INFLUENCE OF MICROSTRUCTURE ON THE SHAPE MEMORY PROPERTIES
OF TWO Ti-LEAN, Ni-Ti-Pt HIGH TEMPERATURE
SHAPE MEMORY ALLOYS

by
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ABSTRACT

Because of NiTi’s superior properties (work output, strength, ductility, recoverable strain, etc.) it is the base system of choice for development of derivative high-temperature shape memory alloys (HTSMAs). Ternary additions of Hf, Zr, Pt, Pd, and Au can be made, in quantities greater than \( \approx 10 \text{ at.\%} \), to increase the transformation temperature of Ni–Ti based SMAs. Pt as an alloying addition is attractive because of (1) its efficiency in raising the martensitic transformation temperature, (2) the relatively stable properties during thermal cycling of Pt–containing Nitinol (NiTi), and (3) the high work outputs of Ni–Ti–Pt alloys relative to other HTSMAs. Platinum containing samples of NiTi were thermally processed to explore the utility of Ti–lean precipitates for matrix strengthening and stabilization of shape memory properties during thermomechanical cycling. Two alloys, \( \text{Ti}_{48.5}\text{Ni}_{30.5}\text{Pt}_{21} \) and \( \text{Ti}_{49.5}\text{Ni}_{29.5}\text{Pt}_{21} \), were heat treated for 1, 5, 24 and 100h at 500, 550, 600, 650, and 700\( ^\circ \text{C} \) and examined using SEM, EDS, DTA, XRD and TEM techniques. Two relevant precipitate phases, the \( P_L \) and \( \text{Ti}_2(\text{Ni,Pt})_3 \) phases, were identified, characterized and the thermodynamic stability and relevant behavior during thermal processing determined. Samples were then subjected to thermomechanical testing that consisted of two parts, (1) two thermal cycles (75\( ^\circ \text{C} \) to 500\( ^\circ \text{C} \) to 75\( ^\circ \text{C} \)) each at stresses of 0, 50, 100, 150, 200, 250, and 300MPa, and (2) 100 thermal cycles at 200MPa. With this combination of systematic microstructural characterization and isobaric thermal cycling, the link between microstructure and shape memory performance was made. The influence the \( P_L \) and \( \text{Ti}_2(\text{Ni,Pt})_3 \) phases have on properties such as martensitic transformation temperatures, transformation strain, and accumulated irrecoverable strain are explained and discussed. Specifically, it was found that the \( P_L \)–phase suppresses transformation temperatures and strains through a matrix strengthening effect, but also stabilizes property evolution, while the \( \text{Ti}_2(\text{Ni,Pt})_3 \) phase plays a dominant role in modifying matrix chemistry, and subsequent transformation temperatures.
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This dissertation is dedicated to my parents who never knew I’d come this far, and to the future students who don’t think they can.
CHAPTER 1

INTRODUCTION

High temperature shape memory alloys (HTSMA’s) are currently under various stages of development. As SMAs are sought for use in high-temperature applications, NiTi’s superior properties, including work output, strength, ductility, and recoverable strain make it the base system of choice for development of derivative high-temperature alloys. Nitinol (Ni-Ti based) SMAs have been used in a wide array of commercial applications such as eyeglass frames, cell phone antennas, appliance controllers, pipe couplings, as well as medical and dental devices. Most of the alloys developed to date are used in low temperature applications given that the maximum transformation temperature of binary NiTi SMA’s is approximately 100°C. There are numerous potential applications for higher temperature SMA’s in the automotive, aeronautical and energy exploration industries, and active efforts are underway to develop viable HTSMA’s, especially for use as solid state actuators.

Ternary additions of Hf, Zr, Pt, Pd, and Au can all be added, in quantities greater than approximately 10 at.%, to increase the transformation temperature of Ni-Ti based SMA’s. Pt as an alloying addition is attractive because of (1) its efficiency in raising the martensitic transformation temperature (the transformation responsible for SMA’s unique properties), (2) the relatively stable properties during thermal cycling of Pt-containing Nitinol, and (3) the relatively high work outputs of Ni-Ti-Pt alloys. However, additional research and development is still necessary to understand how the microstructure affects the shape memory performance in Ni–Ti–Pt alloys.

As alloys are developed for solid state actuation, there are several shape memory properties of interest that must be understood and characterized for adequate design and implementation. Specifically, the characteristic transformation temperatures of the property con-
trolling martensitic transformation (martensite start/finish and austenite start/finish temperatures), the amount of strain a SMA can produce under a biased load, and the amount of irreversible strain accumulated during thermal cycling are of the most importance. While the interplay between microstructure and shape memory properties has been thoroughly studied in the binary Ni–Ti system, there are several aspects of the Ni–Ti–Pt alloys that are not understood. The research presented here will link the microstructures of various samples of two Ni–Ti–Pt alloys with their shape memory performance.

This study will investigate two Ni–Ti–Pt alloys, Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ and Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$. These alloys were chosen to explore the Ti–lean precipitates that are available in a Ni and Pt rich system, and how these precipitates can be used to control microstructures and subsequent shape memory properties. Samples of these alloys were heat treated at various temperatures, for various times, to identify and characterize the precipitates available within these alloys. Two precipitates were found; a small, coherent, and finely distributed phase referred to as the P$_L$–phase, and a Pt containing version of a metastable Ni–Ti phase, Ti$_2$(Ni,Pt)$_3$.

Using various techniques, including scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM), selected area electron diffraction (SADP), X–ray diffraction (XRD) and accompanying Rietveld analysis, the above mentioned precipitates and their accompanying transforming matrices were explored and characterized. One chapter will be dedicated to the microstructural characterization, quantifying the relevant features and differences created by the variation in alloy Ti content, and heat treatment procedure.

A second chapter will describe the results of mechanical testing. As these alloys are being sought for solid state actuator development, isobaric thermal cycling experiments were used to determine shape memory performance. This process used compressive samples that were loaded and thermally cycled through the martensitic transformation. This testing method provided a testing environment that would simulate the loading and thermal cycling
conditions that a HTSMA would experience in service as a solid state actuator. From a discussion and interpretation of these results, the role of characterized microstructural constituents will be identified and explained.

The results of this systematic study provide information on how Ti–lean precipitates can affect various shape memory properties of Pt containing, Ni–Ti HTSMAs. From this work, critical processing and heat treatments routes have been identified that will help enable the future use of Ni–Ti–Pt alloys for use as solid state actuators. Various areas for further research have also been identified for additional development within this alloy system.
CHAPTER 2
BACKGROUND & RELEVANT LITERATURE

2.1 Shape Memory Alloys and the Martensitic Transformation

Shape memory alloys (SMAs) are a class of alloys that show a phenomenon where a sample can experience a seemingly permanent shape change then “remember” its original shape after being heated up to a critical temperature characteristic of the sample’s martensitic transformation. This process is known as the “shape memory effect” and is the aspect of SMAs from which their name is derived. Conversely, SMAs typically also show a phenomenon known as “superelasticity.” This effect occurs when a sample is strained above the critical martensitic transformation temperature and is manifested as a sample showing large amounts (up to 10%) of recoverable, seemingly elastic, strains. Both of these phenomena, and the utility as a whole of SMAs, is based on the martensitic transformations that these alloys experience.

As a shape memory alloy is cooled through its martensitic transformation, characterized by a martensite start and finish temperature ($M_s$ and $M_f$, respectively), the microstructure transforms from a higher symmetry parent/austenite phase to a lower symmetry product/martensite phase. This martensite transformation is characterized as being diffusionless and involves a small (less than one atomic distance) shuffle/shear of the atoms. While the martensitic transformation occurs in various material systems and numerous metallic systems, this review is concerned with thermoelastic martensite and specifically the Ni–Ti SMA system. Thermoelastic martensite is characterized as a martensitic transformation that is fully reversible. As such, the strains that are caused by the crystallographic unit cell changes upon transformation are accommodated elastically. This occurs through the various crystallographically equivalent, but spatially different variants of the low symmetry
martensite that can be formed from the high symmetry parent phase. As the many different variants of martensite are formed upon cooling, neighboring adjacent twins of martensite accommodate and negate the strain produced by the transformation. This is known as self-accommodating martensite and is a characteristic of thermoelastic martensites. The variants of self-accommodating martensite are “chosen” in such a way during transformation that allow for a net volume change near zero. Because of this, there is typically no dimensional change when self-accommodating (thermoelastic) martensite is formed.

When a thermoelastic martensite is stressed below the $M_f$ temperature, there are three main portions characteristic of thermoelastic martensite stress-strain behavior (Fig. 2.1). The first is the linear-elastic loading of the martensite (region 1 of stress-strain space, Fig. 2.1). This is simply elastic loading of the twinned martensite where most/all strain could be recovered upon unloading. The second portion is twin coalescence where twin variants that favorably accommodate the applied load grow at the expense of unfavorable

![Figure 2.1](image.png)  
**Figure 2.1** Schematic plot of the stress-strain-heating behavior of a shape memory alloy undergoing the shape memory effect. The numbers during loading indicate the three phases of loading self accommodated martensite: (1) elastic loading of the martensite, (2) detwinning of the martensite, and (3) the beginning of plastic deformation of the martensite. Figure taken from G.S. Bigelow’s masters thesis [1].
martensite variants (region 2 of stress–strain space, Fig. 2.1). This portion of loading is characterized by a low “work hardening” rate, as twin coalescence can produce large amounts of strain at a relatively constant stress level. The third portion of loading occurs when plastic deformation processes become active in the detwinned martensite and irrecoverable dislocation generation in the martensite occurs (region 3 of stress–strain space, Fig. 2.1). As shown in Fig. 2.1, unloading from the early onset of plastic deformation of martensite allows for elastic unloading of the sample. Upon heating above the $A_f$ temperature, the sample may recover a large portion of the applied strain as the detwinned martensite reverts to the parent austenite phase. This is the shape memory effect, and the effect’s macro–mechanical response can be wholly represented in the the stress–strain–temperature space indicated by Fig. 2.1.

For the purposes of this research, the shape memory effect (SME) was studied to exploit Pt–containing NiTi SMAs for use as high temperature solid state actuators. One method to implement SMAs for actuation purposes is to subject them to a biasing load. Under this load, the martensite will detwin\(^1\), causing a subsequent strain in the actuator. Then through either active heating (resistance from an applied current) or passive heating (change in service environment temperature), the detwinned martensite transforms to austenite, recovering the induced strain from the biasing load, and causing the motion required for actuation. From this loading scenario of in–service parts, a specific mechanical testing procedure was used to simulate the stress/strain conditions of an in–service part, for alloy sample characterization. This testing procedure is referred to as isobaric (or load–biased) thermal cycling and consists of holding a sample at a particular stress, then thermally cycling the sample through the martensitic transformation.

\(^1\)The process that is actually occurring is reorientation and coalescence of twin variants that favorably accommodate the applied load. However, “detwinning” is the term commonly used in the literature, and will be continued to be used, despite that it is misleading with respect to the true mechanism that is operating.
2.2 Load–Biased Thermal Cyclic Response of Martensite

The stress strain response of a sample is slightly different if it is thermally cycled through its martensite transformation under load. While under load, if a sample transforms from austenite to martensite, the variants of martensite that form are those that most favorably accommodate the applied load. The martensite that is formed is textured, where the texture is determined by the applied load, parent grain orientation, and the crystallographically available variants within a specific austenite grain. Macroscopically, this texturing effect is manifested as strain that is much larger than what could be produced by simply loading the martensite to the same load. Upon heating, the textured martensite transforms back to austenite and the strain that was induced upon the initial cooling portion of the thermal cycle is recovered. This recovered strain is known as the transformation strain, and in addition to the characteristic martensitic temperatures (martensite start/finish and austenite start/finish) is one of the characteristics of interest in this research.

This process of loading a shape memory sample and thermally cycling through the martensitic transformation will be referred to as load–biased (LB) or isobaric thermal cycle testing. The mechanical test response of a sample being LB tested is most easily understood in strain/temperature space. However, for understanding, it is beneficial to observe the material response in the conventional stress/strain space. A SMAs LB response can be visualized in Figure 2.2. From this figure, the strain that is generated under load can be seen as the horizontal sections on the green LB stress/strain data. The blue and red arrows represent the heating and cooling cycle(s) of a sample, under stress. The majority of the sample strain is generated while the sample is cooled through the martensite transformation, then recovered as the sample is heated back to the austenite phase. As the stress applied to the sample is increased, there is a slight (primarily elastic) increase in strain, which is shown as the near vertical sections of the stress/strain LB data. Under a constant applied load, a
Figure 2.2  Plot of isothermal (grey) and load–biased (green) stress/strain data collected for a Ni–Ti–Hf HTSMA (Ti\textsubscript{29.7}Hf\textsubscript{20}Ni\textsubscript{50.3}), to demonstrate the concept of how strain is generated during load–biased (LB) testing. The zeroed LB stress/strain data (black line) represents the summation of the near vertical sections of the stress/strain LB data\textsuperscript{2}.

sample can be thermally cycled multiple times and continually recover the reversible strain indicated on the plot.

2.3 Factors Affecting the Martensitic Transformation

There are various factors that can affect the martensitic transformation (MT). The research described here concerns alloys that are slightly lean in Ti, allowing for (Ni+Pt)–rich precipitates. How these precipitates affect the MT is of great importance in providing value to the research at hand. As such, the various factors that affect the martensitic transformation will be explored. Hornbogen proposed a formulation of the factors that affect the martensitic transformation temperatures that is useful in understanding the variables that will later be described in this body of work [2]. From this work, it is useful to describe

\textsuperscript{2}This figure was produced by Glen S. Bigelow of the NASA Glen Research Center.
several characteristic temperatures of the MT. The first is $T_o$, where the Gibbs free energy of the parent austenite phase is equal the free energy of the product martensite phase. This temperature is dependent on the chemical composition of the transforming matrix, degree of order, and the applied stress (or hydrostatic stress) of a transforming sample. A thermodynamically necessary condition for the MT to proceed is the martensite start temperature ($M_s$), the temperature at which martensite begins to form upon cooling, is some quantity below the $T_o$ temperature. It is useful to quantify the amount of undercooling that the $M_s$ is below $T_o$, which is referred to as $\Delta T$ ($\Delta T = T_o - M_s$). The amount of undercooling necessary to nucleate and grow martensite, $\Delta T$, depends on any externally applied shear stresses and any features within a transforming microstructure that act to inhibit shearing of the matrix, such as dislocations, point defects, or precipitates.

Considering these two characteristic temperatures, it is valuable to consider the system specific to this research. As previously mentioned, this work is concerned with Pt–containing NiTi alloys. As this research aims to shed light on the Ni–Ti–Pt system, various relationships are used from the binary system to interpret the data collected and explore the ternary system. One of the most important relationships, is the effect that Ni has on the $M_s$ temperature of the NiTi SMAs. Tang and other researchers have outlined the effects that excess Ni content can have on the $M_s$ temperature [3–5]. These data (Fig. 2.3) indicate the strong effect that Ni in solution has on suppressing the $M_s$ temperature of NiTi SMAs. Additionally, using Tong and Wayman’s treatment for the calculation of $T_o$, given by $(A_f - M_s)/2$ [6, 7], Frenzel also included the calculated values of $T_o$ from their experimental work. These plots indicate not only the strong effect that Ni has on the $M_s$ temperature, but also on the $T_o$ temperature of NiTi alloys, as previously discussed by Hornbogen [2].

Specific to the NiTi system, Panchenko et al. summarized several effects that matrix composition and coherent Ni–rich precipitates (specifically, Ti$_3$Ni$_4$) can have on the $M_s$ temperature of an alloy [8]. These values are based on the thermodynamic equilibrium temperature between parent and product, $T_o$, and the matrix strengthening effects that
Figure 2.3  Plot of experimentally collected (symbols) and modeled (solid line) effect of Ni on the \( M_s \) temperature of NiTi shape memory alloys (SMAs), (A), taken from Tang et al. [4]. Plot of additional \( M_s \) data versus Ni content with accompanying calculated \( T_o \) data (B), taken from Frenzel et al. [5].

determine the quantity of undercooling necessary to nucleate and grow martensite, \( \Delta T \), as previously mentioned. From this work, the change in \( M_s \) temperature per all considered effects is described as:

\[
\Delta M_s = \frac{\delta T_0}{\delta C_{Ni}} \Delta C_{Ni} - \frac{\delta \Delta T}{\delta \Delta \sigma_{0,1}} \Delta \sigma_{0,1} - \frac{\delta \Delta T}{\delta \Delta \sigma_i} \Delta \sigma_i + \frac{\Delta S}{\varepsilon_0} \sigma_{in}
\]  (2.1)

where the four terms of the equation represent the effect of matrix composition, matrix strength, elastic energy from coherent precipitates that are not undergoing a MT, and the coherency stresses that may assist in the nucleation of martensite, respectively. The first term, \( \frac{\delta T_0}{\delta C_{Ni}} \Delta C_{Ni} \), accounts for the precipitation of Ni–rich precipitates that remove Ni from matrix solution. Per Fig. 2.3, excess Ni is understood to drastically decrease the \( M_s \) temperature of NiTi SMAs. Relative to solutionized samples of the same composition, as Ni–rich (or Ti–lean) precipitates form, this term will be positive, effectively acting to increase a sample \( M_s \) through an increase of the \( T_o \) temperature. The second term, \( \frac{\delta \Delta T}{\delta \Delta \sigma_{0,1}} \Delta \sigma_{0,1} \), refers to the strengthening of the B2 parent matrix caused by the formation of coherent precipitates,
essentially acting to increase the shear stresses necessary for the formation of martensite. The term $\Delta \sigma_{0.1}$ refers to the stress difference at 0.1% strain in an aged sample (containing strengthening precipitates) and a solutionized sample. This term increases the $\Delta T$ quantity and lowers the $M_s$ temperature. The third term of Eq. 2.1, $\frac{\delta \Delta T}{\delta \Delta \sigma_i} \Delta \sigma_i$, is meant to account for the elastic energy added to a sample by precipitates that are not undergoing a MT. This effect acts to add an internal stress to the system, $\sigma_i$, and decreases the effective $M_s$ of a sample. The final term, $\frac{\Delta S}{\delta \sigma_{in}}$, accounts for the internal stresses, $\sigma_{in}$, caused by the coherency between precipitate and matrix. This term is added to account for the nucleation of martensite due to $\sigma_{in}$ and should act to increase the $M_s$.

Considering these terms, the effects of precipitates can essentially be grouped into compositional effects that increase the $M_s$ (Eq. 2.1, term 1), or structural effects that act to suppress the $M_s$ (Eq. 2.1, terms 2 and 3). While the fourth term of this equation is posited to increase the $M_s$ temperature of precipitate–containing SMAs, this effect is very difficult to separate from the other two effects that lower the $M_s$, elastic stress of precipitates against transformed martensite and matrix strengthening (resistance to shear). It will be shown that, within the Ni–Ti–Pt alloys of interest, the precipitates present dominate the $M_s$ temperature through both compositional effects (Eq. 2.1, term 1) and structural effects (Eq. 2.1, terms 2 and 3). This, of course, will be discussed in much more detail later.

### 2.4 Pt Containing Shape Memory Alloys

Within the recent NiTi shape memory alloys literature, efforts have been underway to increase the temperature range at which the shape memory effect can be exploited. Specifically, ternary alloying additions that increase the $M_s$ temperatures have been studied [9, 10]. Five main alloying elements have been shown to effectively increase the $M_s$ of NiTi: Au, Pd, Pt, Zr, and Hf. Gold, Pd, and Pt substitute for Ni while Hf and Zr substitute for
Ti. Platinum containing NiTi alloys are attractive for various reasons including their high transformation temperatures (Fig. 2.4) and high work outputs (Fig. 2.5).

Given this justification to study Pt–containing HTSMAs, various contributions have been made to the understanding of these alloys. Lindquist and Wayman were the first authors to characterize the martensitic and austenitic transformation temperatures as well as the deformation and stress–free recovery behavior of Ni–Ti–Pt and Ni-Ti-Pd alloys with compositions ranging from 0 to 50% Pd and 0 to 30% Pt ( Pt and Pd substituted for Ni maintaining 50% Ti) [12, 13]. Hosoda et al. [14] and Lindquist & Wayman [12] both reported similar tensile properties for Ti-Ni-Pt alloys between 0 and 30% Pt. Both investigators also observed a transition from the B19’ (monoclinic) to the B19 (orthorhombic) transformation product for alloys containing $\approx$20% Pt or greater. Meisner and Sivokha also reported test data for an Ni$_{24}$Ti$_{50}$Pt$_{16}$ alloy tested at stress levels up to 700 MPa with limited stress-strain and transformation temperature data [15].

Figure 2.4 Plot of $M_s$ temperature (or martensite peak temperature for the Hf containing alloys) versus alloying content of various Ni–Ti based high temperature shape memory alloys [11].
Figure 2.5  Plot of work output versus transformation temperature for Pt, Pd, and Au containing Ni–Ti based high temperature shape memory alloys. The capabilities of room temperature NiTi and some Ni–Ti–Hf alloys have also been included for reference. The arrows at the right indicate the weight a 1.1mm diameter (0.044in) wire can lift a height of 12.7mm (0.5in). Adapted from [11].

Recent work on the Ni–Ti–Pt system directly relevant to the current research includes that of Rios *et al.* [16, 17] who conducted an investigation of multiple Ni–Ti–Pt alloys near a 50% Ti isoconcentration line and found Ti$_2$(Ni,Pt) present, consistent with the prior Ni–Ti phase diagram [18] on the Ti-rich side of the 50% Ti line. Phases observed in the Ti-lean samples were consistent with previously-reported metastable phases for Ti-lean Ni–Ti alloys, namely Ti$_2$Ni$_3$ [19–23]. The Pt-containing version of this precipitate, Ti$_2$(Ni,Pt)$_3$, and another precipitate phase, the P$_{1}$–phase, will be discussed more below.

Noebe *et al.* [24] provided additional data on the microstructure and mechanical properties of two Ni–Ti–Pt alloys, a 20%Pt and 30%Pt alloy, both with aim compositions of 50%Ti. They reported several important shape memory properties including transformation temperatures, stress-strain data for various temperatures, yield stress at various temperatures, and important work output data for thermal cycling under load. The 20Pt alloy was reported to have transformation temperatures above 230°C, while the 30Pt alloy transformed above 530°C. While, both alloys showed full no-load strain recovery up to fracture limit strains of
3–4%, the 30Pt alloy was not capable of recovering transformation strains while under load. It was found that at 30at%Pt, the martensite phase was either as strong, or stronger than the austenite phase, which resulted in little to no deformation of the martensite under load during load–biased thermal cycling tests. On the other hand, the 20Pt alloy was found to have an increased tensile strength, modulus, and ductility in the austenitic phase, relative to martensite. This resulted in the 20Pt alloying achieving work outputs of up to 8.7 J/cm³. From these data, it was concluded that 30%Pt alloys have work outputs that are too low for applicable use.

Padula et al. built on this work by reporting data for several more Ni–Ti–Pt alloys as well as several Pd containing alloys. Alloy compositions ranged from Pt contents of 20, 25 and 30at%, and Ti contents of 50 or 50.5at% with Ni–Ti–Pd alloys containing Pd contents of 15, 20, 25, 30 and 46at%. All Pd alloys contained 50.5at% Ti, and one alloy (25Pd) contained 5%Pt. From this work, the importance of martensitic yield strength being significantly less than the austenitic yield strength, at temperature, was established as a critical material property for adequate work output. This was explained to be based on the fact that if the martensitic yield strength is too high, and austenite yield strength too low, then less load can be applied to a sample during load–biased thermal cycle testing, otherwise undesirable plastic deformation occurs. This decrease in applied load lowers the amount of reoriented and detwinned martensite that forms, and effectively lowers the transformation strain. This causes these particular alloys to show poor work outputs, as mentioned in the previous paragraph for the 30Pt alloy. However, it was described that an appreciable amount of martensite and austenite strength must be present to avoid a “ratcheting” effect, where sample dimensional changes occur due to the plastic deformation of the martensite. Finally, this study also outlined several methods that can be used to improve shape memory characteristics including solid solution (Pt–containing, Ni–Ti–Pd alloy) and precipitation strengthening and thermomechanical processing [11]. These strengthening effects allow for an austenite phase that is more resistant to plastic deformation during thermal cycling.
Noebe et al. [25] further discussed the effects of processing on a Ti$_{50.5}$Ni$_{29.5}$Pt$_{20}$ alloy. This work thoroughly outlined the effects of amount of hot/cold work and annealing temperature on the hardness, grain size, and transformation temperatures of 1.5 mm rod and 0.5 mm wire. From these results, the recovery temperature range of 450–600°C was identified, and the recrystallization temperature in these alloys was found to be near 700°C. This work also showed the effects of temperature on the stress/strain behavior via isothermal tensile testing. From this it was found that an alloy containing 20%Pt has 4-6 times the 0.2% yield strength as binary NiTi alloys indicating that it is comparatively more difficult to isothermally detwin/reorient martensite in alloys containing relatively high amounts of Pt. Load–biased testing was also completed on the 50.5–Ti alloys showing a peak in specific work output near an applied stress of 400MPa, except for samples of 0.5 mm cold worked wire that showed increasing amounts of work output up to 600MPa. This also showed that Ni–Ti–Pt alloys can be thermomechanically processed into various forms including rod and wire, which is necessary for use of these alloys as final products.

As there has been much work conducted on Ni-Ti alloys, several issues arise when trying to apply the binary alloy tendencies to ternary alloys. Among these issues, the equilibrium precipitate phases that are stable in the Pt–containing alloys are different than those that are present in the binary alloys. This is illustrated in recent work completed by Hatcher (Figure 2.6) [26] where modeling efforts indicate that with increasing Pt content the equilibrium precipitate phase (for Ti-lean alloys) is Ti$_2$(Ni,Pt)$_3$ or the P$_L$–phase, whereas in the binary system, Ni$_3$Ti is the equilibrium phase and metastable Ni$_4$Ti$_3$ is often present. These modeling results have been corroborated with all experimental evidence collected to date. Additionally, the P$_L$–phase does not exist in binary alloys and, as such, its effect on shape memory properties is unknown, especially considering that it forms small precipitates that are coherent within the B2 and martensitic matrices. The literature has various reports of Ni$_4$Ti$_3$ precipitates controlling the martensitic transformation of binary alloys [27–32], thus, it is important to understand how the P$_L$–phase and the Ti$_2$(Ni,Pt)$_3$ phase control/alter
the shape memory properties of Ni–Ti–Pt alloys. As such, the research that is described here concerns Ti-lean precipitates within Pt–containing Ni–Ti alloys. The necessary background for these precipitates is provided in the following sections.

2.4.1 The Ti$_2$(Ni,Pt)$_3$ Phase

Within the Ni–Ti–Pt system, for alloy compositions relevant to this study (Ti-lean–21Pt), two precipitate phases have been observed, the Ti$_2$(Ni,Pt)$_3$ phase and the P$_L$–phase. The P$_L$–phase can be formed as a small, coherent phase that has only been reported in Pt and Pd–containing alloys and has been shown to play an important role in the shape memory properties of Pt–containing HTSMAs [33–35]. The Ti$_2$(Ni,Pt)$_3$ phase is a semi–
coherent, plate like precipitate that has been studied in the binary Ni–Ti system (Ti$_2$Ni$_3$). Within the binary system, the Ti$_2$Ni$_3$ phase is metastable, but appears to be stabilized in the Pt–containing system.

In the binary Ni–Ti system, several phases within Ni-rich (relative to a 1:1 Ni:Ti ratio) alloys have been identified. Nishida, Wayman and Honma [19] reported the presence of Ti$_3$Ni$_4$, Ti$_2$Ni$_3$, and TiNi$_3$, all being present in a Ti$_{48}$Ni$_{52}$ alloy (these and all further compositions are in atomic %), depending on heat treatment time and temperature. The Ti$_3$Ni$_4$ and Ti$_2$Ni$_3$ phases are both metastable while TiNi$_3$ is the equilibrium phase. The Ti$_2$Ni$_3$ phase was reported to contain about 42%Ti, i.e., very close to the 2:3 (Ti:Ni) ratio [19]. In later work, Nishida and Wayman [20, 21] explored the Ti$_2$Ni$_3$ phase further and reported “needle-like” and “antiphase-like” domains arising from a tetragonal $\rightarrow$ orthorhombic and orthorhombic $\rightarrow$ monoclinic phase transformation, respectively.

Additional work was completed by Nishida et al. [22] on various Cu-containing NiTi alloys. It was found that in alloys containing approximately 3-4% Cu, the analog Ti$_2$(Ni,Cu)$_3$ phase was stabilized (below about 850°C) and comprised the majority phase in the alloys investigated. From these samples, a reversible transformation between an orthorhombic (lower temperature) and tetragonal (higher temperature) unit cell of the Ti$_2$(Ni,Cu)$_3$ phase was observed near 120°C. However, no evidence of a lower temperature monoclinic phase was observed in these Cu-containing alloys.

The most recent work on the Ti$_2$Ni$_3$ phase was completed by Hara et al. [23]. They determined that the orthorhombic, low temperature phase had the $Bbmm$ space group, while the higher temperature, tetragonal phase was $I4/mmm$. The lattice parameters of the orthorhombic phase were $a = 0.441$, $b = 0.432$, and $c = 1.352nm$. The previously reported [20, 21] “needle-like” domains were attributed to twinning within the orthorhombic structure with a (110) twin plane [23]. These boundaries were not straight and were concluded to be of a compound type.
Rios et al. explored the phase transformations of various (Ni+Pt)-rich alloys, relative to a 1:1 Ti:(Ni+Pt) ratio and based solely on energy dispersive spectroscopic analysis assumed a range of second phase particles to be the Ti$_2$(Ni,Pt)$_3$ phase [36]. However, this report lacked conclusive confirmation and a formal description of this phase. The most recent work pertaining to the Ti$_2$(Ni,Pt)$_3$ phase was completed by Hudish [37]. In this masters thesis, six Ti–lean Ni–Ti–Pt alloys were explored (Table 2.1). The microstructures of these alloys were found to contain three phases, a matrix near a 1:1 ratio of Ti:(Ni+Pt), a plate like precipitate identified to be Ti$_2$(Ni,Pt)$_3$, and TiC inclusions. The measured compositions of the matrix and Ti$_2$(Ni,Pt)$_3$ phases, varied with both alloy composition and temperature (Figure 2.7). From this figure, it is apparent that the composition of the Ti$_2$(Ni,Pt)$_3$ phase depends on the overall alloy composition. The samples of this study were furnace cooled from 1050°C, so the temperature dependence of this precipitate phase was not explored in this reported work. However, the structure of the Ti$_2$(Ni,Pt)$_3$ phase was confirmed to be the same as that of the binary system, but was designated Cmcm (same as Bbmm, but with a different preference in axis selection) [37].

This work did not consider the mechanical properties of HTSMAs containing this phase, nor the effects that this precipitate has on shape memory properties. In addition to the P$_L$–phase described below, the effects of the Ti$_2$(Ni,Pt)$_3$ precipitate on Pt–containing Ni–Ti alloys will be explored further in the presented work to follow.

**Table 2.1 – Table of Ti-Ni-Pt Nominal Alloy Compositions (atomic %)**

<table>
<thead>
<tr>
<th></th>
<th>Ti</th>
<th>Ni</th>
<th>Pt</th>
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<tbody>
<tr>
<td>F301</td>
<td>48</td>
<td>31</td>
<td>21</td>
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<tr>
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<tr>
<td>F306</td>
<td>45</td>
<td>23</td>
<td>32</td>
</tr>
<tr>
<td>F309</td>
<td>47</td>
<td>28</td>
<td>25</td>
</tr>
<tr>
<td>F310</td>
<td>47</td>
<td>25</td>
<td>28</td>
</tr>
</tbody>
</table>
2.4.2 The P\textsubscript{L}–phase

As mentioned previously, the P\textsubscript{L}–phase is a small, coherent precipitate that has only been observed in Pt and Pd-containing Ni–Ti alloys. This phase is Ti lean with a stoichiometric composition of Ti\textsubscript{11}Ni\textsubscript{9}Pt\textsubscript{4}. Kovarik \textit{et al.} performed the first formal description of the structure of this phase indicating the phase’s space group, atomic ordering, and a unique atomic layering sequence described below [34].

From this work, the crystal structure of the P\textsubscript{L}–phase was identified to be monoclinic (\textit{C}2/c space group, No. 15) with lattice parameters \(a = 0.745 \text{ nm}, b = 1.292 \text{ nm}, c = 1.422 \text{ nm}, \beta = 100.45^\circ\). The structure of this phase is closely related to the parent B2 structure with slight, but significant atomic shifts and an overall ordering of Pt atoms on the Ni sublattice of the B2 parent structure. Therefore, it is useful to describe the P\textsubscript{L}–phase directions in
terms of the B2 phase. As such, the authors described the following relationships between the B2 and $P_L$–phase crystallographic directions:

\[
[100]_P \rightarrow [11\overline{2}]_{B2} \\
[010]_P \rightarrow [3\overline{3}0]_{B2} \\
[001]_P \rightarrow [3\overline{3}2]_{B2}
\]

(2.2)

The $P_L$–phase was also observed to have a layered, or laminate structure, as designated by the subscript L. The layers of this phase share their (001)$_P$ planes with 120° rotations to one another. This leads to 3 different variants with an orientation relationship defined as:

\[
(001)_{P1} \parallel (001)_{P2} \quad (001)_{P1} \parallel [\overline{1}10]_{P2} \\
[100]_{P1} \parallel [\overline{1}10]_{P2}
\]

(2.3)

These different layers, or motifs, are distinguishable if observed in certain crystallographic directions, but not in others. Because of this, during TEM analysis, the $P_L$–phase appears to contain linear “faults.” These faults are the coherent, but crystallographically distinguishable, boundaries between two of the three motifs or layers of the laminated structure.

Recently, Gao et al. attempted to relate the presence of the $P_L$–phase to observed changes in the transformation temperatures in Ni–Ti–Pt alloys [33]. The authors stated that the coherency stresses that occur between the B2 and the $P_L$ phases act to nucleate martensite, effectively lowering the $\Delta T$ necessary for MT (i.e., raising $M_s$, $M_f$, etc.). Using a thermodynamic database, ab–initio calculations, and experimental data, lattice parameters, the matrix/precipitate orientation relationship, elastic constants, and free energy data as inputs, the authors developed a phase field model to describe precipitation of the $P_L$–phase in a Ti$_{50}$Ni$_{30}$Pt$_{20}$ alloy. From this model, the enrichment of Pt in the matrix due to the precipitation of the $P_L$–phase, which has a Pt content of 16.7at% versus the matrix which was at 20%, the $M_s$ temperature was posited to increase by up to 19°C. Further, by considering
the coherency stress fields between the $P_L$–phase and a B19 nucleus, the quantity of elastic energy contribution to the forward MT was estimated to increase the $M_s$ temperature by as much as $100^\circ$C.

As previously mentioned, the $P_L$–phase has been observed in both Pd–containing and Pt–containing alloys. Sasaki et al. studied a Pd containing, Ti–lean alloy of composition $\text{Ti}_{48}\text{Ni}_{27}\text{Pd}_{25}$, and found the presence of the $P_L$–phase to be dependent on heat treatment temperature [35]. When heat treated at $550^\circ$C, the hardness of this alloy decreased slightly, but at heat treatment temperatures of $400^\circ$C, the hardness increased from $\approx 250$ up to about $400$ VHN; this indicates the formation of the $P_L$–phase at temperatures of $400^\circ$C, but not at $550^\circ$C. In addition to hardness increases, it was also reported that samples aged for at least 10h showed an increase in martensitic transformation temperatures of up $120^\circ$C. This increase was attributed to the precipitation of the $P_L$–phase bringing the matrix composition nearer to a 1:1 ratio of Ti:(Ni+Pd). The authors also claimed that the local stress fields around the precipitates provided additional driving force to raise the transformation temperatures, similar to the claims derived from the modeling efforts of Gao et al. [33]. The $P_L$–phase within this alloy was found to have the composition $\text{Ti}_{11}\text{Ni}_7\text{Pt}_6$, maintaining the same 11:13 Ti:(Ni+Pt/Pd) ratio that was reported by Kovarik et al. [34].

The $P_L$–phase within this Pd–containing alloy was also reported to stabilize the mechanical properties of these alloys. The authors reported that samples of the $400^\circ$C–1h aged alloy showed nearly perfect pseudoelastic behavior up to 3% strain, with little to no residual strain. Also, the $P_L$–phase also reportedly stabilized the load–biased thermal cycling properties, and samples resulted in drastically reduced non–recoverable strain compared to a similar Ti–rich alloy (95% reduction strain magnitude) in a similar study by Bigelow et al. [38]. The Ti–lean alloy did have relatively reduced transformation temperatures and transformation strains, however, compared to the Ti–rich alloy.
Given the current understanding of these HTSMAs, there is still a need to clarify the role that Ti$_2$(Ni,Pt)$_3$ and P$_L$-phase precipitates play in affecting shape memory properties. Additionally, to date, there has been no systematic study to explore the phase stability in the Pt-containing Ni–Ti system. The research presented here will provide two main components to the understanding of these alloys. First, the microstructures of two alloys (Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ and Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$) will be characterized over a range of heat treatment time and temperatures. This process will allow for a fundamental understanding of the stability and quantification of the above mentioned precipitate phases. This systematic exploration will provide valuable information for the necessary processing routes for future development of Ni–Ti–Pt HTSMAs.

From this understanding of the microstructure and phase stability, the LB mechanical response of compressive samples will then be characterized. It will be shown that the systematic nature of this study will allow for a deeper understanding of the role that precipitate phases play in controlling shape memory properties (i.e., transformation temperatures and strains). Specifically, the role that the Ti$_2$(Ni,Pt)$_3$ phase plays in controlling matrix chemistry, and the role that the P$_L$-phase plays in both suppressing and stabilizing shape memory properties will be explained. This mechanical response characterization will also be useful for the identification and selection of potential alloys for future development and will guide future alloy design and engineering efforts for development of other precipitate strengthened high temperature shape memory alloys.

The research reported here will be presented in two parts. The following chapter will describe and quantify the microstructural constituents based on their respective heat treatment routes. Next, the results of the extensive load biased testing will be presented and the link between the reported microstructures and load biased shape memory properties will be explained and discussed.
CHAPTER 3

MICROSTRUCTURAL CHARACTERIZATION & PHASE STABILITY

3.1 Introduction

In the binary Ni-Ti system, several phases within Ni-rich (relative to a 1:1 Ni:Ti ratio) alloys have been identified. Nishida, Wayman and Honma [19] reported the presence of Ti$_3$Ni$_4$, Ti$_2$Ni$_3$, and TiNi$_3$ all being present in a Ti$_{48}$Ni$_{52}$ alloy, dependent on heat treatment time and temperature. The Ti$_3$Ni$_4$ and Ti$_2$Ni$_3$ phases are both metastable while the TiNi$_3$ phase is the equilibrium phase. Compositions of the Ti$_2$Ni$_3$ phase were reported to be about 42% Ti and 58% Ni, very near to the 2:3 (Ti:Ni) stoichiometric ratio [19].

Lindquist and Wayman were the first to characterize the martensitic and austenitic transformation temperatures as well as the deformation and recovery behavior of Ni–Ti–Pt and Ni-Ti-Pd alloys with compositions ranging from 0 to 50% Pd and 0 to 30% Pt substituted for Ni maintaining 50% Ti [12, 13]. Hosoda et al. [14] and Lindquist [13] both observed a transition from the B19' (monoclinic) to B19 (orthorhombic) transformation product for alloys containing $\approx$20% Pt or greater.

Recent work on the Ni–Ti–Pt system directly relevant to the current research includes that of Rios et al. [16, 17] who conducted an investigation of the multiple Ni–Ti–Pt alloys near a 50% Ti isoconcentration line and found Ti$_3$(Ni,Pt) present, consistent with the prior Ti-Pt phase diagram [39], on the Ti-rich side of the 50% Ti line. Phases observed in the Ti-lean samples were consistent with previously reported metastable phases for a Ni-Ti alloy that was slightly Ni rich [19]. Additional work investigating the nature of the Ni-rich Ti$_2$(Ni,Pt)$_3$ precipitates and the presence of a newly reported P$_L$–phase was also completed by the author [37] on a portion of this same alloy set. From these studies, it was found that the Ti$_2$(Ni,Pt)$_3$ phase is the prevalent second phase in Ti-lean Ni–Ti–Pt alloys.
Further work in this field includes that of Kovarik et al. [34] who identified and characterized a new precipitate phase, known as the PL–phase (Ti_{11}Ni_{9}Pt_{4}); however, no attention was paid to the stability or bounds of this phase's presence. This precipitate has been observed only in Ni-Ti alloys containing Pt and Pd. From work completed at NASA-Glenn Research Center (GRC), this phase appears to play an important role in the shape memory properties of Ni–Ti–Pt alloys and will be discussed in more detail below.

As there has been much work conducted on Ni-Ti alloys, several issues arise when trying to apply the binary alloy tendencies to ternary alloys. Among these issues, the equilibrium precipitate phases that are stable in the Pt–containing alloys are different than those that are present in the binary alloys. This is illustrated in recent work completed by Hatcher (Figure 3.1, [26]), where modeling efforts indicate that with increasing Pt–content the equi-
librium precipitate phase (for Ti-lean alloys) is $\text{Ti}_2(\text{Ni,Pt})_3$ or the $\text{P}_L$-phase whereas in the binary system, $\text{Ni}_3\text{Ti}$ is the equilibrium phase and metastable $\text{Ni}_4\text{Ti}_3$ is often present. These modeling results have been partially corroborated with the experimental evidence that will be presented below. Additionally, the $\text{P}_L$-phase does not exist in binary alloys and, as such, its effect on shape memory properties is unknown, especially considering its tendency to form small precipitates that are coherent within the B2 and martensitic matrix. The literature has various reports of $\text{Ni}_4\text{Ti}_3$ precipitates controlling the martensitic transformation of binary alloys [27–32]. Thus, in an effort to understand the role that the $\text{P}_L$ and $\text{Ti}_2(\text{Ni,Pt})_3$ phases play on the mechanical properties of Ni–Ti–Pt HTSMA’s, the phase stability and aging behavior was explored in two alloys, $\text{Ti}_{48.5}\text{Ni}_{30.5}\text{Pt}_{21}$ and $\text{Ti}_{49.5}\text{Ni}_{29.5}\text{Pt}_{21}$.

### 3.2 Experimental Methods and Materials

Ingots of both $\text{Ti}_{48.5}\text{Ni}_{30.5}\text{Pt}_{21}$ and $\text{Ti}_{49.5}\text{Ni}_{29.5}\text{Pt}_{21}$ alloys were cast in to water cooled copper molds from high purity starting elements using a vacuum induction melting technique in graphite crucibles. The ingots were homogenized at 1050°C for 72h in a vacuum furnace then sealed in steel cans and extruded into a 0.5in diameter rod at 900°C and left to air cool. Samples were sectioned using wire electrical discharge machining (EDM) and heat treated for 1 and 100h at 500, 550, 600, 650, and 700°C and water quenched. All heat treatments were completed in either a vacuum furnace, or in evacuated quartz ampules that were backfilled with ultra high purity argon. SEM analysis was performed on a JEOL JSM-7000F equipped with an EDAX energy dispersive spectroscopy system. TEM samples were cut into 0.5mm x 3mm disks using wire EDM, thinned, dimple ground and ion milled. Investigation was performed on a Phillips CM12 TEM at an operating voltage of 120kV. Precipitate volume fraction measurements were completed in accordance with the ASTM standard E 562-05. Error bars on volume fraction data represent the 95% confidence limit of the data mean.
Microhardness testing was performed on either a Struers Duramin A300 or a Wilson Tukon M200 Hardness Tester, with a square Vickers indenter. A 500g load, at a 10s dwell time was used. All error bars on hardness data represent one standard deviation of the data mean.

3.3 Results

In the Ti–lean, binary Ni–Ti alloys there are two metastable phases, Ti$_3$Ni$_4$ and Ti$_2$Ni$_3$ which precipitate prior to (temperature and time dependent) the equilibrium TiNi$_3$ phase [19, 20]. However, as Pt is alloyed into Ni–Ti alloys, the phase stability apparently changes with Ti$_2$Ni$_3$ becoming stable. Similarly, the current results indicate that the coherent P$_L$–phase precipitates initially followed by the formation of the more sluggish, equilibrium Ti$_2$(Ni,Pt)$_3$ phase. Figure 3.1 shows the calculated enthalpy of formation versus Pt content of several phases found in both the Ni–Ti system and the Ni–Ti–Pt system. Using heat of formation as a measure of a precipitate’s thermodynamic stability, it is apparent that both TiNi$_3$ and Ti$_3$Ni$_4$ both become less stable as the Pt content is increased. Consistent with these modeling efforts, empirical observations corroborate this phase stability. In both alloys presented here, Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ and Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$, the only precipitate phases observed are the P$_L$–phase and Ti$_2$(Ni,Pt)$_3$. Heat treatment conditions within this investigation spanned 500 to 800$^\circ$C, for times from 1 to 100h, and included a 1000h heat treatment at 700$^\circ$C. In this broad range of investigation, there has been no sign of the Pt-containing versions of TiNi$_3$ or Ti$_3$Ni$_4$.

3.3.1 Microstructural Overview

Initial SEM imaging of both alloys indicated the presence of three phases present (Fig. 3.2). The majority matrix phase is the Pt–containing version of the NiTi austenite/martensite, found to have the B2/B19 structure [12]. Channeling contrast within this phase makes various twin variants of the martensite visible, especially in Fig. 3.2B.
Figure 3.2  Backscattered electron images (BEIs) of both Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ (A) and Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$ (B) alloys extruded at 900°C and air-cooled. The lightest gray matrix is martensite (at room temp.), the dark gray, lenticular shaped precipitate in A is Ti$_2$(Ni,Pt)$_3$ (black arrows), and the black globular phase is TiC (white arrows). The lack of the Ti$_2$(Ni,Pt)$_3$ phase in (B) is consistent with its slightly higher Ti concentration.

plate-like precipitates marked by the black arrows in Fig. 3.2 have been identified previously as the Pt-containing version of the metastable binary phase Ti$_2$Ni$_3$, or in this case Ti$_2$(Ni,Pt)$_3$. The white arrows (Fig. 3.2) indicate the ubiquitous TiC inclusions, common in so many Ni-Ti based SMA’s and related to melting in a graphite crucible [40]. The TiC phase was found to be present in all samples investigated, regardless of heat treatment, at a volume fraction of approximately 3-4%. Not visible in the initial SEM investigation of this alloy is a small, spherical, coherent precipitate previously identified as the P$_L$–phase by Kovarik, et al. where the structure is coherent and the subscript L is related to the unusual lamellar crystallographic arrangement that characterizes this phase. This phase has only been observed in Ni-Ti alloys containing Pt and Pd and a full structural description of this phase was given by Kovarik et al. [34]. The P$_L$–phase was initially found to be present in the alloys of the present study through microhardness testing (Fig. 3.3). The increased hardness present in samples heat treated at 500 and 550°C indicates the precipitation of the P$_L$–phase. Furthermore, classical coarsening and overaging of this phase is apparent as the
Figure 3.3  Plot of Vickers microhardness for both alloys Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ and Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$ after various heat treatment conditions. Error bars indicate a single standard deviation of the data set. All samples were water quenched from the heat treatment temperature indicated in the plot legend.

heat treatment times and temperatures are increased. Evidence of the presence and behavior of this phase will be presented below.

All samples investigated contained TiC inclusions. This phase was confirmed to be TiC through EDS measurements as well as through TEM SADP’s. Through the various heat treatments, the quantity and morphology did not appear to change significantly. For the remainder of the presentation of the results of this study, the TiC phase will be neglected as it appeared to play a minor role in the microstructures presented in this chapter and the mechanical testing results presented in the next chapter.
3.3.2 The Austenite/Martensite Matrix

The binary Ni–Ti system has a high temperature B2 (CsCl) structure which transforms to a monoclinic martensite phase at lower temperatures. Ternary additions of various elements have been shown to modify this martensitic structure, typically changing the martensite from the monoclinic B19' to orthorhombic B19 structure. As reported by Lindquist and Wayman, above approximately 20% Pt, the martensite of Ni-Ti-Pt alloys has this orthorhombic B19 structure [12]. It was assumed that all martensite in the present study had this orthorhombic structure, and specifically the space group \(Pmma\) (#51).

Because the martensitic transformation temperatures of the samples investigated in this study depend so heavily on the sample processing (specifically, thermal treatment), and subsequent microstructure, these data will be saved for discussion for the next chapter. This chapter will report and discuss the various microstructures present in the samples studied, and after this the reader will have sufficient information to understand the variation in transformation temperatures as a function of composition and thermal history. For example, the 48.5–Ti alloy samples had martensite start (\(M_s\)) temperatures ranging from 255 to 345°C, and the 49.5–Ti alloy samples had \(M_s\) temperatures ranging from 237 to 340°C. After an adequate microstructural background has been established, the transformation temperature data, and subsequent explanation of the large difference per sample, will be presented.

3.3.2.1 Martensite Twinning

While the binary Ni-Ti martensite, referred to as B19', is a monoclinic cell (space group \(P2_1/m\), #11) [41], after a critical amount of Pt is added to NiTi (approx. 20at% according to Lindquist and Wayman [12], and down to 7% Pt from currently unpublished data collected at NASA GRC), the martensite structure becomes the B19 orthorhombic structure (space group \(Pmma\), #51). Lindquist reported the twinning mode of the Pt–containing B19 martensite to be on the \((\bar{1}11)\) planes and measured the B19 cell (for a Pt
content of 20\text{at\%}) lattice parameters as $a = 2.75, b = 4.48$, and $c = 4.70\text{Å}$ [13]. The twinning mode of the B19 structure in this study was found to be on the $(11\overline{1})$ planes, as demonstrated in Figure 3.4. From this figure, the shared row of reflections was found to be $(11\overline{1})$, indicating the twinning plane in this martensite. This SADP was collected from the circled area in the corresponding TEM BF image. Notice that the common $(11\overline{1})$ reflections are perpendicular to the martensite plates in the BF image. Additionally, rectangles were added to the upper left of the SADP to demonstrate the two overlapping diffraction patterns comprising the twin pattern. This characteristic twinned diffraction pattern was found in various samples of both the 48.5 and 49.5–Ti alloys, indicating the twinning mode in this alloy system is independent of the processing route. The discrepancy between Lindquist’s reported twinning plane, $(\overline{1}11)$, and the plane found here can be explained by the difference in the “unique” axis choice of

![Figure 3.4](image)

**Figure 3.4** TEM bright field (BF) image of a $600^\circ\text{C}$–1h–WQ sample of alloy Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$, and corresponding selected area diffraction pattern (SADP), taken from the circled area, presenting the twinning mode of the B19 martensite in this alloy system. From the [011] SADP, twinning was found to occur on the $(11\overline{1})$ planes.
the orthorhombic cell. The unit cell parameters will be reported and discussed in the next section.

### 3.3.2.2 Lattice Parameter Determination

From XRD Rietveld analysis, the lattice parameters of the B19 martensitic phase were measured in four samples of the 48.5–Ti alloy. These lattice parameters are summarized in Table 3.1. The error that is included with the lattice parameter measurements refers to the estimated standard deviation (esd’s) for the Rietveld model output. It is worth noting that the esd’s should not be taken as absolute error bars, as they may be as much as an order of magnitude smaller than mean probable errors. They are reported here, however, because they are useful for comparison purposes for similarly collected data sets.

These lattice parameters appear to be in agreement with those reported by Lindquist [13]. Additionally, there is minimal variation in lattice parameters through the various heat treatments. The $a$ and $c$ parameters of the as–extruded condition show the greatest deviation from the rest, which is likely attributable to the fact this condition is furthest from an equilibrium condition, with the most excess Ni and Pt solute in solution. This microstructural condition will be more thoroughly discussed below.

<table>
<thead>
<tr>
<th>Condition</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Extruded</td>
<td>4.4481 ±0.001</td>
<td>2.758 ±0.0005</td>
<td>4.6879 ±0.0005</td>
</tr>
<tr>
<td>600°C–100h–WQ</td>
<td>4.4614 ±0.003</td>
<td>2.7558 ±0.0002</td>
<td>4.7201 ±0.0004</td>
</tr>
<tr>
<td>1300°C–WQ+550°C–100h–WQ</td>
<td>4.4629 ±0.001</td>
<td>2.7638 ±0.0007</td>
<td>4.7076 ±0.0008</td>
</tr>
<tr>
<td>500°C–100h–WQ</td>
<td>4.4624 ±0.0005</td>
<td>2.7613 ±0.0004</td>
<td>4.7122 ±0.0005</td>
</tr>
</tbody>
</table>
3.3.3 The Ti$_2$(Ni,Pt)$_3$ Precipitate

From previous work, the Ti$_2$(Ni,Pt)$_3$ phase was found to have an orthorhombic crystal structure, with the Cmcm space group (#63). The lattice parameters of this phase were found to be $a = 14.2$, $b = 4.5$, and $c = 4.4\AA$. The phase was observed to have a plate-like morphology with a (001)$_{B2}$ habit plane. The composition of this phase was measured using SEM EDS measurements and the Ti:(Ni+Pt) ratios agreed well with the compound stoichiometry ($\approx 40\%$ Ti), while the Ni:Pt ratio varied depending on heat treatment and alloy studied [37]. These factors will be discussed in greater detail below (lattice parameters, habit plane) and in the next chapter (measured compositions).

The Ti$_2$(Ni,Pt)$_3$ phase was observed in both alloys, Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ (48.5–Ti) (all heat treatment conditions) and Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$ (49.5–Ti, 600-700°C heat treatment conditions). While the general Widmanstätten morphology of this phase was consistent between all samples observed, its size, distribution, and volume fraction varied depending on both heat treatment and alloy composition. The structures shown in Fig. 3.2 are in the “as–extruded” condition, i.e., hot extruded at 900°C and air-cooled; these microstructures represent the starting condition for the subsequent heat treatments performed in this study. As is apparent, the Ti$_2$(Ni,Pt)$_3$ phase is present at the extrusion temperature (900°C) in the 48.5–Ti alloy, but not in the 49.5–Ti alloy. In the 48.5–Ti alloy, the volume fraction of the Ti$_2$(Ni,Pt)$_3$ phase was measured to be 9.3% ±1.7%.

Further heat treatments of these alloys elucidated the behavior and stability of the Ti$_2$(Ni,Pt)$_3$ phase. Figure 3.5 presents the microstructures of the 48.5–Ti alloy heat treated at 500, 600, and 700°C for 1 and 100h. Comparatively, Fig. 3.6 is a collection of similar images for the 49.5 alloy. In both alloys, samples heat-treated at 500 and 550°C contain the P$_L$–phase, however, the P$_L$–phase is not resolvable in these SEM images. This phase will be discussed in more detail later.
Figure 3.5 BEIs of alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ heat treated at the indicated times and temperatures. The light gray majority phase is the martensite matrix, the dark gray, plate-shaped phase is Ti$_2$(Ni,Pt)$_3$, and the black phase is TiC.
Figure 3.6  BEIs of alloy Ti\textsubscript{49.5}Ni\textsubscript{29.5}Pt\textsubscript{21} heat treated at the times and temperatures indicated. The light gray majority phase is the martensite matrix, the dark gray, plate–shaped phase is Ti\textsubscript{2}(Ni,Pt)\textsubscript{3}, and the black phase is TiC.
3.3.3.1 $\text{Ti}_2(\text{Ni,Pt})_3$ Morphology and Volume Fraction

From Figures 3.5 and 3.6, the general plate morphology and a coarsening of the $\text{Ti}_2(\text{Ni,Pt})_3$ phase as heat treatment time and temperature are increased is evident. Additionally, it is qualitatively apparent that there is a significantly higher volume fraction of the $\text{Ti}_2(\text{Ni,Pt})_3$ phase in the 48.5–Ti alloy than the 49.5–Ti alloy.

The coarsening of the $\text{Ti}_2(\text{Ni,Pt})_3$ was more thoroughly captured through measurement of the area of individual precipitates, presented in Fig. 3.7. This plot indicates a general coarsening behavior as the heat treatment time is increased from 1 to 100h. This plot also includes the data points for the two samples of alloy $\text{Ti}_{48.5}\text{Ni}_{30.5}\text{Pt}_{21}$ that were furnace cooled (FC) after 1h at their respective heat treatment temperatures and an additional explorative sample heat treated at 800°C for 100h and water quenched.

![Figure 3.7](image.png)

**Figure 3.7** Plot of average area of $\text{Ti}_2(\text{Ni,Pt})_3$ precipitates in the $\text{Ti}_{48.5}\text{Ni}_{30.5}\text{Pt}_{21}$ and $\text{Ti}_{49.5}\text{Ni}_{29.5}\text{Pt}_{21}$ alloys after 1 and 100h at the temperatures indicated. Data was collected by pixel counting using ImageJ [42].
From this plot, several trends are apparent. First, for the 48.5–Ti alloy, the size of the 
\(\text{Ti}_2(\text{Ni,Pt})_3\) phase does not appear to increase for heat treatments at 500°C. The 550°C heat 
treatment has an appreciably higher precipitate area than its 500°C counterpart, with the 
600–700°C–100h samples being slightly higher. While the 600 and 700 samples appear to 
have coarsened significantly relative to their 1h counterparts, they have roughly the same 
sized \(\text{Ti}_2(\text{Ni,Pt})_3\) precipitates. The 800°C–100h sample has a substantially higher precip-
itate area than any other sample investigated. Finally, the FC samples had moderately 
smaller precipitate sizes than their 100h counterparts. For the 49.5–Ti alloy the \(\text{Ti}_2(\text{Ni,Pt})_3\) 
coarsening was less pronounced. The 600°C sample showed the greatest coarsening behav-
ior between the 1 and 100h conditions, with the 700°C sample set having a less dramatic 
coarsening behavior.

As part of this investigation, several samples of the 48.5–Ti alloy were subjected to a 
1300°C homogenization treatment, water quenched, then further heat treated. This was done 
to assess the affect that the 900°C hot extrusion had on precipitate morphology and size and 
to put more solute in solution. One such sample was solutionized and further heat treated at 
600°C for 100h. Figure 3.8 presents the microstructure of the 1300°C–WQ+600°C–100h–WQ 
sample as well as the 800°C–100h–WQ sample, both from the 48.5–Ti alloy. Between these

![Figure 3.8 SEM BSE images of two samples from the 48.5–Ti alloy, (A) 1300°C–
WQ+600°C–100h–WQ, and (B) 800°C–100h–WQ.](image)

Figure 3.8 SEM BSE images of two samples from the 48.5–Ti alloy, (A) 1300°C–
WQ+600°C–100h–WQ, and (B) 800°C–100h–WQ
two micrographs, there is an evident difference in the coarsening behavior of the Ti$_2$(Ni,Pt)$_3$ phase depending on the processing route. The Ti$_2$(Ni,Pt)$_3$ precipitates that grew in Fig. 3.8A came from a solutionized microstructure. These precipitates are in their “unprocessed” form, while the precipitates in Fig. 3.8B grew from a small volume fraction of precipitates left over from the extrusion process. It is apparent from these micrographs that the extrusion of this alloy affects the shape of the Ti$_2$(Ni,Pt)$_3$ phase, truncating the edges of the Ti$_2$(Ni,Pt)$_3$ plates. This makes the Ti$_2$(Ni,Pt)$_3$ plates coarsen to more of a “blocky” morphology, increasing more in plate width than length. The Ti$_2$(Ni,Pt)$_3$ plates grown from the solutionized condition (Fig. 3.8A), however, have a much more apparent lenticular cross section. The precipitate area in this sample, in fact, wasn’t accurately measurable as too many of the precipitates touched one another making individual precipitate areas indeterminable using the implemented pixel counting method. For further comparison, the 600°C–100h condition of Fig. 3.5 can be compared to Fig. 3.8A, where each microstructure received the same exposure at 600°C.

Through volume fraction measurements, the amount of Ti$_2$(Ni,Pt)$_3$ present in several selected alloy conditions is summarized in Fig. 3.9. From this plot, it is apparent that there is more Ti$_2$(Ni,Pt)$_3$ present in the 48.5–Ti alloy than the 49.5–Ti alloy. This is attributed to the fact that the 48.5–Ti alloy is further from the ideal Ti50:(Ni+Pt)50 ratio of the Ti(Ni,Pt) phase. This increased amount of Ni and Pt in solution leads to a greater volume fraction of precipitated second phase, per the lever rule. The amount of Ti$_2$(Ni,Pt)$_3$ peaks at 600°C (Fig. 3.9), with a decreasing quantity of Ti$_2$(Ni,Pt)$_3$ occurring in samples heat treated at increasing temperatures. This trend extends to the 48.5–Ti as–extruded sample, where air cooling from 900°C was assumed to provide a sufficiently high cooling rate to allow for the as–extruded material to adequately represent the microstructure at 900°C (the extrusion temperature). This trend of decreasing Ti$_2$(Ni,Pt)$_3$ content with increased heat treatment temperature also occurs in the 49.5–Ti alloy. As with the 48.5–Ti alloy, 600°C is
Figure 3.9  Plot of volume fraction Ti$_2$(Ni,Pt)$_3$ versus heat treatment temperature for both alloys, Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ and Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$.

the temperature at which there is a maximum of Ti$_2$(Ni,Pt)$_3$, with a decreasing amount as heat treatment temperatures are increased.

Figure 3.9 also shows the volume fraction of Ti$_2$(Ni,Pt)$_3$ in the two samples of alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ that were heat treated for one hour at the indicated temperature and furnace cooled. Apparent from these data, the process of furnace cooling allows the maximum amount of Ti$_2$(Ni,Pt)$_3$ to precipitate in FC samples because the effect is similar to aging at lower temperatures. Furnace cooling allows for more second phase to precipitate versus long term heat treatments at temperatures above 600°C, especially for the 800°C samples (FC vs. 100h–WQ).

For the 48.5–Ti alloy, the samples heat treated at 500 and 550°C had mixed microstructures containing the Ti$_2$(Ni,Pt)$_3$ and P$_L$ phases. To fully explain the results presented here,
the behavior of the \( P_L \)-phase must first be described. An explanation of these volume fraction data will be presented later, after adequate background on the behavior of the \( P_L \)-phase has been established.

Per the lever rule, the amount of \( \mathrm{Ti}_2(\mathrm{Ni},\mathrm{Pt})_3 \) present at a given heat treatment (Fig. 3.9) gives an idea of the shape of the \( \mathrm{B2}/(\mathrm{B2+Ti}_2(\mathrm{Ni},\mathrm{Pt})_3) \) solvus. It is known from DTA analysis that the \( \mathrm{Ti}_2(\mathrm{Ni},\mathrm{Pt})_3 \) phase solvus for the 48.5–Ti alloy is near 1250°C (DTA results will be more thoroughly discussed in the next chapter) and that in the 49.5–Ti alloy the \( \mathrm{Ti}_2(\mathrm{Ni},\mathrm{Pt})_3 \) is fully in solution at 900°C (the extrusion temperature). This confirms that as temperature is increased, the amount of \( \mathrm{Ti}_2(\mathrm{Ni},\mathrm{Pt})_3 \) diminishes.

In order to understand the equilibrium behavior of the \( \mathrm{Ti}_2(\mathrm{Ni},\mathrm{Pt})_3 \) phase in these alloys, a 1000h heat treatment was performed. A sample of the 48.5–Ti alloy that had previously been subjected to a 700°C–1h–WQ heat treatment was heat treated for an additional 1000h and furnace cooled. The microstructure of this sample is presented in Fig. 3.10. It is apparent

![SEM BSE image of a sample of the alloy Ti\(_{48.5}\)Ni\(_{30.5}\)Pt\(_{21}\) subjected to a 700°C–1h–WQ heat treatment, then heat treated for an additional 1000h at 700°C, and furnace cooled.](image)
that the morphology of the Ti$_2$(Ni,Pt)$_3$ phase in this figure does not change drastically from that presented for the 700°C–100h-WQ sample presented in Fig. 3.5, except that the Ti$_2$(Ni,Pt)$_3$ may be slightly coarser in the 1000h sample, as expected. The volume fraction of Ti$_2$(Ni,Pt)$_3$ was measured to be 18.2%±0.98%, similar to the values found for the 600°C–100h–WQ and both FC samples (Fig. 3.9). This value is slightly higher than that in the 700°C–100h–WQ condition (16.2%±0.92%), but this is most likely due to furnace cooling, which allows for the highest volume fraction of Ti$_2$(Ni,Pt)$_3$ to grow during the cooling process.

This 1000h heat treatment is important for understanding the equilibrium second phase in Pt–containing alloys with a relatively high atomic fraction of Pt (21%, in this case). In the binary system, the precipitation sequence was reported by Nishida et al. [19] to be

$$\beta_o \rightarrow \beta_1 + \text{Ti}_3\text{Ni}_4 \rightarrow \beta_2 + \text{Ti}_2\text{Ni}_3 \rightarrow \beta_3 + \text{TiNi}_3$$

where $\beta_o$ is the supersaturated NiTi solution, $\beta_1$ is the matrix composition in metastable equilibrium with the Ti$_3$Ni$_4$ precipitate, and so on. This sequence was found for a Ti$_{48}$Ni$_{52}$ alloy and is generally accepted as the precipitation sequence in the binary system with the Ti$_3$Ni$_4$ precipitate avoided in higher temperature heat treatments ($\gtrsim$680°C). In the binary system, a heat treatment at 700°C for 1000h would yield a microstructure of NiTi and TiNi$_3$, the equilibrium second phase in Ni–rich Ni–Ti alloys. If similar diffusion kinetics between the binary and Ni–Ti–Pt system were assumed, this 700°C–1000h heat treatment should yield the equilibrium phase, Ti$_2$(Ni,Pt)$_3$, in the alloys of this study (Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ and Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$).

### 3.3.3.2 Ti$_2$(Ni,Pt)$_3$ Coherency

Apparent from Fig. 3.3, the Ti$_2$(Ni,Pt)$_3$ phase does not contribute to matrix hardening in these alloys. In both the 48.5 and the 49.5–Ti alloys the samples heat treated above 550°C, containing no P$_L$–phase, showed a consistent hardness (within a standard deviation of the sample mean hardness) through all heat treatment times and temperatures. This point
is further elucidated from the various size and volume fraction distributions of Ti$_2$(Ni,Pt)$_3$ (Figures 3.7 and 3.9) indicating the negligible effect that the Ti$_2$(Ni,Pt)$_3$ phase has on sample hardness. In general, the 48.5–Ti alloy has an increased hardness over the 49.5–Ti alloy which can be attributed to the fact that the 48.5–Ti alloy is further from an ideal 50-Ti stoichiometry leading to an increased amount of disordered matrix, leading to an increased hardness, as suggested by Mousavi et al. [43] and Suzuki and Masumoto [44].

The general morphology of the Ti$_2$(Ni,Pt)$_3$ phase does, however, suggest a habit plane arising from full or semi-coherency between the Ti$_2$(Ni,Pt)$_3$ structure and the B2 matrix (throughout this discussion the B2 matrix will be referred to as this is the phase within which the Ti$_2$(Ni,Pt)$_3$ phase precipitates). The coherency of the Ti$_2$(Ni,Pt)$_3$ phase was observed in various samples as strain centers within the Ti$_2$(Ni,Pt)$_3$ plate. Figure 3.11 presents two TEM BF images taken near the 011 zone axis of the observed Ti$_2$(Ni,Pt)$_3$ plates. From

Figure 3.11 Two TEM BF images showing the nature of strain centers arising from partial coherency between the Ti$_2$(Ni,Pt)$_3$ phase (lighter contrast features running from the upper left to the lower right corner of each image) and the martensite matrix. The image on the left was setup with only 022 reflections excited, while the image on the right was taken using the 200 lattice reflections. Both images were taken near B = [011].
this figure, strain centers caused by the partial coherency of the Ti$_2$(Ni,Pt)$_3$ phase with the martensite matrix are apparent in the image on the left. The image on the right obtained by tilting away from the 022 planes takes the strain centers out of contrast. Note that the strain centers are observable using the 022$_{\text{Ti}_2\text{(Ni,Pt)}_3}$ reflections (left image), but go out of contrast when using the 200$_{\text{Ti}_2\text{(Ni,Pt)}_3}$ reflections, this implies the presence of interfacial dislocations to accommodate the misfit between the B2 and Ti$_2$(Ni,Pt)$_3$ phases.

Knowing the orientation relationships (OR’s) and lattice plane spacings of the B2, B19, and Ti$_2$(Ni,Pt)$_3$ phases, a quantification of the strain centers presented in Fig. 3.11 is possible. The OR’s between the Ti$_2$(Ni,Pt)$_3$ phase was established in previous work [37] as

\[
\langle 110 \rangle_{\text{B2}} \parallel [010]_{\text{Ti}_2\text{(Ni,Pt)}_3} \\
\{001\}_{\text{B2}} \parallel (100)_{\text{Ti}_2\text{(Ni,Pt)}_3}
\]

Additionally, the OR between the B2 austenite and B19 martensite phases has been described by Otsuka and Ren [41]. The B2/B19 OR is actually quite similar to the B2/Ti$_2$(Ni,Pt)$_3$ OR, with $a_{\text{B19}}$ parallel to the [001]$_{\text{B2}}$ direction, with $b_{\text{B19}}$ and $c_{\text{B19}}$ parallel to the [110]$_{\text{B2}}$ and [\overline{1}0]$\overline{1}$$_{\text{B2}}$ directions, respectively.

The lattice parameters of the Ti$_2$(Ni,Pt)$_3$ phase were made using XRD Rietveld analysis. Measurements were made on three samples of the 48.5–Ti alloy, the as–extruded condition, the 600°C–100h–WQ sample, and the 550°C–100h–WQ sample. These values for the Ti$_2$(Ni,Pt)$_3$ phase are presented in Table 3.2. Using these lattice parameters, the d–spacing

<table>
<thead>
<tr>
<th></th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Extruded</td>
<td>14.049 ± 0.012</td>
<td>4.5134 ± 0.0002</td>
<td>4.439 ± 0.0002</td>
</tr>
<tr>
<td>600°C–100h–WQ</td>
<td>14.246 ± 0.006</td>
<td>4.5102 ± 0.0003</td>
<td>4.4351 ± 0.0002</td>
</tr>
<tr>
<td>500°C–100h–WQ</td>
<td>14.206 ± 0.007</td>
<td>4.5084 ± 0.0003</td>
<td>4.4336 ± 0.0002</td>
</tr>
</tbody>
</table>
of the pertinent planes of interest for coherency were calculated. The 011_{\text{Ti}_2(\text{Ni,Pt})_3} planes were calculated to be 3.16Å, while the 101_B19 were calculated to be 3.24Å (per Table 3.1). Also, considering that the Ti_2(\text{Ni,Pt})_3 phase precipitates within the B2 austenite phase, the lattice parameter was measured (via XRD Rietveld analysis, as well) to be 3.0712Å¹. This leads to a 100_{\text{B2}} planar spacing of 3.07Å. These three planar spacings are near enough to each other to warrant a semi-coherent habit plane between the Ti_2(\text{Ni,Pt})_3 plates and both the B2 parent structure and the B19 martensite structure.

Considering the differences in planar spacing between two phases, the case for full or semi coherency can be made. According to Porter and Easterling [45], the misfit between the planar spacing of two phases is defined as:

$$\delta = \frac{d_\beta - d_\alpha}{d_\alpha}$$

where \(d_\alpha\) and \(d_\beta\) refer to the planar spacings of the generic \(\alpha\) and \(\beta\) phases, respectively. Performing this calculation on the above mentioned planes of the Ti_2(\text{Ni,Pt})_3 phase and the B2 and B19 matrix phases the \(\delta\) values are 0.0296 (Ti_2(\text{Ni,Pt})_3–B2) and 0.0253 (Ti_2(\text{Ni,Pt})_3–B19). From this, it is apparent that the martensitic phase has a lower misfit with the Ti_2(\text{Ni,Pt})_3 phase. Additionally, based on the misfit parameter, \(\delta\), the spacing of requisite dislocations to relieve the misfit strain can be calculated. This spacing, \(D\), can be simply calculated as

$$D = \frac{d_\beta}{\delta}$$

Calculating these values, a dislocation spacing of \(\approx 107\text{Å}\) and \(\approx 128\text{Å}\) is predicted between the Ti_2(\text{Ni,Pt})_3/B2 and Ti_2(\text{Ni,Pt})_3/B19 interface, respectively. Measuring the strain centers visible in Fig. 3.11 a value near 320Å was measured. The discrepancy between the calculated

¹The lattice parameter of this phase was found by Rietveld analysis of the 48.5–Ti alloy, as–extruded sample. This particular sample contained so little Ti_2(\text{Ni,Pt})_3 and P_L–phase that there was enough Ni and Pt in solution to suppress the M_s to below room temperature. Because of this, B2 peaks were observed and measured. The value given here is in good agreement with that reported by Hatcher, which was 3.087 for a Ti_{50}Ni_{29}Pt_{21} alloy [26].
and measured values could arise from several sources. First, the imaged strain centers may lack adequate resolution to fully account for all dislocations present. Second, the measurements made on Fig. 3.11 were made between the Ti$_2$(Ni,Pt)$_3$ plate and the martensite. It is difficult to predict how the martensitic transformation affected the semi-coherent interface between the Ti$_2$(Ni,Pt)$_3$ and B2 phases. Finally, depending on how the lattice parameters of the Ti$_2$(Ni,Pt)$_3$ and B2 phases change with temperature, the misfit is likely different at the heat treat temperature and room temperature. Regardless, the imaging conditions presented in Fig. 3.11 suggest the Ti$_2$(Ni,Pt)$_3$ semi-coherency, and subsequent plate morphology, can be observed using the 022$_{\text{Ti}_2(\text{Ni,Pt})_3}$ planes.

3.3.4 The P$_L$–phase

From the hardness data presented in Fig. 3.3, it was speculated that the coherent P$_L$–phase precipitated in samples of both alloys heat treated at 500 and 550°C. However, this phase was very fine and difficult to adequately image in the SEM. As a result, TEM investigations were performed in an effort to observe and characterize the P$_L$–phase. Representative TEM micrographs of the 48.5–Ti alloy are presented in Figure 3.12. From these images, the growth and coarsening of the P$_L$–phase is evident, as heat treatment time and temperature are increased. From these observations, the hardening behavior presented in Fig. 3.3 can be rationalized as the growth and coarsening of the P$_L$–phase. Clearly, as the P$_L$–phase coarsens, the general spherical morphology appears to be maintained in these particular samples.

Figure 3.13 is a similar collection of TEM BF images taken from the 49.5–Ti alloy. As in the 48.5–Ti alloy, the P$_L$–phase can be seen to coarsen as heat treatment time and temperature are increased. Because of its small size and fine distribution, it was difficult to observe the small precipitates present in the 500°C–1h condition, but the phase was
Figure 3.12  BF TEM images of alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ samples containing the P$_L$-phase (arrows).
Figure 3.13  BF TEM images of alloy Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$ samples containing the P$_L$-phase (arrows).
confirmed to be present from the hardness results (Fig. 3.3) and the coarsening behavior of this alloy through heat treatment.

Volume fraction measurements using TEM foils require knowledge of the foil thickness for accurate measurements. As reliable foil thickness determinations were not possible with the current samples, volume fraction measurements of the PL-phase were not made on TEM samples. Using finely-tuned SEM backscatter imaging (images of which will be shown below), the PL-phase was imaged on several of the samples of the 48.5 and 49.5–Ti alloys. Volume fraction measurements were made on the 24 and 100h samples of the 550°C heat treatments, and on the 100h samples of the 500°C heat treatments, presented in Fig. 3.14. In this plot, the 49.5–Ti, 500°C–100h sample has the highest volume fraction of the PL-
phase, with roughly 31%. The 48.5–Ti, 500°C–100h and both 550°C–24h samples have the
next highest volume fractions, near 23%. The 550°C–100h samples have the lowest volume
fractions with the 49.5–Ti sample having near 14% and the 48.5–Ti sample having roughly
10% P_L–phase.

This plot elucidates much of the behavior of the P_L–phase within this system. At
heat treatment temperatures of 550°C, with no Ti_2(Ni,Pt)_3 present, there is a large volume
fraction of P_L–phase present after aging times of 24 and 100h (Figure 3.17). Considering
this, the volume fraction data of the P_L–phase in Fig. 3.14 can be explained by the following.
First, at 500°C the 49.5–Ti alloy has a significantly higher volume fraction of P_L–phase than
the 48.5–Ti alloy. Assuming that the P_L–phase is metastable in this system and Ti_2(Ni,Pt)_3
is the equilibrium phase, then the P_L–phase can be expected to be consumed by the growth
of Ti_2(Ni,Pt)_3. In the 49.5–Ti 500°C–100h sample, there is no Ti_2(Ni,Pt)_3 present, but in
the 48.5–Ti sample, there is an appreciable amount present (10.6%).

This same argument can be used for the 550°C samples. In the 24h condition, the
48.5–Ti alloy has an appreciable quantity of Ti_2(Ni,Pt)_3 present (between 11.6 and 15.2%),
but there is a negligibly small amount of Ti_2(Ni,Pt)_3 in the 49.5–Ti alloy. Because of this,
the Ti_2(Ni,Pt)_3 in the 48.5–Ti alloy has consumed enough of the excess solute to push the
quantity of the P_L–phase below that of the 49.5–Ti alloy. A similar situation is occurring in
the 550°C–100h conditions. In these samples, the 49.5–Ti alloy has a measurable amount of
Ti_2(Ni,Pt)_3 present (3.3%), but not enough to have appreciably decreased the amount of the
P_L–phase. Likewise, in the 48.5–Ti alloy, there is sufficient Ti_2(Ni,Pt)_3 phase (15.2%) to use
the available solute such that the amount of the P_L–phase is decreased appreciably. Simply
put, there is a limited amount of solute available within each alloy to form second/third
phase precipitates. In the 49.5–Ti alloy, all of the excess solute is available for the P_L–phase.
However, in the 48.5–Ti alloy, both the P_L–phase and the Ti_2(Ni,Pt)_3 phase are at volume
fractions where the matrix Ti content is sufficiently near a 1:1 ratio of Ti:(Ni+Pt). Within

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this system, under the heat treatment conditions studied, the amount of P\textsubscript{L}-phase present with the Ti\textsubscript{2}(Ni,Pt)\textsubscript{3} phase is less than the amount in the 49.5-Ti alloy.

A similar interplay between the P\textsubscript{L}-phase and the Ti\textsubscript{2}(Ni,Pt)\textsubscript{3} can be seen by looking at the Feret diameter (defined as the distance between two parallel lines tangent to a particle being measured [46]) of the P\textsubscript{L}-phase with varying heat treatment conditions. Figure 3.15 presents this data. It should be noted that this data set was collected between TEM BF images and SEM BSE images\textsuperscript{2}. From this plot, it is apparent that the P\textsubscript{L}-phase coarsens with increasing heat treatment temperature/time. Similar to the volume fraction data, the 49.5-Ti alloy samples contain coarser P\textsubscript{L} precipitates than those in the 48.5-Ti alloy. Again, this is attributable to the fact that, in the 49.5-Ti alloy samples, there is little to no Ti\textsubscript{2}(Ni,Pt)\textsubscript{3} present to compete with the P\textsubscript{L}-phase. Thus, the P\textsubscript{L}-phase is capable of coarsening more readily in the 49.5-Ti alloy, whereas in the 48.5-Ti alloy the P\textsubscript{L}-phase is coarsening to lower surface energy while at the same time dissolving into the matrix due to the driving force due to the presence of the Ti\textsubscript{2}(Ni,Pt)\textsubscript{3} phase, which is the more stable phase. This would explain the increasing P\textsubscript{L}-phase diameter (Fig. 3.15) and simultaneous decrease in volume fraction (Fig. 3.14), at 550°C.

3.3.4.1 P\textsubscript{L}-phase Coherency

In an ancillary study to understand the coherency of the P\textsubscript{L}-phase with the B2 matrix, high resolution TEM observations were made on a related alloy [37]. Specifically, a non-consumable, vacuum arc melted button of the composition Ti\textsubscript{47}Ni\textsubscript{25}Pt\textsubscript{27} was investigated using high resolution high angle annular dark field (HAADF) imaging. A sample of this alloy was solutionized at 1100°C and water quenched. This process left a microstructure with a small amount of Ti\textsubscript{2}(Ni,Pt)\textsubscript{3}, a large fraction of the P\textsubscript{L}-phase, and a matrix of B2, versus

\textsuperscript{2}It should be noted that corrections for these measurements were not made for the medium from which they were collected as adequate TEM foil thicknesses could not be made. Hence, these data cannot be taken for absolute values, but still allow for qualitative comparisons of the size of the P\textsubscript{L}-phase in differing heat treatment conditions.
Figure 3.15  Plot of Feret diameter vs heat treatment time of the $P_L$-phase for several samples of both the $Ti_{48.5}Ni_{30.5}Pt_{21}$ and $Ti_{49.5}Ni_{29.5}Pt_{21}$ alloys.

martensite. It is well known in the Ni–Ti system that excess Ni in solution dramatically depresses the $M_s$ temperature. This behavior will be more thoroughly discussed in the next chapter, but was taken advantage of in this case to create an observable matrix of B2 at room temperature. Because this alloy was water quenched from such a high temperature, with so much excess solute (Ni and Pt) in solution, the $M_s$ was suppressed to below room temperature allowing for observations of the B2/$P_L$-phase interface without the use of a heating stage.

Figure 3.16 presents a representative HAADF image of a $P_L$-phase precipitate within the B2 matrix. The $P_L$-phase precipitate can be identified in the bottom right corner of the image by the characteristic “dumbell” Pt atom pairs, as described by Kovarik, et al. [34]. Apparent from this image is the coherency between the matrix and the precipitate.
Upon inspection, nearly perfect registry between the matrix and precipitate is found. This is in agreement with the results reported by Gao et al. concerning the P_L–phase and B19 interface [33]. This fact will become important in the next chapter during the discussion of the mechanical testing results on the Ti_{48.5}Ni_{30.5}Pt_{21} and Ti_{49.5}Ni_{29.5}Pt_{21} alloys.

### 3.3.5 Mixed Phase Microstructures

To gain a deeper understanding of the stability of the P_L and Ti_2(Ni,Pt)_3 phases, several heat treatments were completed on the 48.5–Ti alloy after samples were fully solutionized at 1300°C, to dissolve the Ti_2(Ni,Pt)_3, and water quenched. After homogenization, the microstructure contained only TiC inclusions, the martensitic matrix, and a small amount of fine P_L–phase, as indicated by the slight increase in hardness (Fig. 3.3, and confirmed
through TEM observations discussed below) above the other samples containing none of this phase (HT conditions above 550°C). Samples were then aged for 5 and 100h, at 550 and 600°C. Both samples that were heat treated for 5h contained an even distribution of fine, but cuboidially shaped, $P_L$–phase and no $\text{Ti}_2(\text{Ni,Pt})_3$ (Fig. 3.17). The sample aged for 100h at 550°C contained only $P_L$–phase that was coarser than after the 5h age (Fig. 3.17B). The sample aged for 100h at 600°C contained evenly-distributed plates of $\text{Ti}_2(\text{Ni,Pt})_3$ and no $P_L$–phase (Fig. 3.18). Measurements of the 600°C-100h sample indicated a volume fraction of 18.6 ± 0.86% (95%CI) $\text{Ti}_2(\text{Ni,Pt})_3$, which correlate well with those of the sample receiving the same heat treatment prior to homogenization, 18.3 ± 0.48% (95%CI) (Fig. 3.5). The image presented in Fig. 3.18B is the same image presented in Fig. 3.8A. It is being presented again simply for comparison with its 5h counterpart, to show the prevalence of the $P_L$–phase to form as a primary, metastable phase that eventually dissolves, allowing for the growth of the $\text{Ti}_2(\text{Ni,Pt})_3$ phase at 600°C.

Figure 3.17  TEM BF image of the Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ alloy sample solutionized at 1300°C, then heat treated at 550°C for 5h (A), and an SEM BSE image of the same sample heat treated for 100h (B).
Figure 3.18 SEM BSE image of samples of alloy Ti48.5Ni30.5Pt21 solutionized at 1300°C then heat treated at 600°C for 5h (A) and 100h (B). The microstructure in A consists of the Ti-(Ni,Pt) martensite and elongated precipitates of the P_L-phase, while B contains the same martensitic matrix with precipitates of Ti_2(Ni,Pt)_3.

The homogenization experiments presented in this section indicate several things about the stability of the two precipitate phases observed in this system. As previous heat treatments indicated, at 600°C (and higher temperatures) Ti_2(Ni,Pt)_3 has greater thermodynamic stability than the P_L-phase. However, before the homogenization treatments, it was not clear how prevalent the P_L-phase was at early aging times. The presence of the P_L-phase in the 600°C–5h conditions indicates that this phase, while metastable, has faster formation kinetics than the more stable Ti_2(Ni,Pt)_3. Energetically (lower ΔG*, due to lower coherency/misfit strains), this behavior is expected, as the P_L-phase is structurally similar to the B2 parent phase within which it precipitates. Additionally, considering that within the binary Ni–Ti system there are two metastable Ni–rich phases that precipitate before the equilibrium phase, this precipitation sequence is quite similar. This is also reminiscent of the multiple phases that precipitate in the classic Al–Cu system.

To further understand the interplay between the P_L and Ti_2(Ni,Pt)_3 phases, two samples were examined to observe the dissolution of the P_L-phase through the growth of the Ti_2(Ni,Pt)_3 phase, via precipitate free zones (PFZ’s). It was posited that if the Ti_2(Ni,Pt)_3
was the stable phase, and the $P_L$–phase was metastable, then at some point in time–temperature space, the $P_L$–phase should be dissolved, driven by the growth of the $\text{Ti}_2(\text{Ni},\text{Pt})_3$ phase. Figure 3.19 presents the observance of such PFZ’s, at two different heat treatment temperatures. Fig. 3.19A shows the microstructure of the 48.5–Ti alloy in the 550°C–100h–WQ condition. In this sample, the $P_L$–phase precipitates were sufficiently coarse to observe in the SEM (as previously mentioned) and surrounding the $\text{Ti}_2(\text{Ni},\text{Pt})_3$ precipitates there is a clear zone that is void of the $P_L$–phase, indicating that the $\text{Ti}_2(\text{Ni},\text{Pt})_3$ is growing at the expense of the $P_L$–phase. Knowing that solutionized samples heat treated at 600°C for 5h contained only $P_L$–phase precipitates, and those heat treated at 100h contained only $\text{Ti}_2(\text{Ni},\text{Pt})_3$ precipitates, a solutionized sample was heat treated at 36h to observe the transition between the $P_L$–phase and $\text{Ti}_2(\text{Ni},\text{Pt})_3$ phase (Fig. 3.19B). In this figure, the dissolution of the $P_L$–phase as the $\text{Ti}_2(\text{Ni},\text{Pt})_3$ phase grows is even more obvious, likely due to the increased reaction kinetics at the higher heat treatment temperature (550 vs. 600°C).

This same behavior was observed in the 49.5–Ti alloy. As presented earlier, samples heat treated at 500 and 550°C contained little if any $\text{Ti}_2(\text{Ni},\text{Pt})_3$. This occurred because,
in the 49.5–Ti alloy, the extrusion temperature (900°C) was high enough to put all of the Ti$_2$(Ni,Pt)$_3$ in solution, so each heat treatment started with essentially a solutionized microstructure. This is contrasted against the 48.5–Ti alloy as every sample of this alloy initially heat treated started with a small amount of Ti$_2$(Ni,Pt)$_3$ present (Fig. 3.2). Figure 3.20 presents the 550°C–100h–WQ sample of the 49.5–Ti alloy. This alloy was measured to have 4.9%±1.4 Ti$_2$(Ni,Pt)$_3$ present and was the only sample of the 49.5–Ti alloy to have an appreciable amount of Ti$_2$(Ni,Pt)$_3$ present (there were Ti$_2$(Ni,Pt)$_3$ plates observed in the 550°C–24h sample, but in an immeasurably small quantity). Evident from this figure, surrounding the Ti$_2$(Ni,Pt)$_3$ plates (black arrow) there is a distinct lack of the P$_L$–phase (white arrow). This confirms the metastable behavior of the P$_L$–phase, and the stability of the Ti$_2$(Ni,Pt)$_3$ phase, in the alloys of this study, per the previously outlined PFZ argument.

Considering this interplay between the P$_L$ and the Ti$_2$(Ni,Pt)$_3$ phases, the volume fraction of the Ti$_2$(Ni,Pt)$_3$ phase can be more adequately understood for samples heat treated at 500 and 550°C, Fig. 3.9. It can be assumed that the samples of this study have a certain

![Figure 3.20 SEM BSE image of the 550°C–100h–WQ sample of alloy Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$. Both the P$_L$–phase (white arrow) and the Ti$_2$(Ni,Pt)$_3$ (black arrow) were observed in this sample.](image-url)
equilibrium volume fraction of Ti$_2$(Ni,Pt)$_3$, depending on their heat treatment temperature. For samples heat treated above 600$^\circ$C, the equilibrium amount of Ti$_2$(Ni,Pt)$_3$ decreases with increasing heat treatment temperature. Considering the behavior of the samples heat treated at 500 and 550$^\circ$C, it cannot currently be known what the equilibrium amount of Ti$_2$(Ni,Pt)$_3$ is at 500 and 550$^\circ$C. If the B2 phase has increasing solubility for Ni and Pt as temperature decreases, it would be assumed that the amount of Ti$_2$(Ni,Pt)$_3$ would decrease below 600$^\circ$C. If the B2 phase has decreasing solubility for excess Ni and Pt, the amount of Ti$_2$(Ni,Pt)$_3$ would increase below 600$^\circ$C. However, because the reaction kinetics at lower temperatures are decreased, the samples heat treated at 500 and 550$^\circ$C are probably further from equilibrium than their higher temperature counterparts. This lack of attained equilibrium is confirmed by the presence of the P$_L$–phase in all samples heat treated at 500 and 550$^\circ$C. The 550$^\circ$C, 1 and 100h samples of the 48.5–Ti alloy do suggest that the amount of Ti$_2$(Ni,Pt)$_3$ at 550$^\circ$C could approach that of the 600$^\circ$C samples as the volume fraction of Ti$_2$(Ni,Pt)$_3$ increased from $\approx$ 12% to $\approx$ 15% in the 1 and 100h conditions, respectively.

Apparent from Figures 3.17 and 3.18, the morphology of the P$_L$–phase has a dependence on the volume fraction. The morphology of the P$_L$–phase can be contrasted with that of the nearly spherical P$_L$–phase present in Figs. 3.12 and 3.13. The high volume fraction of the P$_L$–phase in these images lends well to the argument of how easily this phase is formed in this alloy system. Additionally, the high volume fractions of this phase after homogenization lend further evidence to the metastability of this phase, at 550$^\circ$C. As all heat treatment conditions of 1h or more appear to contain decreasing fractions of this phase with increasing aging time at 550$^\circ$C (Fig. 3.14).

Viewing Fig. 3.18A, it was thought that the P$_L$–phase may be the product of spinodal decomposition. To address this question, a TEM sample of the 48.5–Ti alloy was solutionized at 1300$^\circ$C and water quenched. Figure 3.21 presents this microstructure. The TEM BF image (Fig. 3.21A) does not indicate that spinodal decomposition occurred in this system. Because of spinodal decomposition’s lack of barrier to nucleation, it would be expected that
Figure 3.21  TEM BF image (A) of a sample of alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ solutionized at 1300°C and water quenched and accompanying TEM DF image showing the early stage formation of the P$_L$–phase precipitates (arrow). The inset [011]$_{B2}$ SADP indicates the reflection used (d=7.12 Å) to form the DF image.

quenching from a high temperature would leave a characteristic modulated microstructure. However, the presented microstructure lacks any kind of detectable compositional modulation. Furthermore, the accompanying DF image (Fig. 3.21B) presents the early stage formation of the P$_L$–phase (arrow). The reflection used to create this DF image is indicated in the inset [011]$_{B2}$ SADP and corresponds to planes with a spacing of approximately 7.12 Å, correlating to the (002)$_{P_L}$ planes ($d_{001} = 14.22$ Å)\[34].

Additional inspection of Fig. 3.17 also indicates evidence for a traditional nucleation and growth of P$_L$–phase, versus a spinodally–decomposed structure. For example, in Fig. 3.17A, toward the center and upper right of the image the P$_L$–phase particles can be seen to be necking in a directional manner. This is further corroborated by the microstructure shown in Fig. 3.17B, which shows a coarser microstructure, but with less of a directional dependence. Comparing Fig. 3.18A to Fig. 3.19B, it appears that the P$_L$–phase coarsens to from the long
rods that are initially formed in early stage heat treatments. More specifically, Fig. 3.18A is dominated by long rod shaped precipitates of the P\textsubscript{L}–phase (darker contrast), but viewing the P\textsubscript{L}–phase in Fig. 3.19B the long rods appear to be coarsening into more spherical precipitates. This is also coincident with an overall decrease in the volume fraction of the P\textsubscript{L}–phase (Fig. 3.14), and consistent with the low volume fraction, spherical morphology of the P\textsubscript{L}–phase in the initial heat treatment conditions of this investigation (Figs 3.12 and 3.13).

To further demonstrate this break up and “spheroidizing” of the P\textsubscript{L}–phase, Figure 3.22 presents the microstructure of a solutionized sample heat treated at 600°C. Image A presents the microstructure after 5h of heat treatment, B after 24h, and C after 36h. Apparent from this is a clear change in morphology from long, thin, rod like precipitates (Fig. 3.22A) to a shorter, wider, more globular morphology (Fig. 3.22C). This is similar to the change in morphology for the sample that was heat treated at 550°C, Fig. 3.17. It is currently unclear what the exact driving forces are to produce the rod/plate–like morphology of the P\textsubscript{L}–phase at high volume fractions. However, this “spheroidizing” effect is consistent with the fact that, in all other heat treatment conditions, the P\textsubscript{L}–phase is present in much lower volume fractions, and maintains a predominantly spherical morphology.

Figure 3.22 Three SEM BSE images of the Ti\textsubscript{48.5}Ni\textsubscript{30.5}Pt\textsubscript{21} alloy solutionized at 1300°C, water quenched, and heat treated at 600°C. Image A was heat treated for 5h, B for 24h, and C for 36h.
3.4 Conclusion

The microstructures through various heat treatment times and temperatures have been explained and quantified in the two alloys, Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ and Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$. All hot extruded samples of the 48.5–Ti alloy contained two phases, the martensitic matrix and the plate-like precipitate Ti$_2$(Ni,Pt)$_3$. Samples of this alloy heat treated at 500 and 550°C contained an additional, small, spherical and highly coherent precipitate known as the P$_L$–phase. Samples of the 49.5–Ti alloy contained either the P$_L$–phase, for samples heat treated at 500 or 550°C, or the Ti$_2$(Ni,Pt)$_3$ phase, for samples heat treated at 600°C and above. Two samples, the 550–24h–WQ and 550–100h–WQ, contained both phases as the metastable P$_L$–phase transitioned to the more stable Ti$_2$(Ni,Pt)$_3$ phase. The P$_L$–phase is metastable but readily forms because of its structural proximity to the B2 parent (austenite) phase, while the Ti$_2$(Ni,Pt)$_3$ phase is the equilibrium phase in this system.

The coherency and long-term stability of each of these phases was also explored. The Ti$_2$(Ni,Pt)$_3$ phase appears to have semi-coherent planes with the B2 phase, and subsequent martensite phase, leading to its characteristic plate-like morphology. The Ti$_2$(Ni,Pt)$_3$ phase was also observed to have little hardening effect on the matrix. The P$_L$–phase was observed to be highly coherent with the B2 structure and its effects on the matrix hardness were readily apparent through microhardness testing, showing a classic hardening and overaging behavior with increasing heat treatment time and temperature.

The quantity of the Ti$_2$(Ni,Pt)$_3$ phase was measured and found to vary with heat treatment. The decrease of Ti$_2$(Ni,Pt)$_3$ with heat treatment temperature suggests a B2 phase field that has an increasing solubility of Ni and Pt with temperature. The P$_L$–phase, it was quantified in the 24 and 100h heat treated samples. These measurements suggest that as heat treatment time and temperature are increased, the quantity of the P$_L$–phase decreases. This fact, in addition to other high temperature quenching experiments, suggests the metastability of the P$_L$–phase. The shape of the B2/Ti$_2$(Ni,Pt)$_3$ equilibrium solvus be-
low 600°C cannot be determined from the presented data, as heat treatment times at lower temperatures were insufficient to reach an equilibrated microstructure.
CHAPTER 4

ISOBARIC THERMAL CYCLING BEHAVIOR

4.1 Introduction

The current research aims to establish relationships between composition, processing, microstructure, and shape memory properties for high temperature shape memory alloys (HTSMA’s) that will be used as solid state actuators. Therefore, the effects of thermal cycling, especially under load, are of the greatest interest. Various contributions have been made to the field of Ni–Ti SMA’s concerning thermal cycling behavior. It is clear from the literature that thermally cycling an SMA affects various properties of the test sample (transformation temperatures, transformation strains, etc.) In general, it is unclear how exactly thermal cycling affects shape memory properties, as various researchers have indicated changes in properties that are sometimes in agreement with previous results, sometimes not. Morgan [47] reviewed the literature available up to 1999 and outlined various discrepancies in which shape memory properties evolved and how they were affected during thermal cycling. This list included increases and decreases in each of the four characteristic transformation temperatures (i.e., martensite start/finish ($M_S$, $M_F$) and austenite start/finish ($A_S$, $A_F$)), as well as increases and decreases in hysteresis and transformation strain. The disagreement between the various studies given were attributed to a lack of specific description of the material chemistry, processing conditions, and testing conditions.

Most recently, De la Flor et al. [48] outlined the conditions for stabilizing the shape memory properties of NiTi drawn wire and reported the effects of cycling temperature on the recoverable strain, while Li et al. [49] reported the effects annealing time and thermo-mechanical cycling conditions (stress and temperature) have on the shape memory response of NiTi wire. In general, the above–mentioned reports indicate that any change in the
transformation temperatures due to thermal and/or thermo-mechanical cycling are due to the effects of dislocation creation and interaction arising from microplasticity accompanying the martensitic transformation. Various researchers including Miyazaki et al. [50] have documented the increased presence of dislocations and dislocation networks after thermal cycling. In addition to this generally accepted explanation of shape memory property ‘drift,’ Wagner et al. [32] also indicated that thermally cycling, even relatively close to the $A_f$ temperature, caused the formation of nano-scale Ni$_4$Ti$_3$ precipitates, which may also contribute to the change of shape memory properties with cycle number, at least in Ni–rich alloys.

Noebe et al. [24] provided additional data on the microstructure and mechanical properties of two Ni–Ti–Pt alloys, namely Ti$_{50}$Ni$_{30}$Pt$_{20}$ and Ti$_{50}$Ni$_{20}$Pt$_{30}$, and reported several important shape memory properties including transformation temperatures, stress-strain data at various temperatures, yield stress at various temperatures, and work output data for thermal cycling under various loads. From these data, it was concluded that 30%Pt alloys have work outputs that are too low for applicable use. Padula et al. extended this work by offering data on several more Ni–Ti–Pt alloys and outlined several methods that can be used to improve shape memory characteristics including both solid solution and precipitation strengthening as well as thermomechanical processing [11]. Noebe et al. [25] further discussed the effects of processing on a Ti$_{50.5}$Ni$_{29.5}$Pt$_{20}$ alloy. Some of the significant results from this work included identification of the temperature range for recovery (450 to 600$^\circ$C) and recrystallization (700$^\circ$C). They also showed that Ni–Ti–Pt alloys can be thermomechanically processed into various forms including rod and wire, which is necessary for use of these alloys as final products.

Despite the contributions made to the understanding of Ni–Ti–Pt HTSMA’s mentioned above, there is still a lack of fundamental understanding concerning the role that Ti-lean precipitates play in controlling shape memory properties (transformation temperatures, transformation strains under load, etc.). In the previous chapter of this work, the phase stability of two alloys, Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ and Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$, was described. This chapter will attempt
to connect the relevant microstructural features explained in the previous chapter with load-biased mechanical testing results collected on various samples of both alloys. Specifically, the role that both Ti-lean precipitates, the P\textsubscript{L}-phase and Ti\textsubscript{2}(Ni,Pt)\textsubscript{3}, play in controlling and altering shape memory properties during isobaric thermal cycling will be explored.

4.2 Experimental method and materials

The samples for mechanical testing were prepared the same way as described in the previous chapter. After heat treatments were completed, cylinders with a 5mm diameter and 10mm length (nominal dimensions) were sectioned using wire electrical discharge machining (EDM) for isobaric thermal cycling. All mechanical testing was performed on an MTS 810 servo-hydraulic load frame managed with an MTS FlexTest SE digital controller allowing operation and triggering of multiple control channels simultaneously. Samples were compressed between Udiment 720 platens, which were backed by hot grip extension rods held by water-cooled MTS 646 hydraulic collet grips. Load was measured with an MTS 100 kN/22 kip load cell. Strain within the gage section was measured with a high resolution Micro-Epsilon OptoControl 2600 LED extensometer. Heating of the sample was managed by a Eurotherm temperature controller with remote set point coupled with an Ameritherm Novastar 7.5 kW induction heater, which heated the hot grip extension rods and platens, heating the sample through thermal conduction. Sample temperature was measured with a type K thermocouple spot-welded directly to the sample surface.

All samples tested using differential thermal analysis (DTA) were run in a Nietzsche STA 409 at a heating and cooling rate of 10K/min, in alumina crucibles in a He atmosphere. For the Ti\textsubscript{48.5}Ni\textsubscript{30.5}Pt\textsubscript{21} alloy, only samples heat treated for 100h were run. These samples were taken from room temperature (RT) up to 1245°C, then cooled to 105°C and cycled again, through 3 thermal cycles, all up to 1245°C. For the alloy Ti\textsubscript{49.5}Ni\textsubscript{29.5}Pt\textsubscript{21}, all samples were run, with 3 thermal cycles between 105 and 500°C and a final fourth cycle going up to
1250°C. For each data peak in the DTA data, the peak onset, peak, and end temperatures were reported. These were determined using the native DTA software which fit a line to a portion of the data set prior to the peak, and one to the maximum slope of the half peak of interest (front half for onset, back half for end), then used the intersection of these two fit lines. Peak onset temperatures will be treated as transformation start temperatures.

Isobaric thermal cycles were conducted in compression by straining the samples at a rate of $1 \times 10^{-4}$/s until the desired stress was reached. Samples were stressed in increments of 50MPa from “no-load” (actually 1-2 MPa due to the load required to maintain contact between the sample and platens and henceforth referred to as 0MPa) to 300MPa, followed by 100 thermal cycles at 200MPa. While at each constant stress level, the sample was thermally cycled twice at 30°C/min heating and 30°C/min cooling, from 75 to 500°C and back. All properties were measured from the second thermal cycle at each stress level. Raw data from the load-biased thermal cycling tests were converted to true strain vs. temperature using NASA GRC-developed software. The true strain-temperature data were fitted using linear regression in three sections: the martensite coefficient of thermal expansion (CTE) region, the transformation region (fitting to the region of maximum slope), and the austenite CTE region (Figure 4.1). Transformation temperatures for the heating ($A_s, A_f$) and cooling ($M_s, M_f$) portions of each cycle were calculated using the intersection of the fit lines. Absolute strains in the austenite and martensite were measured at the beginning and end of each cooling cycle, respectively. Recovered transformation strain was calculated as the relative strain between the austenite finish and austenite start intersections. Relative work output (work per volume (J/cm$^3$)) at each stress level was calculated by multiplying the transformation strain by the applied stress. The amount of unrecovered or “open loop” strain per cycle was measured as the strain difference between the beginning of the heating curve and the end of the cooling curve. It should be noted that this value is the amount of unrecovered strain

1The sample cooling rate was only controllable from 500°C to the beginning of the martensitic transformation. After this, the cooling rate was dictated by transformational heating and heat transfer away from the sample.
Figure 4.1 Schematic diagram of a single isobaric thermal cycle. As the martensite transformation proceeds from a previous cycle, strain is produced within the sample leading to the strain value at the low temperature end of the heating curve. Upon heating, the martensite transforms to austenite and the previously induced strain is recovered, giving rise to the transformation strain. As the sample is then cooled and martensite forms, preferential twins of martensite form to accommodate the applied stress, imparting strain into the sample. The difference in strain before and after the thermal cycle is the open loop or residual strain. Adapted from [38].

per cycle under the given test conditions, without any preconceived notion as to specific transformation/deformation mechanism. It may be possible to recover a part of this strain by subjecting the sample to a change in test environment, such as continued thermal cycling but under a stress-free condition.

4.3 Results and Discussion

In this chapter, the results and discussion will be combined into a single section. Within this section, the transformation temperatures of tested samples will initially be presented. The next section will focus on be transformation strain, and finally the cumulative open loop
strain will be discussed. Throughout this chapter the results of mechanical testing will be linked to the observed microstructures reported in the previous chapter.

4.3.1 Transformation Temperatures

In this section, three main topics will be presented and discussed, namely, (1) the results of sample transformation temperatures based on DTA, (2) the results and explanation of the variable stress cycling, and (3) the results obtained from the constant load thermal cycling. In this section, the interplay between microstructure and isobaric thermal cycling will be discussed.

Throughout this section, the connection between the microstructures presented in the previous chapter will be linked to the mechanical test and DTA data being presented. As a reminder, it is worth noting that there were several general trends in the microstructures of both alloys used in this study. First, at heat treatment temperatures of 500 and 550°C, the P_L–phase, which is present in both alloys, will be shown to have a large effect on the transformation temperatures and strains. For samples heat treated above 550°C, the microstructures contained no P_L–phase, but only the Ti_2(Ni,Pt)_3 phase.

From the data to be presented, it will be shown that the coherency of the P_L–phase is the probable cause for the suppression of the transformation temperatures. In general, the P_L–phase acted to suppress the transformation temperatures of all samples tested and it will be shown that as the P_L–phase volume fraction decreases and diameter increases, the sample transformation temperatures will increase. The Ti_2(Ni,Pt)_3 phase is shown to have no effect on matrix hardness and its effects on microstructure will be linked to the effects it has on altering the matrix chemistry. As such, the transformation temperatures of the tested samples will be linked to the volume fraction and composition of the Ti_2(Ni,Pt)_3 precipitate.
4.3.1.1 Differential Thermal Analysis

One of the first methods used to characterize the difference in the samples being investigated was DTA. This method was performed on the as–extruded, 100h–WQ and both furnace cooled samples of the 48.5–Ti alloy, and on all samples of the 49.5–Ti alloy. Figures 4.2 and 4.3 are presented as representative plots of DTA output ($\mu$V/mg) versus temperature.

For the 48.5–Ti alloy (Fig. 4.2), both the austenite (endothermic) and martensite (exothermic) transformation peaks are clearly visible on the heating and cooling curves, respectively. The austenite peak on the first run appears at a slightly higher temperature than the following two runs (peak onset at 373°C vs 309 and 303°C). The martensite peaks are more consistent for all three cycles. At the upper temperature end of each thermal cycle, near 1200°C, additional peaks are also present. These peaks were found to be from

![Figure 4.2](image.png)

Figure 4.2  Plot of the differential thermal analysis (DTA) results for a sample of the the 600°C–100h sample of alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$. 

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Figure 4.3 Plot of DTA results for a 600°C–100h sample of alloy Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$.

the dissolution and precipitation of the Ti$_2$(Ni,Pt)$_3$ phase. This was confirmed through high temperature (1300°C) homogenization and water quenching experiments, where solutionized microstructures contained no Ti$_2$(Ni,Pt)$_3$. Despite the variation in the sample microstructures (previously discussed), the presented DTA plot is representative of all samples tested, where the $A_s$ temperature of each sample changed slightly after the first run and all samples showed the dissolution and precipitation of Ti$_2$(Ni,Pt)$_3$. The $M_s$ temperatures found from the 48.5–Ti plots were all relatively consistent, regardless of thermal cycle or sample heat treatment (Fig. 4.4). After each 48.5–Ti sample was heated to the maximum test temperature on the first run (1245°C), the samples were essentially homogenized and all microstructures resulting from prior heat treatment were erased. Thus, the only data from the 48.5–Ti samples unique to each sample is the first run $A_s$ temperature. This data and accompanying first run $M_s$ temperature data are presented in Fig. 4.4. From this figure, the effect that heat treatment has on the sample’s transformation temperatures is evident, con-
Figure 4.4  Plot of martensite and austenite DTA peak onset temperatures vs heat treatment temperature for the as-extruded, 100h, and furnace cooled samples of alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$. On this plot the as–extruded sample was plotted at a heat treatment temperature of 900°C because this is the temperature at which the extrusion process was performed.

Considering only the $A_s$ temperatures$^2$. The cause of this will be explained below. Furthermore, if the 48.5–Ti samples had not been heated during DTA cycling to such high temperatures, the $M_s$ temperatures would follow a similar trend to the $A_s$ temperatures. A lower maximum temperature was used on the DTA runs for the 49.5–Ti samples, and the results are discussed next.

The DTA data collected for the 49.5–Ti are represented in Fig. 4.5. Each sample was heated to 500°C for the first 3 runs, then to 1250°C for the final run. Apparent from this

$^2$It is worth noting that the as–extruded sample data are plotted at a heat treatment temperature of 900°C. This was done because the extrusion process took place at 900°C and the extruded bars were then air cooled. In this, and other data trends, the assumption of a 900°C heat treatment fits well with other points of the data set.
plot, the $M_s$ temperatures stay constant through the three thermal cycles (331, 332, and 333°C), and the second and third run $A_s$ temperatures are consistent with each other, but slightly lower than the first run $A_s$ (first 346°C, then 342 and 343°C). On the fourth run, the $A_s$ temperature is the same as the second and third run (345°C), with no notable peaks occurring on heating. On cooling of the fourth cycle, there is a notable exothermic peak at 536°C, then the $M_s$ temperature is suppressed down to 287°C.

As each sample of the 49.5-Ti alloy was tested, the first run martensite and austenite start temperatures are summarized in Figure 4.5. From these data plots, several trends are apparent. First, the 1h samples typically have the lowest start temperatures, while the 100h samples typically have the highest, with the 5 and 24h falling somewhere in between. Second, for the martensite temperatures, the data peaks at the 600°C, with the 500 and 550°C heat treat conditions falling more dramatically than the 650 and 700°C conditions. A similar, but less well defined trend occurs with the $A_s$ temperatures. Finally, the 600°C

![Figure 4.5](image-url)  
Figure 4.5 Plot of $M_s$ and $A_s$ temperatures for the first DTA run of all samples of the alloy Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$.  

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samples have similar peak start temperatures, despite the varying heat treatment times. This is apparent most prominently with the $M_s$ temperatures, and somewhat present with the $A_s$ temperatures, with the 1h sample being an outlier.

The general shape of the DTA start temperatures vs heat treatment conditions for the 49.5–Ti alloy can be understood through the varying microstructures presented in the previous chapter. During microstructural characterization, it was noted that the volume fraction of $\text{Ti}_2(\text{Ni,Pt})_3$ varied significantly with the sample heat treatment (Chapter 3, Fig. 3.9). As both alloys investigated are lean in Ti, there is an expected excess of Ni and Pt in the matrix. Excess Ni (and Pt in this case) has a drastic effect on the $M_s$ temperature of binary Ni–Ti alloys, as summarized by Tang and Frenzel et al., [4, 5]. In the case of a ternary alloy where one element is a Ni substitue (Pt in this research), it appears that moving away from the ideal 1:1 ratio of Ti:(Ni+Pt) has the same effect. As (Ni+Pt) rich precipitates form, the alloy matrix composition shifts closer to the ideal 50Ti:50(Ni+Pt) ratio and the higher the expected and $M_s$ and $A_s$. Subsequently, the maximum volume fraction of Ni+Pt rich precipitates should correspond to the maximum transformation temperatures.

This relationship between transformation temperature and volume fraction $\text{Ti}_2(\text{Ni,Pt})_3$ can be used to explain the variation in transformation temperatures for samples heat treated above 550$^\circ$C, $i.e.$, in samples void of the $P_L$–phase. Concerning the 48.5–Ti alloy, comparison of the volume fraction data presented in the previous chapter (Chapter 3, Fig. 3.9) with the $A_s$ peaks presented in Fig. 4.4 reveals that the general trend of data matches quite well for the 100h samples. The sample heat treated at 600$^\circ$C has the highest volume fraction of $\text{Ti}_2(\text{Ni,Pt})_3$, with the 650 and 700$^\circ$C samples having decreasingly less. Both of the furnace cooled (FC) samples (of the 48.5–Ti alloy only) have similar amounts of $\text{Ti}_2(\text{Ni,Pt})_3$, which is greater than the amount in the 700$^\circ$C sample, thus having a higher $A_s$ temperature. However, it seems this relationship does not hold perfectly considering the $A_s$ temperatures for the FC samples and the 600 and 650$^\circ$C samples. This can be attributed to the fact that the sample $M_s$ temperature is more strongly dependent on matrix chemistry than the $A_s$ temperature.
(per the previously mentioned literature). Finally, the as–extruded sample shows similar behavior between the volume fraction data and the $A_s$ data, both having significantly lower values relative to the 100h samples. Due to the lack of meaningful $M_s$ data for the 48.5–Ti alloy, and 1h sample data, this concept will be further developed later with the presentation of the mechanical test data.

The same correspondence between volume fraction of $\text{Ti}_2(\text{Ni,Pt})_3$ and transformation temperatures, for samples heat treated above 550°C, also holds quite well for the 49.5–Ti samples. In this alloy, however, the improved correlation between volume fraction $\text{Ti}_2(\text{Ni,Pt})_3$ and the $M_s$, versus the $A_s$, is evident. The $A_s$ temperatures somewhat hold this trend, with a substantial discrepancy in the 650°C-1h sample, which will be discussed below. Specifically, the $M_s$ and $A_s$ temperatures for the 100h samples follow the same trend as the volume fraction data, there is a peak at 600°C, with a decreasing trend as heat treatment temperature is increased. For the $M_s$ data, the correlation with the volume fraction data is also quite good. The 600°C–1h values are similar to the 100h values in both $M_s$ and volume fraction, and the differences between the 650 and 700°C data are also similar. The same trend is partially present in the $A_s$ data, but with an added explanation of the 650°C–1h behavior, which will be discussed below. Additionally, because the 5 and 24h DTA data is available, the increasing volume fraction of the $\text{Ti}_2(\text{Ni,Pt})_3$ phase is apparent in the increasing $M_s$ and $A_s$ values (Fig. 4.5). From this, it is evident that 600°C is the temperature where the kinetics of $\text{Ti}_2(\text{Ni,Pt})_3$ precipitation is at a peak for the 49.5–Ti alloy.

The 48.5–Ti alloy samples heat treated at 500 and 550°C have microstructures that contain both the $\text{P_L}$ and $\text{Ti}_2(\text{Ni,Pt})_3$ phases. As such, the DTA data presented above is insufficient to fully describe how the microstructure affects the transformation temperatures. Because of this, the effect of microstructure on these samples will be discussed below along with the mechanical testing results which provide more information about the transformation temperatures of these samples. However, the 49.5–Ti samples heat treated at 500 and 550°C contained only the $\text{P_L}$–phase. Thus, the start temperatures presented in Fig. 4.5, for the
500 and 550°C heat treatment temperatures, show the effect of the P$_L$-phase on the sample transformation temperatures.

Of particular note in Figure 4.5 are the 650°C–1h data. As shown in Figure 4.6, a substantial difference is evident between the martensite/austenite peaks for the 650°C–1h and the 600°C–100h sample (Fig. 4.3). Specifically, the 650°C–1h sample shows two separate peaks on heating and cooling for the first three DTA runs. The first peak on heating (first run) is represented in Fig. 4.5 with the solid circle, where the second peak is represented by the hollow circle. This bulk transformation behavior can be attributed to the presence of two different “zones” within the 650–1h sample, one that contains the Ti$_2$(Ni,Pt)$_3$ precipitates, and one that does not. The presence of these different microstructural areas was observed in the SEM (Figure 4.7). From this figure, the areas containing precipitates of Ti$_2$(Ni,Pt)$_3$ are contrasted against the areas that contain no Ti$_2$(Ni,Pt)$_3$. Using arguments based on the amount of Ni and Pt in solution, and the matrix composition proximity to a 50Ti:50(Ni+Pt)

![](image.png)

Figure 4.6 Plot of DTA results for a 650°C–1h–WQ sample of alloy Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$.
ratio, the areas that are void of \( \text{Ti}_2(\text{Ni,Pt})_3 \) should have the lower \( M_s/A_s \) temperatures, while the areas containing \( \text{Ti}_2(\text{Ni,Pt})_3 \) should have higher \( M_s/A_s \) temperatures. Additionally, the 700°C–1h sample also showed a similar “double peak” behavior in the DTA results. However, the peak doubles were so close in temperature that a single, broad peak was recorded, instead of two distinct peaks. This sample’s microstructure was also relatively inhomogeneous, similar to the 650°C–1h sample.

4.3.1.2 Stress Incremented Thermal Cycling

It is generally accepted in the literature that as a stress is applied to a shape memory alloy, the transformation temperatures also increase [51]. This section reports the results from the stress incremented portion of isobaric thermal cyclic testing. As expected, all samples tested showed increasing transformation temperatures with increasing applied loads. The distribution of the sample transformation temperatures generally followed the same distribution of transformation temperatures as the DTA results presented previously. This
distribution of sample data can be tied back to the microstructural constituents of each sample and will be discussed in more detail below.

Figure 4.8 presents the data collected for the 600°C–100h sample of the 48.5–Ti alloy, and is used here as a representation for all other data sets. This data set shows the seven stresses that isobaric thermal cycling was performed at, where the 200MPa, 100 cycle data has been omitted. The blue data lines represent the cooling data, while the red data lines represent the heating portion of the cycle. From this data, the following data plots were derived, to summarize the characteristics of the martensitic transformation that are outlined in Fig. 4.1. Note that in Fig. 4.1, the absolute strain is plotted (positive strain values), while

![Figure 4.8 Plot of temperature vs. strain data collected for the 600°C–100h sample of alloy Ti_{48.5}Ni_{30.5}Pt_{21}. The applied compressive stresses are indicated, and only the data for the second thermal cycle is presented. The red data lines indicate the heating portion of the cycle while the blue data indicates the cooling portion.](image-url)
in the Fig. 4.8, the true compressive strain is plotted (negative strain values). Similar data plots have been included the appendix.

In both alloys, the $M_s$ and $A_s$ transformation temperatures increased monotonically with increasing applied stress. Most sample data sets could be fit, quite well, to a line. Each zero point of the load depended on the specific heat treatment, and subsequent microstructure, of the sample as well as the slope of each sample data set. Figure 4.9 presents the $M_s$ temperatures vs. stress (only the second cycle at each stress is reported) for all of the 48.5–Ti samples tested. From this figure, the significant effect heat treatment has on the transformation temperatures is apparent. The as–extruded condition has the lowest transformation temperatures for all stresses, where the 500°C samples, in both the 1h and 100h condition, had the next lowest temperatures. Within the 1h sample set, the 550°C sample had the next lowest temperatures, with the 700 and 600°C samples following, respectively, and the 650°C sample having the highest transformation temperatures. In the 100h sample set, the samples

![Figure 4.9](image-url)  
**Figure 4.9** Plots of the martensite start ($M_s$) temperatures versus applied compressive stress during load-biased testing for alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$. The plot on the left presents the data for the as-extruded and 1h samples while the plot on the right displays the data for the 100h and furnace cooled (FC) samples.
ranked in order from lowest to highest as the 500°C, 1300°C–WQ+550°C–100h–WQ, 700, 550, and 650°C samples. Both FC samples, the 1300°C–WQ+600°C–100h–WQ sample and the 600°C sample all had high \( M_s \) temperatures and were closely grouped, with the 600°C sample having the highest \( M_s \) temperatures in the 100h sample set. Within both the 1h and 100h sample sets, all samples appeared to have similar slopes, or \( M_s \) dependence on applied stress, except for the as-extruded and 650°C samples. The same held true in the 100h sample set, with the 650°C–100h sample being the only outlier with respect to \( M_s \) dependence on stress.

The \( A_s \) temperatures versus stress followed nearly exactly the same sample data distribution as the \( M_s \) temperatures vs. stress. Notably, the as-extruded material consistently had the lowest transformation temperatures, followed by the 500°C sample. The 650°C sample had the highest \( A_s \) temperatures in the 1h sample set, while the 600°C sample had the highest in the 100h sample set. One major difference between the \( M_s \) and \( A_s \) temperatures

![Figure 4.10 Plots of the austenite start (\( A_s \)) temperatures versus applied compressive stress during load-biased testing of alloy Ti_{48.5}Ni_{30.5}Pt_{21}. The plot on the left presents the data for the as-extruded and 1h samples while the plot on the right shows the data for the 100h and furnace cooled (FC) samples.](image)

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however, is the spread of the highest and lowest transformation temperatures for a given data set. At zero stress levels, the $M_s$ temperatures span roughly 75°C for the 1h samples and 25°C for the 100h samples, while the spread for the $A_s$ temperatures is $\approx$ 150 and 60°C, for the 1h and 100h data sets, respectively.

As with the 48.5–Ti data presented above, the $M_s$ vs. stress data are presented for the 49.5–Ti alloy in Fig. 4.11 and the effects of thermal processing are readily apparent. The distribution of sample transformation temperatures for the 49.5–Ti alloy relative to the 48.5Ti alloy are similar with a few differences. The as–extruded sample had the lowest $M_s$ temperatures for all stresses, while the 500°C sample had the second lowest temperatures. The 550°C sample had the next lowest $M_s$ temperatures through all stresses in the 1h condition with the 700, 650 and 600°C–1h samples having increasingly higher $M_s$ temperatures for all stresses, respectively. For the 100h samples, the 650 and 600°C samples also had the second highest and highest transformation temperatures, respectively. However, because the

![Figure 4.11](image)

Figure 4.11 Martensite start ($M_s$) versus increasing stress data for the alloy Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$. The as–extruded and 1h sample data are displayed in the plot on the left, the 100h sample data are on the right.
550°C–100h sample \( M_s \) temperature had such a relatively large dependence on the applied stress (high slope), for the stresses 0-150MPa the 550°C sample had a lower \( M_s \) than the 700°C sample, but for stresses greater than 150MPa, the 550°C sample had a higher \( M_s \) temperature. It is interesting to note that the 650 and 700°C–1h samples both have similar \( M_s \) vs. stress slopes that are quite different from the other samples. This can be attributed to the inhomogeneous microstructures of these samples mentioned above. It is likely that the portions of these samples void of the \( \text{Ti}_2(\text{Ni,Pt})_3 \) phase experienced \( \text{P}_L \)-phase precipitation during the LB testing. This precipitation during testing would strengthen the sample matrix, and is a likely explanation for the relatively low slope of \( M_s \) vs. stress.

The \( A_s \) vs. stress data for the 49.5–Ti alloy are shown in Fig. 4.12. The ranking of the sample transformation temperatures for the 1h sample set is rather different from the \( M_s \) temperature data, indicating the different relationship between \( A_s \) and microstructure. Within the 1h sample set, the \( A_s \) temperatures increased in the following order: as–extruded,
650, 500, 700, 550, 600°C. The 100h sample set starts with the 500°C sample having the lowest Aₜ temperatures, followed by the 700°C and the 550°C samples, then the 650°C sample, and the 600°C had the highest Aₜ temperatures, though the overall range is much less than for the 1h conditions.

The transformation temperature vs. stress data presented above (Figs. 4.9–4.12) follows the accepted dependence of transformation temperatures on stress, per the Clausius-Clayperon (CC) relationship. Typically however, the more common form to present such data is on a stress vs. temperature plot. This is similar to the above plots, but with inverted axes. Kato and Pak presented a suitable treatment of the CC relationship for solid-solid phase transformations [52], relating the change in stress with change in temperature to the negative of the transformation entropy divided by the product of the transforming volume and transformation strain. Karaca et al. presented a more physically meaningful form of this equation [53]:

$$\frac{d\sigma}{dT} = -\frac{\Delta H}{T_o\epsilon_{max}^{tr}}$$

(4.1)

where \(\Delta H\) is the transformation enthalpy, \(T_o\) is the equilibrium temperature between martensite and austenite, and \(\epsilon_{max}^{tr}\) is the transformation strain from one grain, or crystal, of austenite transforming to one variant of martensite. Because of the inhomogeneous nature of the samples in this study (the various precipitate phases present and the TiC inclusions), no further analysis of this data will be performed. However, it is useful to understand that the inverse of the slope of the data presented in Figs. 4.9–4.12 is proportional to the transformation enthalpy divided by the product of the equilibrium temperature and transformation strain.

Furthermore, the \(d\sigma/dT\) is an important input parameter for several methods to model the behavior of SMA’s, and is referred to as the stress influence coefficient [51]. The inverted values, \(dT/d\sigma\), for the \(M_s\), \(M_f\), \(A_s\), and \(A_f\) temperatures are reported in Tables 4.1 and 4.2. It is worth noting that the convention is to assume the slope of the \(M_s\) vs. stress line is equal
to that of the $M_f$ vs. stress line, similarly with the $A_s$ and $A_f$ (i.e., $dM_s/d\sigma = dM_f/d\sigma$ and $dA_s/d\sigma = dA_f/d\sigma$). However, upon examination of Tables 4.1 and 4.2, this is often not the case.

Considering that all DTA data were collected on unstressed samples, the extrapolated zero-load transformation start temperatures can be compared to the DTA peak start temperatures. A comparison of the DTA start temperatures and the mechanical testing extrapolated zero load transformation temperatures is presented in Tables 4.3 and 4.4.

For the 48.5–Ti alloy, the $M_s$ temperature data are not well matched between the zero-load due to the high upper temperatures of the DTA runs, as explained above. However, considering the $A_s$ temperatures, there is agreement between the zero-load and DTA transformation temperatures. From Table 4.3, the largest deviation between the two temperatures is $\approx 22^\circ$C (the $650^\circ$C–100h sample), representing a 6% variation from the DTA $A_s$ temper-

Table 4.1 – Table of transformation temperatures vs. stress slopes for the $M_s$, $M_f$, $A_s$, and $A_f$ for all samples of the Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ alloy. Units are $^\circ$C/MPa.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$dM_s/d\sigma$</th>
<th>$dM_f/d\sigma$</th>
<th>$dA_s/d\sigma$</th>
<th>$dA_f/d\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Extruded</td>
<td>0.087</td>
<td>-0.002</td>
<td>0.127</td>
<td>0.080</td>
</tr>
<tr>
<td>500°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1h</td>
<td>0.047</td>
<td>0.089</td>
<td>0.095</td>
<td>0.050</td>
</tr>
<tr>
<td>100h</td>
<td>0.055</td>
<td>0.054</td>
<td>0.045</td>
<td>0.041</td>
</tr>
<tr>
<td>550°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1h</td>
<td>0.045</td>
<td>0.086</td>
<td>0.063</td>
<td>0.045</td>
</tr>
<tr>
<td>100h</td>
<td>0.087</td>
<td>0.055</td>
<td>0.051</td>
<td>0.083</td>
</tr>
<tr>
<td>1300°C +100h</td>
<td>0.074</td>
<td>0.041</td>
<td>0.056</td>
<td>0.076</td>
</tr>
<tr>
<td>600°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1h</td>
<td>0.061</td>
<td>0.058</td>
<td>0.057</td>
<td>0.042</td>
</tr>
<tr>
<td>100h</td>
<td>0.086</td>
<td>0.019</td>
<td>0.009</td>
<td>0.094</td>
</tr>
<tr>
<td>1300°C +100h</td>
<td>0.081</td>
<td>0.033</td>
<td>0.026</td>
<td>0.097</td>
</tr>
<tr>
<td>650°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1h</td>
<td>0.087</td>
<td>0.045</td>
<td>0.045</td>
<td>0.085</td>
</tr>
<tr>
<td>100h</td>
<td>0.106</td>
<td>0.019</td>
<td>0.043</td>
<td>0.094</td>
</tr>
<tr>
<td>1h+FC</td>
<td>0.062</td>
<td>0.063</td>
<td>0.043</td>
<td>0.066</td>
</tr>
<tr>
<td>700°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100h</td>
<td>0.082</td>
<td>0.033</td>
<td>0.043</td>
<td>0.074</td>
</tr>
<tr>
<td>1h+FC</td>
<td>0.077</td>
<td>0.020</td>
<td>0.043</td>
<td>0.057</td>
</tr>
<tr>
<td>800°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1h+FC</td>
<td>0.091</td>
<td>0.026</td>
<td>0.031</td>
<td>0.090</td>
</tr>
</tbody>
</table>
Table 4.2 – Table of transformation temperatures vs. stress slopes for the $M_s$, $M_f$, $A_s$, and $A_f$ for all samples of the Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$ alloy. Units are °C/MPa.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>d$M_s$/d$\sigma$</th>
<th>d$M_f$/d$\sigma$</th>
<th>d$A_s$/d$\sigma$</th>
<th>d$A_f$/d$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Extruded</td>
<td>0.116</td>
<td>0.149</td>
<td>0.217</td>
<td>0.159</td>
</tr>
<tr>
<td>500°C</td>
<td>1h</td>
<td>0.123</td>
<td>0.116</td>
<td>0.074</td>
</tr>
<tr>
<td></td>
<td>100h</td>
<td>0.087</td>
<td>0.076</td>
<td>0.070</td>
</tr>
<tr>
<td>550°C</td>
<td>1h</td>
<td>0.148</td>
<td>0.118</td>
<td>0.119</td>
</tr>
<tr>
<td></td>
<td>100h</td>
<td>0.157</td>
<td>0.102</td>
<td>0.099</td>
</tr>
<tr>
<td>600°C</td>
<td>1h</td>
<td>0.092</td>
<td>0.047</td>
<td>0.116</td>
</tr>
<tr>
<td></td>
<td>100h</td>
<td>0.091</td>
<td>0.029</td>
<td>0.047</td>
</tr>
<tr>
<td>650°C</td>
<td>1h</td>
<td>0.033</td>
<td>0.195</td>
<td>0.192</td>
</tr>
<tr>
<td></td>
<td>100h</td>
<td>0.110</td>
<td>0.057</td>
<td>0.049</td>
</tr>
<tr>
<td>700°C</td>
<td>1h</td>
<td>0.048</td>
<td>0.124</td>
<td>0.144</td>
</tr>
<tr>
<td></td>
<td>100h</td>
<td>0.099</td>
<td>0.044</td>
<td>0.058</td>
</tr>
</tbody>
</table>

ature. For the 49.5–Ti alloy, the DTA and zero-load $M_s$ values matched quite well, with the largest temperature deviation (9.5°C) occurring in the 700°C–1h sample. The $A_s$ (DTA) and $A_s$ (zero-load) temperatures deviated much more for the 49.5–Ti alloy, with the largest difference, from the 600°C–1h sample, being ≈ 69°C. From this generally positive correlation between the DTA and zero-load transformation temperature data, the two values may be used interchangeably in the following discussion.

Just as with the discussion of the DTA results, the variation in zero stress transformation temperature with sample heat treatment can be explained through the presence and quantity of the microstructural constituents described in the previous chapter (however, an explanation for the variation $d\sigma/dT$ was not found). Figure 4.13 presents the zero load $M_s$ temperatures for both the 48.5 and 49.5–Ti alloy. This figure shows the familiar relationship already seen in Figs. 4.4 and 4.5, where, for a given heat treatment time, the sample $M_s$ temperature increases up to a peak at heat treatment temperatures of 600°C, then decreases with the as-extruded samples having the lowest $M_s$ temperatures, for the alloy sample set. As before, samples heat treated at 600°C and higher contain only the Ti$_3$(Ni,Pt)$_3$ phase. Com-
Table 4.3 – Table of DTA peak start temperatures and extrapolated zero load compressive testing transformation start temperatures for the alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$.

<table>
<thead>
<tr>
<th></th>
<th>DTA $M_s$</th>
<th>Zero Load $M_s$</th>
<th>DTA $A_s$</th>
<th>Zero Load $A_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Extruded</td>
<td>320</td>
<td>255</td>
<td>262</td>
<td>184</td>
</tr>
<tr>
<td>500°C 1h</td>
<td>–</td>
<td>270</td>
<td>–</td>
<td>231</td>
</tr>
<tr>
<td>100h</td>
<td>318</td>
<td>315</td>
<td>317</td>
<td>300</td>
</tr>
<tr>
<td>1h</td>
<td>–</td>
<td>294</td>
<td>–</td>
<td>278</td>
</tr>
<tr>
<td>550°C 100h</td>
<td>318</td>
<td>333</td>
<td>348</td>
<td>340</td>
</tr>
<tr>
<td>1300°C +100h</td>
<td>–</td>
<td>324</td>
<td>–</td>
<td>332</td>
</tr>
<tr>
<td>1h</td>
<td>–</td>
<td>332</td>
<td>–</td>
<td>321</td>
</tr>
<tr>
<td>600°C 100h</td>
<td>319</td>
<td>348</td>
<td>373</td>
<td>360</td>
</tr>
<tr>
<td>1300°C +100h</td>
<td>–</td>
<td>344</td>
<td>–</td>
<td>353</td>
</tr>
<tr>
<td>650°C 1h</td>
<td>–</td>
<td>332</td>
<td>–</td>
<td>334</td>
</tr>
<tr>
<td>100h</td>
<td>320</td>
<td>333</td>
<td>369</td>
<td>347</td>
</tr>
<tr>
<td>1h</td>
<td>–</td>
<td>325</td>
<td>–</td>
<td>324</td>
</tr>
<tr>
<td>700°C 100h</td>
<td>318</td>
<td>330</td>
<td>353</td>
<td>334</td>
</tr>
<tr>
<td>1h+FC</td>
<td>322</td>
<td>343</td>
<td>357</td>
<td>347</td>
</tr>
<tr>
<td>800°C 1h+FC</td>
<td>324</td>
<td>345</td>
<td>356</td>
<td>349</td>
</tr>
</tbody>
</table>

paring the $M_s$ temperatures to the volume fractions (VFs) of Ti$_2$(Ni,Pt)$_3$ the data trends correlate quite well, qualitatively. The trends for the 600–700°C samples of the 48.5–Ti alloy match with the separations between the 1h and 100h samples being nearly identical. Additionally, the same trend of the two FC samples having similar Ti$_2$(Ni,Pt)$_3$ VFs as the 600°C–100h sample, so too do they have similar $M_s$ temperatures. The same trends also hold well for the 49.5–Ti alloy. The 600°C samples have nearly identical Ti$_2$(Ni,Pt)$_3$ VFs and $M_s$ temperatures. The 650°C samples also have similar behavior between $M_s$ temperatures and VFs. The only discrepancy is that of the 700°C sample, between the 1 and 100h conditions.

Again, this correlation between the VF of Ti$_2$(Ni,Pt)$_3$ and the $M_s$ temperature can be explained through an excess solute argument of Ni and Pt in the matrix, per the previously reported literature [4, 5]. As the amount of Ti$_2$(Ni,Pt)$_3$ increases, the amount of Ni and Pt in solution in the matrix decreases. As Ni in solution acts to (drastically) decrease the $M_s$
Table 4.4 – Table of DTA peak start temperatures and extrapolated zero load compressive testing transformation start temperatures for the alloy Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$.

<table>
<thead>
<tr>
<th></th>
<th>DTA M$_s$</th>
<th>Zero Load M$_s$</th>
<th>DTA A$_s$</th>
<th>Zero Load A$_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Extruded</td>
<td>228</td>
<td>226</td>
<td>245</td>
<td>200</td>
</tr>
<tr>
<td>500°C 1h</td>
<td>237</td>
<td>234</td>
<td>260</td>
<td>250</td>
</tr>
<tr>
<td>100h</td>
<td>301</td>
<td>298</td>
<td>354</td>
<td>304</td>
</tr>
<tr>
<td>550°C 1h</td>
<td>260</td>
<td>261</td>
<td>299</td>
<td>270</td>
</tr>
<tr>
<td>100h</td>
<td>314.6</td>
<td>311.06</td>
<td>361.1</td>
<td>319.67</td>
</tr>
<tr>
<td>600°C 1h</td>
<td>338</td>
<td>336</td>
<td>371</td>
<td>302</td>
</tr>
<tr>
<td>100h</td>
<td>340</td>
<td>336</td>
<td>353</td>
<td>339</td>
</tr>
<tr>
<td>650°C 1h</td>
<td>305/318</td>
<td>310</td>
<td>241</td>
<td>213</td>
</tr>
<tr>
<td>100h</td>
<td>331</td>
<td>328</td>
<td>348</td>
<td>335</td>
</tr>
<tr>
<td>700°C 1h</td>
<td>293</td>
<td>302</td>
<td>313</td>
<td>259</td>
</tr>
<tr>
<td>100h</td>
<td>319</td>
<td>321</td>
<td>342</td>
<td>323</td>
</tr>
</tbody>
</table>

Temperature, removing excess Ni (and in this case Pt) acts to increase the M$_s$ temperature. Therefore, as the amount of Ti$_2$(Ni,Pt)$_3$ increases, so too should the sample/matrix M$_s$. This relation is summarized with the correlations presented in Fig. 4.14.

For the samples heat treated at 500 and 550°C the explanation becomes more complicated, as all 48.5–Ti alloy samples and the 550°C–100h sample of the 49.5–Ti alloy contain both Ti$_2$(Ni,Pt)$_3$ and the P$_L$–phase, while both the 500°C samples and 550°C–1h sample of the 49.5–Ti alloy contain only the P$_L$–phase. For the three samples of the 49.5–Ti alloy that contain only the P$_L$–phase there are several mechanisms that must be addressed. First, as the P$_L$–phase is a (Ni+Pt) rich precipitate, with a Ti:(Ni+Pt) ratio of 11:13 (i.e., Ti$_{11}$Ni$_9$Pt$_4$), and as the volume fraction of this phase increases, so should the M$_s$ temperature of the matrix, per the discussion above. However, from volume fraction measurements presented in the last chapter, it appears that the amount of P$_L$–phase continually decreases as heat treatment time increases at 550°C. Thus, from simply a matrix composition argument, the behavior of the 49.5–Ti, 500°C and 550°C–1h samples seems counterintuitive. These sam-
Figure 4.13  Plot of the extrapolated zero load $M_s$ temperature and volume fraction $\text{Ti}_2(\text{Ni,Pt})_3$ vs. heat treatment temperature for both alloys $\text{Ti}_{49.5}\text{Ni}_{29.5}\text{Pt}_{21}$ (closed symbols) and $\text{Ti}_{48.5}\text{Ni}_{30.5}\text{Pt}_{21}$ (open symbols).

Samples have an increasing $M_s$, but decreasing VF of $P_L$–phase, with increasing heat treatment time/temperature.

Additionally, the 48.5–Ti alloy samples heat treated at 500 and 550°C contain both the $P_L$–phase and the $\text{Ti}_2(\text{Ni,Pt})_3$ phase. From a composition standpoint, considering the amount of $\text{Ti}_2(\text{Ni,Pt})_3$ present, the transformation temperatures do not always correlate with matrix composition, as they do with the samples heat treated at 600°C and above. To reconcile this, a consideration of the role that the $P_L$–phase plays on the martensitic transformation must be made. This discrepancy was addressed by accounting for the solute present in the matrix of each sample. Using the volume fraction measurements of the $\text{Ti}_2(\text{Ni,Pt})_3$ and $P_L$–phase, plus a knowledge of the precipitate compositions, an estimate of the sample matrix composition was made. To complete this, EDS measurements were made on all of the 100h heat treatment conditions of the 48.5–Ti alloy. These results are presented in Figure 4.15. There are several points of interest in the composition data presented here.
Figure 4.14 Plot of volume fraction $\text{Ti}_2(\text{Ni,Pt})_3$ vs. $M_s$ temperature for both alloys, $\text{Ti}_{48.5}\text{Ni}_{30.5}\text{Pt}_{21}$ and $\text{Ti}_{49.5}\text{Ni}_{29.5}\text{Pt}_{21}$. Note that the symbol color indicates heat treatment temperature.

First, note that the composition of the $\text{Ti}_2(\text{Ni,Pt})_3$ phase was reasonably near 40% Ti in all samples measured. This is the stoichiometric composition, i.e. two parts Ti in five parts total, or 40%. Typically, the Ti content was measured to be greater than 40% (between 40 and 42%), which is attributable to a tangent construction of the free energy surfaces between the $\text{Ti}_2(\text{Ni,Pt})_3$ phase and the B2 matrix. Additionally, the EDS interaction volume was found to be $\approx 1\mu m^3$, for an operating voltage of 15kV, using a Monte Carlo simulation program. Also of interest are the matrix compositions for samples heat treated at 500 and 550°C. These samples contain the P_L-phase, and the probe size in the SEM used was not small enough to reliably gather data from these precipitates, so this data represents the combined composition of the matrix and the P_L-phase. As such, considering the P_L-phase stoichiometry ($\text{Ti}_{11}\text{Ni}_9\text{Pt}_4$ [34]) or composition of $\text{Ti}_{45.8}\text{Ni}_{37.5}\text{Pt}_{16.7}$, it is expected that the measured
compositions of the matrix and Pₜ–phase, relative to the alloy composition (Ti₄₈.₅Ni₃₀.₅Pt₂₁), would result in a lower quantity of Ti, a higher quantity of Ni, and a depletion of Pt. The results presented in Fig. 4.15 indicate just that, for those samples that contain the Pₜ–phase (HT temperatures of 500 and 550°C).

It is also evident from Fig. 4.15 that the Ti₂(Ni,Pt)₃ phase contains less Pt than the overall alloy composition (21%). Because Pt increases the Mₛ temperature in Ni–Ti alloys, the amount of Pt being put into the matrix by the precipitation is worth consideration. For the purposes of this study however, this point was neglected. Looking at the binary alloy system, Ni suppresses the Mₛ by approximately 100°C per at.% Ni in solution [5]. According to data collected by Rios et al., Pt increases the Mₛ (beyond additions of ≈10%) by 25°C per at.% Pt. Considering that the proximity to a 1:1 Ti:NI ratio has nearly four times more potency to affect the Mₛ temperature than Pt matrix Pt content, the effect of increasing matrix Pt content with changing Ti₂(Ni,Pt)₃ VF was not considered.
From this Ti$_2$(Ni,Pt)$_3$ composition data, the volume fraction data presented in the previous chapter, and an assumption of the P$_L$-phase composition (Ti$_{45.8}$Ni$_{37.5}$Pt$_{16.7}$), the matrix composition was estimated for several samples of both alloys. This was done by summing the products of each microstructural constituent’s volume fraction with composition, as shown in Equation 4.2:

$$f_{matrix} \cdot C_{matrix} + f_{Ti_2(Ni,Pt)_3} \cdot C_{Ti_2(Ni,Pt)_3} + f_{TiC} \cdot C_{TiC} = C_{alloy}$$  \hspace{1cm} (4.2)

where $f_{matrix}$ is the volume fraction of the matrix, $C_{matrix}$ is the composition of the matrix for a specific element, and so on. This equation is then applied to each individual element (Ni, Ti, and Pt in this case) to evaluate the matrix composition. It is worth noting that the Ti content of TiC can vary from 50 to 68%, dependent on temperature, per the Ti–C phase diagram [54]. Because of this, the Ti content of the TiC composition was chosen to be 68%, as this value gave the most realistic calculated compositions. The calculated compositions are presented in Tables 4.5 (the 48.5–Ti alloy) and 4.6 (the 49.5–Ti alloy). It should be noted that while the relative error associated with the data presented in these tables is likely greater than the magnitude of differences within the table data values, the fact that all data was collected and processed in the same way allows for the values to be qualitatively compared to one another. Even though these data likely have considerable overlap, they are still useful to understand the matrix compositions, relatively, within a given alloy set.

From these tables, it is apparent that the samples that contain the P$_L$-phase have matrix compositions closest most near the ideal 1:1 ratio of Ti:(Ni+Pt). This can be easily verified by looking at how near the Ti content is to 50%. This ratio between the quantity of Ti and (Ni+Pt) is related to the thermodynamic equilibrium between the austenitic parent phase, and the martensitic product, referred to as T$_o$. The M$_s$ temperature is then at some temperature, $\Delta T$, below T$_o$, where $\Delta T$ is related to the undercooling required to drive the martensitic transformation forward. The magnitude of $\Delta T$ is related to factors inhibiting the
Table 4.5 – Calculated Sample Matrix Compositions (atomic %) for Alloy Ti_{48.5}Ni_{30.5}Pt_{21}

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Time</th>
<th>Ti</th>
<th>Ni</th>
<th>Pt</th>
</tr>
</thead>
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<tr>
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<td></td>
<td>48.8</td>
<td>29.9</td>
<td>21.8</td>
</tr>
<tr>
<td>500°C</td>
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<td>26.3</td>
<td>23.9</td>
</tr>
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<td></td>
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</tr>
<tr>
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<td>22.7</td>
</tr>
<tr>
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<td></td>
<td>100h</td>
<td>49.8</td>
<td>28.3</td>
<td>22.4</td>
</tr>
<tr>
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<td>1h</td>
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<td>28.3</td>
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</tr>
<tr>
<td></td>
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<td>28.3</td>
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</tr>
<tr>
<td></td>
<td>100h</td>
<td>49.7</td>
<td>28.5</td>
<td>22.3</td>
</tr>
<tr>
<td>800°C</td>
<td>1h+FC</td>
<td>49.7</td>
<td>28.6</td>
<td>22.2</td>
</tr>
</tbody>
</table>

Table 4.6 – Calculated Sample Matrix Compositions (atomic %) for Alloy Ti_{49.5}Ni_{29.5}Pt_{21}

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Time</th>
<th>Ti</th>
<th>Ni</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>500°C</td>
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<td>26.2</td>
<td>24.0</td>
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<tr>
<td>550°C</td>
<td>100h</td>
<td>49.9</td>
<td>28.0</td>
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<tr>
<td>600°C</td>
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<td></td>
<td>100h</td>
<td>49.7</td>
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</tr>
<tr>
<td>650°C</td>
<td>1h</td>
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<td>29.0</td>
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<tr>
<td></td>
<td>100h</td>
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<td>700°C</td>
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<tr>
<td></td>
<td>100h</td>
<td>49.6</td>
<td>29.0</td>
<td>22.0</td>
</tr>
</tbody>
</table>
shearing of the lattice associated with the martensitic transformation, such as the inherent friction generated during the transformation, or strengthening mechanisms in the matrix, such as dislocations and/or coherent precipitates. This has been summarized and discussed by Hornbogen [2], and this cursory explanation is only meant to provide the reader with enough information to understand the data at hand.

The data presented in Tables 4.5 and 4.6 is critical to the understanding of the role that the PL–phase plays in these alloys for the following reason. Generally, it is accepted that coherent precipitates will strengthen the matrix and inhibit the martensitic transformation, increasing the necessary undercooling, ΔT, required to drive the transformation forward, essentially depressing the Ms temperature [55–58]. However, there is a fair amount of speculation in the literature concerning binary NiTi alloys [8, 27, 59, 60], and specifically Gao et al., pertaining to the current alloy system [33], that suggests the coherency stress fields that arise from coherent particles within a transforming matrix may act as nucleation sites for martensite formation. These coherency–generated stress fields would reduce ΔT and effectively increase the Ms temperature. If we relate the To temperature of a sample to the Ti content within that sample (proximity to an ideal 1:1 ratio of Ti:(Ni+Pt)), then samples heat treated at 500 and 550°C, in both alloys, should have the highest To temperatures, as they have matrices with the highest Ti contents (least Ni and Pt in solution). If the PL–phase was in fact nucleating martensite and reducing the ΔT for these samples, this would increase the Ms temperatures even further. However, even though we can assume that the 500 and 550°C samples have significantly higher To temperatures, from a matrix composition argument, it is apparent that the presence of the PL–phase is suppressing the Ms temperature of these samples, Fig. 4.13.

It is known, for the samples that were mechanically tested, that the volume fraction of the PL–phase decreases as heat treatment time increases, at 550°C (Chapter 3, Fig. 3.14), and through this consideration, the transformation temperatures presented in Fig. 4.13 can be understood. Per the prior argument of the PL–phase suppressing the Ms temperature,
as the $P_L$–phase decreases in quantity and volume fraction, the suppression of $M_s$, or the magnitude that the $P_L$–phase affects $\Delta T$, lessens. This occurs because there is less $P_L$–phase to inhibit the martensitic transformation (with increasing heat treatment time/temperature), and also because coarser precipitates of the $P_L$–phase have a less potent strengthening effect on the transforming matrix. It is clear however, that in the 48.5–Ti alloy, 550°C–100h sample, which has the lowest volume fraction and largest $P_L$–phase precipitates, the $M_s$ is suppressed below the maximum obtained $M_s$ in this sample set, namely the 48.5–Ti alloy, 600°C–100h sample.

### 4.3.1.3 Constant–Stress Thermal Cycling

This section will discuss the results of the constant stress, 100 thermal cycle portion of testing. The distribution of sample transformation temperatures followed closely to those found from the stress incremental portion of cycling. As such, the effects that the various microstructural features have on a repeatedly cycled sample will be discussed. Generally, there are two main processes that effect the transformation temperatures through multiple thermal cycles, dislocation generation and precipitation of the $P_L$–phase during testing. Samples that did not contain the $P_L$–phase were more prone to be affected by dislocation generation, and samples with lower amounts of $\text{Ti}_2(\text{Ni,Pt})_3$, and excess Ni and Pt in solution, were observed to precipitate the $P_L$–phase during testing. Samples that contained the $P_L$–phase at the beginning of testing (heat treatment temperatures of 500 and 550°C) showed the most stable properties, as the pre-existing $P_L$–phase acted to prevent most microstructural changes that would alter the transformation temperatures. This will be explained in more detail below. First however, the cycling data will be presented and explained, with an explanation of the underlying behavior to follow.

Similar to increasing load conditions, the 100 thermal cycle runout results varied significantly with the heat treatment of each sample. Figure 4.16 presents the $M_s$ versus cycle
data for the 48.5-Ti alloy (100 thermal cycles from 75 to 500°C and back to 75°C, under a constant 200MPa load). Through cycling, the sample trends are nearly identical to the previously presented incremental stress data. Additionally, transformation temperatures for all samples heat treated above 550°C increased during thermal cycling, while those samples heat treated at 500 and 550°C, plus the as-extruded material, maintained very low slopes (except for the 500°C–1h sample). It appears that the samples heat treated at 600 and 650°C–100h, as well as the FC samples, appear to have Ms values that increase non-linearly, until they stabilize near cycle #75, while the 700°C–100h sample appears to have a linearly increasing Ms and does not plateau.

The As temperatures during thermal cycling held relatively the same sample order as with the As versus stress data, for both the 1h and 100h conditions (Fig. 4.17). The as-extruded material changed the most through cycling. The 500 and 550°C samples exhibited a slight and gradual increase in As through cycling, while the 600-700°C samples maintained relatively low, positive slopes. For the 100h samples, a similar sample data distribution is seen during cycling, with few differences from the As vs. stress data. These samples showed little variation, and maintained quite low slopes during cycling.
Figure 4.17  Austenite start ($A_s$) temperatures for samples of alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ for all heat treatment conditions tested, during the 100 thermal cycle, 200MPa runout test.

Through thermal cycling, the ranking of the 49.5–Ti alloy samples maintained the same order as described for the $M_s$ vs. stress data (Fig. 4.18) The as–extruded and 500°C–1h samples were consistently the lowest, with the 550°C–1h sample being ($\approx 40^\circ$C) higher. The 700, 650, and 600°C samples were the next highest, respectively. All 1h samples showed an increasing $M_s$ trend in the beginning of cycling, with a plateauing behavior near the 75$^{th}$ cycle. The magnitude of the low–cycle $M_s$ increase can be seen to be roughly correlated with the transformation temperature, as samples with lower $M_s$ temperatures generally have a more rapid $M_s$ increase at low cycles. This is demonstrated by the as–extruded and 500°C

Figure 4.18  Plots of the martensite start ($M_s$) vs. cycle# data collected for the Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$ alloy.
samples having the greatest $\Delta T$’s through cycling (23.5 and 16.7°C, respectively), while the 600 and 650°C samples have the lowest (3.7 and 1.2°C, respectively). As the thermal cycling proceeded, however, several notable changes occurred. First, in the 1h sample set at the beginning of cycling, the 500°C sample maintained a higher $M_s$ temperature over the as–extruded sample, as is the typical behavior from previously reported results, but, through cycling, the $M_s$ of the as–extruded sample increased enough to reach the $M_s$ of the 500°C sample. Second, while the $M_s$ temperature of the 650°C sample slightly increased through cycling, the 700°C samples $M_s$ temperature increased sufficiently to surpass the 650°C sample near the 30th cycle. Except for the 700°C sample, all of the sample $M_s$ temperatures, seemed to stabilize, or plateau, by the end of cycling.

For the 100h sample set, the 500°C sample appeared to maintain a nearly unchanging $M_s$ temperature during thermal cycling. The $M_s$ temperatures of the 550 and 700°C samples, however, increased gradually until they converged to the same $M_s$ temperatures of the 600 and 650°C samples, by the end of cycling, i.e., slightly above 360°C.

The thermal cycling results for the $A_s$ temperatures of the 49.5–Ti alloy were similar to the $A_s$ vs. stress plot (Fig. 4.19). The $A_s$ temperature for all samples in the 1h condition, except for the 600°C sample, appeared to increase through cycling until they plateaued near

Figure 4.19  Plots of the austenite start ($A_s$) vs cycle# data collected for the Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$ alloy.
the 75th cycle. The 600°C–1h sample maintained a consistent A_s through all cycles. All of the 100h samples seemed to maintain consistent A_s temperatures through cycling, except for the 550°C sample, which increased gradually, but again, seemed to plateau near cycle #75.

From the previous discussions, the ranking (by temperature) of samples as the thermal cycling begins, and how they evolve through the cycling process, can be explained by the starting microstructures. This discussion will begin with the 48.5–Ti alloy, then move to the 49.5–Ti alloy, and finish with a comparison of the two against each other. It is important to note that the upper cycle testing temperature for all tests was 500°C, as mentioned previously. This temperature is high enough to allow for noticeable changes to occur in the microstructure through diffusional transformation processes. Specifically, because the P_L–phase is observed to form at 500°C, this phase was observed to precipitate during mechanical testing (as will be discussed later in this chapter). It is reasonable to assume that, if the diffusional kinetics are sufficient to allow for the precipitation of the P_L–phase, they are also sufficient to allow for the evolution of this phase as well, such as coarsening and compositional changes. Currently, it is not clear how much the Ti_2(Ni,Pt)_3 phase evolves during the tests. However, considering the composition difference between the Ti_2(Ni,Pt)_3 and P_L phases, and the large structural deviation between the Ti_2(Ni,Pt)_3 phase and the B2 matrix (whereas the P_L–phase is structurally similar to the B2 phase), it was assumed that variations in P_L–phase quantity were the dominant transient components of microstructural precipitate evolution during testing.

First, the as–extruded sample of the 48.5–Ti alloy has a rather variable cycling curve, which averages to be fairly flat through all 100 cycles. This microstructure was found to contain small amounts of the Ti_2(Ni,Pt)_3 phase, and a large amount of the P_L–phase and is considered to have the least stable microstructure (furthest from equilibrium over the thermal cycling temperatures, 75–500°C) which continually evolves during cycling. This sample data is so scattered because the microstructure is continuously evolving during testing. At the peak testing temperature (500°C), the Ti_2(Ni,Pt)_3 is likely in a smaller quantity than
equilibrium and the $P_L$–phase is precipitating and evolving. It will be shown and discussed later that, during isobaric thermal cycling, the $P_L$–phase has a tendency to precipitate, given enough supersaturation of Ni and Pt.

The 500°C–1h sample is also in a fairly unstable microstructural state at the beginning of thermal cycling, as the kinetics operating at 500°C, for only 1h, are insufficient for the microstructure to reach a state of reasonable metastability. Thus, as the sample is thermally cycled, the $P_L$–phase coarsens and/or further precipitates, explaining the increased transformation temperatures during cycling. This is also evident in the hardness difference between the as–extruded material and the 500°C–1h sample, namely, 321 vs. 415HV, respectively. For the 500°C–100h sample, the $P_L$–phase does not undergo evolution through the thermal cycling process as 100h was sufficiently long to establish a microstructural state that is stable through cycling. Thus, the presence of the (metastable) $P_L$–phase stabilizes the transformation temperatures.

In the samples heat treated above 550°C, the $P_L$–phase is not present, and the transformation temperatures are observed to increase monotonically with increased thermal cycling. This behavior is well documented in the literature and is attributed to the generation of dislocations during thermal cycling [50]. The stress fields generated by these dislocations then act to help select preferential variants of martensite during the forward transformation (austenite $\rightarrow$ martensite), which act to reduce the required undercooling for transformation, i.e., reduce $\Delta T$. Hence, while the thermodynamic equilibrium of these samples is not changing, the $T_o$ temperature, the $M_s$ still increases due to the in-situ dislocation generation that promote the transformation of preferential martensite variants.

For the samples of the 49.5–Ti alloy, Figs. 4.18 and 4.19, there is a slightly different behavior during cycling. The $M_s$ and $A_s$ temperatures of these samples appear to go through more of an initial increase through the first $\approx 60$ cycles before plateauing. A comparison of samples before and after testing gives an explanation of this behavior, as shown in Fig-
From the micrographs presented in this figure, the $P_L$–phase can be seen to have precipitated during the mechanical testing process in the 49.5–Ti alloy sample heat treated at 600°C for 100h and water quenched. Considering that within the 49.5–Ti alloy sample set, the 600°C–100h sample has the most $\text{Ti}_2(\text{Ni},\text{Pt})_3$ present, it can be assumed that if this sample had enough excess solute to precipitate the $P_L$–phase, it is probable that all other samples also underwent $P_L$–phase precipitation during testing. This precipitation process is the proposed cause of the cycling behavior variation between the 48.5 and 49.5–Ti alloys. Further evidence of the role that the $P_L$–phase precipitation plays can be seen in the 500°C–100h sample, which shows the same monotonic increase of $M_s$ with increased thermal cycling, just as in the majority of the 49.5–Ti alloy samples. The similarity between this 500°C–100h sample (49.5–Ti) alloy and the 48.5–Ti alloys can attributed to the fact that the 500°C–100h sample contains the maximum amount of $P_L$–phase available in that alloy such that additional $P_L$–phase precipitation likely did not occur. Therefore, the microstructural changes occurring in the 500°C–100h sample are the same as those occurring in most of the 48.5–Ti alloy samples, which amounts to dislocation generation and accumulation.

Figure 4.20 SEM BSE image of the 600°C–100h–WQ sample of alloy $\text{Ti}_{49.5}\text{Ni}_{29.5}\text{Pt}_{21}$ before (A) and after (B) isobaric thermal cyclic testing. The black arrow in B is pointing to the $P_L$–phase precipitates that formed during isobaric thermal cycling.
The $M_s$ data in the 100h samples of the 49.5–Ti alloy, except for the 500°C sample, gave interesting evidence concerning the transformation capabilities of this alloy (Fig. 4.18). Apparent from this data, $\approx 360°C$ is the maximum temperature attainable in this alloy, given the prior thermal processing routes of this study. This data can be explained by the effect of the P$_L$–phase. Through thermal cycling, enough of the P$_L$–phase precipitates to stabilize the sample’s $M_s$ temperatures, while suppressing it to levels below that of the 48.5–Ti alloy samples, which has a maximum $M_s$ of $\approx 380°C$ (Fig. 4.16).

4.3.1.4 Summary of Transformation Temperature Data

To summarize the effects of microstructure, it is useful to separate the sample into two categories, those that contain the P$_L$–phase (heat treatments of 500 and 550°C) and those that do not (heat treatments so 600°C and above). This distinction can be made because the P$_L$–phase controls transformation temperatures when it is present, and the Ti$_2$(Ni,Pt)$_3$ phase controls transformation temperatures when there is no P$_L$–phase present.

For the samples heat treated at 500 and 550°C, the P$_L$–phase suppressed all transformation temperatures through a strengthening effect on the matrix (determinable from increased sample hardness). It was observed that as the P$_L$–phase coarsened and decreased in volume fraction, the sample transformation temperatures increased. This was due to the precipitates decreasing ability to strengthen the matrix because (1) coarser particles are less potent matrix strengtheners, and (2) the less precipitates that are present, the less they will be able to effectively strengthen a matrix. An estimation of the matrix composition was made by considering the volume fraction and composition of the overall alloy, the precipitates present (either P$_L$–phase, Ti$_2$(Ni,Pt)$_3$, or both), and the TiC. From this estimation, it was concluded that, while samples containing the P$_L$–phase likely have the highest $T_o$ temperatures, their transformation temperatures are suppressed due to the coherency effects of the P$_L$–phase.
It was found that the transformation temperatures of samples that only contained the Ti$_2$(Ni,Pt)$_3$ phase were controlled by the amount of this phase present. Since this phase was semi-coherent and relatively coarsely distributed, it did not effect the matrix in structurally similar way as the P$_L$–phase. Instead, the influence of the Ti$_2$(Ni,Pt)$_3$ phase was derived from how it modified the matrix composition. Therefore, as the amount of Ti$_2$(Ni,Pt)$_3$ increased, the matrix composition was pushed closer to a 1:1 ratio of Ti:(Ni+Pt), and the transformation temperatures increased. Because of this, it was shown that the volume fraction of Ti$_2$(Ni,Pt)$_3$ had a positive correlation with the transformation temperature, within a given alloy.

Fundamentally, it was shown that the P$_L$–phase affected the transformation temperatures through modification of the driving forces needed to nucleate and grow martensite. Subsequently, as the P$_L$–phase likely increased a sample’s T$_o$ temperature, the magnitude that ∆T was increased dominated the effect this precipitate had. Conversely, the Ti$_2$(Ni,Pt)$_3$ had little effect on the ∆T of a transforming matrix, but dominated the T$_o$ temperature of the martensitic transformation.

In general, it was observed that samples of the 48.5–Ti alloy had higher transformation temperatures than the 49.5–Ti samples. This was due to the lower driving forces in the 49.5–Ti alloy for the precipitation of second phases. Samples of the 48.5–Ti alloy precipitated volume fractions of the P$_L$ and Ti$_2$(Ni,Pt)$_3$ phases nearer the equilibrium volume fractions, allowing for matrix compositions that were nearer the ideal 1:1 ratio of Ti:(Ni+Pt). If the 49.5–Ti samples were given longer heat treatments, it is likely that their transformation temperatures would be similar to those of the 48.5–Ti samples.

### 4.3.2 Transformation Strain

As described above, the transformation strain of each sample was measured to be the recovered strain upon heating (the martensite → austenite transformation), comparing the
strain at the $A_s$ and $A_f$ temperatures. The transformation strain quantity is a measure of how much strain the sample is capable of producing during back transformation. This characteristic of shape memory alloys is critical to the use of these alloys as solid–state actuators as these strain values determine the quantity of work output that each sample is capable of producing. From the classic definition of work, the product of a force applied over a distance, the work of a transforming SMA can be calculated as the product of the transformation strain and applied stress. Also, the samples mechanically tested all had the same nominal dimensions. As such, the transformation strain is the fundamental property controlling the work output of each sample. The work output of each sample is directly related to the transformation strain through the applied stress and this property will be used to investigate the influence of microstructure, instead of work output. The calculated work output results will not be presented or discussed here. As with the transformation temperatures reported above, the transformation strain was measured for the initial regime of testing where the compressive load was incrementally increased (0–300 MPa in 50 MPa increments), and through the 200MPa, 100 thermal cycle portion of testing. The transformation strain data will be presented in the same order as above.

### 4.3.2.1 Stress Incremented Thermal Cycling

From the explanation of the origin of the transformation strain during isobaric thermal cycling in Chapter 2, the effects of incremental stress testing can be easily understood. As the transformation strain is related to the amount of favorably oriented martensite variants that are formed to accommodate an applied load during the martensitic transformation, it would be expected that, as the load increases, so does the amount of preferentially–oriented martensite. As such, as the applied load is increased, so too is the transformation strain. This effect does however, have a limit. If too much load is applied, then plastic deformation begins to accommodate the applied load instead of the formation of preferred variants of martensite. This section will describe the results of the incremental stress testing on the
transformation strain produced. As before, the data will be presented for each alloy, then discussed afterward.

Figure 4.21 presents the absolute (otherwise the values would be negative due to the compressive stress state) transformation strain data for the 48.5–Ti alloy as it was thermally cycled through the 7 different stress increments. Between all of the heat treatments, the as–extruded condition had the lowest transformation strain. For the 1h conditions, the 500 and 550°C generally had the next lowest strains. For the low applied stresses the 600°C condition had comparable strains to the 550°C sample, but for the higher applied loads (> 150MPa), the 600°C sample had higher transformation strains than the as–extruded, 500, and 550°C samples. The 650 and 700°C had the highest transformation strains for all applied loads above 50MPa. Additionally, the trend lines plotted for these data sets indicated that the amount of transformation strain per applied stress was beginning to plateau for the

Figure 4.21 Plot of transformation strain versus compressive stress for all samples of the Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ alloy tested. Samples in the plot on the left were heat treated for one hour (plus the as–extruded sample), and samples in the plot on the right were heat treated for 100 hours (plus the furnace cooled samples).
as–extruded, 500 and 550°C-1h samples at the higher applied stresses. This indicates that, for the heat treatments studied, 300MPa (possibly lower for the as–extruded condition) represents the highest applied load needed to achieve the maximum transformation strain.

For the 100h and furnace cooled conditions, a slightly different behavior was observed. The sample with the lowest transformation strain was the 1300°C–WQ+550°C–100h–WQ sample. The 500 and 550°C samples had the next lowest transformation strain through the majority of applied stresses, with the 700°C–FC sample having the next highest strains. The 600, 650, 700°C (100h) and the 800°C–FC sample all had approximately the same amount of strain through all the stresses, as the individual data points are indistinguishable on the plot. The 1300°C–WQ+600°C–100h–WQ sample consistently had the highest transformation strain for all the applied stresses. As with the 1h samples, the 500°C sample tended toward a transformation strain saturation at the highest applied stresses.

Similar to Fig. 4.21, the transformation strain versus applied compressive load is shown for the 49.5–Ti alloy in Figure 4.22. Again, the as–extruded condition had the lowest transformation strain for all applied loads. The 500°C samples had the next lowest transformation strains in 1h samples, and the lowest strain in the 100h samples. Within the 1h data set, the 550, 650, and 700°C samples all had very closely grouped strains, with the 700°C sample having slightly higher strains for the three highest loads. The 600°C sample had the highest transformation strains through all testing stresses for the 1h samples. Within the 100h samples, the 550°C sample had the second lowest strains. The 600, 650, and 700°C–100h samples were closely grouped through all stresses with the 700°C sample having slightly lower strains and the 650°C sample had the highest strains at the highest applied stress (300MPa).

As can be seen in Figures 4.21 and 4.22, the samples of this study follow the same general trend where an increase in applied load causes a larger transformation strain. Several samples of the 48.5–Ti alloy (Fig. 4.21), however, start to show a strain saturation, where the data trends to a maximum level of strain within that sample, regardless of the applied load. These
Figure 4.22  Plot of transformation strain versus compressive stress for all samples of the Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$ alloy tested. Samples in the plot on the left were heat treated for one hour (plus the as–extruded sample), and samples in the plot on the right were heat treated for 100 hours.

samples include the as–extruded, 500 and 550°C–1h, and 500°C–100h samples. The other samples continue a linear trend up to the maximum applied load (in this study 300MPa). All samples of the 49.5–Ti alloy (Fig. 4.22) show this behavior or begin and trend toward a maximum strain at the upper stresses of testing. These samples responded with higher strains relative to the 48.5–Ti alloy, namely, a maximum strain of 2% in the 49.5–Ti alloy vs. a max strain of 1.3% in the 48.5–Ti alloy.

The general transformation strain performance of each sample follows a similar trend to the distribution of sample transformation temperatures. The as–extruded samples of both alloys have the lowest transformation strains, followed by the 500 and 550°C samples. This general trend of the 500 and 550°C samples confirms that the P$_L$–phase not only inhibits the transformation temperatures of each alloy, as previously discussed, but also inhibits the formation of strain–accommodating variants of martensite.
4.3.2.2 Constant Stress Thermal Cycling

Through each thermal cycle, the martensitic transformation causes transient changes in the microstructure. As discussed previously, the two main microstructural features that evolve in this system are the generation and accumulation of dislocations, or the precipitation of the \( P_L \)-phase. This section will present the results of the constant load thermal cycling portion of testing, then provide a microstructurally based explanation of the various sample behavior.

Figure 4.23 presents the absolute transformation strain data collected during the 200MPa, 100 thermal cycle, isobaric portion of mechanical testing. Similar to the change in transformation temperatures, the shape of the constant stress (200 MPa) cycling data trend lines varied depending on the sample heat treatment. The as-extruded sample exhibited the most scatter and fit a linear trend of increasing transformation strain through cycling. Among all the samples tested, the as-extruded condition and the 1300°C–WQ+550°C–100h–WQ sample had the lowest strain values during cycling. The 500 and 550°C samples had the next lowest values of strain, which were fairly consistent between the 1 and 100h conditions. All four of these conditions, 500 and 550°C, 1 and 100h, fit well with a linear trend through

![Figure 4.23](image-url) Plots of absolute transformation strain vs. # of thermal cycles for all Ti_{48.5}Ni_{30.5}Pt_{21} samples tested. The plot on the left presents the data for the as-extruded condition and samples heat treated for one hour. The plot on the right presents the data for samples heat treated for 100h and the furnace cooled (FC) samples.
cycling. For the 1h samples, the 600°C condition had the next highest strain values, with the 650 and 700°C values having the highest transformation strains for the 1h samples, all fitting well to linear, or fairly flat parabolic curve fits. For the 100h and FC samples, the 700°C–FC sample had the next highest transformation strain above the 500 and 550°C samples. For this sample, the data trend was fit well with a parabolic trend. The 600, 650, 700, and the 800°C–FC samples all started at nearly the same transformation strain values at the beginning of testing, but then several of these samples diverged through cycling. The 600, 650°C, 800°C–FC, and 1300°C–WQ+600°C–100h–WQ samples all had decreasing transformation strains that fit well with parabolic curve fits while the 700°C sample strain linearly decreased through cycling.

Figure 4.24 presents the 49.5–Ti data for the 100 thermal cycle, 200MPa “runout” test. During the 100 cycle testing, both the 500°C samples, had the lowest transformation strains. For the 1h samples, the as-extruded sample had the next lowest strains, with the 550 and 650°C samples having the next lowest. All four of these samples in the 1h condition had stable and unchanging (flat) strains throughout the entire test. The 700°C sample had the second highest strains in the 1h samples, and gradually (and linearly) increased in strain during testing. The 600°C sample had the highest strain of all the 1h samples and the

![Figure 4.24](image_url)  
**Figure 4.24** Plots of absolute transformation strain for all Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$ samples tested. The plot on the left presents the data for the samples heat treated for one hour while the plot on the right presents the data for samples heat treated for 100h.
amount of strain decreased linearly with continued cycling. In the 100h sample set, the 550°C sample had the second lowest transformation strain. The strains produced by the 600, 650, and 700°C samples were relatively similar and close to the values produced by the 600°C–1h sample. All of these samples had a decreasing amount of transformation strain through continued cycling while the severity of this change (slope of linear fit) varied among the samples.

Before the distribution of sample strains is discussed, an explanation of the general transformation strain behavior will be given. As discussed previously, as an SMA is thermally cycled, dislocations are generated during the martensitic transformation [61]. This was previously mentioned to explain the increase in the transformation temperatures with thermal cycling. From this prior argument, it was stated that, due to the generation of dislocations during the transformation, the stress fields of these dislocations helped the nucleation of preferred martensite variants, and acted to ultimately increase the transformation temperatures of each sample during thermal cycling (except for those samples containing the $P_L$–phase, which were stabilized against dislocation generation). Apparent from Figs. 4.23 and 4.24, the generation of these dislocations also acts to decrease the available transformation strain.

To verify the process of dislocation generation during thermal cycling, several samples of the 48.5–Ti alloy were examined after LB testing through TEM investigations. Figure 4.25 presents the microstructures of the 48.5–Ti, 600°C–100h sample, before (A) and after (B) LB testing. The pre-cycled martensite shows very crisp and clear twin boundaries (Fig. 4.25A) that are relatively dislocation–free. In contrast, the martensite presented after LB testing (114 thermal cycles) appears quite different, showing distorted and non–linear martensite twin boundaries. The martensite in this image is distorted as the dislocations generated during LB testing act to disrupt the prior well–defined and linear martensite.

In addition to the generation of dislocations during thermal cycling, it was also noted that the $P_L$–phase precipitated during thermal cycling (e.g. Fig. 4.20). This phenomenon was
Figure 4.25 TEM BF images of the Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ alloy heat treated at 600°C for 100h before isobaric thermal cycling (A), and after cycling (B).

Also observed in the 48.5–Ti alloy, but in a much lower quantity, and had to be imaged using TEM techniques. Figure 4.26 presents TEM BF images of three different samples of the 48.5–Ti alloy, 600°C–100h, 650°C–1h, and 700°C–1h. Using micro diffraction, a characteristic diffraction pattern was captured from one of the PL–phase precipitates in the 600°C–100h sample (inset of Fig. 4.26A). The 600°C–100h sample contained a negligible amount of the PL–phase whereas the 650°C–1h and 700°C–1h samples contained an increasing amount of PL–phase. The amount of PL–phase within these samples was based on the amount of Ti$_2$(Ni,Pt)$_3$ that was present in each sample. As the amount of Ti$_2$(Ni,Pt)$_3$ decreased from the maximum allowable in this alloy (near 18% in the 600°C–100h sample) excess solute in the matrix formed PL–phase precipitates during LB testing. As the 650 and 700°C–1h samples had a lower amount of Ti$_2$(Ni,Pt)$_3$ than the 600°C–100h sample, there was more PL–phase precipitated during testing.
Figure 4.26 TEM BF images of several samples of the Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ alloy after isobaric thermal cycling. The arrow shows the presence of the P$_L$-phase that precipitated during LB testing. The 600$^\circ$C–100h sample (A) had the lowest P$_L$-phase content, while the 650$^\circ$C–1h (B) and 700$^\circ$C–1h (C) samples contained increasingly more P$_L$-phase, respectively.

To further examine this in-situ precipitation and which samples were most affected, microhardness testing was performed on samples after LB testing (Figure 4.27). The hardness differences before and after LB testing (closed vs. open symbols, respectively) give a clue to whether just dislocation generation, or both dislocation generation and P$_L$-phase precipitation was operable during LB testing. For example, looking at the 600$^\circ$C–100h sample, it was observed that little P$_L$-phase was precipitated during LB testing, and this sample has one of the lowest pre/post LB testing microhardness differences. In contrast to this, the 700$^\circ$C–1h sample had some of the highest amounts of P$_L$-phase precipitation, in the 48.5–Ti alloy and has one of the greatest microhardness differences. However, there is a limit to the amount of hardening that the P$_L$-phase can produce through precipitation. Looking at the 49.5–Ti samples, it is known that the 600$^\circ$C–100h sample precipitated a large amount of P$_L$-phase during LB testing, yet its microhardness was not increased as significantly as the 700$^\circ$C–1h sample of the 48.5–Ti alloy, which is likely due to a coarsening effect of the P$_L$-phase. The P$_L$-phase present in the 49.5–Ti alloy was coarser than the P$_L$-phase precipitated in the 48.5–Ti alloy, making it less effective at matrix hardening. Two samples of the 49.5–Ti alloy
Figure 4.27  Plots of Vickers hardness data for both the Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ and Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$ alloys before and after isobaric thermal cycling. Note that the 1h and 100h data points have been off–set for ease of data interpretation, not due to a difference in heat treatment temperatures. The error bars indicate one standard deviation of the sample data.

with the largest pre/post LB testing microhardness differences are the 650 and 700°C–1h samples. The 650°C–1h sample was discussed previously as being unique in the DTA section of this chapter. This sample had an inhomogeneous microstructure with portions of the microstructure that were void of Ti$_2$(Ni,Pt)$_3$. This microstructural inhomogeneity manifested as a double DTA peak on heating and cooling, suggesting that the two portions of the microstructure were going through the MT at different temperatures. The 700°C–1h sample also had a similar double DTA peak, and an inhomogeneous microstructure. Considering this, the interpretation of the microhardness differences implies that the portions of the microstructure void of Ti$_2$(Ni,Pt)$_3$ likely formed a fine distribution of P$_L$–phase, substantially increasing the overall sample hardness. This point will be important later in the discussion of transformation strain and will be revisited.
This explanation of the dislocation generation and P$_L$-phase precipitation is relevant to the discussion of transformation strain because these processes are most readily detected by examining the change in transformation strain through multiple LB thermal cycles. Figure 4.28 presents three samples taken from Fig. 4.23, the 500, 600°C-100h, and 700°C-1h samples. From this plot, several effects that sample microstructure has on cycling behavior are readily apparent. First, in the 500°C sample, because of the presence of a large amount of fine P$_L$-phase, the transformation strain is relatively constant, but rather low. The 600°C sample, has a transformation strain that decreases in an exponential decay manner and the 700°C sample’s transformation strain monotonically decreases through cycling. The difference in these samples arises from the fact that, during LB testing, in the 600°C sample, only dislocation generation is affecting the decrease in transformation strain. In the 700°C sample, the microstructure is generating dislocations, but also precipitating P$_L$-phase during cycling. This precipitation of P$_L$-phase acts to inhibit the generation of dislocations, and in

![Figure 4.28](image)

Figure 4.28 Plot of absolute transformation strain vs. cycle # of the 100 cycle, 200MPa portion of isobaric thermal cycling performed on samples of the Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ alloy. This plot contains the same information as in Figure 4.23, but with only three samples presented for ease of data interpretation.
turn helps to partially stabilize the microstructure against the loss of transformation strain through thermal cycling. Considering that a linear decrease with cycling indicates a microstructure precipitating P\textsubscript{L}–phase, re-examination of Fig. 4.24 indicates that all samples of the 49.5–Ti alloy precipitated P\textsubscript{L}–phase during LB testing, as previously posited from the fact that the 600\textdegree C–100h sample contained a large amount of P\textsubscript{L}–phase after LB testing, and this sample was the least likely to precipitate P\textsubscript{L}–phase from a solute balance argument (maximum amount of Ti\textsubscript{2}(Ni,Pt)\textsubscript{3} present).

To understand the microstructural features controlling the transformation strain a sample was capable of producing, the mean free distance (MFD) between precipitates of each microstructure was measured. The MFD was described by Fullman [62] as:

\[ \lambda = 1 + \frac{(V_v)\alpha}{N_L} \]  

where \((V_v)\alpha\) is the volume fraction of the \(\alpha\) phase (Ti\textsubscript{2}(Ni,Pt)\textsubscript{3} or P\textsubscript{L}–phase in this case) and \(N_L\) is the average intercept length per unit length of test line for the given phase of interest. This measure of interparticle spacing is useful for the samples at hand as it is independent of particle shape or distribution [63].

Comparing the MFD between the property–controlling precipitate phase, Ti\textsubscript{2}(Ni,Pt)\textsubscript{3} for samples heat treated above 550\textdegree C and the P\textsubscript{L}–phase for samples heat treated at 500 and 550\textdegree C, a useful relationship was found, Figure 4.29. This figure shows the transformation strain of each sample plotted against the heat treatment temperature (A), and these transformation strains plotted against the MFD of the property controlling precipitate phase (B). From the strain vs. MFD plot, it is apparent that all samples of the 48.5–Ti appear to have a linear dependence between the MFD and transformation strain produced under a load of 200MPa. For the 49.5–Ti alloy, it appears a similar dependence exists, but that the maximum strain achievable within this alloy is reached near a precipitate mean free spacing of \(\approx 5\mu m\). This relationship can be explained by the following argument. As the
Figure 4.29  Plot of absolute transformation strain (%) during the first cycle (cycle #16, overall) of the 100 thermal cycle isobaric portion of mechanical testing versus heat treatment temperature (A), and versus the mean free distance (MFD) between precipitates (B). For samples heat treated at 500 and 550°C, the MFD was measured between the P$_L$–phase precipitates, for all other samples the MFD was measured between the Ti$_2$(Ni,Pt)$_3$ precipitates. In plot B, the 600°C–100h data point with the ‘x’ is the 1300°C–WQ+600°C–100h–WQ sample.

Sample is loaded and cooled through the MT, variants of the martensite that accommodate the applied load are preferentially formed. If it is assumed that the volume fraction of these preferred martensite variants is directly related to the amount of transformation strain a sample is capable of producing, then the more room a microstructure has to produce these preferred variants, the more transformation strain this sample will produce. As second phase precipitates are added to a microstructure, these precipitates act to inhibit the continuous and strain accommodating growth of the preferred (by the applied load) martensite variants. It then follows that, as the space between these precipitates (MFD) is decreased, so too will the strain that a sample is capable of producing.
Considering this argument, several points of interest arise from Fig. 4.29B. First, for the 48.5–Ti alloy, the samples HT at 500 and 550°C contained both the P_L–phase and the Ti_2(Ni,Pt)_3 phase, as discussed previously. However, the MFD between the P_L–phase precipitates in these sample was much smaller than the MFD between the Ti_2(Ni,Pt)_3 precipitates. Considering the MFD between the P_L–phase precipitates, the trend of the 500 and 550°C samples falls on the linear fit with the other samples of the 48.5–Ti alloy implying that the P_L–phase inhibits the transformation strain in a similar way to the Ti_2(Ni,Pt)_3 phase. This is significant because the P_L–phase is a fine, coherent, and spherically–shaped precipitate, while the Ti_2(Ni,Pt)_3 phase is a semi–coherent, relatively coarse, plate–shaped precipitate. Considering that these two rather different precipitates have similar effects on the transformation strain of these samples is revealing of the role that precipitates, or likely second phases in general, play in suppressing the transformation strains of SMA’s. Ultimately, these data suggest that the size, shape, and coherency of a second phase is irrelevant, and only its volume fraction and inter–particle spacing need to be considered, for a particular alloy.

The second point to be discussed from Fig. 4.29B is the difference between the 48.5 and 49.5–Ti alloys. Considering the increased transformation strain of the 49.5–Ti alloy samples and their comparable MFD measurements between precipitates, there is an inherent difference in the performance of each of these alloys. Two of the 49.5–Ti samples, however, show strains that would be extrapolated from the 48.5–Ti alloy samples, the 650 and 700°C, 1h samples. These two samples were previously discussed as having inhomogeneous microstructures, and it was posited that these samples likely precipitated a large amount of P_L–phase during LB testing. As the strain data presented in the plot of Fig. 4.29 was taken from cycle #16, the second cycle of the 200MPa isobaric portion of LB testing, it is likely that the supersaturated portions of these microstructures precipitated large amounts of fine P_L–phase during the first 15 cycles of LB testing. This P_L–phase would then act to inhibit and decrease the transformation strains in these samples, producing results that were more representative of microstructures already containing the P_L–phase at the beginning of
LB testing, such as the 500 and 550°C samples. Considering this, it is worth noting that the MFDs of the 650 and 700°C–1h samples were measured between the existing Ti$_2$(Ni,Pt)$_3$ phase from pre–LB microstructures and the MFD distance between any P$_L$–phase is not represented in Fig. 4.29. With this consideration of these two 49.5–Ti samples, it is apparent that the sample MFDs between the property–controlling precipitate does not capture the fundamental transformation strain determining property of these microstructures.

4.3.3 Cumulative Open Loop Strain

While the transformation strain of these shape memory alloys is a measure of the strain produced by the martensite $\rightarrow$ austenite transformation during a thermal cycle, the open loop strain is a measure of the dimensional change of the test sample after a single cycle (Fig. 4.1). Taking these strain values and summing them from the beginning to end of thermal cycling provides a measure of the total non-recoverable strain\(^3\) accumulated during the entire mechanical tests, or the cumulative open loop strain (COLS). The behavior of cumulative open loop strain is critical to understand for development of these alloys as dimensional stability will be key when HTSMA components are put into service.

The COLS results for the 48.5–Ti alloy under increasing stress increments are presented in Figure 4.30. From this plot, several trends from the previously presented transformation strain data are apparent. First, the as–extruded condition has the lowest COLS, compared with the 1h samples for the majority of the stresses tested. The 500°C sample has the next lowest COLS, with the 650°C sample having similar to higher COLS, depending on the stress level. The 600 and 700°C samples have nearly identical COLS values through all stress levels and have the highest COLS at the highest stress levels. The 550°C–1h sample had a relatively high COLS at lower stress levels, but as the stress was increased, these

\(^3\)The term “non-recoverable” refers to strain that cannot be recovered by heating the sample to the same temperatures as the sample experienced during testing, or the upper cycle temperature. However, it is possible to recover some/all of this strain if the sample is heated above the upper cycle temperature experienced during mechanical testing.
Figure 4.30  Plots of absolute cumulative open loop strain versus applied compressive stress for the alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$. The plot on the left presents the data for the as–extruded and 1h samples while the plot on the right presents the data for the 100h and furnace cooled (FC) samples.

values leveled off, presenting a less consistent dependence of COLS on the applied stress, relative to the 1h samples. The as–extruded, 500, and 550°C samples all seemed to have COLS values with a decreasing dependence on increasing stress levels, while the 600, 650, and 700°C samples had a more linear dependence of increasing COLS with increasing stress.

The 100h samples exhibited similar results, with a few differences. Again, the 500°C sample consistently had the lowest COLS, with the 1300°C–WQ+550°C–100h–WQ sample having very similar results. The 550, 650, 700°C and 700°C–FC samples all had similar results up to 150MPa, then diverged into the following order. The 550°C sample had the next highest COLS values after the 500°C sample, with a linear fit through increasing stresses. The 700°C sample had the next lowest COLS, with the 700°C–FC sample having slightly higher values at the highest stresses. The 650°C sample had a slightly steeper increase than the previously mentioned samples. The 1300°C–WQ+600°C–100h–WQ and 800°C–FC samples had nearly identical COLS values, all larger than the previously mentioned 100h
samples. The 600°C had the highest COLS values of all the 48.5–Ti samples. All samples of
the 100h set, except for the 500, 550, 700°C and the 1300°C–WQ+550°C–100h–WQ samples,
had an increasing dependence of COLS on stress, meaning that the curve fit for each data
set had an increasing slope with increasing stress.

The COLS versus stress data for the 49.5–Ti alloy are presented in Figure 4.31. The
accumulated strain for this alloy is fairly different from the collected data for the 48.5–Ti
alloy. Within the 1h sample set, the 650°C sample consistently has the lowest COLS, while
the 500, 550, and 700°C samples COLS values are grouped so closely, their differences are
nearly indiscernible. From the 100MPa stress level and higher, the 600°C sample has the
highest COLS values. Additionally, while all samples except the 600°C sample appear to
have a decreasing dependence of COLS versus stress, the 600°C sample has a significantly
increasing dependence of COLS on stress.

Figure 4.31 Plots of absolute cumulative open loop strain versus applied compressive
stress for the alloy Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$. The plot on the left presents the data
for the as–extruded and 1h samples while the plot on the right presents the
data for the 100h samples.
The 100h samples are more similar to the 48.5–Ti alloy than their 49.5–Ti, 1h counterparts. The 500°C sample has the lowest COLS through all stresses, with a weakly–decreasing dependence on stress. The COLS of the 550 and 700°C samples has a linear dependence on stress, with both sample values nearly overlapping. The 650°C sample has the next highest COLS for all stresses above 50MPa, and the 600°C sample has the highest values through all stresses. The COLS for both the 600 and 650°C samples has an increasing dependence on stress.

Generally, the behavior of the COLS during incremented stress testing follows the same distribution and behavior as the transformation strain. This is apparent from a comparison of Figures 4.21 and 4.30 as well as Figs. 4.22 and 4.31. Looking at the transformation strain and COLS in the 48.5–Ti alloy (Figs. 4.21 and 4.30), the as–extruded, 500 and 550°C–1h samples show a similar trend to saturate in both transformation strain and COLS as the maximum stress (300MPa) is reached during testing. Similarly, in the 100h samples, the 1300°C–WQ+550°C–100h–WQ, 500°C, and 550°C–100h samples show similar plateauing (500°C–100h) or linear trends between transformation strain and COLS. Interestingly however, it appears that the 100h samples of the 48.5–Ti alloy that show a slight downward concavity in transformation strain data show a corresponding upward concavity in the COLS data. This implies that samples that are capable of the maximum transformation strain also have a propensity to dimensionally drift, or accumulate OLS, and this effect is exacerbated with increasing load biasing stresses.

Similar behavior holds true for the 49.5–Ti alloy. In the 1h samples, it seems that for all samples except for the 600°C–1h sample, the COLS maintained a consistent value per applied stress, regardless of microstructure. This implies a saturation of COLS for samples from a 1h heat treatment. Interestingly, the 650°C–1h sample consistently showed the lowest values of COLS. The 100h samples showed similar behavior to the 48.5–Ti alloy samples. The 500, 550, and 700°C samples had a linear increase in COLS with increasing applied stress while the 600 and 650°C had “accelerating” levels of COLS with increasing applied
stresses. These two last samples (600 and 650°C) coincidentally had the highest levels of transformation strain during the stress incremented portion of testing.

For the 48.5–Ti alloy, the COLS versus cycle # data, for the 100 cycle “runout” portion of testing, are presented in Fig. 4.32. For the 1h samples the as-extruded and 500°C samples had the lowest COLS, with the as-extruded sample starting at a lower value but gradually, and linearly, catching up to the 500°C sample by the end of the 100 cycles. The 550°C sample had the next lowest COLS. Both the 500 and 550°C–1h samples had nearly flat COLS lines through all 100 cycles indicating very little to no increase of the COLS in these samples through repeated thermal cycles under load. The 600, 650, and 700°C samples all had similar and gradually increasing values of COLS through cycling. The 650°C sample had a slightly higher slope than the 600 and 700°C samples.

For the 100h samples, the results were slightly different. In general, the 100h samples accumulated more OLS per cycle (curve fits had a higher slope) than their 1h counterparts. However, the 500°C sample had a relatively stable and the lowest amount of COLS. The 1300°C–WQ+550°C–100h–WQ sample had the next highest amount of accumulated strain which increased slightly through cycling. The 550, 700, 700–FC, and 800°C–FC samples

![Figure 4.32](image.png)  
Figure 4.32  Plots of absolute cumulative open loop strain versus thermal cycle, for the alloy Ti_{48.5}Ni_{30.5}Pt_{21}, during the 200MPa, 100 cycle “runout” test. The plot on the left presents the data for the as–extruded and 1h samples while the plot on the right presents the data for the 100h and furnace cooled (FC) samples.
all had respectively increasing amount of COLS, and all had similar curve fit slopes. The 650°C sample had a similar amount of accumulated strain as the 800°C–FC sample, but had a slightly higher dependence on cycling (i.e. higher slope). The 1300°C–WQ+600°C–100h–WQ sample and the 600°C had the next highest values of COLS, respectively, with the 1300°C–WQ+600°C–100h–WQ sample having a high enough slope that after the 100 thermal cycles it had overlapping values of accumulated strain with the 600°C sample.

Figure 4.33 presents the COLS data for the 49.5–Ti alloy for the 100 thermal cycle, 200MPa “runout.” As with the increasing stress tests, the 1h samples performed in a similar sequence. The 650°C sample had the lowest COLS through all of the cycles with the 500°C sample having similar, but slightly higher values. Both samples had fairly unchanging values of COLS through cycling. The 700°C sample had the next highest values of COLS, with the 550°C sample having slightly higher values. Both of these samples showed gradually increasing amounts of COLS through cycling, with the latter having a slightly higher slope than the former. The 600°C sample had COLS values that started nearly 3 times greater than the other samples and ended nearly 6 times greater.

![Figure 4.33](image-url)  

Figure 4.33 Plots of absolute cumulative open loop strain versus thermal cycle, for the alloy Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$, during the 200MPa, 100 cycle “runout” test. The plot on the left presents the data for the as–extruded and 1h samples while the plot on the right presents the data for the 100h and furnace cooled (FC) samples.
The 100h samples followed the same pattern as the stress increment tests. The samples went in order of increasing COLS as follows: 500, 700, 550, 650, and 600°C. The 500°C sample had the most flat (least increasing) curve of COLS versus cycle #, while the 550 and 700°C samples had similar and positive slopes. The 600 and 650°C samples also had equal and positive slopes, but had a slightly more positive slope than the 500 and 700°C samples.

To better understand the distribution of sample COLS and microstructure, each sample’s COLS data from the 100 cycle, 200MPa, (“runout”) portion of testing was plotted versus sample heat treatment time, and also plotted against the transformation strain at the beginning of the 100 cycle “runout,” Figure 4.34. From this plot a correlation between the amount of strain a sample is producing and the amount of COLS a sample produces is likely. This link indicates that as a sample produces more strain upon loading, more COLS will be accumulated in the sample.

Figure 4.34 Plot of cumulative open loop strain versus heat treatment temperature for both alloys Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ and Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$, (A), and cumulative open loop strain versus absolute transformation strain, (B), for both alloys.
The accumulated strain of a sample can be related to the generation of dislocations within the structure, which can inhibit the reverse transformation of certain variants of martensite [64, 65]. It appears, however, that from the data presented here, the more that a sample’s microstructure is capable of producing transformation strain, the more that microstructure is free to generate lattice defects that will cause irreversible strain. This concept can be thought of in terms of lattice strengthening mechanisms. First, consider the samples that contain the P\textsubscript{L}–phase, \textit{i.e.} those samples heat treated at 500 and 550\degree C. While the P\textsubscript{L}–phase within these samples reduces the amount of transformation strain produced in a thermal cycle, these precipitates also inhibit the generation of dislocations and irreversible martensite variants. Because of this, these samples also show the lowest amounts of COLS. Then looking at samples heat treated at 600–700\degree C, the amount of COLS peaks at heat treatment temperatures of 600\degree C, then reduces as heat treatment temperature is increased (Fig. 4.34A). This can be explained by the fact that samples heat treated at 600\degree C have the highest amount of Ti\textsubscript{2}(Ni,Pt)\textsubscript{3}, and thus matrix stoichiometries nearest an idea ratio of 1:1 Ti:(Ni+Pt). These microstructures have little to no strengthening from the semi–coherent Ti\textsubscript{2}(Ni,Pt)\textsubscript{3} phase, and have the least amount of non-stoichiometric solute in solution. Assuming that excess solute helps to strengthen the matrix through a solid solution strengthening effect, it can be posited that samples with a less stoichiometric matrix are better strengthened against the generation of defects that lead to COLS. The trade off from this strengthened matrix however, is that there is an apparent decrease in transformation strain.

This argument appears to only apply within a single alloy, however. It has been shown previously that the 49.5–Ti alloy has a larger amount of excess solute, from Tables 4.5 and 4.6 and Fig. 4.20, but the samples of this alloy show much higher transformation strains than those of the 48.5–Ti alloy. Within the sample set of the 49.5–Ti alloy, the same trends are apparent, where samples containing the P\textsubscript{L}–phase have much smaller COLS values, there is a peak in transformation strain and accompanying COLS for the sample heat treated at
600°C which then decreases with increasing heat treatment temperature, but these trends do not compare well with the 48.5-Ti alloy.

Finally, it is interesting to note that while various samples of this study, especially those of the 48.5-Ti alloy showed a lower bound of transformation strain, or rather a stabilized transformation strain, after 100 thermal cycles, the COLS for all samples did not appear to plateau within the limits of these mechanical tests during the 100 cycle “runout” portion of testing. Various samples of both alloys did however, show a plateau COLS near the maximum load of 300MPa (Figs. 4.30 and 4.31). This point only represents a maximum amount of COLS per a single thermal cycle however, whereas the 100 thermal cycle test results show how the sample behavior evolves through numerous cycles. As the COLS represents an overall dimensional change of the sample, there must be a limit to the overall amount of this irrecoverable strain that can be accumulated. From the collected data, it is difficult to determine where this strain limit may be with respect to these Pt-containing HTSMA’s. For future development, the limit of this accumulated irrecoverable strain may need to be a point of further research.

4.3.3.1 The 600°C–1h Sample of Alloy Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$

The 600°C–1h, 49.5–Ti sample is of particular interest within the samples studied here. This sample had comparable microstructural features (starting hardness, ending hardness, volume fraction Ti$_2$(Ni,Pt)$_3$, starting martensite type, etc.) as the other samples of this alloy, but showed different amount of COLS (Figs. 4.31 and 4.33). Considering the transformation temperatures of this alloy and the volume fraction Ti$_2$(Ni,Pt)$_3$ (Fig. 4.13), there is little that microstructurally sets this sample apart from other samples of the 49.5–Ti alloy. In the previous chapter, this sample was chosen as the example for the type of martensite in these alloys because of its consistency with other samples.
Looking more closely at the data collected from the LB tests, there is a unique behavior that was observed. Figure 4.35 shows the collected true strain vs. temperature data that was collected for the 600°C–1h sample. In this plot, a discrepancy is apparent on the heating portions of cycling during the reverse transformation of martensite to austenite. While the forward transformation (austenite → martensite) has a reasonable temperature range ($M_s – M_f$, blue data lines), the temperature range of the reverse transformation ($A_f – A_s$, red data lines) is larger than expected. For comparison, Figure 4.36 has been included. This data set is representative of most all other samples tested, and has been presented to elaborate the difference that make the 49.5–Ti, 600°C–1h sample unique. In

![Figure 4.35](image)

**Figure 4.35**  Temperature–strain (true strain) data collected for the 600°C-1h sample of alloy Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$. The red data lines are the heating portions of cycling while the blue data lines are the cooling portions of cycling. Thermal cycling begins at 0% strain under a load of 0MPa, then two thermal cycles were performed at 50, 100, 150, 200, 250, and 300MPa, followed by 100 thermal cycles at 200MPa, ending near 12% strain.
Figure 4.36  Temperature–strain (true strain) data collected for the 500°C-100h sample of alloy Ti_{48.5}Ni_{30.5}Pt_{21}. The red data lines are the heating portions of cycling while the blue data lines are the cooling portions of cycling. Thermal cycling begins at 0MPa, then two thermal cycles were performed at 50, 100, 150, 200, 250, and 300MPa, followed by 100 thermal cycles at 200MPa.

In contrast to the data presented in Fig. 4.35, there are two main features that set the 49.5–Ti, 600°C–1h sample apart. Looking at the 48.5–Ti, 500°C–100h sample, first, notice how the martensite→austenite transformation (red data lines) occurs over a relatively narrow temperature range. The temperature range of this back transformation is of the same magnitude as the forward, austenite→martensite, transformation. Second, while the overlapping data lines of the 200MPa, 100 cycle portion of testing indicate a small amount of accumulated irrecoverable strain (≈ 0.2%), this amount of strain is much less than that accumulated by the 49.5–Ti, 600°C–1h sample (≈ 7.5%).

This behavior of the 49.5–Ti, 600°C–1h sample indicates a microstructural mechanism that is stabilizing the martensite, and inhibiting the back transformation. To further investigate this, the microstructure post–LB testing was examined using SEM BSE imaging.
While the Ti$_2$(Ni,Pt)$_3$ phase appeared coarser after testing (which also appeared coarser in the 600°C–100h sample), there was little else that differed between the pre and post–LB sample microstructures. Also, there was no evidence of P$_L$–phase growth during testing. This poses few options to explain the unusual data of the 600°C–1h sample.

4.4 Conclusion

Based on the microstructural characterization of the samples investigated in this study, the isobaric thermal cycling response of various samples was explained and discussed. Through the first portion of LB testing, stress incremented thermal cycling, the samples of this study were found to generally follow the established Clausius–Clayperon relationship where increasing applied load increases all transformation temperatures. The effects of multiple thermal cycles (100 cycles) were also assessed and found that, generally, transformation temperatures increased through multiple thermal cycles. The individual sample transformation temperatures of these samples could be closely correlated to the amount and type of (Ni+Pt)–rich precipitates that were present in the microstructure. For samples heat treated at 500 and 550°C, the P$_L$–phase precipitate dominated transformation temperatures through its effect on the undercooling ($\Delta T$) based on its size and general distribution. Small, closely distributed precipitates of the P$_L$–phase suppressed the transformation temperatures the most. As this phase coarsened and the interparticle spacing increased, the suppression effect it maintained on transformation temperatures lessened. For samples heat treated above 550°C, the quantity of the Ti$_2$(Ni,Pt)$_3$ phase dominated the transformation temperatures. This precipitate appeared to affect the matrix composition, and hence the chemical equilibrium temperatures of the martensitic transformation ($T_o$) through consumption of Ni and Pt in the matrix solution. Consequently, the transformation temperatures of most samples of this study (those heat treated above 550°C) were linked to the volume fraction of the Ti$_2$(Ni,Pt)$_3$ phase.
The 49.5–Ti alloy (Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$) samples of this study were shown to have nearly a factor of 2 times greater transformation strain than the 48.5–Ti alloy (Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$) samples. The transformation strain was also found to increase with increasing load, during LB thermal cycling. Through multiple thermal cycles under load, the samples of this study showed a decrease in the transformation strain produced. The behavior of this transformation strain decrease was dependent on the microstructural processes occurring during thermal testing, either stable transformation between austenite and martensite (500 and 550°C samples containing P$_L$–phase), dislocation generation during cycling (samples heat treated at 600°C), or dislocation generation and precipitation of the P$_L$–phase (samples heat treated at 700°C). The amount of strain that a sample was capable of producing was linked to the mean free distance (MFD) between the property–controlling phase within each sample (the P$_L$–phase for samples containing it, and the Ti$_2$(Ni,Pt)$_3$ phase in the other samples). This relationship between the MFD and transformation strain was found to be categorized by alloy, where the 49.5–Ti alloy samples showed significantly higher transformation strains for the same measured MFD’s.

The accumulated irrecoverable strain, or cumulative open loop strain (COLS), was also measured for all of the samples tested in this study. This inherent property of these alloys was found to correlate to the amount of transformation strain produced by each sample. This connection between COLS and transformation strain showed a bottom limit with samples containing the P$_L$–phase, which helped to significantly decrease the amount of COLS through a strengthening and stabilization of the transforming matrix. This Ti$_2$(Ni,Pt)$_3$ did not appear to play a significant role in the control of the COLS, except for the effect that it plays in inhibiting the available amount of transformation strain through changes in the MFD of Ti$_2$(Ni,Pt)$_3$ precipitates.
CHAPTER 5

CONCLUSIONS & SUMMARY

In this research, two alloys, Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ and Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$, were investigated to understand how microstructure influences the shape memory properties of Pt–containing, Ti-lean high temperature shape memory alloys (HTSMAs). The presented investigation spanned samples heat treated at 500, 550, 600, 650, and 700°C, for times of 1, 5, 24, and 100h, with various other heat treatments to explore and support various aspects of microstructural development. These samples were investigated using techniques such as SEM, TEM, and EDS, as well as a load biased, compressive, thermal cycling mechanical testing regime. This mechanical testing procedure allowed for sample to be subject to various stresses between 0 and 300MPa (in 50MPa increments), as well as 100 thermal cycles at a constant stress (200MPa). The results of this research are summarized below.

Microstructural Characterization Conclusions

Within the alloys explored, Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ and Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$, two (Ni+Pt) rich precipitates were found, depending on the heat treatment route. In the samples that were heat treated at 500 and 550°C, the highly coherent and finely distributed P$_{L}$–phase was observed. For heat treatments above 550°C (e.g. 600, 650 and 700°C), the P$_{L}$–phase was not observed (except in short heat treatment times, at 600°C, after special homogenization experiments). Instead, these microstructures contained the Ti$_2$(Ni,Pt)$_3$ phase. The Ti$_2$(Ni,Pt)$_3$ phase was also observed in various samples heat treated at 500 and 550°C, if it was present in the microstructure prior to heat treatment (in the as–extruded condition). Evidence was found to suggest that the P$_{L}$–phase is metastable at 550°C while the Ti$_2$(Ni,Pt)$_3$ phase is thought
to be the equilibrium second phase in this alloys system. There was not enough data to speculate on the stability of the P\textsubscript{L}–phase stability at 500°C.

The P\textsubscript{L}–phase was observed to have a hardening effect on the matrix, showing classic peak and overaging hardening behavior with increasing heat treatment time. It was observed that this phase coarsened with increasing heat treatment time/temperature and decreases in volume fraction with increasing heat treatment time/temperature. This is one of the factors that led to the conclusion that this is a metastable phase. This phase was also observed to precipitate in high volume fractions, in a rod or plate morphology in the most Ti–lean alloy (48.5–Ti), at short heat treatment times and lower heat treatment temperatures (550 and 600°C) after homogenization treatments.

The Ti\textsubscript{2}(Ni,Pt)\textsubscript{3} phase did not noticeably harden the sample matrix, regardless of heat treatment condition. This phase was observed to peak in volume fraction for heat treatment temperatures of 600°C, showing a decreasing volume fraction as heat treatment temperature increased. At 500 and 550°C the equilibrium behavior of the Ti\textsubscript{2}(Ni,Pt)\textsubscript{3} phase could not be determined as the longest heat treatment time of 100h was likely insufficient to allow for adequate reaction kinetics to bring the various microstructures to equilibrium.

**Mechanical Testing Conclusions**

From the isobaric thermal cycling procedure, various insights were made into the nature of the studied Pt–containing alloys. First, it was found that the coherent P\textsubscript{L}–phase suppresses the M\textsubscript{s} and other martensitic transformation temperatures. Through quantification of the volume fraction and using the stoichiometric composition of this phase (Ti\textsubscript{11}Ni\textsubscript{9}Pt\textsubscript{4}), it was discovered that this phase’s affect on the martensitic transformation temperature was due to an increase in the driving force needed to grow the martensitic phase through a matrix strengthening effect due to its coherent nature and fine distribution. It was found that while this phase increases the compositionally dependent T\textsubscript{o} temperature of transformation, it also
increases the magnitude of $\Delta T$ enough to decrease $M_s$ temperatures of $P_L$–phase containing samples below the maximum $M_s$ temperatures found in other samples of this study. As the size of the $P_L$–phase increased and the volume fraction decreased, $M_s$ temperatures were observed to increase.

It was found that the $M_s$ temperature (and other MT temperatures) of sample void of the $P_L$–phase, were controlled by the volume fraction of $\text{Ti}_2(\text{Ni,Pt})_3$. This phase was found to only affect the matrix composition, and hence the $T_o$ temperature, through altering the Ni and Pt content in solution. As such, the $M_s$ temperatures of samples containing only the $\text{Ti}_2(\text{Ni,Pt})_3$ phase, were directly linked to the volume fraction of $\text{Ti}_2(\text{Ni,Pt})_3$.

As the $P_L$–phase inhibited the $M_s$ temperatures, it was also observed to inhibit the transformation strain under load. In general, the transformation strain was correlated to the mean free distance (MFD) between precipitate phases. As the samples that contained the $P_L$–phase contained a finer distribution of precipitates, these samples had some of the lowest observed transformation strains. This correlation between sample transformation strain and MFD was found to have a good correlation for samples of a single alloy, however, comparing samples between the two alloys, indicated there may be a more fundamental aspect of these microstructures that controls the transformation strain produced.

Though the $P_L$–phase was shown to suppress the $M_s$ temperature and lower the available sample transformation strain, it was also shown to stabilize the microstructure against property evolution during load biased thermal cycling. It was shown that sample properties evolved during cycling by either dislocation generation or precipitation of the $P_L$–phase during cycling, depending on the starting microstructure.

Finally, the amount of non–recoverable strain, or cumulative open loop strain (COLS), that a sample produced was related to the amount of transformation produced. It was found that as transformation strain increased, so did the non recoverable strain produced. However, as the $P_L$–phase was shown to stabilize sample property evolution during cycling,
it also reduced the COLS produced during cycling. Samples that contained the $P_L$-phase showed the lowest amount of COLS in this study.

**General Conclusions and Future Work**

From this research, it is evident that there are several trade-offs within this alloy system, concerning desirable shape memory properties. First, as dimensional stability is critical for any designed component, the reduction of COLS is critical. While it was noted that samples containing the $P_L$-phase showed the lowest values of COLS, the presence of the $P_L$-phase also suppressed two critical shape memory properties, the transformation temperatures and strains. If these alloys are sought for maximum transformation temperatures, the presence of the $P_L$-phase will have to be optimized to ensure that there is minimal suppression of the $M_s$ temperature, while maintaining maximum microstructural stabilization. Sample of this study that maximized transformation temperature, while minimizing COLS included the 48.5-Ti, 550°C–100h and 700°C–1 & 100h samples. The 550°C–100h sample, however, showed suboptimal transformation strains. Additionally, while all of the 48.5-Ti alloys had the highest $M_s$ temperatures, it is possible that the 49.5-Ti alloy samples are capable of similar transformation temperatures through longer heat treatment times.

Given the significant difference between the transformation strains produced between the 48.5 and 49.5-Ti alloys, it is recommended that designs requiring the maximization of the transformation strain, use alloy compositions nearer a 1:1 ratio of Ti:(Ni+Pt). However, these samples did show the highest amount of COLS, so it would be advantageous to design alloy processing steps to allow for the formation of the $P_L$-phase (heat treatments near 550°C). As noted above however, longer heat treatment times may be needed to obtain desirable microstructural constituents (coarse $P_L$-phase) and appreciably higher $M_s$ temperatures.
There are several points necessary for future work. First, while the precipitation of the P_L–phase was observed in several samples (48.5–Ti, 700°C–1h, 49.5–Ti, 600–700°C–100h samples), the effect this caused during isobaric thermal cycling (100 cycles at 200MPa) did not plateau. This means that the property evolution this precipitation process affected, namely the transformation strain, did not saturate, and is not currently fully quantifiable. While it is likely that these properties will not deviate substantially from other similar samples (48.5–Ti, 600°C–100h), this data does not exist and may be of future concern. Similarly, considering the trends in the COLS data with repeated thermal cycling, it is not currently understood at what magnitude this phenomenon will saturate. Considering that the transformation strain typically stabilized at 75 thermal or less, it is unclear what is driving the continual evolution of COLS and how to predict how many cycles it might take to saturate this property.

Concerning the microstructural component of this research, a full description of the P_L–phase behavior with heat treatment time/temperature is still unknown. Specifically, it would be beneficial to perform longer term heat treatments (100h) at 500 and 550°C to further investigate the metastability of this phase. Additionally, a more thorough investigation into the nature of this phase at low heat treatment times would be necessary to understand the interaction of this phase with the matrix. The nature of the rod/plate morphology of the P_L–phase at 550 and 600°C after homogenization treatments is currently lacking full description.

More generally, there is also a wide range of information that could be collected concerning the role that Pt plays in stabilizing Ti–lean precipitate phases. Considering that Ti_2(Ni,Pt)_3 appears to be stable with this alloy system, but is metastable in binary alloys, it would prudent to further explore how this precipitate stability is affected at lower Pt contents.
REFERENCES CITED


APPENDIX

Transformation Strain vs. Temperature Plots

This appendix contains the strain vs. temperature plots for all samples isobaric thermally cycled for both alloys, Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ and Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$. The applied compressive loads are indicated and the 200MPa, 100 cycle portion of testing has not been included for data clarity. Note that as a testing stress level was increased, one thermal cycle was required for the sample to reach a steady state. Thus, only the second thermal cycles are included on these plots. The thermal cycling range was 75 to 500 to 75$^\circ$C. The red indicate the heat portion (75 to 500$^\circ$C), while the blue data lines indicate the cooling portion (500 to 75$^\circ$C) of testing.

A.1 Alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$ Samples

The plots below are for samples of the alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$. These samples include heat treatment temperatures of 500, 550, 600, 650, and 700$^\circ$C for 1 and 100h. These samples were all heat treated from the as extruded condition and water quenched. Additional samples include heat treatments at 700 and 800$^\circ$C that were furnace cooled (FC), and two samples that were heat treated at 550 and 600$^\circ$C for 100h after a solutionization treatment at 1300$^\circ$C.
Figure A.1  Plot of temperature vs. strain data collected for the as-extruded sample of alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$. The applied compressive stresses are indicated, and only the data for the second thermal cycle is presented. The red data lines indicate the heating portion of the cycle (75 to 500°C) while the blue data indicates the cooling portion (500 to 75°C).
Figure A.2 Plot of temperature vs. strain data collected for the 500°C–1h sample of alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$.

Figure A.3 Plot of temperature vs. strain data collected for the 500°C–100h sample of alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$. 
Figure A.4   Plot of temperature vs. strain data collected for the 550°C–1h sample of alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$.

Figure A.5   Plot of temperature vs. strain data collected for the 550°C–5h sample of alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$. 
Figure A.6  Plot of temperature vs. strain data collected for the 550°C–100h sample of alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$.

Figure A.7  Plot of temperature vs. strain data collected for the 1300°C–WQ+550°C–100h–WQ sample of alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$. 
Figure A.8  Plot of temperature vs. strain data collected for the 600°C–1h sample of alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$.

Figure A.9  Plot of temperature vs. strain data collected for the 600°C–100h sample of alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$. 
Figure A.10  Plot of temperature vs. strain data collected for the 650°C–1h sample of alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$.

Figure A.11  Plot of temperature vs. strain data collected for the 650°C–100h sample of alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$. 

Figure A.12 Plot of temperature vs. strain data collected for the 700°C–1h sample of alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$.

Figure A.13 Plot of temperature vs. strain data collected for the 700°C–100h sample of alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$.
Figure A.14 Plot of temperature vs. strain data collected for the 700\degree C–1h–FC sample of alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$.

Figure A.15 Plot of temperature vs. strain data collected for the 800\degree C–1h–FC sample of alloy Ti$_{48.5}$Ni$_{30.5}$Pt$_{21}$.
A.2 Alloy Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$ Samples

For this alloy, samples were heat treated at 500, 550, 600, 650, and 700°C for 1 and 100h. Again, thermal cycling was performed from 75 to 500 to 75°C, and the red data lines indicate sample heating while the blue indicate sample cooling.

Figure A.16 Plot of temperature vs. strain data collected for the as-extruded sample of alloy Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$.
Figure A.17 Plot of temperature vs. strain data collected for the 500°C–1h sample of alloy Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$.

Figure A.18 Plot of temperature vs. strain data collected for the 500°C–100h sample of alloy Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$.
Figure A.19  Plot of temperature vs. strain data collected for the 550°C–1h sample of alloy Ti_{49.5}Ni_{29.5}Pt_{21}.

Figure A.20  Plot of temperature vs. strain data collected for the 550°C–100h sample of alloy Ti_{49.5}Ni_{29.5}Pt_{21}.
Figure A.21 Plot of temperature vs. strain data collected for the 600°C–1h sample of alloy Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$.

Figure A.22 Plot of temperature vs. strain data collected for the 600°C–100h sample of alloy Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$.
Figure A.23  Plot of temperature vs. strain data collected for the 650°C–1h sample of alloy Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$.

Figure A.24  Plot of temperature vs. strain data collected for the 650°C–100h sample of alloy Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$.
Figure A.25  Plot of temperature vs. strain data collected for the 700°C–1h sample of alloy Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$.

Figure A.26  Plot of temperature vs. strain data collected for the 700°C–100h sample of alloy Ti$_{49.5}$Ni$_{29.5}$Pt$_{21}$.