

Similar to the prior ternary elements discussed above for the equiatomic and Ti-rich compositions, they were also alloyed with Ni-rich Nitinol. For the Pt and Pd additions, a new type of precipitate was observed, denoted as the P-phase. These precipitates were complicated in their identification by a multivariate stacking of the unit cells. The true identity of the precipitate was not identified until 2010 in the seminal work [65]. Later work, then computational, confirmed the thermodynamic stability of the phase as well as its compositional range [66]. The formation of this precipitate was observed to remove Ni content from the shape memory matrix phase which biased the matrix to become Ti-rich and an increase in the transformation temperatures, well over 100°C, were noted and retained the superior dimensional stability. However, these alloys still did not yield the same energy output as their equiatomic and Ti-rich counterparts. Ongoing efforts are now being addressed how to optimize the precipitate microstructure (volume fraction, inter-precipitate spacing, etc.) to increase the matrix phase and hence the work out of the alloys.

As noted above, Hf and Zr provided a lower cost alternative to the prior precious metals. Similar to the precious metals, additions of Hf and Zr for the Ni-rich Nitinol compositions have resulted an increase in the transformation temperature and the precipitation of new types of precipitates [24], [67]. Of these two ternary alloys, the Ni-rich Ni-Ti-Hf system has been studied more in-depth. This is likely contributed to the Ni-Ti-Hf system being the initial alloy that showed a Ms temperature near 230°C with aging in a 50.6Ni-29.4Ti-20 Hf (at. %) alloy [23]. The increase in transformation temperature was attributed to the presence of nanoscale precipitates who exhibited an extra reflection seen at x/7 positions along the <321> reciprocal vector of the B2 matrix looking along the [111] zone axis. Theses identified reflections matched that of those seen in Ni-rich binary NiTi for the metastable Ni4Ti3 precipitates, leading Meng et al, to identify the
precipitates as Ni₄(Ti+Hf)₃ [23]. However, as well be discussed later, this identification may not be correct.

Based on this promising transformation temperature, efforts were taken to determine if it retained good dimensional stability. Bigelow et al. [17] performed a series of mechanical test on a 50.3Ni-29.7Ti-20Hf (at. %) alloy which demonstrated an alloy with high work output in tension and compression, tremendous dimensional stability at stresses up to 500 MPa, and near perfect superelastic behavior while having a Ms transformation temperature near 150°C. These mechanical behavior properties are very different than what was reported for the Ti-rich Ni-Ti-Hf alloy. In that same report, Bigelow et al. [17] reported a fine dispersion of a secondary precipitate phase that was different from the Ni₄(Ti+Hf)₃ reported by Meng et al. [23] and was contributing to the improved mechanical properties of this alloy. Yang et al. [68] provided complementory set of work on the same alloy to determine the crystal structure and reported it to be the H-phase precipitate that was previously reported by Han [24]. The H-phase is an orthorhombic unit cell with a 192 atom basis. Yang et al. [68] reported the composition of the H-phase in this alloy to be 50Ni-16.7Ti-33.3Hf (at. %) for an overall alloy of 50.3Ni-29.7Ti-20Hf (at.%). Figure 1.7 shows the unit cell of the H-phase as well as a BF (bright field) image illustrating the morphology of the spindle-like precipitates.
Despite having similar precipitation to Ni-Ti-Hf alloys, Ni-Ti-Zr has shown some different responses in mechanical testing. Evirgen et al. [19] reported on a 50.3Ni-29.7Ti-20Zr alloy similar to the prior report of 50.3Ni-29.7Ti-2Hf by Bigelow et al. [17]. Though both alloys revealed good dimensional stability, the Zr containing alloy had a less vertical response during its load-bias thermal cycling. This implies that the Zr alloy will have a more gradual transformation over the temperature range.

Since Zr provides an even less expensive alternative than Hf, efforts have now been done to determine if similar properties can be achieved with this ternary. Santamarta et al. [25] completed an investigative study on Zr additions to a Ni-rich NiTi alloy in the range of 15-20 at.% Zr. H-phase precipitates, the same type reported by Han et al. [24] in Hf work, were identified. However this study lacked the investigation of the transformation behavior, and also the mechanical behavior, to determine the functionality of Ni-Ti-Zr alloys. This dissertation aims at helping to bring that gap by conducting a series of studies on a 50.3Ni-32.2Ti-17.5 (at.%) alloy (Chapter 3).
Interestingly, a review of the ternary Ti-Ni-Hf or Ti-Ni-Zr phase diagrams does not reveal the H-phase phase field, as shown in Figure 1.8. For the macro-alloy compositions reported in the literature (15-20 at%), these ternary elements are believed to be in solution with a B2 phase. This demonstrates that the phase equilibrium is still needed to be thoroughly understood in these alloys. To demonstrate this point further, the Ti2Ni precipitate, noted to be in the Ti-rich compositions, have also been reported to appear in the Ni-rich compositions of Ni-Ti-Hf [69]. Though this paper provides sufficient diffraction patterns to support this phase’s presence, no confirmation was provided on the actual composition of the targeted alloy and/or how impurities may have effect the phase stability, which may have contributed to its formation. It is unclear why such a Ti-rich precipitate would form in the Ni-rich compositions.

![Figure 1.8. Ni-Ti-Zr ternary phase diagram generated from Thermocalc ® at (a)400°C and (b)550°C.](image)

Since the H-phase has only been reported to form in higher Hf or Zr concentrations, it is unclear the compositional stability range for this phase. Recent work in very Ni-rich Nitinol alloys with Hf additions of 1- 4at% have shown, given sufficient aging time at 400°C, the precipitation of the H-phase. Though one could expect in more dilute limits, Hf and Zr sit
substitution for Ti, this does not appear to be the case. These former studies were done on potential bearing applications for Nitinol and no work relating the effect of dilute ternary additions on the shape memory behavior have been reported. Consequently, Chapter 4 explores both the phase and shape memory properties for a 50.3Ni-48.7Ti-1 Zr (at. %) and a 50.3Ni-48.7Ti-1Hf (at. %) alloy.

Finally to bridge the gap between 1% and 17.5% Zr, a series of 7% alloys have been studied where a compressive microstructure-to properties links is made at two aging temperatures at various times across all three compositions. From which a more informed understanding of the Ni-Ti-Zr alloy system can be ascertained for its shape memory attributes.
1.5 References


376–387.


CHAPTER 2
EXPERIMENTAL DETAILS

This chapter provides a review of the scientific methods and data analysis procedures used in the research.

2.1 Synthesis

Various compositions with X ranging from 1 at. % to 17.5 at. % Zr and Hf were made of 50.3Ni-(49.7-X)Ti-(X)Zr or 50.3Ni-(49.7-X)Ti-(X)Hf alloys obtained through a collaboration with NASA Glenn Research Center. By fixing the Ni content, a comparison between each alloy can more readily be made. All alloys were prepared by vacuum induction melting of high purity elements (99.98% Ni; 99.8% Zr/Hf; 99.95% Ti) in a graphite crucible with argon atmosphere. The ingots were vacuum homogenized for 72 hours at 1050°C and furnace cooled. They were then hot extruded at 900°C with an area reduction ratio of 7:1. The extruded bars were then re-solution annealed at 1050°C for 10 hours then water quenched in preparation for the aging treatments. The rods were sectioned into smaller pieces then aged at 400°C and/or 550°C for various times after which they were water quenched. In all solutionizing and aging treatments, the samples were wrapped in Ta foil with flowing argon over the sample while in the tube furnace to eliminate possible oxidation.

2.2 Property Characterization

Vickers Hardness testing – this testing was performed to determine the change in hardness as a function of aging time for each alloy. This provided the classical age hardening curve from
which the onset of precipitation can be gleaned by the change in hardness. The samples were measured using a Buehler Vickers hardness tester under a load of 1000g with a dwell time of 15s. To ensure accuracy, 12 separate measurements were taken with the mean hardness and standard deviation reported for each hardness data point.

Thermomechanical tension and compression testing- This testing was performed at Glenn Research Center (GRC) using an MTS 810 servo-hydraulic load frame equipped with a multi-channel TestStar™ IIIs controller. Heating and cooling was accomplished using a combination of a thermal chamber and induction heating elements. Temperature was controlled and measured using a GC-Controls digital controller and type-K thermocouples spot welded directly to the samples. Cylindrical dog-bone samples with a 5.08 mm diameter and 15.24 mm in gage length were machined from the extruded rod and were subjected to two stress-free thermal cycles while mounted in the test frame to relieve any residual stresses resulting from the machining and sample handling. Constant-force thermal cycling experiments were performed in series at stresses ranging from 0 to ±400 MPa (series of increasing loads on the same sample). Each sample was thermomechanically cycled twice at each stress level.

Differential scanning calorimetry – DSC was able to provide the temperature points for the phase transformation as a function of the heat absorbed or released. UA has a TA Q200 unit that has a temperature range of -90°C to 400°C. Each sample was run for 3-5 cycles in the temperature range of -90°C to 300°C at a rate of 10°C/min. The chamber was equipped with flowing argon in order to keep the sample from oxidizing. The sample to be tested was cut to be 5 mm diameter desk, and tested in a standard aluminum DSC pan. Through these scans the amount of heat released can be related to where the transformation temperature initiates and concludes. This transformation behavior was directly related to the microstructure and precipitate chemistry in the alloys.
2.3 Phase and Microstructure Characterization

**Transmission electron microscopy** (TEM) – TEM was a vital tool in imaging the precipitates and identifying the phases through electron diffraction. Specimens were prepared by cutting a 3 mm disc from the sample of interest using a Fischione Model 170 ultrasonic disc cutter. The disc was then thinned down to ~100 µm using 800 grit SiC paper followed by dimple polishing to < 15 µm using a diamond abrasive. The specimens were Ar ion milled using the Precision Ion Polishing system (GATAN 691) to create an electron transparent area near the perforated hole. The TEM was performed in a 200 keV field emission FEI TECNAI (scanning) transmission electron microscope ((S)TEM), to view the microstructure and provide phase identification. The STEM is equipped with a High Angle Annular Dark Field Detector (HADDF) that provides a semi-quantitative image where brightness scales with the atomic number, $Z^{-1.7-2}$. Therefore, any difference in contrast between phases observed in the image provides insist to composition of the two phases with the brighter contrast phase containing higher atomic numbered atoms relative to the darker contrast phase. More information on TEM can be found in references [1].

**Atom probe tomography** – APT provided the chemical identification of the matrix and precipitates as well as the volume fraction and number density of precipitates. This was then related to the phase and mechanical behavior of these alloys. APT provided a three dimensional reconstruction of each atom in the material by field evaporating atoms from a needle like specimen. More details on the technique can be found in references [2].

The atom probe specimens were prepared using a FEI Quanta 200 3D Dual Beam electron-focus ion beam (FIB) microscope equipped with an Omniprobe micro-manipulation system with details of the preparation given in reference [3]. The extracted material is annular-milled into the required atom probe tips using a 30 keV beam energy at beam currents between 0.3-0.5 nA. The
final shaping of the tip is done by using a 5 keV – 70 pA ‘clean up’ step to reduce the surface damage created from the Ga ion implantation at the higher energy settings. For the Leap 3000XSi, APT was performed at 40 K, 200 kHz pulse repetition rate, and 0.4 nJ pulse energy with a target evaporation of 0.5 per pulse whereas the LEAP 5000XS APT was performed at 40K, 100 kHz, and 100-200 pJ pulse energy with a target evaporation of 1 per pulse. The atom probe data is to be analyzed using the IVAS 3.6 software package and reconstructed using the procedures outline by Hornbuckle et al. [2]

Due to Zr and Ti have a higher affinity for hydrogen, we did note the presence of elemental hydrogen and hydride complexes in the mass spectrum, which typically accounted for < 2-5% (depending on the amount of Zr and Ti present in the initial composition) of the total composition. This hydrogen is either an artifact due to processing incorporated in making the alloy or a known vacuum contaminate gas in the LEAP chamber. An example of an indexed spectrum is shown in Figure 1.9. To ensure accuracy in measuring the three constituent elements in the analysis, we removed the elemental hydrogen from our composition and have included the metallic species of the hydride to the overall composition from which we normalized to the three constituent elements. This is done by decomposing the complex ions to obtain the number of counts for Ni, Ti, and Zr/Hf without hydrogen. For example, if there was a precipitate with 17716 counts of Ni, 14533 counts of Ti, and 1171 counts of Zr, first, all these counts would be summed together (this would equal 33420 total counts). Then to obtain the at. % of Ni in those total counts, this formula would be used:

\[
\text{Ni (at.\%)} = \frac{100}{\text{Total counts}} \times \text{Ni counts}
\]

The Ni (at. %) counts would be 53.01 for this example. The composition of the matrix and precipitates that will be reported in this dissertation are an average of several interfaces for
accuracy. This method ensured that the composition of the ternary alloy added to 100%; in doing so our overall composition matched with the targeted process composition of the alloys.

Figure 2.1. An example of an indexed mass spectrum showing ZrH and Zr$^{2+}$.

**Inter-precipitate spacing measurements** – Using both the TEM and APT datasets, the inter-precipitate spacing was calculated using the method developed by Törrönen [4]. The inter-precipitate spacing can be obtained by using the following equation:

$$L_v = \alpha N_v^{-1/3},$$

The $\alpha$ is a unity constant and $N_v$ (number of precipitates per unit volume) is calculated by dividing the number of precipitates per unit area divided by the thickness of the TEM foil and the mean precipitate diameter. Since the particles can come in a range of shapes, we have adopted the following morphology guide from reference [4] to consistently measure the precipitates in the same manner, shown in Figure 1.10. More details can be obtained about the process from the above reference. This method was originally developed to calculate inter-precipitate spacing using 2D images; however, a concern with this method would be overlapping precipitates in the extrapolation of the findings to 3D. The addition of APT eliminates the need for this extrapolation. To validate the use of APT in this analysis, we applied and compared both methods for the forthcoming inter-precipitate spacing measurement results.
**Figure 2.2.** Morphology guide from ref [4] illustrating how to measure precipitates from various morphologies.
2.4 References


CHAPTER 3

INFLUENCE OF PRECIPITATE COMPOSITION, SIZE, AND SPACING ON THE MARTENSITIC TRANSFORMATION AND FUNCTIONAL BEHAVIOR OF A 50.3Ni-32.2Ti-17.5Zr (at.%) SHAPE MEMORY ALLOY

Suzanne Kornegay¹, Monica Kapoor¹, B.C. Hornbuckle¹, Othmane Benafan², Glen S. Bigelow², Ronald D. Noebe², Mark L. Weaver¹, and Gregory B. Thompson¹*

¹ The University of Alabama
Department of Metallurgical & Materials Engineering
Box 870202, Tuscaloosa, AL 35401-0202

² NASA Glenn Research Center
Materials and Structures Division
21000 Brookpark Road, Cleveland, OH 44135

*contact author: gthompson@eng.ua.edu

Abstract
Ternary addition of Zr to Ni-rich Nitinol have been shown to facilitate nanoscale precipitation that results in an increase and stabilization of the shape memory transformation temperatures over solid-solution conditions. In the present study, we investigated the relationship between precipitate evolution and the martensitic transformation temperatures and functional behavior of a 50.3Ni-32.2Ti-17.5Zr (at. %) alloy. No transformation (at least to -90°C) was observed in the solutionized condition. Upon aging at 550°C, the onset of a martensitic transformation (Ar) was noted at approximately -10°C after aging for 24 hours and increased to ~75°C after aging for 300
hours. The transformation temperature was found to be sensitive to the precipitate size, number
density, and inter-precipitate spacing. The precipitate phase was identified as the orthorhombic
H-phase via selected area electron diffraction. For selected aging conditions, the load-biased
shape memory behavior was determined under compressive and tensile loading through constant
stress thermal cycling. A small tension-compression asymmetry was noted with slightly larger
transformation strains achieved in tension than compression at constant stresses up to 400 MPa.
In addition, the superelastic behavior of the 4 and 72 hour aged samples was determine in
compression at $A_f + 20^\circ$C. The samples exhibited classical ‘flag-like’ behavior and minimal
residual strain when loaded to 1 GPa with the 4 hour aged sample exhibiting a lower critical
stress and a more defined unloading “plateau” than the 72 hours sample.

3.1 Introduction

NiTi alloys, commonly referred to as Nitinol, are the most common commercial shape
memory alloys. The shape memory effect is a phenomenon whereby a material undergoes a
reversible, crystal structure change when heated and cooled through a critical temperature range
between a martensitic and austenitic crystal structure. Below the martensite finish temperature
($M_f$) the material is fully martensitic (monoclinic or orthorhombic in structure) and deforms
predominately via reorientation and/or (de)twinning, whereas, above the austenite finish
temperature ($A_f$) the stable phase is a higher symmetry B2 cubic structure, commonly referred to
as austenite. Dependent on composition, the transformation temperatures for NiTi typically range
between -100$^\circ$C to 100$^\circ$C, with the Ni-rich compositions having the lower transformation
temperatures. Upon cycling through the transformation multiple times, the equi-atomic and Ti-
rich compositions typically retain strain after each cycle creating dimensional instability which can
contribute to low cycle fatigue failure [1]. These types of dimensional instability effects can be
reduced or eliminated through ‘training’ the alloy by thermomechanical cycling, which leads to a two-way shape memory effect, albeit requiring more processing time and cost. In contrast, the Ni-rich NiTi alloys exhibit superior dimensional stability during pseudoelastic stress cycling [2] and constant force thermal cycling [3],[4], requiring little or no ‘training’. The improved dimensional stability is attributed to the precipitation of Ni$_4$Ti$_3$ precipitates [3,4,6], which are absent in the equiatomic and Ti-rich compositions. However, the sub-room temperature transformation temperatures for the Ni-rich compositions have prevented them from becoming a viable system for high temperature solid-state actuators and similar devices.

One means of increasing the transformation temperature in both Ti- and Ni-rich NiTi alloys has been through the use of ternary macro-alloying additions of Pt [7], Pd [8], Hf [5,9], Zr [10], [11], or Au [12]. Such alloying has provided transformation temperature increases of more than a 150% while maintaining or improving basic shape memory and other functional properties [13]-[18]. These ternary additions have resulted in several, only recently characterized, precipitate phases [19], [20], [5], [21], which are largely considered responsible for the improved properties [22], [23].

For example, Hf in the Ni-rich 50.3Ni-29.7Ti-20Hf (at.%) alloy facilitates the precipitation of an orthorhombic 192 atom unit cell precipitate referred to as the ‘H-phase’ [5] (after its original report by Han et al. [24]). This alloy has a transformation temperature above 100°C while exhibiting excellent mechanical and functional stability [16], [25]. Yang et al. [5] reported the composition of this H-phase in the 50.3Ni-29.7Ti-20Hf alloy to be 50Ni-16.7Ti-33.3Hf (at. %). This has led investigators to suggest that these precipitates compositionally bias the shape memory alloy matrix through a depletion of Ni and
enrichment in Ti leading to increased transformation temperatures [26], [27]. Similar compositional bias concepts have been put forth for the Ni-Ti-Pt/Pd alloys [22, 28].

Besides compositional effects, the transformation temperature can be influenced by residual strain in the matrix. One source of such strain can be coherent precipitates, with the level of strain a function of misfit, precipitate size and inter-precipitate spacing and ultimately governed by the thermodynamic volume fraction of the second phase. In the limit, when the inter-precipitate spacing is smaller than or comparable to the critical martensite nuclei size, the martensitic transformation is suppressed even in the presence of a Ti-rich matrix [27].

The same type of H-phase precipitates found in the Ni-Ti-Hf alloys have also been reported in Ni-Ti-Zr alloys [21], which also exhibit significantly enhanced superelastic properties [29], [30] and shape memory behavior [17], [31]. The use of Zr over Hf offers several advantages including a 20% reduction in weight between a NiTi-20Hf vs. NiTi-20Zr alloy and a significant reduction in cost [31]. However, several subtle differences in the H-phase precipitation behavior between Zr- and Hf-containing alloys have been noted [21] and would need to be resolved before realizing the full commercial potential of either alloy. For instance, in equivalent compositions, H-phase precipitates coarsen in Zr-containing alloys faster than those in Hf-containing alloys [21]. This difference is likely attributed to different rates of diffusivity for the Zr and Hf in the matrix. This coarsening difference would influence the martensitic transformation temperatures of Ni-Ti-Hf and Ni-Ti-Zr alloys for equivalent aging conditions because the precipitate size and inter-precipitate spacing - and thus potential compositional and strain effects - would be different. While the Ni-Ti-Hf alloys have been investigated previously in some detail, in this study the compositional effects, precipitate size, and inter-precipitate spacing are evaluated and referenced to the martensitic transformation temperature.
for a new 50.3Ni-32.2Ti-17.5Zr (at. %) alloy along with evaluation of the functional and mechanical behavior of the alloy.

3.2 Experimental Procedure

The 50.3Ni-32.2Ti-17.5Zr (at.%), alloy was prepared by vacuum induction melting of relatively high purity elemental materials (99.98% Ni, 99.95% Ti, 99.5% Zr) using a graphite crucible and casting into a 25.4 mm diameter by 102 mm long copper mold. The resulting ingot was vacuum homogenized within the single B2 phase field at 1050°C for 72 hours. The alloy was then extruded at 900°C with an area reduction ratio of ~7:1. The extruded bar was then re-solutionized at 1050°C for 10 hours followed by a water quench, and sectioned into smaller pieces, which were aged at 550°C for various times followed by a water quench. During all solutionizing and aging treatments, the samples were wrapped in Ta foil and placed in a tube furnace under flowing Ar to reduce oxidation as much as possible.

The hardness for each sample was measured using a Buehler Vickers hardness tester under a load of 1000 g at a dwell time of 15 s. Each hardness data point represents the average from 12 separate measurements with one standard deviation reported. Differential scanning calorimetry (DSC) was performed in a TA Instruments Q200 calorimeter. Each sample was cycled in the instrument five times between -90°C to 300°C using a heating/cooling rate of 10 °C/min.

Transmission electron microscopy (TEM), performed in a 200 keV field emission FEI TECNAI (scanning) transmission electron microscope ((S)TEM), was used to view the microstructure and provide phase identification via selected area electron diffraction (SAD). The STEM is equipped with a High Angle Annular Dark Field (HAADF) detector that provides a semi-quantitative image of the microstructure where brightness scales with the atomic number as $Z^{-1.7}$.
TEM samples were prepared by cutting samples into 3 mm diameter discs that were < 100 µm in thickness followed by dimple polishing to < 15 µm using a diamond abrasive. The samples were subsequently Ar ion milled using the Precision Ion Polishing system (GATAN 691) to create an electron transparent area near the perforated hole.

A Cameca Local Electrode Atom Probe (LEAP) 3000XSi was employed to study the composition of the phases. The atom probe tomography (APT) samples were prepared using a FEI Quanta 200 3D Dual Beam electron-focus ion beam (FIB) microscope equipped with an Omniprobe micro-manipulation system. Details of the sample preparation process are provided in reference [32]. The extracted material was annular-milled into the required atom probe tip geometry using a 30 keV beam energy at beam currents between 0.3-0.5 nA. The final shaping of the tip was done using a 5 keV – 70 pA ‘clean up’ step to reduce the surface damage created from the Ga ion implantation at the higher energy settings. APT was performed at 40 K, 200 kHz pulse repetition rate, and 0.4 nJ pulse energy with a target evaporation rate of 0.5 atoms per pulse. The atom probe data was analyzed using the IVAS 3.6 software package and reconstructed using the procedures outlined by Hornbuckle et al. [33]

Using both the TEM and APT datasets, the inter-precipitate spacing was calculated using the method developed by Törrönen [34]. The inter-precipitate spacing can be obtained by using the following equation:

\[ L_v = \alpha (N_v)^{-1/3} \]  

(1)

where the \( \alpha \) is a unity constant and \( N_v \) (number of precipitates per unit volume) calculated by dividing the number of precipitates per unit area by the thickness of the TEM foil and the mean precipitate diameter. Törrönen [34] provided a variety of different shape geometries to calculate the mean precipitate diameter. As will be shown in this work, the precipitates were plate-like and
the corresponding appropriate geometric factor from Törrönen [34] was used. The readers are referred to [33] for more details on the analysis procedure.

Törrönen’s [34] method was originally developed to calculate inter-precipitate spacing using 2D TEM images from which the 3D information was acquired. However, an obvious concern with this method would be the potential for overlapping precipitates which would undercount the number density. The addition of APT in this study was used to validate the 2D to 3D extrapolation assumptions used in equation (1), as APT provides direct 3D inter-precipitate measurements. Both the 2D and direct 3D measurements for inter-precipitate spacing will be compared in the forthcoming sections.

Thermomechanical tension and compression testing was performed using an MTS 810 servo-hydraulic load frame equipped with a multi-channel TestStar™ IIIs controller. Heating and cooling was accomplished using a combination of a thermal chamber and induction heating. Temperature was controlled and measured using a GC-Controls digital controller and type-K thermocouples spot welded directly to the samples. Cylindrical dog-bone samples with a 5.08 mm diameter and 15.24 mm gage length were machined from the extruded rod and used for both tension and compression loading. The samples were initially subjected to two stress-free thermal cycles while mounted in the test frame to relieve any residual stresses resulting from the machining and sample handling. Constant-force thermal cycling experiments were performed in series at stresses ranging from 0 to ±400 MPa (series of increasing loads on the same sample). Two conditions (i.e., samples aged at 550°C for 4 and 100 hours) were tested between the lower and upper cycle temperatures of -50 and 180°C for the 4 hour aged sample and between 70 and 250°C for the 100 hour sample. Each sample was thermomechanically cycled twice at each stress level.
Pseudoelastic behavior was determined in compression using cylindrical samples measuring 10 mm in length and 5 mm in diameter. The pseudoelastic tests were performed by straining the sample at a constant rate of $1 \times 10^{-4}$ s$^{-1}$ to a set stress level followed by unloading. The samples with measurable transformation temperatures were tested at the austenite finish temperature $(A_F) + 20^\circ$C, as determined from the strain-temperature response at 0 MPa, (Figure 7). The samples were cyclic tested in compression starting at 1000 MPa up to 2500 MPa at increments of 500 MPa. At pre-selected stresses/strain values, the samples were cycled 5 to 10 times to measure stability.

3.3 Results and Discussion

Age hardening behavior

Figure 3.1 shows Vickers hardness as a function of aging time for the 50.3Ni-32.2Ti-17.5Zr alloy aged at 550°C. VHN (Vickers Hardness Number) is a minimum of $397 \pm 6$ for the solution-annealed condition and peaks at $566 \pm 7$ after aging for 4 hours at 550°C. Subsequent aging resulted in a decrease in VHN to $\sim 470 \pm 7$ after 300 hours. The plot confirms typical precipitation hardening behavior indicative of peak and over-aged conditions.
Figure 3.1. Evolution of Vickers hardness as a function of aging time for 50.3Ni-32.2Ti-17.5Zr (at. %) aged at 550°C.

**Effects of precipitation on transformation temperatures: strain versus chemical effects**

Figure 3.2 is a collection of DSC curves for the 50.3Ni-32.2Ti-17.5Zr alloy after aging for various times at 550°C. Several observations are readily apparent. First, the solution-annealed sample did not show evidence of any martensitic transformation peak over the temperature range scanned. After aging for 4 hours (the peak-aged condition for strength), a very modest peak in the DSC curves was noted on heating and is indicated by the arrow in Figure 3.2; the plot to the right is a magnified image of the reverse transformation. After aging for 24 hours, further evidence of the martensitic transformation can be seen during both heating and cooling. At 100 and 300 hours aging, a clearly distinct series of transformation peaks can be seen. An inset image to the right for the 300 hour aged condition clearly revealed a variation in the transformation temperature with cycling indicating an unstable response to thermal cycling. With increasing cycle count, the transformation peaks for the forward and reverse transformations slowly shifted to lower temperature values.
A second observation to note from the data in Figure 3.2 is that as the aging time increased, the transformation temperatures increased, with the austenite finish temperature ($A_f$), for example, increasing from ~58°C (after 24 hours of aging) to ~135°C (after 300 hours of aging). A summary of the start and finish transformation temperatures are included in Table 3.1. These transformation temperatures were determined from the second cycle DSC curves using the baseline tangent method.

**Table 3.1.** Approximate transformation temperatures for Ni-32.2Ti-17.5Zr after aging at 550°C for various times and the corresponding hardness values.

<table>
<thead>
<tr>
<th>Aging time (Hrs)</th>
<th>Transformation Temperatures (°C)</th>
<th>Hardness (VHN)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_s$</td>
<td>$A_f$</td>
</tr>
<tr>
<td>SA</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>~15</td>
<td>~-10</td>
</tr>
<tr>
<td>24</td>
<td>~0</td>
<td>~58</td>
</tr>
<tr>
<td>100</td>
<td>~20</td>
<td>~115</td>
</tr>
<tr>
<td>300</td>
<td>~58</td>
<td>~135</td>
</tr>
</tbody>
</table>
Figure 3.3 shows a series of TEM bright field (BF) images, STEM-HAADF images, and selected area diffraction (SAD) patterns for samples aged at various times at 550°C. Figure 3.3(a) is a TEM BF image of the solution annealed sample clearly revealing an absence of precipitation within the microstructure, which is more conclusively demonstrated with the corresponding [100]_{B2} SAD pattern with only the primary reflections of the B2 austenite phase observed. Figure 3.3(b) is a BF image of the 4 hour (peak-aged) sample revealing nano-scale, plate-like precipitates that are ~15 nm in length and ~5 nm in width (indicated by the arrows in the image). Details of the precipitate sizes are summarized in Table 3.2.

Table 3.2. Size and inter-precipitate spacing of the H-phase precipitates in the 50.3Ni-32.2Ti-17.5Zr alloy aged at 550°C, as measured from TEM images. The uncertainty in the size and inter-precipitate spacing measurements represent one standard deviation of the distribution.

<table>
<thead>
<tr>
<th>Aging time (Hrs)</th>
<th>Size (nm)</th>
<th>Inter-precipitate Spacing (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Length</td>
<td>Width</td>
</tr>
<tr>
<td>4</td>
<td>15 ± 4.1</td>
<td>5 ± 1.4</td>
</tr>
<tr>
<td>72</td>
<td>40 ± 3.3</td>
<td>15 ± 1.8</td>
</tr>
<tr>
<td>100</td>
<td>65 ± 5.4</td>
<td>18 ± 2.3</td>
</tr>
</tbody>
</table>

The identification of the precipitate phase was confirmed by the diffraction pattern of the 4 hour aged sample, Figure 3.3(b), taken from the [110]_{B2} zone axis with the primary reflections indexed to the B2 matrix phase and secondary reflections indexed to the H-phase [21]. These secondary reflections are highlighted by the arrowheads in the diffraction pattern. The STEM-HAADF image of the 72 hours aged sample, Figure 3.3(c), revealed that these precipitates were enriched in Zr compared to the matrix, evident by their bright contrast, and coarsened to ~40 nm in length and ~15 nm in width (Table 3.2). The SAD patterns for the 72 hour sample taken along
[100]_{\text{B2}}, [110]_{\text{B2}}, and [111]_{\text{B2}} zone axes are shown in Figure 3.3(d). In the [100] zone axis, the primary reflections are consistent with B2 matrix phase with two sets of secondary reflections (1/3<110> and 1/4<210>), indicated by white arrowheads, consistent with the two variants of H-phase precipitates that are associated with either the vertical or horizontal growth morphology in the matrix, which are clearly evident in the STEM-HAADF image in Figure 3.3(c). Further confirmation of the H-phase can be observed from the additional 1/3<110> secondary reflections in the [110]_{\text{B2}} zone axis, with these reflections also indicated by the white arrowheads in Figure 3.3(d) [21].

Figure 3.3(a-d). A series of TEM bright field (BF), STEM-HAADF, and selected area diffraction (SAD) patterns for (a) solution annealed material and samples aged for (b) 4 hours, and (c-d) 72 hours at 550°C.

With the onset of H-phase precipitation, the alloy follows a classical age hardening behavior as shown in Figure 3.1, with an initially increasing hardness with aging time followed by a peak hardness and over-aging conditions. However, the peak age condition did
not correspond with the highest martensitic transformation temperature, Figure 3.2, for this alloy. The martensitic transformation temperatures continued to increase with over-aging, suggesting that a particular precipitate size, number density, and inter-precipitate spacing also contributed to regulating the shape memory transformation in conjunction with a compositional effect that would accompany the precipitation.

This chemical effect occurs as the Ni-Ti-Zr elements partition between the matrix and new precipitate phase. Figure 3.4(a) is the atom probe reconstructed image, with the precipitates delineated with a 13.66 at.% Zr isoconcentration surface. These precipitates revealed the H-phase morphology consistent with their shape and orientation with respect to each other as observed in the TEM images of Figure 3.3. Figure 3.4(b) is the corresponding proximity histogram (or proxigram) of the H-phase precipitates from the atom probe reconstruction. A proxigram is a 3D average composition profile of the precipitates as a function of the distance from an interface [39]. The matrix and precipitate compositions of this 100 hour aged sample as well as those APT data sets for the 4 and 72 hour aged alloys are tabulated in Table 3.3. (Atom probe tomography was also done for the solution annealed condition, and consistent with the diffraction patterns, a solid solution (no precipitation) phase was found.)
Figure 3.4. (a) 3D reconstructed atom map of the H-phase precipitates delineated with a 13.66 at. % Zr isoconcentration surface, and (b) corresponding proximity histogram of the H-phase precipitates. The alloy 50.3Ni-32.2Ti-17.5Zr was aged for 100 hrs at 550°C.

Table 3.3. Average composition (at. %) of the H-phase precipitates in the 50.3Ni-32.2Ti-17.5Zr alloy aged at 550°C as measured by atom probe tomography with the proxigram concentration profile method [39]. The uncertainty in composition for each concentration was indicated as standard deviation in the data.

<table>
<thead>
<tr>
<th>Aging time (hrs)</th>
<th>Matrix</th>
<th>Precipitate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Ti</td>
</tr>
<tr>
<td>4</td>
<td>53.50 ± 0.10</td>
<td>36.20 ± 0.13</td>
</tr>
<tr>
<td>72</td>
<td>53.10 ± 0.38</td>
<td>35.10 ± 0.57</td>
</tr>
<tr>
<td>100</td>
<td>51.10 ± 0.04</td>
<td>34.00 ± 0.02</td>
</tr>
</tbody>
</table>

In the time of flight mass spectrum from the atom probe data sets, ZrH+ and ZrH++ were noted and would be consistent with zirconium’s high affinity for hydrogen [40]. By including the zirconium present in these hydrides, the bulk composition was found to be consistent with the nominal composition of the alloy, when the hydrogen was not included. The hydrogen
content was typically < 2 at.% for all the APT data sets. The proxigram of Figure 3.4(b) revealed significant partitioning of Zr to the precipitate phase which was consistent with the STEM-HAADF images in Figure 3.3. The proxigram also showed that Ni was slightly enriched in the precipitate (57.10 at. %) relative to the matrix (51.10 at. %), consistent with prior atom probe analysis of the Hf-based H-phase in Ni-Ti-Hf SMAs [26]. Such changes in the Ni content in the matrix would contribute to the increase in the transformation temperature the prescribed chemical effect. In Table 3, one can see that the 300 hour aged condition, which had the highest transformation temperature, also had the lowest Ni content in the matrix as compared to the other aged alloys.

Interestingly, the Ni content in the matrix appeared relatively similar between the 4 and 72 hour aged conditions in Table 3.3. This provides insights of a competing factor in regulating the transformation temperature, as the transformation temperature increases with aging time, Figure 3.2. This apparent contradiction where the transformation temperature increases but the Ni content in the matrix is relatively invariant can be explained by considering the mechanical effect created by overlapping strain fields from the precipitates as proposed by Evirgen [27]. In this work, Evirgen described that when the inter-precipitate spacing was smaller or comparable to the critical martensite nuclei size, the martensitic transformation was suppressed. Hence, if the precipitates are too close together, even if a favorable chemical effect is present, the transformation temperature can be suppressed. The concept of overlapping strain fields then explicitly implies the existence of a strained coherent or semi-coherent interface between the precipitates and matrix. Such a condition can be inferred from the morphology of these precipitates based on their acicular shape. The orientation relationship (OR) of the H-phase and B2 matrix has previously been reported by Han et al. [24] to be [100]_{H\text{-phase}} \parallel [001]_{h2},
[010]_H-phase || [110]_H-phase, and [001]_H-phase || [-110]_H-phase with three directions defined because of the orthorhombic structure of the H-phase. Based on the H-phase and B2 lattice parameters reported by Han et al., the misfit strain along the two [110]_B2 would be approximately ≈ 0% strain whereas the [100]_H-phase || [001]_B2 would yield ≈ 4% strain.

Table 3.4 contains the precipitate number density, determined by APT, for the various aging conditions. As the aging time increased, the precipitate number density decreased, which corresponded to an increase in the inter-precipitate spacing, Table 3.2. When precipitation starts, the number density of the precipitates is high and inter-precipitate spacing small. This small inter-precipitate spacing will result in large regions of overlapping strain fields in the matrix [17], schematically shown in Figure 3.4. These overlapping strain regions will pin the martensite requiring a larger driving force for its phase transformation, even though the alloy has a favorable chemical effect for increasing the transformation temperature. The low heat flow response in the DSC curves of Figure 3.2 are proportional to the amount of transformable martensite, and one can glean on a small proration of the 4 hour aged condition is able to transform evident by its very modest DSC peak. Upon further aging, where the precipitates have now coarsened and the inter-precipitate spacing increased, Figure 3.3 and Table 3.2, the extent of overlapping strain fields will be reduced as schematically shown in Figure 3.4. Consequently, the previously pinned martensite is now able to readily transform. This is manifested as distinct and more apparent transformation peak in the DSC scan. By increasing the size of transformable region, which is the unpinned region, the necessary driving force for transformation temperature is reduced and a corresponding increase in the martensitic transformation temperature is observed where the chemical effects on transformation are now able to be observed. Hence even though the Ni content in the matrix is relatively similar between
4 and 72 hours (Table 3.3), the further increase in the inter-precipitate spacing, Table 3.2, enabled the transformation temperature to increase as shown in Figure 3.2.

**Table 3.4.** Number density of the H-phase precipitates in 50.3Ni-32.2Ti-17.5Zr aged at 550°C as measured by atom probe tomography. The error in number density is based on counting statistics.

<table>
<thead>
<tr>
<th>Aging time (hrs)</th>
<th>Number Density ($\times 10^{24}/m^3$)</th>
<th>Error ($\times 10^{22}/m^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>2.21</td>
<td>0.22</td>
</tr>
<tr>
<td>48</td>
<td>1.62</td>
<td>0.18</td>
</tr>
<tr>
<td>72</td>
<td>0.15</td>
<td>8.46</td>
</tr>
<tr>
<td>100</td>
<td>0.14</td>
<td>6.48</td>
</tr>
</tbody>
</table>

To quantify the unpinned martensite between the precipitates, we have adapted the procedure given by Tirry *et al.*[36]. In their study, the calculated strains were measured from the [101]$_{\text{B2}}$ direction along the edge of a Ni$_4$Ti$_3$ oblate precipitate where the maximum strain was found to be at a distance of ~15 nm from the precipitate/matrix interface. Though the original report was for a binary Nitinol system and this is a ternary based Nitinol alloy, both the Ni$_4$Ti$_3$ and H-phase precipitates share a similar acicular morphology within the matrix where trends in similar behavior can be gleaned. For example, it is reasonable to assume than the maximum martensitic pinning will coincide with regions where maximum strain occurs. Based on Tirry *et al.*’s [36] results, a 50% or greater maximum strain would span a region between 5 to 25 nm from the precipitate/matrix interface. Hence, if two precipitates are more than 50 nm apart (or, alternatively, 25 nm from each precipitate/matrix interface), the martensite would not be pinned and the transformation will occur more readily at a higher temperature. For the 100 hour aged sample,
which demonstrated one of the higher martensitic transformation temperatures, the inter-precipitate spacing is ~43 nm, Table 3.2. This value is very near the assumed unpinned spacing, based upon the previous argument. Conversely, the peaked aged sample had a near absence of a transformation peak, Figure 3.2, suggesting that the inter-precipitate spacing of ~12 nm, Table 3.2, was well within the overlapping strain fields. As already discussed above, once these strain fields are no longer overlapping, the chemical effect created by the partitioning of the elements between the shape memory matrix and precipitate become significant and the increase in the transformation temperature can be observed [17], [37], [38]. This interconnection between the transformation temperature, inter-precipitation spacing, and chemical partitioning is plotted in 3.6 where one can ascertain how both the mechanical and chemical effects compete with each other in regulating the transformation temperature.

![Figure 3.5](image)

**Figure 3.5.** A 3D plot correlating the relationship between transformation temperature, inter-precipitate spacing, and Ni-content in the matrix for various aging times.
Shape memory and superelastic behavior

With the microstructure characterized, certain aging conditions were chosen for detailed functional and mechanical testing. Figure 3.7 shows a series of constant-force thermal cycling tests under compressive (a-b) and tensile (c-d) loading for the 4 hours (a,c) and 100 hours (b,d) aged conditions, with the second thermal cycle at each constant stress level (up to 400 MPa) displayed in the figure. For each stress level, a notable change in the transformation strain response was noted. As each alloy is subjected to a greater stress, an increase in the strain response was found indicating that the external load assisted in the transformation by aligning more of the martensitic variants with increasing stress, over the range of stresses investigated.

**Figure 3.6.** A series of constant-load thermal cycling test results for the Ni-32.Ti-17.5Zr alloy under (a-b) compressive and (c-d) tensile loading for the (a,c) 4 hour and (b,d) 100 hour aged conditions.
For an actuator application, a narrow hysteresis would be preferred in order to increase the cycling rate. Here, the hysteresis is defined as the difference between the austenite finish (A_f) and martensite start (M_s) transformation temperatures. In general, the 100 hour alloy aged condition resulted in a relatively stable response with little or no residual strain during each cycle, and we noted that this alloy was not subjected to the added benefit of any significant training under these testing conditions. However, since the stress levels were applied in series, the initial 100 MPa stress may have served as a training cycle which assisted in the decrease of the residual strain. A comparative plot of the actuation and residual strain taken under compression and tension from Figure 3.7 are plotted in Figure 3.8.

The minimal strain response in this alloy is likely related to the martensite variant interfaces with the precipitates [17,30,31,38,41]. It has now become widely recognized that small precipitates, especially in Ni-rich NiTiZr and NiTiHf alloys (as cited above) are easily absorbed by the martensite variants allowing the martensite to form large lathe structures along preferred directions that minimize energy in the sample and maximize the transformation strain. The martensite variants in samples with larger precipitates are generally observed to form between the larger precipitates in less ideal orientation because of the physical constraint imposed by the precipitates.
Finally, since the stress levels were applied in series, the initial 100 MPa stress served may have served as a training cycle, which resulted in a decrease of the residual strains during successive cycling. Figure 3.8(b) showed that for the 100 hour aged sample at 100 MPa in compression and tension, a sharp increase in residual strain occurred; however, with increasing applied stress to 400 MPa, the amount of residual strain was lower and nearly constant.

Finally, the pseudoelastic response of the Ni-32.2Ti-17.5Zr alloy after aging at 72 hours was determined. In general, the pseudoelastic response of a shape memory alloy can take two generally accepted forms – (1) A conventionally recognized “flag-like” pseudoelastic response, where the upper stress plateau region corresponds to the austenite-to-martensite reverse transformation and the unloading portion of the plateau represents the forward transformation. At lower stresses, the deformation is dictated by the elastic response of the austenite phase. (2) The other form, referred to as “linear” pseudoelasticity, occurs in which there is no apparent stress plateau but large deformations of several percent are induced on loading with little hysteresis and near perfect
recovery upon unloading. Of these two responses, linear pseudoelasticity can be developed through training or significant cold work while flag-like pseudoelasticity is generally considered an inherent property of a shape memory material.

Figure 3.9(a) is the load-biased strain-temperature response at 0 MPa showing how the Af temperatures were chosen for the isothermal testing at 72 hours. Figure 3.9 (b) is the isothermal mechanical testing curve for the 72 hour aged condition, respectively, loaded to the stress level of 1000 MPa. The 72 hour aged alloy was tested at 90°C and 140°C (Af + 20°C, where Af was obtained from the strain-temperature response at 0 MPa). With the sample tested up to 1000 MPa, the residual strains were still small, with 0.027% residual strain after seeing 1.655% strain at 1000 MPa. At stresses higher than 1000 MPa, the alloy began to accumulate residual strain. At 2000 MPa, 5.797% strain was measured with 1.936% residual after the first cycle and 2.517% residual after the 5th cycle.

(A) (B)

Figure 3.8(a-b). (a) Load-biased at 0 MPa (strain-temperature response) showing the Af temperatures and how the Af + 20°C were chosen. (b) Isothermal stress-strain behavior including the unloading response for sample 72 hours to investigate the superelastic behavior of that alloy at Af + 20°C.
3.4 Conclusions

In this study, the addition of Zr and its effect on precipitation and in turn how precipitation affects the dominant mechanisms controlling the martensitic transformation were explored and yielded the following conclusions:

(1) Upon aging at 550°C for various times, the 50.3Ni-32.2Ti-17.5Zr (at.%) alloy exhibited classical age hardening behavior, with peak hardness at 566 VHN at 4 hours. Electron diffraction confirmed the precipitates to be the H-phase.

(2) In the solution annealed condition, no notable transformation peak was observed over the DSC scan range of -90 to 300°C. M_s was approximately -10°C after aging for 24 hours and increased to ~75°C after aging for 300 hours. The increase in the transformation temperature was explained by the coarsening behavior of the H-phase precipitates. The transformation at early aging times (4-72 hours) was dominated by the strain fields induced by the precipitate phase, which reduced the driving force for transformation. Over this range of aging times, the composition of the matrix was little changed and the increase in transformation temperature was attributed predominantly to coarsening of the precipitate phase and relaxation of the internal strains. At aging times greater than 72 hours the Ni content of the matrix decreased significantly and the precipitates were relatively coarse leading to a more dramatic increase in transformation temperatures.

(3) APT was used to quantify the composition of the matrix and precipitate phases. The results revealed the contribution of compositional effects to the increasing transformation temperature. As the precipitates coarsened, the matrix phase became
increasingly Ti-enriched, especially for aging times beyond 72 hours, becoming a dominant effect on transformation temperatures, especially given the coarse microstructure and relaxation of internal strains with coarsening.

(4) When thermally cycled under constant load in compression and tension, the 100 hour aged alloy exhibited good dimensional stability under repeated thermal cycling at various loads. It also exhibited the classical ‘flag-like’ pseudoelastic response.
3.5 References


CHAPTER 4
INFLUENCE OF DILUTE ZIRCONIUM AND HAFNIUM TERNARY ADDITIONS ON PRECIPITATION SHAPE MEMORY PROPERTIES IN 50.3Ni-48.7Ti-1 Zr or Hf (at.%)
Upon precipitation of these phases, a symmetric R-phase transformation pathway was observed. Similarly, the solutionized and water quenched 50.3Ni-48.7Ti-1Hf alloy formed the B2 solid solution phase. However, upon aging, metastable Ni$_4$Ti$_3$ precipitates were observed and exhibited a single shape memory transformation temperature. At 48 hours of aging, the Ni$_4$Ti$_3$ precipitates were absent and the S- and H-phase were found to be in the microstructures whereupon an asymmetric R-phase transformation pathway was observed. The links of microstructure – precipitate size, composition, and volume fraction – on the transformation pathways as well as the load bias mechanical testing in tensile and compression (up to 400 MPa) are discussed.

4.1 Introduction

The shape memory effect is a phenomenon whereby a material undergoes a reversible phase change when heated and cooled through a transformation cycle. This transformation is reversible and the original shape, even against an opposing load, can be recovered. The shape memory effect in NiTi-based alloys was discovered in the 1960s and since has been commonly referred to as Nitinol. Since its discovery, this type of alloy has been used in various engineering applications such as cardiovascular stents, braces, and eyeglasses [1]. In addition, shape memory alloys (SMAs) are ideal for solid-state actuators offering similar or superior energy densities (per volume/weight) when compared to conventional actuators [1]–[3]. In addition, the total part count for a shape memory actuator is less than a conventional actuator design thereby reducing design complexity and maintenance requirements [4], [5]. Consequently, the aerospace industry has been keen on their potential use in aircrafts. In addition, SMAs are also being considered for applications in small motors and fasteners in automobiles as well as safety valve actuators for down-hole oil and gas drilling [1]–[3],[6], [7].
While SMAs are anticipated for many actuator applications, there are several aspects of their metallurgy that are unknown or not fully resolved leading to a delay in integration. Some of these limitations are low transformation temperature, generally between -100°C to 100°C, or dimensional instabilities that results from multiple cycling through the phase transformation. In terms of the former concern, prior work in the binary NiTi system showed that Ni-rich compositions exhibit transformation temperatures that are well below room temperature. However, these Ni-rich Nitinol alloys exhibit superior dimensional stability as compared to their equiatomic and Ti-rich NiTi counterparts during pseudoelastic and constant force thermal cycling [8]. Dimensional stability refers to the alloy retaining minimal to no strain upon repeated thermal cycling through the transformation temperature under load. Though we do note that these Ni-rich Nitinol alloys are subject to long term durability and fatigue behavior concerns.

The functional mechanical properties in these Ni-rich Nitinol alloys are attributed to the precipitation of a Ni₄Ti₃ phases which are absent in the equiatomic and Ti-rich NiTi alloys [9]. Additionally, the R-phase can form and contribute to variations in the functional mechanical properties. The Ni₄Ti₃ phase has a R3 space group symmetry with a lenticular shaped precipitate morphology whereas the R-phase is a tetragonal B33 structure that alters the transformation pathway between the martensite and austenite phases as will be further discussed below. The Ni₄Ti₃ precipitates are metastable and generally decompose to a Ni₃Ti₂ then to the thermodynamically stable Ni₃Ti phase dependent upon heat treatment [1]. In contrast, the R-phase is a lower energy transformation phase that forms between the martensite and austenite phases over a finite temperature range.

With the formation of Ni₄Ti₃ precipitates, they can provide both a compositional and strain effect upon regulating the transformation temperature. The Ni-rich precipitates deplete the matrix
of Ni which then compositionally biases the transforming matrix phase to become more Ni-lean. Consequently, the transformation increases because of this compositional effect. In addition, the inter-precipitate spacing yields various strain fields which influence the critical martensitic nuclei size needed for the transformation [10]. However, after long term aging, these precipitates become more widely spaced and this strain effect becomes less significant.

The shape memory transformation pathway between the lower symmetry martensitic phase and a higher symmetry austenitic B2 phase occurs predominately via (de)twinning mechanisms [11]. As revealed by Otsuka [12], Nitinol based alloys offer three possible martensite candidates: the B33 (or commonly referred to as the R-phase), B19, and B19’. The transformation path will be determined by which of these three phases is the most stable. The different transformation paths to these martensite candidates are then further divided into three cases which can be reviewed in reference [12]. For this work, two of the three cases will be briefly reviewed as they will be relevant to the forthcoming results and discussion. The third case, which encompasses the B19 structure, was not observed in this work and is not discussed but has been observed in NiTi alloyed with Cu [12].

In the first case, the monoclinic B19’ phase is the most stable; therefore, the other martensite phases do not appear below the B2 to B19’ transformation temperature. Since the transformation path is for a single phase or step (B2 to B19’), a single transformation peak is measured in a differential scanning calorimetry (DSC) scan, where exothermic and endothermic heat associated with the phase transformation are measured as a function of temperature. However, if there is a temperature at which the R-phase is thermodynamically favored over B19’, the R-phase will initially form. The B2 parent phase then transforms into the R-phase (Step 1) followed by a subsequent lower temperature transformation from the R-phase to B19’ (Step 2) with
continual cooling. These two different martensitic phases yield two transformation peaks during the thermal cycle in the DSC.

Recent studies on the use of ternary macro-alloying of Nitinol with either Pt[13], Pd[14] Hf[15] Zr[16], [17] or Au[18] has also shown significant increases in the transformation temperature for the Ni-rich compositions [1], [10], [19]–[22], with the majority of the transformations being a single step pathway. For example, in a Hf-containing 50.3Ni-29.7Ti-20Hf (at.%) alloy, the transformation temperature was a single step above 100°C [23]. Upon aging, and subsequent precipitation of a 192 atom orthorhombic unit cell referred to as the “H-phase” after its original report by Han et al. [24], the increase in transformation temperature and functional mechanical properties became more tunable and stable over repeated thermal cycles and loads. These H-phase precipitates are oblate spindle-like in morphology in the Nitinol matrix. Yang et al. [9] reported the composition of this H-phase in this alloy to be 50Ni-16.7Ti-33.3Hf (at. %). The depletion of Ni from the matrix to this precipitate leads to a compositional effect which is believed to help stabilize the shape memory properties. More recently, Santamarta et al. [26] completed a complementary study to the Hf alloys by studying various Zr additions between 15 to 20 at.% to an equivalent Ni-rich NiTi alloy. In their study, the H-phase precipitates were also observed with these H-phase precipitates found to significantly enhance both the superelastic and shape memory properties.

To date, most of the ternary addition research has focused on macro-alloy amounts (>15 at.%) with very little to no work for dilute Zr or Hf in Nitinol alloy. This could be contributed to an assumption that these elements would likely site substitute for the Ti sublattice as all three elements are from the group IVB transition metals. Nevertheless, for very Ni-rich NiTi (54 at.%), with Hf additions of 1 to 4 at. %, the H-phase has been found [27] suggesting the possibility of its
presence at much lower concentrations. Furthermore, even if these ternary elements are found to be in solution, the localized strain field created by any sublattice site substitution would likely effect shape memory transformation properties. This work aims at beginning to bridge these phase and shape memory property gaps by experimentally investigating the effect of 1 at. % Zr or Hf in a 50.3Ni-48.7Ti-1Zr or Hf alloy.

4.2 Experimental Procedure

Both 50.3Ni-48.7Ti-1Zr (at.%) and 50.3Ni-48.7Ti-1Hf (at. %) alloys were prepared by vacuum induction melting of high purity elements (99.98% Ni; 99.8% Zr/Hf; 99.95% Ti) in a graphite crucible with argon atmosphere. The ingots were vacuum homogenized for 72 hours at 1050°C and furnace cooled. They were then hot extruded at 900°C with an area reduction ratio of 7:1 (Ext. 135 and 125). The extruded bars were then re-solution annealed at 1050°C for 10 hours then water quenched in preparation for the aging treatments. The rods were sectioned into smaller pieces then aged at 400°C for various times after which they were water quenched. In all solutionizing and aging treatments, the samples were wrapped in Ta foil with flowing argon over the sample while in the tube furnace to eliminate possible oxidation.

The hardness for each aged sample was measured using a Buehler Vickers hardness tester under a load of 1000g with a dwell time of 15 s. Each hardness data point represents the average from 12 separate measurements, with the standard deviation for each reported. Differential scanning calorimetry (DSC) was performed in a TA Instruments Q200 where the temperature was cycled five times between the temperature ranges of -90°C to 300°C.

Transmission electron microscopy (TEM) was performed in a 200 keV field emission FEI TECNAI (scanning) transmission electron microscope. This instrument was used to view the
microstructure and provide phase identification by selected area diffraction (SAD). The TEM samples were prepared by cutting the samples into 3 mm diameter discs that were < 100 µm in thickness followed by dimple polishing to < 15 µm using a diamond abrasive. The samples were then Ar ion milled using the Precision Ion Polishing system (GATAN 691) to create an electron transparent area near the perforated hole.

Atom probe tomography (APT) was also employed to study the composition of the phases and was conducted in a Cameca Local Electrode Atom Probe (LEAP) 3000XSi and 5000XS. The atom probe samples were prepared using a FEI Quanta 200 3D Dual Beam electron-focus ion beam (FIB) microscope equipped with an Omniprobe micro-manipulation system with details of the preparation process outlined in reference [28]. The extracted material was annular-milled into the required atom probe tip geometry using a 30 keV beam energy at beam currents between 0.3-0.5 nA. The final shaping of the tip was done using a 5 keV – 70 pA as a ‘clean up’ step to reduce the surface damage created from the Ga ion implantation at the higher energy settings. For the LEAP 3000XSi, APT was performed at 40 K, 200 kHz pulse repetition rate, and 0.4 nJ pulse energy with a target evaporation of 0.5 per pulse whereas the LEAP 5000XS APT was performed at 40K, 100kHz, and 100-200 pJ pulse energy with a target evaporation of 1 per pulse. The atom probe data was analyzed using the IVAS 3.6 software package and reconstructed using the procedures outline by Hornbuckle et al. [29]. Since Zr and Ti have a high affinity for hydrogen, we did note the presence of elemental hydrogen and hydride complexes in the atom probe mass spectrum, which typically accounted for < 2% of the total composition. This hydrogen is either a processing artifact incorporated in the making of the alloy or a vacuum contaminate gas in the LEAP chamber. In the analysis, we have removed the elemental hydrogen from our composition and have included the metallic species of the hydride to the overall composition from which we
normalized to the three constituent elements. This ensured that the composition of the ternary alloy added to 100%; in doing so our overall composition matched with the targeted process composition of the alloys.

Thermomechanical tension and compression testing was performed at Glenn Research Center (GRC) on both alloys after various aging conditions. Testing was completed using an MTS 810 servo-hydraulic load frame equipped with a multi-channel TestStar™ IIIs controller. Heating and cooling during testing was generated using a combination of a thermal chamber and induction heating elements. The temperature was controlled and measured using a GC-Controls digital controller and type-K thermocouples spot welded directly to the samples. Cylindrical dog-bone samples were machined from the extruded rod and measured 5.08 mm in diameter and 15.24 in gage length. The samples were subjected to two stress-free cycles while mounted in the test frame to relieve any residual stresses resulting from the machine and sample handling. Constant-force thermal cycling experiments were conducted in series at stress levels ranging from 0 to ±400 MPa.

4.3 Results and Discussion

Age hardening behavior

The Vickers hardness number (VHN) as a function of aging time for the 50.3Ni-48.7Ti-1Zr and 50.3Ni-48.7Ti-1Hf alloys aged at 400°C are shown in Figure 4.1(a) and (b). In Figure 4.1(a), the plot revealed that the VHN for the solution annealed condition was 251 ± 3 and eventually achieving a peak hardness of 298 ± 4 after 10 hours. Subsequent aging times resulted in a decrease in the VHN to 289 ± 6 at 100 hours. In comparison the solution annealed condition for the Hf sample, Figure 4.1(b), had a VHN of 233 ±2 with a peak hardness of 299 ± 9 after 24 hours. As with the Zr alloy, further aging resulted in a decrease in the hardness to a VHN of 279 ± 6 after 100 hours. Though the peak hardness values are similar between the two samples, Zr was
able to achieve this value in approximately one-half the time. This more rapid increase in precipitation hardening is contributed to Zr being a faster diffusing species than Hf in the Nitinol alloy [26].

**Figure 4.1(a-b).** Evolution of Vickers hardness as a function of aging time at 400°C for (a) 50.3Ni-48.7Ti-1Zr (at. %) alloy, and (b) 50.3Ni-48.7Ti-1Hf.

**DSC measured transformations**

Figure 4.2 are the corresponding DSC curves for the alloys at specific aging treatments. In Figure 4.2(a), which is the 50.3Ni-48.7Ti-1Zr alloy, the solution annealed condition contained one peak upon heating and one peak upon cooling for each of the thermal cycles, though the onset and finishing temperatures varied slightly for each thermal cycle. This is most evident on the cool down transformation where the transformation temperature decreased with each repetitive cycle.
Figure 4.2. DSC curves of (a) 50.3Ni-48.7Ti-1Zr (at. %) and (b) 50.3Ni-48.7Ti-1Hf (at. %) alloys aged at 400°C for various times.

The single exothermic heat flow peak is indicative of the B2 - B19' transformation. After aging for 10 hours and 24 hours, two peaks, rather than a single peak, are now present upon the heating and cooling cycles in Figure 4.2(a). In addition, the variation in start and finishing temperatures, particularly for the cool down cycle, are no longer present indicating a temperature stability for this transformation. Comparing these results with Figure 4.1, the onset of precipitation appears to have altered the phase transformation route as well as stabilize the onset of the transformation for repeated thermal cycling. This two-stage transformation noted for these aged alloys is indicative of a symmetric R-phase transformation as described in the introduction [11]. Upon further aging up to 100 hours, this two-stage transformation was retained; however, upon the cooling down portion of the DSC curve, the austenite to R-phase and R-phase to B19' transformation temperature transitions are further separated from each other than the lower aging time conditions. Table 4.1 summarizes the transformation temperatures for each of these conditions.
Table 4.1. Measured transformation temperatures for a 50.3Ni-48.7Ti-1Zr (at.%) alloy at various aging times on the last (5th) cycle.

<table>
<thead>
<tr>
<th>Aging Time (Hours)</th>
<th>Heating Cycle Temperatures (°C)</th>
<th>Cooling Cycle Temperatures (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Start</td>
<td>Finish</td>
</tr>
<tr>
<td>SA</td>
<td>-24</td>
<td>6</td>
</tr>
<tr>
<td>10 hrs</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>24 hrs</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100 hrs</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

In Figure 4.2(b), the DSC curves are shown for the 50.3Ni-48.7Ti-1Hf alloy. The solution annealed alloy, similar to the 1 at. % Zr alloy, revealed one transformation peak indicating the one-step transformation path of B2 - B19’. This transformation peak also showed signs of instability similar to what was observed in the Zr alloy. After aging 24 hours, one broad transformation peak, which was low in intensity, was present (unlike the 1 at. % Zr alloy which had a two-stage transformation). The broad nature of this peak is suggestive that an increased change in temperature is required in order for the transformation to propagate [10]. Further aging to 48 to 120 hours, reveals a clear onset of an asymmetric R-phase transformation is observed, with a two-stage transformation (two peaks – B2 to R and then R to B19’) noted upon cooling and a single transformation (one peak – B19’ to B2) upon heating in the DSC curve. Table 4.2 summarizes the transformation temperatures for each of these conditions. It is worth to note that prior reports of higher Hf concentrations for equivalent Ni Nitinol concentrations, i.e. 50.3Ni, did not show this type of symmetric or asymmetric R-phase transformations [30]. Rather they revealed a single stage transformation. Thus, the dilute additions of Zr or Hf appear to retain the R-phase type transformations noted in the Ni-rich Nitinol binary alloys. The differences in the R-phase pathway
between the two ternary alloys – symmetric vs. asymmetric - suggest a difference in the kinetic barriers to form the R-phase between the two alloys [11].

**Table 4.2.** Measured transformation temperatures for a 50.3Ni-48.7Ti-1Hf (at.%) alloy at various aging times on the last (5th) cycle.

<table>
<thead>
<tr>
<th>Aging Time (Hours)</th>
<th>Heating Cycle Temperatures (°C)</th>
<th>Cooling Cycle Temperatures (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA</td>
<td>-47</td>
<td>-13</td>
</tr>
<tr>
<td>24 hrs</td>
<td>8</td>
<td>50</td>
</tr>
<tr>
<td>48 hrs</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>120 hrs</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**TEM and electron diffraction for the 50.3Ni-48.7Ti-1Zr**

The TEM bright field (BF) and selected area diffraction (SAD) patterns for the 1 at. % Zr alloy are shown in Figure 4.3. The SAD patterns were taken along the [100]$_{B2}$ and [111]$_{B2}$ zone axes for the solution annealed, 10 hours, 24 hours, and 100 hours aging conditions. In the solution annealed condition, the SAD patterns were consistently indexed to the austenite B2 structure with no evident secondary reflections from precipitates, which is in agreement with the bright field image (no precipitates observe). After 10 hours aging, the SAD patterns revealed secondary reflections present in the [111] zone axis. These secondary reflections were indexed to the R-phase [27] and would be consistent with the two-stage transformation observed in the DSC curve in Figure 4.2(a). A closer look at the TEM bright field also revealed the presence of a secondary precipitate within the matrix. Since the R-phase is a transforming matrix phase, which would not be a precipitate, one could speculate that this could be in the early onset of H-phase precipitation as well, as the H-phase precipitates have been reported in Ni-Ti-Zr alloys albeit at much higher Zr contents (>15 at.%) [26]. Moreover, the identified R-phase reflection in Figure 4.3(e), pointed to
by the arrows, also overlaps the H-phase reflections in this same zone axis [27]. However, the diffraction pattern in the [100] zone axis does not reveal additional secondary reflections which would be present if the H-phase had precipitated [27]. Hence, the precipitates in Figure 4.3(f) are not the H-phase.

Figure 4.3(a-l). A series of TEM bright field and selected area diffraction (SAD) patterns for 50.3Ni-48.7Ti-1Zr (at. %) at various aging times at 400°C. Each set is a diffraction patterns taken from [100] and [111] zone axes and a micrograph representing microstructure for (a-c) solution annealed condition, (d-f) 10 hrs, (g-i) 24 hrs, (j-l) 100 hrs. The H-phase is indicated by the arrows on the diffraction patterns.

To further confirm that the reflections in Figure 3.3(e) are from the R-phase, and not this precipitate, the 10 hours sample was heated up to 100°C using a Gatan in situ TEM holder. This
temperature is well above the R-phase transformation temperature in Figure 4.2(a). As seen in Figure 4.4(a), these reflections are now absent confirming that they were associated with the R-phase. Diffraction patterns and bright field images were also taken at 100°C using an in situ TEM Gatan heating stage for this 100 hour aged alloy. As shown in Figure 4.4(b), the diffraction patterns and bright field images for the 100 hours aged sample, also at 100°C, revealed the same reflections that were present at room temperature (Figure 4.3(j)). This provides clear evidence for the H-phase by removing the prior R-phase overlapping reflections in the [111] diffraction condition.

**Figure 4.4.** Bright field image and diffraction patterns taken at 100°C, indicating that secondary reflections are not the S-phase for (a) 10 hours and the H-phase for (b) 100 hours.

The absence of these reflections, which as mentioned previously, could also be indexed to the H-phase in this zone axis, provides additional evidence, along with absence of secondary reflection in the [100] zone axis, that the spherical precipitates are not the H-phase. This is significant because the H-phase has been reported to initially nucleate with a spherical morphology [26].
Coughlin et al. [41] have recently reported the existence of an H’ phase in a 51Ni-29Ti-20Hf alloy. This precipitate was found to be present after aging for 3 hours at 500°C. Aging for the equivalent time but at 600°C and 700°C resulted in the loss of this phase. Though the authors did not discuss the morphology of the H’ phase, the high resolution TEM micrographs of it suggest a spherical shape precipitate based upon its circular projection. Diffraction along the [011]B2 results in a series of distinct diffuse reflections between the B2 fundamental reflections, shown schematically in Figure 4.5(a). Diffraction of this phase along the [111]B2 also results in diffuse scattering lines between the fundamental diffraction reflections of B2, as shown in Figure 4.5(b). More importantly, these diffuse reflections in this zone axis are absent if the H-phase is present. Hence, this zone axis, i.e. [011]B2, would provide the clearest evidence if the spherical precipitates found here are the H’ phase. Figure 4.5(c) is the diffraction pattern from this zone for the 50.3Ni-48.7Ti-1Zr alloy aged at 10 hours. Figure 4.5(d) is the diffraction pattern for the [111] zone for this work for additional comparison. It is apparent that the distinguishing diffuse reflections are absent when comparing to Figure 4.5(a-b). Hence, we will identify this new spherical precipitate as the S-phase for the remainder of this paper.
Meng et al [31] reported a similarly shaped (spherical) nanoscale precipitate in a 44Ni-36Ti-15Hf-4Cu (at.%) alloy. These precipitates were indexed as the Fd3m Ti$_2$Ni phase, which is a stable precipitate for Ti-rich binary alloys [31]. Its stabilization in Ni-rich alloys has been suggested to occur from potential oxygen contamination [32]. However, this Ti$_2$Ni phase’s reflections could not be consistently indexed to the current patterns shown in Figure 4.3. Figure 4.6 (a-c) shows a bright field image and diffraction pattern taken along the [100]$_{\text{B}2}$ zone axis.
Figure 4.6. (a-b) Bright field image of 100 hours sample showing lattice fringes to measure d-spacings, and (c) corresponding reflection on [100] diffraction pattern.

In Figure 4.6(a-b), the lattice fringes are evident in the S-phase and measured to have a d-spacing of 2.28 Å, which is very comparable to the 2.23Å d-spacing for the \{110\} reflections of B2. This would explain the lack of clearly distinguishable S-phase reflections seen in the SAD pattern from those of the matrix reflections. The lack of additional and clearly separated SAD reflections from the strong B2 reflections, as well as other lattice fringes that could be measured from the S-phase, made crystallographic identification of the S-phase difficult and is the subject of a future investigation.

Upon aging to 24 hours for the 1 at.% Zr alloy, some of the precipitates appeared to have a different shape than the prior S-phase precipitates. These new precipitates were oblate or spindle-like in morphology measuring ~ 25 nm in length in comparison to the S-phase measuring ~ 12 nm in diameter, Figure 4.3(i). The SAD patterns in the [111] zone again can be indexed to the R-phase and the B2 matrix. However, upon viewing the [100] zone axis, additional secondary reflections were now noted (indicated by the arrows, Figure 4.3(g)). These reflections are consistent with the H-phase [26]. The morphology of the oblate precipitate would also be consistent with the H-phase [26]. Hence, the prior secondary reflections in the [111] zone, indexed
as the R-phase, can now also be indexed to the H-phase since each of these reflections overlap in this viewing orientation. The two-stage transformation from the DSC curve in Figure 4.2 provides the necessary evidence of the R-phase presence in the microstructure. Finally, aging at 100 hours provides the clearest visual evidence of the two precipitates – the oblate H-phase and spherical S-phase. The H-phase now measured ~100 nm in length while the S-phase coarsened to ~20 nm.

**Atom probe tomography characterization for the 50.3Ni-48.7Ti-1Zr**

APT was conducted at various aging times to capture the size, volume fraction, and composition evolution of the S-phase in the 1 at.% Zr alloy, Figure 4.7.

![Atom probe reconstructions](image)

**Figure 4.7.** Atom probe reconstructions for (a) 1 hour, (b) 10 hours, (c) 24 hours, and (d) 100 hours aging time at 400°C

Table 4.3 contains the matrix and precipitate compositions for four different aging times - 1 hour, 10 hours, 24 hours, and 100 hours - at 400°C. Table 4.4 includes additional S-phase precipitate information including the average radius of the S-phase and its volume fraction for each of these aged conditions. Upon initially nucleating the S-phase (1 hour), the precipitate is Zr enriched and further enriches itself with aging up to 10 hours. Interestingly, at 24 and 100 hours, the S-phase precipitates then deplete in Zr, Table 4.3. Recall that at 24 hours of aging, the alloy began to precipitate the H-phase, Figure 4.3(g–i). The H-phase is also known to be enriched in Zr [26] similar to the H-phase in the Hf-alloys [30], although those reports were for alloys with an
overall much higher ternary alloy composition. Consequently, upon precipitating the H-phase, a
competition for the Zr’s partitioning between these two precipitates appears to occur, with Zr in
the S-phase being depleted. The composition of the S-phase at 100 hours was approximately 54Ni-43Ti-3Zr (at. %), which again confirms that these spherical precipitates are not of the Ti₂Ni variation previously discussed above from the work of Meng et al. [31]. Efforts to capture the H-
phase’s composition in the APT samples for the 1 at.% Zr alloy were attempted but unsuccessful.
This has been contributed to the low volume fraction of the H-phase in this alloy, as shown in
Figure 4.8, where it was difficult to capture this precipitate within the ~100 nm field of view of
the atom probe sample needle. In contrast, the S-phase was present throughout the microstructure.

Table 4.3. Average precipitate and matrix compositions for the S-phase precipitates at various
aging times for 1 at. % Zr at 400°C.

<table>
<thead>
<tr>
<th></th>
<th>Matrix Composition (Average, at.%)</th>
<th>Precipitate Composition (Average, at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Ti</td>
</tr>
<tr>
<td>1 hr</td>
<td>54.26 ± 0.0</td>
<td>45.06 ± 0.02</td>
</tr>
<tr>
<td>10 hrs</td>
<td>52.29 ± 0.02</td>
<td>46.44 ± 0.02</td>
</tr>
<tr>
<td>24 hrs</td>
<td>52.06 ± 0.02</td>
<td>47.26 ± 0.01</td>
</tr>
<tr>
<td>100 hrs</td>
<td>49.80 ± 0.02</td>
<td>49.75 ± 0.02</td>
</tr>
</tbody>
</table>
Table 4.4. The calculated volume fraction and average precipitate diameter of the S-phase precipitates at various aging times for 1 at. % Zr at 400°C.

<table>
<thead>
<tr>
<th>Time</th>
<th>Volume Fraction (%)</th>
<th>Average Precipitate Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 hr</td>
<td>1.1</td>
<td>6 ± 1.3</td>
</tr>
<tr>
<td>10 hrs</td>
<td>1.4</td>
<td>8 ± 2.4</td>
</tr>
<tr>
<td>24 hrs</td>
<td>32.8</td>
<td>16 ± 1.6</td>
</tr>
<tr>
<td>100 hrs</td>
<td>42.1</td>
<td>20 ± 1.2</td>
</tr>
</tbody>
</table>

Figure 4.8. STEM-HAADF image showing S-phase and H-phase precipitates at 100 hours aging at 400°C.

TEM and electron diffraction for the 50.3Ni-48.7Ti-1Hf

In comparison to the 1 at. % Zr alloy, the TEM micrographs and selected diffraction patterns at 1 at. %Hf are shown in Figure 4.9(a-l). The solution annealed condition’s SAD patterns, Figure 4.9(a)-(b), contained only the B2 matrix phase reflections which was consistent with the
lack of precipitates in the BF image in Figure 4.9(c). This was equivalent to the prior findings observed in the 1 at.% Zr alloy. Upon aging to 24 hours, Figure 4.9(d-e), the SAD pattern revealed the R-phase reflections, indicated by the arrows in the [111] zone axis and whose reflections are consistent with the asymmetric DSC curve in Figure 4.2(b). In addition, the [111] zone contained a series of extra reflections occurring at the x/7 positions along the \( \langle 123 \rangle \) vector of B2 which index as the Ni\(_4\)Ti\(_3\) precipitate [33]. For ease of viewing, these reflections can be seen in the oval that captures two each of these reflections around the fundamental reflection in Figure 4.9(e). The Ni\(_4\)Ti\(_3\) reflections do overlap with the primary reflections of B2 NiTi in the [011] and [001] zone axes making the [111] zone axis the best primary axis for this particular phase’s identification [27]. One should also note that the [100] zone does not reveal the H-phase reflections for this 24 hour aging condition, which was previously seen in the 1 at.% Zr alloy (figure 4.3 (g)). Consistent with the diffraction patterns, the STEM-HAADF image, Figure 4.9(f), showed the precipitates with a acicular morphology consistent with Ni\(_4\)Ti\(_3\) [27].

Upon aging to 48 and 120 hours, the SAD patterns and BF micrograph for the 1 at. %Hf alloy revealed a two precipitate microstructure consistent with the prior longer aged 1 at. %Zr alloy. Viewing along the [111] zone for these times, Figure 4.9(h) and 4.9(k), the former Ni\(_4\)Ti\(_3\) reflections are now absent. The arrows clearly indicate either or both the R-phase and H-phase are present, due to their overlapping diffraction conditions in this viewing direction as previously discussed. From the DSC curve, Figure 4.2(b), the asymmetric transformation is noted providing support that the reflections can also be indexed to the R-phase. Upon tilting to the [100] zone, the H-phase reflections were noted, indicated by the arrows in Figure 4.8(g) providing the additional support (along with the microstructure images, Figure 4.9(l)) that the H-phase is now present in
the microstructure. The BF TEM micrographs, Figure 4.9(i) and 4.9(l), also revealed both the spherical, S-phase, and oblate shaped, H-phase, morphologies in these microstructures.

![Image of BF TEM micrographs](image)

**Figure 4.9(a-l).** A series of bright field and selected area diffraction (SAD) patterns for 50.3Ni-48.7Ti-1Hf (at. %) at various aging times at 400°C. The diffraction patterns are taken from [100] and [111] zone axes for (a-c) solution annealed condition, (d-f) 24 hrs of aging, (g-i) 48hrs of aging, and (j-l) 120 hours of aging. In (e), the Ni₄Ti₃ are shown in the circles while the R-phase is denoted by the arrows. Figure 8(g-h) and (j-k) has H-phase present in both zone axes, indicated by the arrows.

In Ni-rich binary alloys, after a solution anneal and water quench, Ni₄Ti₃ are known to readily precipitate within microseconds. The lack of these precipitates in either the Zr or Hf alloys upon solution annealing and quenching does demonstrate that dilute additions appear sufficient to suppress this rapid nucleation. Nonetheless, upon aging, the precipitation sequence to form or not to form the Ni₄Ti₃ phase appears to be dependent on the diffusivity of Zr or Hf. As reported by
Hornbuckle et al. [27], Hf’s slow diffusivity in NiTi can reduce the kinetics for the metastable Ni$_4$Ti$_3$ phase’s decomposition to Ni$_3$Ti$_2$ and eventually to the stable Ni$_3$Ti phase. In this work, the slower diffusivity of Hf (as compared to Zr) was readily apparent in the time to peak age, Figure 1. In the case of the 1 at.% Zr alloy, Zr diffusivity and/or strain in the matrix appeared to be sufficient to bypass the precipitation of the metastable Ni$_4$Ti$_3$ phase and directly form the S-phase (1 and 10 hours) with the accompaniment of the H-phase at 24 hours and longer aging.

In contrast, the slower diffusivity of Hf delayed the H-phase precipitation at 24 hours and directly precipitated the Ni$_4$Ti$_3$ phase, as B2 NiTi has no excess solubility of Ni [34]. Since the S-phase does not readily provide clear and separate reflections from the matrix phase in the SAD patterns and the strain contrast created by the Ni$_4$Ti$_3$ precipitates in the micrographs, Figure 4.8(f) [27], [35], one cannot definitely determine if the S-phase is or is not present at this stage of aging.

**Atom probe tomography characterization for the 50.3Ni-48.7Ti-1Hf**

Similar to the 1%Zr alloy, APT was done for this alloy at 24 and 120 hours of aging shown in Figure 4.10(a-b). At 24 hours of aging, consistent with the selected area diffraction (Fig. 4.9(e)), the reconstruction only revealed precipitate morphologies and compositions consistent with the Ni$_4$Ti$_3$ phase, with Hf slightly enriching this precipitate, Table 4.5. Though the atom probe has a limited field of view of ~ 100 nm, the absence of the S-phase in this reconstruction could indicate that this phase has yet to precipitate as alluded to in the prior electron diffraction and imaging section. Nonetheless, both the H-phase and S-phase are clearly evident after 48 and 120 hours of aging, Fig. 4.9, with the absence of the Ni$_4$Ti$_3$ phase. The presence of the two different phases can be seen in atom probe reconstruction of Figure 4.10(b) for 1% Hf alloy after 120 hours aging. The lack of Ni$_4$Ti$_3$ and its subsequent decomposition phases, e.g. Ni$_3$Ti$_2$ and Ni$_3$Ti, in either the Zr or
Hf alloys demonstrates that the S-phase and H-phase are more likely candidates for the equilibrium phases for this ternary alloy, even in the dilute ternary alloy limit.

**Figure 4.10.** Atom probe reconstruction of 1% Hf specimen (a) after 24 hours of aging with Ni₄Ti₃ precipitates delineated with a 45.01 at.% isoconcentration Ti surface, and (b) after 120 hours of aging with both S-phase and H-phase precipitates present, with each phase delineated by a 52.82 at. % isoconcentration Ni surface.

**Table 4.5.** Average precipitate and matrix composition for the S-phase and H-phase precipitates at various aging times.

<table>
<thead>
<tr>
<th></th>
<th>Matrix Composition (Average, at.%)</th>
<th>Precipitate Composition (Average, at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Ti</td>
</tr>
<tr>
<td>24 hr</td>
<td>54.12 ± 0.04</td>
<td>45.28 ± 0.04</td>
</tr>
<tr>
<td>48 hrs</td>
<td>48.96 ± 0.03</td>
<td>47.42 ± 0.03</td>
</tr>
<tr>
<td>120 hrs (S)</td>
<td>49.13 ± 0.04</td>
<td>49.57 ± 0.01</td>
</tr>
<tr>
<td>120 hrs (H)</td>
<td>48.94 ± 0.07</td>
<td>49.74 ± 0.03</td>
</tr>
</tbody>
</table>

**Influence of precipitation on the transformation temperature**

With the phase and microstructure evolution now quantified as a function of either Zr or Hf at various aging times, the influence of these changes on the martensitic start temperature (Mₘ) are now discussed. The increased Mₘ with aging time can be associated with several factors including a mechanical effect, a chemical effect, or a combination of each of these two effects.
The mechanical effect pertains to the influence of strain fields that are present around the precipitates. These strain fields act as obstacles to the transformation requiring a certain undercooling (driving force) for the transformation to occur [36], [37]. This mechanical effect is a function of both the precipitate size and its inter-precipitate spacing as reported in the previous work by Evirgen [38] for a 50.3Ni-34.7Ti-15Hf (at. %) alloy. In that study, the inter-precipitate spacing was smaller than or comparable to the critical martensite nuclei size. This suppressed the martensitic transformation meaning that more undercooling was necessary to drive the transformation which was manifested as a decreased in Ms. As seen in Figure 4.2(a), the 100 hours DSC curve for the 1 at. % Zr alloy in the cooling cycle experienced a drop in its transformation temperature upon the second step transformation from R-phase to B2. This is likely contributed to the high number density of S-phase particles as seen in the bright field image in Figure 4.3(l) as well as a nearly equivalent d-spacing, Figure 4.5, which could yield a strained interface. With the inclusion of the H-phase, which has been reported to not shear when the martensitic transformation takes place and has a coherent orientation relationship with the B2 austenite phase, it too would contribute to the mechanical effect [26]. These types of mechanical effects appear to be less sensitive to the Hf alloy, evident that its B2 to R-phase and then R-phase to B19’ phase shifts being closer together in the cooling cycle as compared to the Zr alloy. It has been reported that the hardening of shear modulus facilitates the formation of the R-phase, where Zr and Hf may contribute to a slightly different sublattice site substitution response in the matrix phase.

With the precipitation of both the S-phase and H-phase in each of the alloys, the composition of the matrix phase changes. Each of these precipitates, Table 4.3 and 4.5, have extracted Ni from the surrounding matrix which would help make the transforming phase Ni-lean [39] as well as alter the elastic constants. In Nitinol, as the alloy becomes more Ni-lean, a
corresponding increase in the Ms occurs. We do note some variation in the Ni composition between each of the aged conditions here via our APT measurements; nonetheless, the transformation temperatures are relatively invariant, Figure 4.2 and Tables 4.1 and 4.2.

In the binary Nitinol, such minor Ni alterations in the Ni-rich compositions have been reported to yield dramatic reduction in the Ms [40]. The lack of chemical sensitivity here demonstrates the likely complex interaction of the mechanical effect’s influence in offsetting a purely chemical effect. For richer Hf or Zr ternary alloys (>15 at%) [30], the Ms is > 100°C where these dilute alloys Ms are < 50°C. This difference in Ms as a function of ternary compositions for equivalent 50.3Ni content could be contributed to the volume fraction and type of precipitation events. The dilute alloys of this study have a qualitatively lower volume fraction of the H-phase (Figure 4.8) as compared to higher ternary compositions [26]. By reducing the fraction of this particular phase, one could conclude that an insufficient number of H-phase precipitates were present to extract a sufficient Ni content from the matrix and/or have a mechanical strain effect on the transforming phase. Such a conclusion though is compounded by the influence of the S-phase, which is not reported in the higher ternary alloy phases. The Ni-richness of the S-phase precipitate, Table 4.3 and 4.4, clearly assists in contributing to the chemical effect in extracting Ni from the matrix; however, its high number density with its corresponding short inter-precipitate spacing likely offsets dramatic Ms increases from any chemical effect because of their overlapping strain fields. Achieving an optimal balance of these precipitates, which is a function of the ternary composition and its processing conditions, is needed to fully balance the effect of microstructure on the transformation temperature properties.
Functional thermomechanical responses

With the shape memory transformation temperature relationship and microstructure links established, the functional thermomechanical behavior of these alloys is now discussed in terms of the prior connections. As discussed in the introduction, dimensional stability is crucial for shape memory alloys to be used in actuator designs, where the SMA will perform work against an applied load as well as undergo multiple cycles. The compressive and tensile constant force thermal cycling strain-temperature curves for the 50.3Ni-48.7-1Zr (at. %) after 10 hours and 100 hours of aging are shown in Figure 4.11(a-d).

By comparing the two plots, the sample revealed greater strain percent in tension than in compression. However, at 10 hours of aging shown in Figure 4.11(a), there is almost no residual strain until loading to 300MPa in tension, after which a noticeable gap in the strain is observed between the beginning and ending portions of the hysteresis curves between the heating and
cooling cycle. After loading to 400 MPa, the amount of unrecovered strain is approximately 0.5%. Figure 4.11(b) are equivalent loading plots under compressive loading. As before, there was no notable change in unrecovered strain at low loads. At -300 MPa, the onset of unrecoverable strain was observed. At -400 MPa, the unrecoverable strain was \(\sim 0.25\%\), or half of what was measured in tension in Figure 4.11(a). Upon aging to 100 hours, the onset of residual strain in tension is apparent at 300 MPa and higher loads, Fig. 4.11(c) whereas the compression load for the equivalent aging condition is readily observed at -400 MPa, Fig. 4.11(d). In terms of microstructure, the largest difference between the 10 and 100 hour aged condition is the presence of S-phase in both alloys but the absence of the H-phase at 10 hours but precipitated at 100 hours. The onset of H-precipitation does not appear to have a marked change in the residual strain response between the two alloys, and is likely contributed to its low volume fraction, as seen in Fig. 4.8. However, the thermomechanical response does seem sensitive to the phase transformation pathway.

In Fig. 4.11(a), in general, the cool down portions of the tensile load after 10 hours of aging reveal a continuous and relatively vertical response, with the slope becoming more vertical with load, for the alloy. The heating up portion of the curve also shows a similar response, but one can notice a subtle slope change near 0°C, indicated by the solid red arrow. Recall that this alloy exhibited a symmetric R-phase transformation, with the doublet peaks in Fig. 4.2 very near each other and tens of degrees Celsius above 0°C, Table 4.1. This subtle change in slope is believed to be a signature of this two-step transformation pathway, and for this alloy, appears most sensitive to the heating portion of the thermal cycle under load. The modest reduction of this transformation temperature on the thermomechanical test is contributed to a mechanical energy bias effect. In comparisons this subtle change in slope upon heating is not as present in the compressive sample in Fig. 4.11(b). However, in compression, at lower loads, a ‘double slope’ is observed at -50 MPa.
as well as -100 MPa, indicated by the blue arrow for each of these curves, which was not observed in tension. The location of this response is also lower in temperature than the DSC curve in Fig. 4.2. Upon increasing the load, the cooling curves response becomes more continuous and vertical and the ‘double slope’ effect is lost indicating a sensitivity of the R-phase transformation to loading.

In comparison, the 100 hour aged sample, where upon clear H-phase precipitation has occurred, albeit at a low volume fraction, retained the ‘double slope’ response in the cool down portion of loading in tension or compression, Fig. 4.11(c-d). Unlike the 10 hour aged sample, where the double slope temperature value was slightly lower than the DSC determined value, this peak was at a much higher temperature location. Recall in Fig. 4.2, the cool down portion of the DSC curve resulted in widening of the two-step transformation pathway. Under loading, with the maturation of the alloy’s microstructure from further aging, the load bias appears to shift the second step (R-phase to B19') to a higher temperature, ~ -25°C vs. ~ -65°C. The heating curves also reveal a subtle change in slope, indicated by the red arrow in Fig. 4.11(c-d), which is retained up to the highest loads. As with the 10 hour aged condition, these slope dependent variations appear near temperatures where the doublet responses are observed in the DSC. From both aged conditions, the R-phase transformation temperature, particularly upon cool down, appears sensitive to loading, with increases in load reducing the two-step wise transformation.

Figure 4.12(a-d) illustrates strain (%) vs. temperature (°C) plots for 24 hours aging time (a-b) and 48 hours (c-d) aging time for 50.3Ni-48.7Ti-1Hf (at.%) sample tested in tension (a,c) and compression (b,d). Recall at 24 hours of aging, only the Ni₄(Ti,Hf)₃ precipitates were noted in the B2 matrix microstructure as compared to only the S- and H-phase at 48 hours. As with the prior alloy, the shape of the hysteresis gives clues to the transformation behavior. According to the DSC curve in Fig. 4.2(b), a modest and board single step transformation peak is noted. There is
good agreement with the transformation temperatures between the DSC and thermomechanical response in both compression and tension for this particular alloy. With increasing the load, the vertical response of the transformation is more readily apparent up to ±200 MPa, where upon the slope decreases. It is interesting to note, that a ‘double-slope’ response was observed for the -50MPa alloy, but it is not clear what its origin would be as this aged condition did not promote the ready observation of any R-phase based transformation. After loading to ±200 MPa, a small amount of residual strain was present. This amount of residual strain increased with increasing load, with the amount of residual strain present for both loading configurations being very similar, Figure 4.13.

Figure 4.12 (a-d). Strain (%) vs Temperature graph for the 50.3Ni-48.7Ti-1Hf (at.%) alloy in tension(a, c) and compression (b,d) at 24 hours aging time (a-b) and 48 hours aging time (c-d) under various loads.
The retention of strain was also apparent for the 48 hour aged condition. Unlike the 24 hour aged condition, where the DSC curve revealed a one-step transformation, the 48 hour aged condition was an abnormal R-phase transformation. Though this multi-step transformation is clearly evident in Fig. 4.2(b), no clear ‘double-slope’ or subtle change in slope is noted upon cooling or heating through the transformation, Fig. 4.12(c-d), as previously seen in the 10 hour aged condition. As with the 24 hour aged condition, upon increasing the load resulted in a more vertical transformation response up to ±200 MPa with further increases resulting in a loss of this vertical response on both cooling and heating through the transformation. At ≥ 200 MPa, a residual strain was noted in this tensile loaded alloy, whereas this residual strain became more apparent at ≤ -50MPa for the compression sample in Fig. 4.12 (c-d). The overall amount of residual strain present in the 48 hours sample was found to be greater than the 24 hours sample, Fig. 4.13.

Figure 4.13(a) is the summary plot of all 1 at. % Zr and 1 at. % Hf samples tested in both tension and compression. This plot reveals the actuation strain (%) vs. applied stress (MPa). In both tension and compression, the 1 at. % Zr sample aged at either 10 hours or 100 hours has higher actuation strain then the Hf containing alloy. When the 1% Zr alloy only contains the S-phase (10 hours) – which is at a very low volume fraction of 1.4% - the actuation strain was slightly larger as compared to the microstructure with both S- and H-phase (100 hours) with the S-phase volume fraction over 42%, Table 4.4. Though the S-phase volume fraction is significantly increased, the actuation strain is still within ~ 0.5% of each other between these two aging conditions.
Similarly, the Zr alloy performed better than the Hf alloy for the residual strain in either tension or compression, Figure 13(b). For all alloy types, the residual strain for the equivalent alloy was higher in tension than compression as well. Interestingly, the 24 and 48 hour Hf alloy resulted in a near equivalent response in actuation strain and residual strain between the two alloys in tension but showed a clear deviation when loaded in compression. Since these two alloys had very different precipitate types - Ni₄(Ti,Hf)₃ (24 hours) vs. S- and H-phase (100 hours) - this suggest a potential load dependence connected with the type of precipitates in the microstructure.

Though the alloys revealed relatively poorer dimensional stability under increasing loads during thermal cycle as compared to higher Zr or Hf ternary concentrations, these alloys may still hold promise as alternatives to the binary Ni-rich Nitinol. As noted in the introduction, the Ni-rich Nitinol alloys have durability and fatigue concerns that have been linked to the precipitation of the Ni₄Ti₃ precipitates. It is clear that the addition of these dilute ternary elements, with proper aging, can result in a B2 matrix absent of this precipitate which could offer alternative
microstructure with potential improvements in fatigue life. This is the subject of future investigations by the authors.

4.4 Conclusions

In this study, the additions of dilute Zr and Hf and its effect on precipitation, transformation behavior, and functional mechanical behavior were explored and yielded the following conclusions:

(1) In a 50.3Ni-48.7Ti-1Zr (at. %) alloy, after 10 hrs of aging at 400°C, a VHN of ~ 298 was observed. DSC results indicated that upon aging there is two-step transformation (B2-R-B19') behavior upon heating and cooling which is commonly referred to as a symmetric R-phase transformation.

(2) In a 50.3Ni-48.7Ti-1Hf (at. %) alloy, after 24 hrs of aging at 400°C, a VHN of ~ 299 was observed. Both peak hardness values were essentially the same for the Zr and Hf sample; however, Zr achieved that hardness value in less than half the time of Hf. DSC results indicated that upon aging to 24 hours a one-step transformation (B2-B19') occurred. On further aging to 48 hours and 120 hours, a multi-step transformation pathway was observed which is commonly identified as either an abnormal asymmetric (48 hours) to asymmetric (120 hours) R-phase transformation.

(3) In the 50.3Ni-48.7Ti-1Zr alloy, TEM BF and SAD patterns revealed the presence of two different precipitates after aging at 400°C. One with a spindle morphology and one that was spherical, with the latter being the first phase to form. The SAD patterns revealed a B2 matrix phase after solution annealing and secondary reflections upon aging consisted with the R-phase and H-phase, which were linked to the transforming matrix phase and spindle-like precipitates respectively. The spherical precipitate was not identified to being either the early onset of H-phase precipitation or the recently reported H’ phase. It appears to be a new phase within the Ni-T-Zr alloy. This spherical phase has been denoted as the “S-phase.”
In the 50.3Ni-48.7Ti-1Hf alloy, TEM BF and SAD patterns revealed the presence of two different microstructures dependent on aging time at 400°C. After 24 hours, Ni₄Ti₃ precipitates were observed to form from the B2 solution annealed matrix. Upon aging to 48 and 120 hours, the Ni₄Ti₃ precipitates were absent and the prior discussed S-phase and H-phases were identified.

The thermomechanical functional responses were studied under tensile and compressive loading. For the 50.3Ni-48.7Ti-1Zr alloy revealed more actuation strain and less compressive strain than the 50.3Ni-48.7Ti-1Hf alloy, with the 10 hour aged (S-phase containing microstructure) having the highest performance metrics. Upon loading, the Zr alloy exhibited the multi-step transformation pathway in its thermomechanical responses, with lower loads and the cooling cycle being the most prominent in displacing this response. Optimal transformation responses (vertical strain transformations vs. temperature) were noted at ±200 MPa loading. Finally, the 50.3Ni-48.7Ti-1Hf alloy revealed a load dependent strain response between the 24 and 48 hour aged conditions. This is likely linked to the differences in precipitate types (Ni₄(Ti,Hf)₃ vs. S- and H-phase) between the alloys, with less strain response under compression as compared to tensile loading.
4.5 References


[25] K. F. Hane and T. W. Shield, “Microstructure in the cubic to monoclinic transition in
1999.

Noebe, “TEM study of structural and microstructural characteristics of a precipitate phase


[28] K. Thompson, D. Lawrence, D. J. Larson, J. D. Olson, T. F. Kelly, and B. Gorman, “In situ
site-specific specimen preparation for atom probe tomography,” Ultramicroscopy, vol. 107,

[29] B. C. Hornbuckle, M. Kapoor, and G. B. Thompson, “A procedure to create
isoconcentration surfaces in low-chemical-partitioning, high-solute alloys,”
Ultramicroscopy.

Thompson, “Structure–property relationships in a precipitation strengthened Ni–29.7Ti–

Hf–Cu quaternary alloy ribbons containing (Ti,Hf)2Ni precipitates,” Acta Mater., vol. 58,


[34] T. B. Massalski, H. Okamoto, P. R. Subramanian, and L. Kacprzak, Binary alloy phase

[35] W. Tirry and D. Schryvers, “Quantitative determination of strain fields around Ni4Ti3


CHAPTER 5
THE INFLUENCE OF ZIRCONIUM ON MICROSTRUCTURE AND TRANSFORMATION TEMPERATURES IN NICKEL-TITANIUM BASED SHAPE MEMORY ALLOYS

Suzanne Kornegay¹, Othmane Benafan², Florian Vogel¹, and Gregory B. Thompson¹*

¹ The University of Alabama, Department of Metallurgical & Materials Engineering, Box 870202, Tuscaloosa, AL 35401-0202

² NASA Glenn Research Center, Materials and Structures Division, 2100 Brookpark Road, Cleveland, OH 44135

*corresponding author: gthompson@eng.ua.edu

Abstract

A series of Ni₅₀.₃Ti(₄₉.₇-x)Zrx, where x = 0, 1, 7 and 17.5, alloys were aged at 400°C and 550°C for various aging times up to 300 h with their shape memory transformation temperatures analyzed by differential scanning calorimetry (DSC) from -90°C to 300°C. The shape memory transformations were then compared to microstructures and chemistry characterized by transmission electron microscopy (TEM) and atom probe tomography (APT). In some cases, the addition of Zr was found to form H-phase precipitates - a 192 atom unit cell orthorhombic structure. This phase was also accompanied by a spherical precipitate, denoted the S-phase, for the 1 at.% Zr alloy after aging at 400°C. Upon aging at 550°C, both types of precipitates were
absent in the B2 microstructure. The presence of these precipitates accompanied a symmetric R-phase transformation at 400°C aging and a single stage B2-19’ transformation at 550°C aging. The addition of 7 at.% Zr revealed no measureable transformation over the DSC scan region range up to 300 h of aging, even though H-phase precipitates were observed. Upon aging at 550°C, the onset of a transformation was noted at 48 h. Finally, the 17.5 at.% Zr alloy revealed a transformation temperature after 300 h of aging at 400°C and 24 h at 550°C aging. The H-phase precipitate was noted in each of these conditions. The variation in transformation temperatures as a function of aging condition and Zr alloy content is discussed in terms of the precipitate sizes, inter-precipitate spacing and matrix compositions.

5.1 Introduction

NiTi alloys, commonly referred to as Nitinol, are common commercial shape memory alloys, but are limited in applications by either a low transformation temperature (generally between -100 °C to 100 °C) or dimensional instabilities caused by retained strain through multiple cycling through the transformation temperature. Upon cycling through the transformation multiple times, the equi-atomic and Ti-rich compositions, which are more sensitive to retained strain, are susceptible to low cycle fatigue failure; however, these failures can be reduced through ‘training’ the alloy. In contrast, the Ni-rich NiTi alloys exhibit excellent dimensional stability during pseudoelastic stress cycling and constant force thermal cycling [1] experiments with little to no training. The excellent dimensional stability of Ni-rich NiTi alloys, as opposed to the equi-atomic and Ti-rich alloys, is attributed to the precipitation of Ni₄Ti₃ precipitates. The Ni₄Ti₃ phase is a metastable phase that is lenticular shaped with a R3 space group crystal structure. Depending on the thermal history, this precipitate will eventually decompose to another metastable Ni₃Ti₂ phase.
and then to thermodynamically stable Ni$_3$Ti phase [2]. Even though Ni-rich NiTi alloys exhibit superior dimensional stability, the shape memory transformation temperature readily reduces well below room temperature which has hindered these compositions from being viable alloys for high temperature solid-state-based actuators and similar devices.

During the shape memory transformation, the alloy undergoes a reversible crystal structure change from a low temperature, low symmetric phase, termed martensite, to a higher temperature, higher symmetric phase, termed austenite. It has been established that there are three possible martensite candidates in Ni-Ti based alloys - the R-phase, B19, and B19’ - with the austenite phase being the B2 structure [3]. The transformation paths from martensite-to-austenite are broken into three cases, which can be reviewed in reference [3], with the pathways determined by which of these phases martensite phase is the most stable. Here, we briefly review two of the pathways – referred to as Case 1 and Case 2 by Otsuka et al. 2005 [3] - as they are relevant to the findings that will be forthcoming.

In Case 1, the transformation path is directly between B2-B19’. In this single transformation path, the higher temperature austenite is able to convert directly to the B19’ martensite phase upon cooling or vice versa upon heating resulting in one transformation peak visible in the differential scanning calorimetry (DSC) scan for the cooling portion and one transformation peak upon the heating portion of the thermal cycle. Recall that DSC provides the heat flow into or out of a sample that is undergoing a phase transformation. In Case 2, the B19’ phase becomes unstable from a hardening effect on the shear modulus - which can occur from the presence of defects such as dislocations, precipitates, and impurity elements [4] - the R-phase becomes stabilized and the transformation path now involves a multiple step pathway such as B2-R-B19’. The R-phase has a trigonal crystal structure and belongs to either
the P3 or P-3 space group. In this case, two transformation peaks will now be observed in the DSC curves in either thermal cycles. When this intermediate R-phase occurs between the B2 and B19’ phases upon both the heating-up and cooling-down portions, it is referred to as a symmetric R-phase transformation. If the R-phase transformation is only observed in one of the thermal ramps (typically upon cooling), it is then referred to as an asymmetric R-phase transformation. These R-phase transformations are typically observed by [3] (1) increasing the Ni content, (2) aging at lower temperatures between 300 °C and 500 °C after solution treatment to form Ni₄Ti₃ precipitates, (3) annealing below the recrystallization temperature immediately after cold-working, (4) adding a third element, and (5) thermal cycling.

In addition to the symmetric and asymmetric R-phase transformations, there have been other reports of an ‘abnormal R-phase transformation’ [5], [6]. In this transformation pathway – which can occur in either symmetric or asymmetric R-phase transformations – an additional, or now third DSC peak, is present upon the cooling portion of the thermal cycle. This abnormal three-stage transformation behavior has been attributed to preferential grain boundary precipitation of Ni₄Ti₃ precipitates at and very near the grain boundaries [6]. This generates macro-scale heterogeneity in the microstructure and in the chemical composition between the grain boundary region and the matrix interior of the grain. Consequently, the grain boundary portion of the microstructure undergoes a B2-R-B19’ two-stage transformation and the grain interior, which is considered to be relevantly precipitate free, directly undergoes the B2-B19’ transformation. The combination of these microstructures then is believed to facilitate the three transformation peaks upon cool down present in the DSC scans.

With the basic shape memory transformation pathways reviewed, we now focus on how these transformations can be altered or engineered through the use of ternary additions. It has been
reported that ternary macro-alloying of Nitinol with Pt [7] Pd [8], Au [9] Hf [10], or Zr [11], [12] can significantly increase the transformation temperature for both Ti-rich and Ni-rich compositions. In particular to the Ni-rich compositions, the increase in transformation temperature has been above room temperature while allowing the alloy to retain excellent dimensional stability [13]–[18]. Such a balance of properties have now made these alloys candidates for solid state actuators and similar devices used in warmer environments. The improved properties have been attributed to their ability to facilitate the precipitation of new types of phases within the shape memory matrix. In some cases, the proper identification of the precipitate had alluded scientists for years [ref]. For example, in the Pt and/or Pd ternary alloys a complex monoclinic unit cell, referred to as the P-phase, was found with a variant stacking sequence that confounded the diffraction identification [19]. More recent efforts have now been undertaken to address the compositional solubility range of this precipitates [20]. Collectively, these types of precipitates changed both the composition and strain within the shape memory matrix which are believed to promote the increases in transformation temperature [19], [20]. However, the prohibitive cost of precious metal additives like Pt or Pd for these alloys has made the Hf and Zr additions to be considered a more economically viable solution which have also shown promising increases in transformation temperature and mechanical properties.

Of these two ternary additions, the Ni-rich Nitinol with Hf, arguably, have been more investigated. This is likely attributed to their initial report of having excellent transformation and mechanical properties for a Ni50.3-Ti29.7-Hf20 (at.%) alloy [21]. Subsequent to this paper, it was found that the oblate spindle-like precipitates observed in the matrix where those previously identified by Han et al. [22]. These precipitates, now referred to as the H-phase, consisted of a192 atom orthorhombic unit cell. The composition of the H-phase in this particular alloy was
determined to be Ni$_{50}$-Ti$_{16.7}$-Hf$_{33.3}$ (at.%) by Yang et al. [2] using atom probe tomography. Recently, Zr has attracted attention because of its 20% reduction in weight [23] for a comparable Hf alloy composition and significantly less cost than Hf. It has been found that an equivalent H-phase precipitate was observed in a Ni$_{50.3}$-based alloy, with the Zr overall composition spanning 15 to 20 at.% [24]. Though the same precipitate phase has been noted in both systems, some differences were reported in the coarsening of the H-phase [25] as well as the transformation temperatures and superelastic and shape memory thermo-mechanical responses [24], [25].

To date, the majority of these ternary studies have been in the higher ternary additions. Recently, the authors reported on the precipitation, transformation temperature and thermo-mechanical responses for a series of 400°C aged Ni$_{50.3}$Ti$_{48.7}$(Zr or Hf)$_{1}$ alloys. It was found that these additions were not in solid solution occupying the Ti sublattice but precipitated out the H-phase as well as a nanoscale spherical phase, denoted as the S-phase [26]. These alloys also revealed a difference in the initial precipitation, with the Hf forming Ni$_{4}$(Ti,Hf)$_{3}$ precipitates that eventually decomposed to the H- and S-phases. In contrast, the Zr alloy by-passed the Ni$_{4}$Ti$_{3}$ precipitate structure and directly formed the S- and H-phases. Even the transformation pathways were noted to be different, with the Hf promoting an asymmetric R-phase and the Zr promoting a symmetric R-phase.

In this paper, we aim at expanding those studies by comparing the precipitation and shape memory transformation behavior for a range of Zr contents up to 17.5 at.%. In the prior studies by the authors, the 1 at.% Zr was reported at 400°C aging conditions [26] whereas their work at 17.5 at.% was done at 550°C [25]. Since major phase and transformation differences were noted, we have provided here a complimentary study for each alloy at the other aging condition as well as bridging the large compositional gap between those aging conditions by adding studies of a
7 at.% alloy. Therefore, this research will bridge the gap of microstructural evolution, transformation behavior, and phase composition at two different aging temperatures as a function of Zr additions in a Ni-rich NiTi shape memory alloy. The results of which provide a better understanding of how the precipitation behavior in these alloys regulates the shape memory transformation behavior.

5.2 Experimental Procedures

Four alloys were prepared with the following compositions: Ni50.3Ti49.7-xZrx with (1) x = 0 known as the binary or control for the study, (2) x = 1 and (3) x = 7 and (4) x = 17.5 (all compositions in at.%). All of these alloys were prepared by vacuum induction melting of high purity elements (99.98% Ni; 99.8% Zr; 99.95% Ti) in a graphite crucible under an argon atmosphere. These ingots were then vacuum homogenized for 72 h at 1050°C and furnace cooled followed by a hot extrusion at 900°C with an area reduction ratio of 7:1. The alloys were then re-solutionized at 1050°C for 10 h followed by a water quenching. To prepare the samples for the aging treatments, the rods were sectioned into smaller pieces then aged at 400°C or 550°C for various times after which they were again water quenched. In all solutionizing and aging treatments, in order to eliminate possible oxidation, the samples were wrapped in Ta foil with flowing argon over the sample while in the tube furnace. For convenience, we have adopted the subsequent nomenclature to describe each alloy in its processed state with the designation sequence of [solute content/aging temperature/aging time] - for example, the Ni50.3-Ti48.7-Zr1 (at.%) alloy that was aged at 550 °C for 10 h would be labeled in the Results and Discussion section as [1Zr-550C-10h].

Following solution annealing and subsequent aging, the hardness for each sample was measured using a Buehler Vickers hardness tester under a load of 1 kg with a dwell time of 15s.
Each hardness data point reported represents the average from 12 separate measurements with the standard deviation for each reported. The transformation behavior of these alloys was quantified using differential scanning calorimetry (DSC), which was performed in a TA Instruments Q200 where the temperature was cycled five times between the temperature ranges of -90°C to 300°C, with the heating portion of the curve located on the bottom portion of the scan and the cooling portion of the thermal cycle located on the top portion of the scan. The transformation temperatures that are tabulated in Tables 5.1, 5.2, and 5.3 and were extracted from the DSC curves using the baseline tangent method.

Transmission electron microscopy (TEM) was performed in a FEI TECNAI (scanning) transmission electron microscope ((S)TEM) equipped with a field emission electron source operated at 200 keV, to characterize the microstructure and provide phase identification via bright field (BF) imaging, STEM-high angle annular dark field (HAADF) imaging and selected area diffraction (SAD) patterns. The HAADF provides a semi-quantitative image where the brightness scales with atomic number $Z^{-1.7-2}$; hence the brighter phases are those with higher atomic numbered atoms. The TEM samples were prepared by cutting the sample of interest into a 3 mm diameter disc that was polished to be $< 100 \, \mu m$ in thickness followed by dimple polish to $< 15 \, \mu m$ using a diamond abrasive. The samples were then Ar ion milled using the Precision Ion Polishing system (GATAN 691) to create an electron transparent area near the perforated hole in the dimpled region of the disc. Using these images, the precipitate sizes and inter-precipitate spacing were calculated. For the inter-precipitate spacing, the method by Törrönen (1980) [27] was employed. Further details in the use of this technique can be found in the authors’ prior paper [25] and/or the original reference for the technique in reference [27]. Atom probe tomography (APT) was performed in a Cameca Local Electrode Atom Probe (LEAP)
3000XSi and 5000XS to study the composition of the identified phases. The atom probe samples were prepared using a FEI Quanta 200 3D Dual Beam electron-focused ion beam (FIB) microscope that is equipped with an Omniprobe Autoprobe 200 micro-manipulation system. Details on the lift out procedure can be found in reference [28]. The extracted material was then annular-milled into the required atom probe tip geometry using a 30 keV beam energy at beam currents between 0.3-0.5 nA. The final shaping of the tip was done using 5 keV and 70 pA as a ‘clean up’ step in order to reduce the surface damage created from the Ga ion implantation at the higher energy settings. The running parameters used for the LEAP 3000XSi were 40 K, 200 kHz pulse repetition rate, and 0.4 nJ pulse energy with a target evaporation of 0.5 % per pulse. The LEAP 5000XS was performed at 40K, variable pulse frequencies to maintain a minimum range of 110 Da in the mass spectrum, and 100-200 pJ pulse energy with a targeted evaporation of 1 % per pulse. The atom probe data was analyzed using the IVAS 3.6.12 software package and analyzed using the procedures outlined by Hornbuckle et al. 2015 [29]. Since Zr and Ti have a high affinity for hydrogen, we noted the presence of elemental hydrogen and hydride complexes in the atom probe mass spectrum, which typically accounted for < 2-5 at.% (depending on overall Zr and Ti content) of the total composition. This hydrogen is either a processing artifact incorporated in the making of the alloy or a vacuum contaminate gas in the LEAP analysis chamber. In the analysis, we have removed the elemental hydrogen from our composition and have included the metallic species of the hydride to the overall composition from which we then normalized to the three constituent elements. This ensured that the composition of the ternary alloy added to 100 at.%.
5.3 Results and Discussion

In this study, four Ni-rich NiTi alloys, with varying Zr ternary additions, were investigated to determine the effect of Zr content on the microstructural evolution and shape memory behavior. Figure 5.1a-h is a collection of Vickers hardness plots as a function of aging time for the 0, 1, 7 and 17.5 at.% Zr aged at 400°C (a-d) and 550°C (e-h) for different times.

**Hardness after aging at 400 °C**

In Figure 5.1(a), the [0Zr-400C] series achieves a peak hardness at 24 h with a Vickers Hardness Number (VHN) of 370 ± 4 VHN. The [0Zr-400C] control series has been extensively studied [5], [6] where precipitates of Ni₄Ti₃ were observed which contributed to the hardness of this alloy [30], [31]. Figure 5.1(b) depicts the evolution of hardness for the [1Zr-400C] revealing a hardness of 298 ± 4 VHN after 10 h and 289 ± 6 VHN after 100 h in the overaged condition, which had previously been reported by the authors group [26] and was added here for convenience to the reader for the subsequent comparisons. In this prior work, this particular microstructure consisted of nanoscale spherical precipitates, denoted as the S-phase and eventually the H-phase within the B₂ matrix. It is interesting to note that its hardness was lower than either the control or subsequent alloys with higher Zr content. By increasing the ternary addition amount to 7 at.% Zr when aged at 400 °C for 24 h the peak hardness value increased to 549 ± 5 VHN with an hardness of 486 ± 7 VHN after 300 h in the overaged condition as shown in Figure 5.1(c). Finally, for the [17.5Zr-400C] series, the peak hardness of 628 ± 9 VHN was achieves after 48 h of aging followed by a steady decrease in hardness to 540 ± 8 VHN after 300 h. Both, the [7Zr-400C] and [17.5Zr-400C] alloy are characterized by H-phase precipitates, which contributes to the precipitation strengthening of these alloys which will be further developed later in this paper.
Figure 5.1. Vickers Hardness (VHN) as a function of aging time for 0\% Zr, 1\% Zr, 7\% Zr, and 17.5\% Zr at 400\°C (a-d) and 550\°C (e-h). Hardening curves (b) and (h) have been re-plotted from references [26] and [25] respectively.
Figure 5.2. DSC curves for 0% Zr, 1%Zr, 7%Zr, and 17.5%Zr at 400°C (a-d) and 550°C (e-h). The arrow in the DSC curves indicated direction of increasing thermal cycles. DSC curves (b) and (h) have been previously reported in references [26] and [25].
Hardness after aging at 550 °C

The temporal evolution of the alloys hardness after aging at 550°C of samples with equivalent compositions is plotted in Figure 5.1(e-h). The [0Zr-550C] series showed a continually increasing hardness up to 100 h of aging, with a hardness value of 350 ± 9.4 VHN in the peak aged condition (Figure 5.1(e)). The [1Zr-550C] series achieves a peak hardness of 334 ± 6 VHN after 10 h of aging. Though this is approximately equivalent to the peak aged condition observed at 400°C, the hardness value had increases slightly more than in the lower temperature condition. The [7Zr-550C] and [17.5Zr-550C] series revealed peak hardness values of 540 ± 7 VHN and 566 ± 7 VHN after 10 h and 4 h respectively. The peak hardness of both of these conditions is lower than those of their respective peak aged condition at 400°C, which is attributed to the faster coarsening kinetics due to the increased mobility at higher temperatures. The [7Zr-550C] alloy reveals a nearly equivalent peak hardness value between the two different aging times while the [17.5Zr-550C] alloy had a reduction in peak hardness with the increase in aging temperature. Collectively, these results confirm that precipitation strengthening occurs in these alloys and the resulting microstructure determines the hardness values as a function of composition and aging temperature and time.

Since precipitates have a crucial influence on the shape memory transformation temperature, the aging curves are now compared to their respective transformation temperatures. Figure 5.2(a-h) is a collection of DSC curves of Ni50.3Ti49.7-xZrx alloys for (a) x = 0, (b) x = 1, (c) x = 7 and (d) x = 17.5 after aging at 400°C (a-d) and 550°C (e-h) for different times. A summary of the transformation temperatures is compiled in Table 5.1, 5.2, and 5.3.
Transformation behavior after aging at 400 °C

The transformation behavior for [0Zr-400C] alloy, Figure 5.2(a), reveals a one-step transformation peak (B2-B19’) in both the heating and cooling cycles for the solution annealed condition. This transformation shows some instability evident by the variation of the onset and completion of the phase transformation with repeated thermal cycling in the heat flow peaks. This is highlighted by the trending arrow in Figure 5.2a on the cooling portion of the curve for the [0Zr-400C-solution anneal (SA)] sample. After 10 h of aging, the DSC peaks no longer reveal this instability; however, the DSC curve reveals a change in transformation path. Rather than retaining a one-step transformation, multiple peaks are now seen on both the cool down and heating up portions of the curve. For the cool down (upper curve), a single phase transformation is noted near 50°C and an additional transformation near -50°C. A closer evaluation of the shape of this peak at ~ -50°C reveals a doublet symmetry (denoted by the two arrows). Upon heating up (lower portion of the curve), these two peaks were again observed (denote by the arrows), whose onset and finish values are very near to each other. If two peaks had occurred upon cool down and two peaks present upon heating up, this would be a classical ‘symmetric R-phase’ transformation [4], as discussed in the introduction. The presence of the doublet peak upon the second stage of the cool down suggests that the transformation to the final martensite phase does not occur in a single, uniform manner but is an abnormal R-stage transformation [6]. Clearer evidence of this doublet peak is revealed with further aging at 24 h and 100 h in Figure 5.2(a) where these peaks further separate. Collectively these lower temperature doublet transformation peaks gradually increase their onset and finish transformation temperatures with aging, particularly for the cool down portion of the DSC scans. In contrast, the transformation peaks upon the heating up portion of these curves only show a modest increase in its onset and finish
temperatures with aging. The measured transformation temperatures for the binary alloy at 400°C are listed in Table 5.1.

Table 5.1. Measured transformation temperatures for [0Zr-400C] and [0Zr-550C]. A single dash indicates that a transformation path response of that type did not occur for the alloy/aging time tested.

<table>
<thead>
<tr>
<th>Aging Time (h)</th>
<th>Heating Cycle</th>
<th>Cooling Cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Start</td>
<td>Finish</td>
</tr>
<tr>
<td>SA</td>
<td>-25</td>
<td>-10</td>
</tr>
<tr>
<td>10 h (400C)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>24 h (400C)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100 h (400C)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10 h (550C)</td>
<td>23</td>
<td>38</td>
</tr>
<tr>
<td>24 h (550C)</td>
<td>12</td>
<td>30</td>
</tr>
<tr>
<td>100 h (550C)</td>
<td>60</td>
<td>75</td>
</tr>
</tbody>
</table>

The solution annealed condition of the sample containing 1 at.% Zr reveals a similar response as the [0Zr-400C] sample (shown in Figure 5.2b). A one step transformation is noted upon cooling and heating with respective to the onset and finishing temperature as well as their instability with repeated thermal cycling. When aged for 10 h or 24 h, two peaks are present upon the cool down and heating up portions of the curve. These have been previously reported by the authors as a symmetric R-phase transformation. The addition of 1 at.% Zr appears sufficient to suppress the prior abnormal R-phase transformation. Also, the two peaks on the cool down portion of the curve become further separated with the lower temperature
peak’s onset and finish temperatures occurring well below 0°C. Finally, the two peaks upon the heating up portion of the curve are well separated as compared to the near overlapped peaks observed in the [0Zr-400C] series.

With an increased amount of Zr, the [7Zr-400C] series shows a substantial change in the DSC responses from the prior two alloys, Figure 5.2c. Here, no transformation peaks are observed over the temperature range of -90°C to 300°C, even for the sample aged up to 300 h where precipitation has clearly occurred as indicated by the hardness evolution shown in Figure 5.1(c). A similar set of DSC response curves are also observed for the [17.5Zr-400C] series, i.e. no notable transformation peaks except for the sample aged for 300 h where a one stage transformation is noted and the onset and finish temperature revealing instabilities with thermal cycling (Figure 5.2d). A summary of the observed transformation temperatures for the 1 and 17.5 at.% Zr containing samples aged at 400°C is listed in Table 5.2. Since none of the aged conditions for the 7 at.% Zr containing alloy exhibits a transformation response in the tested range, this alloy is not included in the table.

**Transformation behavior after aging at 550 °C**

Upon increasing the aging temperature to 550°C, Figure 2(e-h), marked differences in the transformation pathways and transformation temperatures are found. In the [0Zr-550C] series, the onset of aging results in a loss of the abnormal R-phase transformation to an asymmetric R-phase transformation. When aged for 24 h and 100 h, the two peaks associated with the cool down transformation are present and slightly increase the onset and finish temperatures. Similarly, the one stage transformation peak associated with the heating up portion of the curve increases with aging time. With the addition of 1 at.% Zr, aging at 550 °C, Figure 5.2(f), results in a loss of the prior symmetric R-phase transformation noted after aging at 400°C (Figure 5.2(b)), now resembling a
single step transformation upon cooling and heating. However, the onset and finishing temperatures for this transformation appear to be lower than for the solutionized condition and all of these transformations exhibited instabilities for all of the aging conditions.

Unlike the prior [7Zr-400C] series which exhibits no notable DSC peaks within the scanned range, the [7Zr-550C] series exhibits the onset of a heating up transition after 48 h and 100 h of aging. Further with the transformation peak becoming stronger either with increased thermal cycling or for the longer aged condition. The transformation to the martensite phase with cooling is not evident in the scan and must therefore occur below -90°C, which is outside the scan range of the DSC used. Finally, the DSC responses for the [17.5Zr-550C] series are shown in Figure 5.2(h). As previously reported by the authors [25] and added here for convenience to the reader in the comparisons, a slight onset of a transformation was noted after 24 h aging, with it becoming stronger and shifted to higher temperatures as a function of aging time. The width of these peaks is attributed to either the increase or decrease in temperature necessary for facilitating a sufficient driving force for the transformation to continue to propagate upon heating or cooling. A summary of the transformation temperatures for the samples aged at 550°C are listed in Table 5.3.
Table 5.2. Measured transformation temperatures for [1%Zr/400°C] and 17.5%Zr/400°C]. The transformation temperatures for [7%Zr/400°C] are not included in the table because there was no transformation response detected in the tested range of -90 to 300°C. A single dash indicates that a transformation path response did not occur for the alloy/aging time tested.

<table>
<thead>
<tr>
<th>Aging Time (Hours)</th>
<th>1% Zr at 400°C</th>
<th>17.5% at 400°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA</td>
<td>-24</td>
<td>6</td>
</tr>
<tr>
<td>10 hrs</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>24 hrs</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100 hrs</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>300 hrs</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 5.3. Measured transformation temperatures for the [1Zr-550C], [7Zr-550C], and [17.5Zr-550C] series after aging for different times. A single dash indicates there was no transformation response for that condition. A double dash indicates that the transformation behavior data was not collected for that aged condition. Temperatures are reported in °C.

<table>
<thead>
<tr>
<th></th>
<th>1 at.% Zr</th>
<th></th>
<th>7at.% Zr</th>
<th></th>
<th>17.5 at.% Zr</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Start</td>
<td>Finish</td>
<td>Start</td>
<td>Finish</td>
<td>Start</td>
<td>Finish</td>
</tr>
<tr>
<td>SA</td>
<td>-24</td>
<td>6</td>
<td>-35</td>
<td>-70</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10 h</td>
<td>-29</td>
<td>-13</td>
<td>-42</td>
<td>-62</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>24 h</td>
<td>-29</td>
<td>0</td>
<td>-42</td>
<td>70</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td>48 h</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>-22</td>
<td>-5</td>
</tr>
<tr>
<td>100 h</td>
<td>-27</td>
<td>-5</td>
<td>-42</td>
<td>-62</td>
<td>85</td>
<td>115</td>
</tr>
<tr>
<td>300 h</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>65</td>
<td>135</td>
</tr>
</tbody>
</table>

To link the transformation temperatures to the microstructure, a series of transmission electron microscopy (TEM) and atom probe tomography (APT) studies for selected conditions was undertaken.

Microstructure after aging at 400 °C for 100 h

Figure 5.3(a-c) shows a series of bright field (BF) TEM and selected area diffraction patterns (SAD) for Ni\(_{50.3}\)Ti\(_{49.7-x}\)Zr\(_x\) alloys with (a) x = 1, (b) x = 7 and (c) x = 17.5 aged at 400°C for 100 h. By comparing the alloys of the same aging condition, the evolution of the microstructure can be directly correlated to the Zr content. For the binary or control alloy, several reports exist already in the literature concerning its phase and microstructure, specifically since these slightly Ni-rich compositions are used as biomedical stents [13]. The reader is referred to those references for further information. We now focus the balance of the paper on the characterization of the microstructures with the Zr additions.
The BF-TEM image of the [1Zr-400C-100h] sample shown in Figure 5.3(a) reveals a microstructure comprised of two different types of precipitates. For this aging condition, these precipitates, have previously been identified as the S-phase for the spherical and as the H-phase for the oblate, spindle-like morphology [26]. The presence of two distinct precipitate morphologies aids to identify that the S-phase is not a precursor phase of the H-phase. Along the [111]_{B2} zone axis, a set of secondary reflections (indicated by arrows) can be indexed to be either the R-phase or the H-phase [26], [30], as these precipitate reflections overlap in this particular zone axis. By tilting to the [100]_{B2} zone axis the additional reflections in Figure 5.3(a), indicated by the arrows, would be absent if it was the R-phase but are observed confirming the H-phase. The S-phase is best identified by its physical presence in the microstructure, as its secondary reflections overlap with the B2 \{110\} reflections [26]. The clear identification of the R-phase is compounded by the overlapping H-phase reflections, based on the DSC curves shown in Figure 5.2(b), the R-phase is also present in the microstructure.
Figure 5.3. SAD and BF-TEM depicting the microstructural evolution of Ni<sub>50.3</sub>Ti<sub>49.7-x</sub>Zr<sub>x</sub> alloys for (a) x = 1, (b) x = 7 and (c) x = 17.5 after aging at 400 °C for 100 h. Compositions in at.%.

For the [7Zr-400C-100h] sample shown in Figure 5.3(b), the same secondary reflections present in the [100] and [111] zone axes are those noted in Figure 5.3(a). Small precipitates are present in the microstructure. Based on morphology alone, one could deduce that these could be the S- and/or H-phases previously observed in the [1Zr-400C-100h] sample, with the H-phase in the early stages of nucleation since a clear acicular morphology is absent. *Santamarta et al. 2013* reported that the H-phase appears with a spherical shape in its early stages of precipitation [24]. However, the SAD pattern in Figure 5.3(b) confirms the precipitates to be H-phase and even after longer aging times only the H-phase having an acicular morphology is found. Thus, it is concluded that only the H-phase is present in this [7Zr-400C-100h] sample. Finally, for the [17.5Zr-400C-100h] sample, the SAD and corresponding BF-TEM in Figure 5.3(c) reveal a B2
structure. There are no secondary reflections present in either the [100] or [111] zone axes consistent with the precipitate-free microstructure.

**Microstructure after aging at 400 °C for 300 h**

With the absence of a transformation response in the DSC scan in the scanned range for either the 7 or 17.5 at.% Zr containing alloy after aging at 400°C for 100 h, samples with these compositions were also subjected to aging at 400°C for 300 h. As noted in Figure 5.2(c-d), a transformation temperature is observed for the [17.5Zr-400C-300h] sample but not for the [7Zr-400C-300h] sample. The microstructure of the [7Zr-400C-300h] sample shown in Figure 5.4(a) is comprised of precipitates with an oblate, spindle-like morphology and the corresponding SAD pattern can consistently be indexed to the H-phase (secondary reflections are indicted by the arrows). The prior nanoscale spherical precipitates achieved after aging at 400°C for 100 h (Figure 5.3(c)) have now coarsened into the more recognizable H-phase morphology [24]. Similarly, the spindle-like shaped precipitates of the H-phase, along with the confirming SAD, for the [17.5Zr-400C-300h] sample are displayed in Figure 5.4(b). Clearly between 100 and 300 h of aging, sufficient time occurred to nucleate and coarsen the precipitates. However, this [17.5Zr-400C-300h] condition exhibits a transformation temperature in the DSC scan, which is absent in the prior [7Zr-400C-300h] sample though it contained H-phase precipitates. Thus, the precipitation of the H-phase in of itself seems to be insufficient to raise the transformation temperature in the 7 at.% Zr containing alloy.
Figure 5.4. SAD and BF-TEM depicting the microstructural evolution of Ni$_{50.3}$Ti$_{49.7-x}$Zr$_{x}$ alloys for (a) $x = 7$, and (b) $x = 17.5$ after aging at 400 °C for 300 h. Compositions in at.%.

**Microstructural quantities and composition of phases after aging at 400 °C**

To elucidate the correlation between the microstructure and the transformation temperature, the inter-precipitate spacing and the compositional effects of precipitation were quantified. Two effects - a mechanical and a chemical - have been shown to determine the transformation in Nitinol alloys [14], [32]. The mechanical effect pertains to the influence of strain fields that are present around the precipitates and are a function of their size and inter-precipitate spacing [32]. These strain fields can act as obstacles to the transformation, making further undercooling necessary for the transformation to occur. The chemical effect appears when more Ni is partitioned to the precipitate phase than to the matrix phase [14], [24], [25] enabling the shape memory matrix phase to increase its transformation temperature. Which one of these effects dominates is a function of the processed microstructure. For example, the inter-precipitate spacing must be sufficiently large enough to not suppress the critical martensitic
nuclei from which the chemical effect's influence can be observed. The precipitate size and inter-precipitate spacing for the samples aged at 400°C are tabulated in Tables 5.4 and 5.5.

**Table 5.4.** Average precipitate sizes after various aging treatments of Ni$_{50.3}$Ti$_{49.7-x}$Zr$_x$ (with x = 1, 7 and 17.5) alloys as determined by TEM. A single dash indicates there was no TEM data acquired for that sample. A double dash depicts there were no precipitates present in that condition. The H-phase is designated H-(l) for the major axis and the minor axis is designated H-(w). For the [7Zr-400C-100h] sample, the precipitates have spherical morphology and the measurement represents the diameter.

<table>
<thead>
<tr>
<th></th>
<th>1 at.% Zr alloy</th>
<th>7 at.% Zr alloy</th>
<th>17.5 at.% Zr alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Type</td>
<td>Size (nm)</td>
<td>Type</td>
</tr>
<tr>
<td>400 °C / 100 h</td>
<td>S</td>
<td>20 ± 2.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H-(l)</td>
<td>100 ± 7.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H-(w)</td>
<td>30 ± 1.7</td>
<td></td>
</tr>
<tr>
<td>400 °C / 300 h</td>
<td>-</td>
<td></td>
<td>H-(l)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-(w)</td>
</tr>
<tr>
<td>550 °C / 24 h</td>
<td>--</td>
<td></td>
<td>H-(l)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-(w)</td>
</tr>
</tbody>
</table>

**Table 5.5.** Average inter-precipitate spacing after various aging treatments of Ni$_{50.3}$Ti$_{49.7-x}$Zr$_x$ (with x = 1, 7 and 17.5) alloys as determined by TEM. A single dash indicates there was not TEM data gathered for that alloy. A double dash means there were no precipitates present in the microstructure. The inter-precipitate spacing was calculated between precipitates regardless of the precipitate type of its neighbor.

<table>
<thead>
<tr>
<th></th>
<th>1 at.% Zr alloy</th>
<th>7 at.% Zr alloy</th>
<th>17.5 at.% Zr alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Spacing (nm)</td>
<td>Spacing (nm)</td>
<td>Spacing (nm)</td>
</tr>
<tr>
<td>400 °C / 100 h</td>
<td>18 ± 0.8</td>
<td>12 ± 0.0</td>
<td>--</td>
</tr>
<tr>
<td>400°C / 300 h</td>
<td>-</td>
<td>15 ± 0.7</td>
<td>25 ± 0.5</td>
</tr>
<tr>
<td>550°C / 24 h</td>
<td>--</td>
<td>60 ± 1.7</td>
<td>27 ± 1.2</td>
</tr>
<tr>
<td>550°C / 100 h</td>
<td>--</td>
<td>48 ± 0.5</td>
<td>43 ± 1.5</td>
</tr>
</tbody>
</table>
It is reasonable to infer for the [7Zr-400C] series that its transformation behavior is governed by the mechanical effect. The clear onset of precipitates after aging at 400°C for 100 h is evident (Figure 5.3) and after aging for 300 h the microstructure is determined by coarsened H-phase precipitates (Figure 5.4(a)) whereas no transformation peak is observed in the DSC scan (Figure 5.2(c)). After 100 h of aging, the precipitates are ~10 nm in size with an inter-precipitate spacing of ~12 nm. Due to the precipitate size and spacing being close to the same length, it is likely that the strain fields that are surrounding the precipitates are pinning the martensite and not allowing a transformation [25]. Even after continuous aging up to 300 h, the precipitates have only coarsened to ~24 nm with the inter-precipitate spacing now being ~15 nm, Table 5.5, and no transformation is observed in the DSC scans for this condition. However, it appears that strain fields (mechanical effect) are playing a dominant role and consequently, the chemical effect was also investigated to determine the partitioning of Ni between the matrix and precipitates. Figure 5.5(a) shows an atom probe reconstruction of the [7Zr-400C-300h] sample. The compositions for the matrix and precipitates are given in Table 5.6. The matrix is Ti-rich as compared to the precipitate, with the precipitate enriched in Ni and Zr. Though the necessary Ni partitioning has occurred, the lack of a notable transformation in the scanned range confirms that the still close inter-precipitate spacing, ~15 nm (given in Table 5.5) appears to be sufficient to suppress an increase in the shape memory transformation for the [7Zr-400C-300h] condition.
Figure 5.5. APT reconstruction of (a) Ni$_{50.3}$Ti$_{42.7}$Zr$_7$ delineated using a 6.57 at.% Zr isoconcentration surface, and a (b) Ni$_{50.3}$Ti$_{42.7}$Zr$_{17.5}$ delineated by a 14.57 at.% Zr isoconcentration surface. Both of these samples were aged at 400°C for 300 h.

Table 5.6. Average matrix and H-phase precipitates compositions for [7Zr-400C-300hr] and [17.5Zr-400C-300h]. The composition values are average values and correspond to the datasets shown in Figure 5.5 (a and b) respectively.

<table>
<thead>
<tr>
<th>Zr addition (at.%)</th>
<th>Matrix Composition (at.%)</th>
<th>H-phase Precipitate Composition (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Ti</td>
</tr>
<tr>
<td>7</td>
<td>50.3 ± 0.01</td>
<td>43.36 ± 0.00</td>
</tr>
<tr>
<td>17.5</td>
<td>48.94 ± 0.04</td>
<td>32.57 ± 0.02</td>
</tr>
</tbody>
</table>

For the [17.5Zr-400C-100h] condition, the SAD reveals a B2 structure as shown in Figure 5.3(d). The absence of distinct precipitates, which when present would result in chemical partitioning within the matrix, may explain why no transformation peaks are evident in the DSC scans shown in Figure 5.2(d). However, upon the clear formation of H-phase precipitates after 300 h (Figure 5.4(b)), a transformation peak in the DSC curve can be observed (Figure 5.2d). APT of the [17.5Zr-400C-300h] sample (Figure 5.5(b)) reveals that the increase of Zr solute content
results in a reduction of Ni content in the matrix upon precipitation. Increasing the amount of Zr solute appears to offset the amount of Ti in the H-phase when comparing both alloys. Hence, the further reduction of Ni to ~49 at.% as compared to ~50.3 at.% in the matrix for the 17.5 and 7 at.% alloys respectively after aging at 400°C for 300 h contributes as chemical effect to raising the transformation temperature. The inter-precipitate spacing for the [17.5Zr-400C-300h] condition is ~25 nm, which is larger than the prior ~15 nm for the [7Zr-400C-300h] condition (Table 5.5). Thus, a critical inter-precipitate spacing appears to have been reached enabling the chemical effect to be more dominant.

When comparing the microstructure for all three alloys after 100 h of aging (or 300 h), the H-phase is present. This suggests a fairly large Zr solubility range for the H-phase. It is also likely the equilibrium phase, considering its complex and large unit cell that must be formed. In addition, the lack of any of the traditional binary Ni-rich precipitates, such as Ni$_4$Ti$_3$, to form for any of these compositions. However, using ThermoCalc®, neither the S- nor the H-phase could be predicted for varying Zr content (1-20 at.%) and temperature (400-550°C). Instead, with increasing Zr content, the Ni$_4$(Ti,Zr)$_3$ precipitate in a B2 matrix is predicted, indicating the need to further develop thermodynamic databases for this type of alloy.

In addition, at the very dilute limit of 1 at.% Zr, a clear indication of a secondary precipitate phase, the S-phase, exists along with the H-phase evident by two distinct precipitate morphologies, Figure 5.3(a) [26]. The Zr solubility of the S-phase is much more limited as it is not observed in either the 7 or 17.5 at.% Zr containing alloys. Interestingly, these low Zr concentrations can facilitate H-phase precipitates, as prior work has only reported this at higher Zr concentration between 15 and 20 at.%}. This provides new insights into the solubility limits of each of these
phases. Since the H-phase formation and coarsening require longer aging times for higher Zr concentrations at 400°C, it also indicates the slow diffusivity of Zr in these alloys.

With the characterization and discussion of the samples aged at 400°C finished we now focus on the samples aged at 550°C for different times. Hereafter the two aging temperatures are compared.

**Microstructural quantities and composition of phases after aging at 550 °C**

The hardness and transformation responses for this alloy have been previously introduced when the hardness data and transformation behavior after 400°C of aging was discussed; therefore, the links to the microstructure are established and ready to be discussed.

After aging samples containing 1, 7 and 17.5 at.% Zr at 550 °C for 24 and 100 h the resulting microstructures were characterized (opposed to aging for 100 and 300 h at 400°C). Figure 5.6(a-c) are a series of BF-TEM and SAD patterns for Ni_{50.3}Ti_{49.7-x}Zr\_x alloys with (a) x = 1, (b) x = 7 and (c) x = 17.7 aged at 550 °C for 24 h. In contrast to aging at 400 °C, at this higher temperature, a B2 microstructure with no apparent S- or H-phase precipitates is observed for the [1Zr-550C-24h] sample. The lack of these clear precipitates appears to alter the transformation pathway, as previously discussed above in reference to Figure 5.2. The [1Zr-550C] series retained a single transformation, albeit it with instability upon multiple thermal cycles, with near similar onset and finish transformation temperatures. In contrast, the binary alloy, without the 1%Zr, retains an asymmetric R-phase transformation. This difference indicates the influence of Zr on the transformation pathway, even in dilute concentrations.
Figure 5.6. Microstructural evolution of (a) 50.3Ni-48.7Ti-1Zr (at.%), (b) 50.3Ni-42.7Ti-7Zr (at.%), and (c) 50.3Ni-32.2Ti-17.5Zr (at. %) as a function of ternary addition amount at 550°C after 24 h of aging.

The microstructure for the [7Zr-550C-24h] sample is shown in Figure 5.6(b). In the SAD pattern, along the [111] zone axis, secondary reflections (marked by the arrows) is evident and is consistent with either the H-phase or R-phase. After tilting to the [100] zone axis, it was determined that these reflections were that of the H-phase. The lack of an R-phase transformation peak, where the R-phase reflections could be masked by the H-phase as previously discussed, indicates that the R-phase is not present in this alloy. Additionally, the morphology of oblate, spindle-like precipitates captured in the microstructure are consistent with the H-phase. With the continual addition of Zr to the Ni_{50.3}Ti_{32.2}Zr_{17.5} alloy, there is still evidence in the SAD patterns and BF image that the H-phase precipitates are present. However, these precipitates are smaller than the precipitates in the 7% Zr alloy at 550°C, Table 5.4. This difference in size could
be contributed to either slower kinetics because of the increase Zr content in the matrix and/or a change in the phase equilibrium conditions as both the increased Zr content and temperature would shift its phase position relative to the ternary equilibrium phase boundaries. Since the phase field of the H-phase has yet to be defined either experimentally or computationally, determining how is phase fraction and composition change with either temperature or composition is still unknown. It is interesting to note that the transformation behavior, Figure 5.2, revealed a transformation peak for the [17.5Zr-550C-24h] alloy but no transformation peak for the [7Zr-550-24h] alloy, where both alloys have H-phase precipitation. A similar observation was noted above for these two alloys at 400°C after 300 h of aging, where the higher content alloy had a transformation and the lower content alloy did not. Again, this could be contributed to either a differences in inter-precipitate spacing and/or a chemical difference in the precipitate. To determine this difference, we have compared the microstructure of these two alloys at 550°C-100 h.

Figure 5.7 (a-c) are the series of TEM SAD patterns and BF images that capture the microstructure of (a) Ni_{50.3}-Ti_{48.7}-Zr_{1} (at.%), (b) Ni_{50.3}-Ti_{42.7}-Zr_{7} (at.%), and (c) Ni_{50.3}-Ti_{32.2}-Zr_{17.5} (at. %) at 550°C after 100 h of aging. Consistent with the 24 h aging condition, the [1Zr-100hr-550C] alloy was indexed to the B2 phase. For both the 7% Zr and 17.5% Zr alloys, the H-phase precipitate was confirmed from the SAD pattern in the [111] and [100] zone axes as well as their microstructures in the micrographs, Figure 5.7 (b-c). The increased time allowed the precipitates in the 17.5% Zr alloy to approximately double in size, Table 5.4. Interesting, the H-phase precipitates in the 7% Zr alloy did not significantly change from 24 to 100 h, Table 5.4, with their average values within each other’s standard error suggesting that for this composition and temperature the precipitates readily nucleated and grew to their size as compared to a higher concentration of Zr.
As tabulated in Table 5.5, the inter-particle spacing at 24 h for the 7% alloy is ~60 nm while the spacing for the 17.5% alloy is ~27 nm. Since the higher Zr content alloy has a smaller spacing, and a very modest onset of a transformation peak, Figure 5.2, it suggestive that the lack of a transformation in the 7% Zr alloy is not from a mechanical effect. Rather it likely resides in a chemical effect. Upon longer aging up to 100 h, a transformation upon heating was noted in the 7% Zr alloy, where the inter-precipitate spacing was found to be ~50 nm. Though this is slightly smaller than the 24 h aged inter-precipitate spacing for the equivalent 7% Zr composition, Table 5.5, where one could expect the same value since the precipitates did not coarsen significantly, the difference likely resides in the limited field of view provided by a TEM micrograph. Even though
the 100 h aged condition has a shorter inter-precipitate than then 24 h, the values are similar and these differences are contributed to sampling sizes. In contrast, the inter-precipitate spacing was found to be sufficiently larger between 24 and 100 h at 550°C for the 17.5% Zr alloy, Table 5.5, with an increase in the transformation temperature, Figure 5.2(d). Upon longer aging at 100 and 300 h for this 17.5% Zr alloy, the transformation peak position further increased. With the increased inter-precipitate spacing, the chemical effects of the precipitation events on the matrix and its subsequent transformation temperature become more prominent. After 24 h of aging time, the size of the H-phase precipitates is ~25 nm in length and ~11 nm in width with an inter-precipitate spacing of ~27 nm. Here, the inter-precipitate spacing is similar to the size of the precipitates where upon overlapping strain fields created by the precipitate will hinder the martensitic transformation [14], [25], [32] With continued aging, the precipitates coarsen to ~65 nm in length and ~21 nm in width, Table 5.4, with an inter-precipitate spacing is ~43 nm, Table 5.5. As discussed previously by the authors in reference [25], as these precipitates coarsen in the size, the strain at the interface increases until it is relieved by the insertion of misfit dislocations. Such an insertion would change the surrounding strain fields. Coupled with the increased inter-precipitate spacing, the influence of the mechanical effect is reduced, albeit likely not diminished as will be discussed below.

Figure 5.8 and Table 5.7 are the respective APT reconstructions and compositions for the 7 and 17.5% Zr alloys. First one can glean that the 7% Zr alloy has a higher Ni matrix content than the 17.5% Zr alloy, ~54% vs. 51% respectively. In a comparison of transformation temperatures, Figure 5.2 and Table 5.3, this would provide a chemical effect argument considering that both of these alloys have near equivalent and tens of nanometer inter-precipitate spacings, where the mechanical effect would be lessened. However, comparing the compositions of the precipitates
and matrix for the same overall alloy composition but different aging temperatures, Tables 5.6 and 5.7, a chemical difference is noted between the alloys and aged temperature, with a lower Ni content in the matrix for the lower aged temperature alloys. Such differences in composition as a function of aged temperature could be expected since these alloys are subjected to annealing in a different region of their ternary phase field which was water quenched in. However, the higher aged temperature alloys had a higher transformation temperature with a higher matrix Ni content for equivalent compositions. This would seem contradictory to a strict chemical effect. Upon a closer look at the inter-precipitate spacing between the equivalent alloys at the different aging temperatures reveals a larger inter-precipitate spacing with increased temperature, Table 5.5. This provides support that the higher temperature aged alloys are able to phase transform at a higher temperature because the mechanical effects created by closely spaced precipitates have lessened, even though the matrix composition is slightly more Ni-rich. This demonstrates the complex interaction of precipitate composition, size, and spacing on the transformation behavior and how different aging conditions, even in the same alloy composition, will result in marked differences in the shape memory transformation temperature.

Figure 5.8. Atom probe reconstruction of (a) Ni$_{50.3}$-Ti$_{42.7}$-Zr$_7$, and (b) Ni$_{50.3}$-Ti$_{32.2}$-Zr$_{17.5}$ at 550°C after 100 h aging.
Table 5.7. Average matrix and H-phase precipitates compositions for [7Zr-550C-100hr] and [17.5 Zr-550C-100h]. These compositions correspond to the reconstructions shown in Figure 5.8.

<table>
<thead>
<tr>
<th></th>
<th>Matrix Composition (Average)</th>
<th>H-phase Precipitate Composition (Average)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Ti</td>
</tr>
<tr>
<td>100 h (7%)</td>
<td>53.96 ± 0.05</td>
<td>43.62 ± 0.75</td>
</tr>
<tr>
<td>100 h (17.5%)</td>
<td>51.1 ± 0.04</td>
<td>34.0 ± 0.02</td>
</tr>
</tbody>
</table>

5.4 Conclusions
In this comparative study, the additions of varying Zr content in Ni-rich NiTi alloys were explored at two aging temperatures, 400°C and 550°C, to determine the effect of Zr additions on microstructure and transformation behavior. The following conclusions were noted:

i. In a 50.3Ni-48.7Ti-1Zr (at. %) alloy, aging at 400°C yielded two different precipitate phases - the S-phase and H-phase after 100 h. DSC results revealed upon aging a two-step transformation pathway (B2-R-B19') upon heating and cooling. This is more commonly referred to as a symmetric R-phase transformation. Aging at 550°C yielded no secondary phases in the microstructure. The DSC curves indicated a one-step transformation; however, the onset and finishing temperatures for this transformation appeared to be lower than the solutionized condition and all of these transformations exhibited instabilities for all of the aging conditions.

ii. In a 50.3Ni-42.7Ti-7Zr (at. %) alloy, aged at 400°C for 100 h, yielded small H-phase precipitates that were ~10 nm. With continued aging to 300 h, these precipitates coarsened to ~24 nm in length and ~8 nm in width. Though precipitates were present in the microstructure, there was no evidence of a transformation response in the tested range. This is
attributed to a mechanical effect where the close proximity of the precipitates (~12 nm in spacing) created strain fields that suppressed the transformation. At 550°C, after 24 h aging, the microstructure revealed coarsened H-phase precipitates ~72 nm in length and ~20 m in width at an inter-precipitate spacing of ~60 nm. The precipitates remained approximately the same size after continued aging up to 100 h. A transformation upon heating was detected in the DSC scan for the 48 h aged alloy which became more stable after 100 h aging time. This was attributed sufficient spacing between the precipitates coupled with a higher Ni content in the precipitate that enabled the chemical effect to increase the transformation temperature to evident.

iii. Finally, in a 50.3Ni-32.2Ti-17.5Zr (at. %) alloy aged at 400°C after 100 h aging, a B2 structure was found along with no apparent transformation within the DSC scan range of -90°C to 300°C. Upon further aging to 300 h, coarsened H-phase precipitates were found in the microstructure that were ~28 nm in length and ~10 nm in width with a transformation peak upon heating. Thus between 100 and 300 h of aging at 400°C, sufficient time occurred to nucleate the H-phase and for them to coarsen to a size where their inter-precipitate spacing (~25 nm) would not suppress the transformation. Since this alloy’s matrix composition was more Ni-lean than the 7% alloy for the same aging condition, with an inter-precipitate spacing nearly twice as large, the 17.5%Zr was able to reveal an increase in the transformation temperature whereas it was absent in the 7%Zr alloy. Previous work reported by the authors for 550°C aging [25] revealed a H-phase precipitation after 24 h with precipitates being ~26 nm length and ~11 nm in width with an inter-precipitate spacing near 27 nm and an observable single transformation pathway peaks in the DSC scan. With continued aging, the H-phase coarsen to ~65 nm in length and
~21 nm in width with an increased inter-precipitate spacing of ~ 43 nm. The single pathway transformation DSC peaks increased in temperature and become more prominent providing more evidence of a lessening of the mechanical effect in suppressing the transformation temperature.

iv. The competitive interaction between the mechanical and chemical effect could be ascertained through these comparisons. For example, at 550°C/100 h, the 17.5% Zr and 7%Zr alloy had nearly equivalent inter-precipitate spacing of ~43 and ~48 respectively, the increased transformation temperature in the 17.5% Zr alloy is contributed to it having a more Ni-lean matrix composition (~51%) than the 7%Zr alloy’s matrix composition (~54%). In this comparison, the chemical effect on transformation was readily observable. Similarly, the 400°C/300 h conditions for these two alloys revealed an H-phase inter-precipitate spacing of ~ 15 nm and ~25 nm for 7%Zr and 17.5%Zr respectively; however, the 17.5%Zr alloy revealed a transformation peak in the DSC which was absent in the 7%Zr alloy. The 17.5%Zr alloy’s matrix was also more Ni-lean (~49%) as compared to the 7%Zr alloy’s matrix (~50.3%). Though the 400°C aged alloys had less Ni content in the matrix as compared to their 550°C aged counterparts, the increased inter-precipitate spacing was nearly twice as large which reduced the suppression of the transformation temperature created by the overlapping strain fields from the mechanical effect. This is suggestive of the strong influence the mechanical effect has on the transformation temperature even in alloys where the composition is more favorable for an increase in the transformation temperature but whose inter-precipitate spacing is too close.
5.5 References


CHAPTER 6

CONCLUSIONS AND FUTURE WORK

6.1 Summary of findings

In this work, the influence of Zr additions on phase stability, transformation temperatures, and thermomechanical behavior in Ni-rich Nitinol was investigated through various microanalysis techniques. This work explored the effects of Zr in three different ranges: (1) the microstructural and thermo-mechanical characterization of a 17.5% Zr alloy to optimize the alloy in terms of transformation behavior and dimensional stability, (2) the characterization and mechanical behavior of a 1%Zr Ni-rich Nitinol alloy to determine what phases precipitated and their effect on the dimensional stability- a complimentary 1%Hf alloy was compared to the 1%Zr alloy also in this work, and (3) the microstructural evolution and transformation behavior of 1, 7, and 17.5% Zr at 400°C and 550°C aging temperature to determine the solubility of phases present and their effect of transformation behavior. These findings how significant contributions to the shape memory alloy field. First, this work was able to quantify inter-precipitate spacing as well as the chemical effect using atom probe tomography. This is significant because this brings light to the closely competing effects and their impact on shape memory transformation. In addition, to the author’s knowledge, this is the first study that includes dilute additions. The importance of this study was showing that the dilute additions still resulted in precipitation, despite the small amount of the ternary alloying element.
As previously discussed, the phases found present in these alloys do not appear on the ternary phase diagram. Consequently, the experimental results from this study were plotted on the ternary phase diagrams shown in Figure 6.1 and 6.2. Using APT for the longest time, the compositions of the phases reveal the location of their solvus line. First starting with 550°C (Figure 6.1), the APT data for the H-phase will be used. The compositions previously reported for 7% and 17.5% were 54Ni-37Ti-8Zr (at.%) and 57Ni-22Ti-21Zr (at.%). The two compositions are plotted as points on the diagram and the dash line represents the solvus line. The arrow is at the end of the line because it has not been experimentally developed where this line ends.

![Figure 6.1](image)

**Figure 6.1.** Schematic of experimental results plotted on a Ni-Ti-Zr phase diagram generated at 550°C.

Building from the plot shown in Figure 6.1, the phases from the experimental results at 400°C. The H-phase boundary will be taken from the previously plotted data at 550°C due to the fact that no H-phase APT data could be collected at 1% Zr compositions. The compositions for
the S-phase are plotted in the phase diagram shown in Figure 6.2. The S-phase composition that was used for the plot is 54Ni-43Ti-3Zr.

![Phase Diagram](image)

**Figure 6.2.** Schematic of experimental results plotted on a Ni-Ti-Zr phase diagram generated at 400°C.

### 6.2 Summary results of a 50.3-32.2Ti-17.5Zr (at.%) alloy

In chapter 3, a 50.3-32.2Ti-17.5Zr (at.%) alloy had its transformation behavior and thermomechanical behavior correlated to the microstructure as a function of aging times at 550°C. Upon solution annealing, no transformation response was detected in the tested range; however, after 4 hours of aging or longer the onset of a martensitic transformation was noted to initiate at ~ -10°C (4 hours) with continued increase in this transformation temperature to ~ 135°C with aging to 300 hours. Using TEM, a precipitate phase was found to be present in the B2 shape memory matrix phase and it was identified to be the H-phase. This precipitate phase was present starting at 4 hours aging time and continued to coarsen with increased aging. These precipitates played an
important role in the transformation behavior of the alloy as the increase in transformation
temperature was correlated to the precipitate size, number density, inter-precipitate spacing, and
composition. When the precipitates were closely spaced with an inter-precipitate spacing of 12
nm, the transformation temperature was suppressed due to overlapping stain fields. Upon
coarsening, the inter-precipitate spacing increased to 43 nm, and the transformation temperature
was able to be detected and increased to 115°C.

Selected aged conditions (4 hours and 72 hours) were tested via compression and tensile
loading through constant stress thermal cycling and it was found that the residual strains in both
samples were very small up to 1000 MPa. The room-temperature superelastic response in
compression determined that the 4 and 72 hours aged samples exhibited the classical ‘flag-like
behavior’ with the 4 hour aged sample exhibiting a lower yield stress and more defined unloading
“plateau” than the 72 hour sample.

6.3 Summary results of a 50.3-48.7Ti-1Zr or 50.3-48.7Ti-1Hf (at.%) alloy

Chapter 4 explored dilute additions of Zr (1 at.%) to a Ni-rich Nitinol alloy and the effect
on transformation behavior and microstructure at 400°C. In addition, the 1% Zr alloy was
compared to a 1% Hf alloy to determine differences in precipitation, transformation temperatures,
and functional mechanical behavior.

For the 50.3Ni-48.7Ti-1Zr alloy, solution annealing followed by water quenching resulted
in a solid solution B2 phase microstructure. This condition resulted in a B2-B19’ transformation
pathway upon thermal cycling which was indicated by one transformation peak in the DSC scan.
However, with aging of 1, 10, 24, and 100 hours a nanoscale spherical precipitate was formed that
has been denoted as the S-phase. These spherical precipitates slightly coarsened with increased
aging time. At 24 hours and 100 hours aging time, there were another precipitate was observed. This latter formed precipitate was oblate, spindle-like in morphology with the selected area diffraction revealing it to be the H-phase. Upon precipitation of these phases, the transformation pathway changed from B2-B19’ in the solution annealed condition to a B2-R-B19’ pathway or a symmetric R-phase transformation pathway. This was indicated by two transformation peaks that was seen in both heating and cooling cycles of the DSC.

The 50.3Ni-48.7Ti-1Hf alloy behaved similarly to the 1% Zr alloy upon solution annealing, showing a B2 phase microstructure and a B2-B19’ transformation pathway. Upon aging to 24 hours, Ni₄Ti₃ precipitates were observed, and the transformation pathway remained the same as in the solution annealed condition, i.e. a one-step transformation. However, at 48 hours of aging, the Ni₄Ti₃ precipitates were absent and both the S-phase and H-phase were found to be in the microstructure. In addition, the transformation pathway changed to an asymmetric R-phase transformation.

The mechanical behavior was then linked to the microstructure evolution of these alloys. The 1% Zr alloy aged at 10 hours and the 1% Hf alloy aged at 24 and 48 hours, were tested in tension and compression under various loads to determine the amount of actuation strain and residual strain for each alloy/aging condition. The 1% Zr alloy had the most actuation strain % in both tension and compression at 400 MPa, while the 1% Hf alloy aged at 48 hours at the least amount of actuation strain % in both tension and compression at 400 MPa. In measuring residual strain, in compression the 1% Hf alloy aged at 48 hours at the most residual strain at ~0.44% under the maximum load of 400 MPa, and the 1% Zr sample had the lowest at ~0.15%. In tension, all alloys had approximately the same amount of residual strain at ~0.52% with the applied stress of 400 MPa.
To the researcher’s knowledge, this is the first time the S-phase has been reported in the Ni-rich Nitinol alloys. The secondary reflections for the S-phase were found to overlap those of the \{110\} reflections of B2 making clear phase identification difficult and a recommendation for future work.

6.4 Comparison of transformation temperatures as a function of Zr content and aging conditions

Finally in Chapter 5 a comparative study of transformation as a function of Zr and various aging conditions at 400°C and 550°C were completed. This study helped bridge gaps in processing not done in Chapters 3 and 4 as well as included an additional 50.3Ni-42.7Ti-7Zr alloy that spanned the compositional divide from the prior two studies. By adding a new range of Zr addition, as well as investigating the other additions at various temperatures, the microstructural evolution, transformation behavior, and phase composition at two different aging temperatures as a function of Zr additions in a Ni-rich NiTi shape memory alloy was determined.

As noted above, the 1% Zr work was reported in Chapter 4 to have precipitated two phases: the S-phase and H-phase. However, in this same alloy aged at 550°C up to 100 hours, neither of these precipitates or any other secondary phases were observed in the B2 matrix. This alloy at 550°C also exhibited a single transformation pathway of B2-B19’ for all aging conditions.

The 7% alloy at 400°C after 100 hours aging time yielded nanoscale precipitates that were determined to be the H-phase from the indexed diffraction patterns. With continued aging to 300 hours, these precipitates coarsened and formed the familiar shape of the H-phase spindle precipitate. There was no transformation response detected in the tested range for this alloy.
between -90°C to 300°C, indicating the transformation was well below room temperature. At
550°C, a transformation was noted to occur at 48 hours and became more apparent after 100 hours
of aging. After 24 hours of aging, coarse, H-phase precipitates were noted in the microstructure
indicating that the onset of H-phase precipitation in of itself is insufficient to increase the
transformation temperature. The precipitates were also noted not to substantially change size with
increasing time, with a size of approximately $67 \pm 2.4$ nm in width and $18 \pm 3.4$ nm in length. This
led to the rational that the transformation was being governed by a compositional effect, as a
transformation peak was noted for the longer aged samples.

For the 17.5% alloy at 400°C, at 100 hours of aging, the microstructure was a B2 matrix
phase and there was no transformation response detected in the DSC tested range. With further
aging to 300 hours, a transformation response was detected and with corresponding coarsened H-
phase precipitates $10 \pm 1.7$ nm in width and $28 \pm 2.3$ nm in length present in the microstructure.
As reported in Chapter 3, aging at 550°C also formed the H-phase precipitates after 4 hours aging
time. These precipitates grew up to $21 \pm 2.6$ nm in width and $65 \pm 5.4$ nm in length and the
transformation temperature increased to $\sim 135^\circ C$ with continued aging.

The major findings of this comparison revealed that the precipitation of the H-phase in of
itself does not increase the transformation temperature. Even more interestingly was that the inter-
precipitate spacing of $\sim 45$ nm was found to exist for both the 7% and 17.5% Zr alloys at 100 hours
aging time at 550°C; however, the transformation temperature was 115°C for 17.5% and -5°C for
7%. The precipitates were approximately evenly separated where the overlapping strain field
effects that suppress the alloys could be considered approximately equivalent, the transformation
temperatures were different. This demonstrated the complex interplay of the mechanical and
chemical effect in regulating the transformation temperature in these alloys.
6.5 Future work and direction

With regard to future work, two main areas have been identified. First, the S-phase has been identified by its distinct spherical morphology, with its composition being 54Ni-43Ti-3Zr (at.%) determined by atom probe but its crystallography was not determined. Determining this phase’s crystal structure would be important as it could lead to new insights into what and why this phase formed. Second, the H-phase was able to form over a composition range from 1 to 17.5% Zr. Though Zr shares the same transition metal group family as Ti, it obviously does not prefer to form a site substitution for Ti in yielding a solid solution, even in dilute limits. Experimentally determining the compositional and temperature phase field of this precipitate is critical. It will then help improve thermodynamic data bases where upon more systemic means of engineering the precipitate can be made. Clearly its precipitate has both a strong mechanical and chemical effect on the shape memory transformation temperature.

Finally, NASA, the supporter of this research has been very keen on low temperature transformation temperatures for more space based alloys, in particular alloys around 7%Zr. Such alloys would be ideal for passive aeronautical applications in a space environment for chevrons, engine chines, and vortex generators. Some preliminary work has been completed for 50.3Ni based alloys with a Zr content of 6.5% Zr, 7.5% Zr, and a quandary 7%Zr-1%Cr alloys. The Vickers Hardness curves and the DSC curves for these are shown in Appendix A. In this preliminary work, differences in hardness as well as the transformation behavior were observed, particularly for the Cr added alloy. Future work in exploring the microstructures, as done above, offers new areas of research exploration. The work provided in this dissertation provides the ground work of comparison to these alloys, where minute changes in Zr content could be further examined.
APPENDIX A

The following figures are a collection of preliminary data for 6.5%Zr, 7%Zr-1%Cr, and 7.5% Zr alloys at 400°C and 550°C. The compiled data consisting of Vickers hardness curves, and DSC curves are shown below.

**Figure A.1.** Vickers hardness curves as a function of aging time for (a) 6.5%Zr, (b) 7%Zr-1%Cr, and (c) 7.5%Zr at 400°C. All of these alloys achieved a peak hardness value after 24 hours aging time.

**Figure A.2.** Vickers hardness curves as a function of aging time for (a) 6.5%Zr, (b) 7%Zr-1%Cr, and (c) 7.5%Zr at 550°C. These alloys achieved a peak hardness much faster than at 400°C.
Figure A.3. DSC curves for (a) 6.5%Zr, (b) 7%Zr-1%Cr, and (c) 7.5% Zr at 400°C. There was no transformation response detected for any of the alloys in the tested range.

Figure A.4. DSC curves for (a) 6.5%Zr, (b) 7%Zr-1%Cr, and (c) 7.5% Zr at 550°C. For alloys (a) and (b), there was a transformation at 24 hours; however, with an increase in Zr content (alloy (c)) a transformation does not occur until 100 hours. It is interesting to note that all transformation pathways are B2-B19' with the exception of alloy (b) where at 24 hours of aging on the heating cycle it is starting to form a doublet peak and upon aging at 100 hours has a symmetric R-phase transformation pathway.