STRUCTURE AND THERMOMECHANICAL BEHAVIOR OF
NITIPT SHAPE MEMORY ALLOY WIRES

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STRUCTURE AND THERMOMECHANICAL BEHAVIOR OF
NITIPT SHAPE MEMORY ALLOY WIRES

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<tr>
<td>ΔH</td>
<td>transformation latent heat</td>
<td></td>
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<tr>
<td>ε_o</td>
<td>transformational strain</td>
<td></td>
</tr>
<tr>
<td>σ</td>
<td>applied stress</td>
<td></td>
</tr>
<tr>
<td>A_f</td>
<td>austenite finish temperature</td>
<td></td>
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<tr>
<td>at%</td>
<td>atomic percentage</td>
<td></td>
</tr>
<tr>
<td>COF</td>
<td>chronic outward force</td>
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<tr>
<td>Cu</td>
<td>Copper</td>
<td></td>
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<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
<td></td>
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<tr>
<td>FIB</td>
<td>focused ion beam</td>
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<tr>
<td>Li</td>
<td>Lithium</td>
<td></td>
</tr>
<tr>
<td>M_f</td>
<td>martensite finish temperature</td>
<td></td>
</tr>
<tr>
<td>M_s</td>
<td>martensite start temperature</td>
<td></td>
</tr>
<tr>
<td>M to A</td>
<td>martensite to austenite</td>
<td></td>
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<tr>
<td>Ni</td>
<td>Nickel</td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>Palladium</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>Platinum</td>
<td></td>
</tr>
<tr>
<td>RRF</td>
<td>Radial Resistive Force</td>
<td></td>
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<tr>
<td>R-Phase</td>
<td>rhombohedral phase</td>
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<tr>
<td>Si</td>
<td>Silicon</td>
<td></td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
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<tr>
<td>T</td>
<td>temperature</td>
<td></td>
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<tr>
<td>Ti</td>
<td>Titanium</td>
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SUMMARY

The objective of this work is to understand the structure-property relationships in a pseudoelastic composition of polycrystalline NiTiPt (Ti-42.7 at% Ni–7.5 at% Pt). Structural characterization of the alloy includes grain size determination and texture analysis while the thermo-mechanical properties are explored using tensile testing. Variation in heat treatment is used as a vehicle to modify microstructure. The results are compared to experiments on Ni-rich NiTi alloy wires (Ti-51.0 at% Ni), which are in commercial use in various biomedical applications. With regards to microstructure, both alloys exhibit a <111> fiber texture along the wire drawing axis, however the NiTiPt alloy’s grain size is smaller than that of the Ni-rich NiTi wires, while the latter materials contain second phase precipitates. Given the nanometer scale grain size in NiTiPt and the dispersed, nanometer scale precipitate size in NiTi, the overall strength and ductility of the alloys are essentially identical when given appropriate heat treatments. Property differences include a much smaller stress hysteresis and smaller temperature dependence of the transformation stress for NiTiPt alloys compared to NiTi alloys. Potential benefits and implications for use in vascular stent applications are discussed.
CHAPTER 1

INTRODUCTION

Nickel Titanium Alloys

Nickel-Titanium (NiTi) alloys are an equiatomic or near equiatomic intermetallic compound of titanium and nickel. They were first discovered in 1958 by William J. Buehler at the Naval Ordinance Laboratory (NOL). The parent or austenite phase is a highly ordered derivative of the BCC unit cell known as B2. The martensite phase can exist in several variants but is considered as a monoclinic distortion of the B19 cell. A third phase known as the rhombohedral phase (R-Phase), often precedes the martensitic transformation, but can also occur independently.[1] The microstructure of NiTi is primarily single phase with trace amounts of other phases in the matrix. Due to the presence of oxygen, second phase precipitates can form. For instance, titanium rich alloys can have TiNi₃ present, while nickel rich alloys precipitate Ti₂Ni. Presence of these precipitates can have significant affect on the processibility and mechanical properties of NiTi.[2]

The stress-strain response of NiTi is highly dependent on the applied load and temperature. Figure 1 represents a typical tensile stress-strain response. In general, Stage I is a linear elastic response of either the martensite or parent phase. After further deformation, Stage II marks the formation of stress induced martensite or martensitic reorientation depending on the sample temperature. Stage III represents the elastic deformation of martensite with indications of slip and dislocation motion. The last stage indicates plastic deformation of the martensite phase.[1, 3]
Figure 1. Stages during tensile formation of NiTi shape memory alloys.

Figure 2. Stress induced martensite (SIM) formed during loading and disappears upon unloading.
The thermoelastic martensitic phase transformation in NiTi enables unique strain recovery properties such as pseudoelasticity and shape memory. Pseudoelastic (or superelastic) NiTi is capable of recovering large inelastic strains (at times up to 10%) spontaneously upon unloading.[3] For NiTi alloys, pseudoelastic response occurs above $A_S$, the parent phase start temperature, but below $M_F$, which is the highest possible temperature for the martensitic phase to exist. As seen in Figure 2, when loaded in tension, the parent phase transforms into martensite, also known as stress induced martensite (SIM). Once unloaded, the martensite reverts to the parent phase not immediately due to the interfacial energy required to generate new austenite interfaces.[3]

Another unique property of NiTi alloy is the one way shape memory effect or its unique ability to return to its original undeformed shape after heating. Shape memory is exhibited when NiTi recovers large strain deformation upon heating.[4] The foundation for this effect is generally due to the notion that martensite has less symmetry compared to the parent phase as shown in Figure 3. Therefore upon cooling from the parent phase, the martensite phase can take on many variants through deformation. However when heated and transforming back into the parent phase, the more symmetrical parent phase allows only one structure and therefore the material reverts back to its original shape.[2]
Medical Applications

These unique properties have been used in the design of medical devices in cardiology, interventional radiology and orthopedics.[5] In particular, the properties of NiTi have made it an excellent material choice for use in self-deploying endovascular stents.[4, 6, 7] Stents are mesh-like tubes that can be used as a supplement or an alternative to conventional balloon angioplasty for treating arterial occlusion disease. Given the superelastic behavior of NiTi alloys, medical device manufacturers have developed compressible stents for use in arteries where gross deformation can occur. Mainly used in peripheral arteries, NiTi stents are self-expanding upon deployment and can conform more readily to the shape of the obstructed vessel. Stainless steel balloon
expandable stents are neither crush resistant (in a gross displacement controlled application) nor self-expanding.

In order to optimize the pseudoelastic properties of the stent at human body temperature, heat treatments are applied to the final product. Stents are manufacturing from either the expansion of a pattern cut from a small tube or the cutting of a design directly into a larger tube. Depending on the fabrication method, stents can be exposed to single or multiple treatments to achieve the desired properties.[8] It is well known that heat treatments influence transformation temperatures through the formation of precipitates.[1, 9-11] These precipitates do not exhibit shape memory properties and can greatly affect mechanical response of the final stent.

The procedure to place a stent involves the use of a delivery catheter guided through the femoral artery to the area deployment. Interventional radiologists use X-ray or fluoroscopy to help guide the catheter and track the location of stent deployment.[5] Stents with thicker struts are more radiopaque than those with thin wire filament struts.[12] Also less dense NiTi possesses lower inherent radiopacity compared to stainless steel. Moreover, future stents are utilizing thinner struts, and, as a consequence, new NiTi stents are often radiolucent. Current solutions involve the use of coatings or gold, platinum, and tantalum radiopaque markers [4, 9] adhered to the stent. Since tantalum and Nitinol are galvanically similar, corrosion is not a major issue. But since gold is more noble than Nitinol, a substantial decrease in corrosion resistance is observed when these materials are combined. Stents with gold markers are usually coated with a thin polymer layer to protect against corrosion.[4] In addition to local markers, gold and
platinum coatings have also been used to increase biocompatibility and overall radiopacity.[13]

**Alloying Elements**

The alloying of NiTi with heavy elements is an alternative solution to improve inherent radiopacity of NiTi based biomaterials. Possible ternary elements include iridium, platinum, gold, rhenium, tungsten, palladium, rhodium, tantalum, silver, ruthenium, or hafnium. The addition of alloying elements provides a way to control transformation temperatures, control the hysteresis width, and affect the martensitic and austenitic strength.[10] Ni-Ti-Hf systems have been investigated due to the relatively low cost of addition and high transformation temperatures. The stress-strain behavior of a Ni<sub>49</sub>Ti<sub>36</sub>Hf<sub>15</sub> differs from that of NiTi in that the stress plateau disappears and high work hardening is observed. This greatly decreases the shape memory properties by premature dislocation slip during martensite variant orientation or stress-induced martensitic transformation. Addition of Zr up to 30 at.% significantly increases phase transformation temperatures and has similar microstructure and shape memory properties as NiTiHf alloys. Alloying element additions of Zr, Hf, Au, Pt, and Pd also can embrittle the alloy decreasing ductility. [10, 14-16] Increased transformation temperature and decreased ductility are undesirable for medical devices taking advantage of the pseudoelastic properties of NiTi.

The effects of platinum and palladium addition to NiTi have also been previously investigated.[2, 17] This pioneering work demonstrated that transformation temperatures decrease with increasing Pt or Pd at.% additions between 0-10%, and above 10%, the
transformation temperatures increase linearly with Pt or Pd addition. The slight decrease in transformation temperatures with Pt addition is desirable from the standpoint of maintaining pseudoelasticity at body temperature. Moreover, the Pt and Pd doped alloys exhibited reasonable strain recovery when deformed below $M_f$ and heated to room temperature, with little dependence on the percentage of alloying element[2]. Although this prior work provides rationale to consider Pt as a doping element for NiTi, the structure and resulting thermo-mechanical properties of the Ni-Ti-Pt materials have not been thoroughly examined.

The objective of this work is to provide a foundation to understand the structure-property relationships in a targeted composition of Ni-Ti-Pt. A single composition was selected since there is a small composition window where the material has the appropriate transformation temperatures for use in pseudoelastic biomedical applications. Structural characterization of the NiTiPt material included grain size determination and texture analysis while the thermo-mechanical properties were explored using tensile testing. Variation in heat treatment was used as a vehicle to modify structure and thus understand the link between structure and properties in the NiTiPt alloys. The results are compared to experiments on Ni-rich NiTi alloys, which are in commercial use in various biomedical applications.
CHAPTER 2
MATERIALS AND METHODS

The NiTi and NiTiPt wires examined were polycrystalline in nature. The NiTi wire had a composition of Ti-51.0 at% Ni (Ti-56.0 wt% Ni), while the NiTiPt wire had a composition of Ti-42.7 at% Ni–7.5 at% Pt (Ti-39.4 wt% Ni–23.0 wt% Pt). Wires of both NiTi and NiTiPt were cold drawn to a nominal diameter of 0.34 mm. Cold work percentage reductions were in the range of 40% to 45%. The final step in the manufacturing process for both wires involved a final heat treatment of 505 °C for 1.5 minutes.

Subsequent heat treatments of both the NiTi and NiTiPt were performed as follows. Each sample was heat treated in a furnace for 1.5 hours at seven different temperatures starting at 300 °C and increasing to 600 °C in 50 °C increments. Surface oxidation caused by the heat treatment was removed prior to testing through light sanding. All wires without a secondary heat treatment (only the 1.5 minute 505 °C heat treatment) were designated as “as-received”.

For texture measurements, 10 mm long segments were cut from the wires and embedded parallel in epoxy. Next, the segments were ground and polished down to the midplane. In this way, a thin slice of parallel wires with a large area of about 10 mm x 3.5 mm was obtained that provided sufficient x-ray intensity for the texture measurements. Measurements were performed with a Philips X'pert Pro system using CuKa radiation. Orientation information was obtained from the {110}, {200} and {211} planes in the B2 parent phase. In order to make sure that only the austenitic phase was present, the wires were heated up to 100 °C during the measurements. The inverse pole
figures presented here are shown in the form of equal area projections and were calculated using popLA software.[14] For local compositional analysis, polished metallographic cross-sections of the wires were analyzed in a scanning electron microscope using an ultrathin Si(Li) EDAX detector.

Samples for transmission electron microscopy (TEM) were prepared from the thin wires using a focused ion beam (FIB). The microstructures were studied with a Philips CM 200 TEM operated at a nominal acceleration voltage of 200 kV, and two-beam conditions were used for imaging whenever possible. In each case, the plane of the TEM foil cut by the FIB was normal to the wire axis, i.e. the viewing direction in the images shown is normal to the wire drawing direction.

Transformation peaks were measured for both NiTi and NiTiPt wires in the as-received and heat treated states using a differential scanning calorimeter (DSC). DSC test specimens were cut from the wire, weighed, and sealed in pure aluminum sample pans. An identical empty aluminum sample pan was used for reference. The pans were placed inside a nitrogen-filled dry box and given the following temperature scan: hold for 1 min at 20 °C, cool to -70 °C at 10 °C/min, hold for 2 min at -70 °C, heat to 150 °C at 10 °C/min, hold for 2 min at 150 °C, cool to -70 °C at 10 °C/min.

Mechanical test specimens with length of 0.3 m were cut from the NiTi and NiTiPt as-received wire and heat treated as described in the heat-treating procedures. The samples were mounted on a uniaxial screw driven load frame (MTS Systems Corp., Eden Prairie, MN) contained within a thermal chamber with thermo-electric heating and liquid nitrogen cooling. The samples were run under strain control upon loading and in
load control during unloading. Wire samples were held using spooling grips to minimize stress concentrations at the grip junction.

Tensile testing of each sample was performed per ASTM F-2516. The test protocol involved pulling the wire to 6% strain, unloading to less than 7 MPa, and then pulling to failure. All tests were conducted at a strain rate of 0.002 s⁻¹ with a nominal gage length of 20 mm, inside a thermal chamber at 37 °C. Prior to loading, the specimens were held at 37 °C for 5 minutes to ensure a steady state temperature. In order to measure recovered strain as a function of applied strain, the wires were loaded and unloaded in 3% strain increments up to 9% strain followed by loading in 1% increments until failure. The test was performed at a strain rate of 0.002 s⁻¹ with a nominal gage length of 20 mm in a temperature controlled chamber at 37 °C. To obtain the critical transformation stress as a function of temperature, the wires were loaded to 6% strain and then unloaded through a temperature range from -50 °C to 200 °C in 25 °C increments until failure. After unloading, samples showing residual strains were heated to induce shape recovery.
CHAPTER 3
EXPIMENTAL RESULTS

Material Structure

Figure 4 shows transmission electron microscope (TEM) images of the NiTiPt wire as-received under (a) low and (b) high magnifications and furnace heat treated for 1.5 hours at 600 °C under (c) low and (d) high magnifications. TEM images for as-received NiTi wire are shown in Figure 4(e,f). The images reveal that as-received NiTiPt wire has a grain size on the order of tens of nanometers. When the NiTiPt wire is heat treated for 1.5 hours at 600 °C, grain growth occurs resulting in a grain size on the order of hundreds of nanometers. The NiTiPt material given a 300 °C heat treatment was also analyzed and the grain size was the same as observed in Figure 4(a,b). Other intermediate heat treatments were not analyzed, but are expected to have a structure in between the two extremes in Figure 4(a,b) and Figure 4(c,d). The grain size in the as-received NiTiPt wires is extremely small, on the same order as nanocrystalline metals. The inset diffraction patterns indicate a textured polycrystalline material for both the as-received and furnace heat treated samples. The NiTi grains are approximately twice the size of the NiTiPt wire grains (Figure 4e). Elongated grains due to drawing were also observed in the NiTi (Figure 4f), and such grains likely exist in the NiTiPt even though they were not observed in the particular cross section extracted from the wire.
Figure 4. Transmission electron microscope images from the NiTiPt and NiTi wires. The images display NiTiPt as-received wire at (a) low magnification and (b) high magnification. NiTiPt wire heat treated for 1.5h at 600 °C at (c) low magnification and (d) high magnification (e,f) NiTi as-received wire.
Figure 5 displays the measured crystallographic texture in the NiTiPt wires. The 1-axis represents the wire drawing direction, while the 2-axis and 3-axis represent the transverse cross directions of the wire. There is a weak preferred grain orientation in the drawing direction of the wire $\langle 111 \rangle$. The crystallographic texture in the transverse directions was essentially random, indicating no strong preferential orientation of the grains. This texture is basically identical to cold-drawn NiTi wires. [1]

**Figure 5.** Steriographic unit triangles illustrating crystallographic texture in the NiTiPt wire along with a diagram of the corresponding wire axis orientation.
Thermal transformation

Figure 6 shows the thermal transformation of NiTi and NiTiPt wires after 1.5 hour furnace heat treatments ranging from 300 °C to 600 °C in 50 °C increments. Heat flow in the DSC curves is defined as endothermic up and exothermic down. For both NiTi and NiTiPt, the transformation becomes more evident with higher temperature furnace heat treatments. The NiTi always shows a more distinct thermally-induced transformation relative to the NiTiPt. With increasing heat treatment temperature, either R-phase (rhombohedral phase) or two-step martensitic transformations appear as indicated by the multiple peaks observed in the DSC curves.[18-21] For the NiTi material (Fig 6a), the M to A (martensite-to-austenite) transformation temperature gradually increases with increasing heat treatment temperature, while the R-phase transformation remains relatively constant. Numerous papers exist in the literature to explain the appearance and movement of multiple transformation peaks in Ni-rich NiTi.[18-22] For the NiTiPt material (Fig 6b), there is a slight increase in both the M to A transformation temperature and A to M transformation temperature with increasing heat treatment temperature. The transformation temperatures for the NiTiPt material are considerably lower than that of the NiTi material, and some multi-step phase transformations were observed but not studied in detail given the breadth of this work. In general, the diffuse nature of the thermally-induced phase transformation in NiTiPt significantly limited the utility of DSC studies, especially in samples aged at low temperature.
Figure 6. DSC graphs for (a) NiTi wires and (b) NiTiPt wires with 1.5h furnace heat treatments at various temperatures.
**Mechanical Behavior**

Figure 7 shows representative stress-strain curves for NiTi and NiTiPt wires after selected furnace heat treatments. The stress-strain behavior of the as-received wires (Fig 7a) are similar and follow typical tensile deformation characteristics in NiTi materials.[3] A noticeable difference is the smaller hysteresis in the NiTiPt compared to the NiTi wire. The difference in hysteresis is consistent across all furnace heat treatments. Figure 7b represents the stress-strain response of the wires after a 350 °C furnace heat treatment for 1.5 hours. The behavior is similar to the as-received wires, with some variability in the transformation plateau stress. In Figure 7c, the ultimate, upper and lower plateau strengths for both the NiTi and NiTiPt wires begin to decrease. With a 1.5 hour 550 °C furnace heat treatment (Figure 7d), the ultimate failure strength of both alloys drop considerably. In addition, the NiTi material no longer exhibits pseudoelastic properties. The NiTiPt wire still retains its pseudoelasticity and the upper and lower plateau stresses remain roughly unchanged from the 450 °C heat treatment sample.
Figure 7. Representative stress-strain graphs at 37 °C following ASTM2516-06 for NiTi and NiTiPt wire (a) as-received, (b) with a 1.5h furnace heat treatment at 350 °C, (c) with a 1.5h furnace heat treatment at 450 °C, and (d) with a 1.5h furnace heat treatment at 550 °C.

Figure 8 summarizes critical mechanical properties as a function of wire furnace heat treatment temperature, highlighting trends and variability (± 1 standard deviation). The ultimate tensile strength, shown in Figure 8a, is relatively constant for the NiTi and NiTiPt wires up to the 450 °C heat treatment. Above the 450 °C furnace heat treatment, the ultimate strength declines for both alloys. The NiTiPt wire loses approximately 40%
of its failure strength at the 600 °C heat treatment. Also, as a result of the higher temperature heat treatments (~550 °C), the failure strain increases for both materials as shown in Figure 8b. The NiTi wire becomes ductile and deforms beyond the range of the extensometer before failing. The NiTiPt shows similar behavior with increased failure strain at the 550 °C heat treatment and deforms beyond the extensometer range at the 600 °C treatment. Failure strain is constant within experimental error below the 500 °C heat treatment for both alloys, which is partially driven (especially at low aging temperatures) by the 5 minute 505 °C heat treatment given both materials prior to secondary heat-treating.
Figure 8. Mechanical properties at 37 °C from ASTM2516-06 as a function of wire furnace heat treatment for (a) ultimate tensile strength, (b) failure strain, (c) martensite yield strength, (d) plateau stresses and (e) residual elongation.
To gain a better understanding of the mechanical properties, the martensite yield strength (0.2\% offset method) was plotted as a function of furnace heat treatment temperature (Figure 8c). The martensite yield strength between the binary and ternary alloy are similar and fairly consistent for the heat treatment temperatures below 500 °C. Above that temperature, the strength significantly decreases for both alloys though the NiTiPt wire has slightly higher, but insignificant, resistance to plastic flow compared to the NiTi wire.

Figure 8d shows the upper and lower plateau strengths for both the NiTi and NiTiPt wires. The upper plateau strength is defined as the stress at 3\% strain during loading of the sample. The lower plateau strength is the stress at 2.5\% strain during the unloading of the sample after being loaded to 6\% strain. Both alloys demonstrate a declining plateau stress with increasing heat treatment temperature; however the decline is significantly greater with the NiTi wire. Furthermore, the hysteresis is significantly smaller across all heat treatments with the NiTiPt wire as indicated by the difference between the upper and lower plateau strengths. The difference in hysteresis is about a factor of two for most of the heat treatments.

The residual elongation as a function of furnace heat treatment temperature is shown in Figure 8e. The residual elongation is defined as the unrecovered displacement upon unloading measuring at a stress of 7.0 MPa. The NiTiPt wire recovers the applied strain showing small residual elongation values below the 550 °C heat treatment. The NiTi wire loses a significant amount of pseudoelasticity at higher temperature heat treatments as indicated by the increased residual elongation values. In these tests, the NiTi material is transitioning to a shape memory response where the permanent strain at
unloading can be recovered upon heating. The shift to shape memory is in line with the increasing transformation temperatures observed in DSC testing (Figure 6).

Figure 9 shows recoverable strain as a function of applied strain for as-received wire samples deformed at 37 °C. This test helps to assess the recoverable strain limit in the two materials. Up to 12% strain, the NiTi and NiTiPt wires display similar recoverable pseudoelastic strains. Above 12%, the curves diverge and NiTi begins to show slightly larger recoverable strain limits compared to NiTiPt, although the difference is minimal.

![Figure 9. Recovered strain as a function of applied strain for as-received wire at 37 °C.](image)

To measure the effect of temperature on the critical stress to induce the martensitic transformation, tensile tests were performed on as-received wires heated from -50 °C to 200 °C (Figure 10a and 10b). The samples were loaded to 6% strain and then unloaded at a strain rate of 0.002 s⁻¹. At temperatures significantly below the M to A
transformation, the material does not exhibit pseudoelastic behavior and is believed to deform due to martensite reorientation. In the range of stress-induced transformation based inelasticity, both materials show increasing critical stress with increasing test temperature. At temperatures greater than 125 °C, the austenite phase remains stable.

**Figure 10.** Stress-strain response as a function of temperature for (a) NiTi wire and (b) NiTiPt wire. All tests were performed on as-received wire.
upon loading and stress-induced martensite transformation is not observed. A 0.2% offset from linearity was used to determine the critical martensitic transformation stress, and these stresses are plotted as a function of test temperature in Figure 11. A linear curve fit comparing the critical stress temperature sensitivity, in the appropriate temperature range, demonstrates that the transformation in the NiTi material is slightly more sensitive to test temperature than the transformation in the NiTiPt.

**Figure 11:** Critical transformation stress as a function of temperature for NiTi and NiTiPt as-received wire.
CHAPTER 4

DISCUSSION

From an overall perspective, the thermo-mechanical properties of NiTiPt are very similar to the Ni-rich NiTi shape memory alloys. In regards to microstructure, both alloys exhibit a weak 〈111〉 fiber texture along the wire drawing axis, however the NiTiPt alloy’s grain size is smaller than that of the Ni-rich NiTi wires. Given the microstructural similarities, the overall strength and ductility of the alloys are essentially identical when given appropriate heat treatments. This work has revealed several fundamental aspects regarding the structure and deformation of NiTiPt wires to be further discussed herein.

Aging treatments of Ni-rich NiTi alloys cause the formation of Ti$_3$Ni$_4$ precipitates which are well known to affect both transformation temperatures and mechanical properties. [18, 20-23] Examining the DSC results, Figure 6a demonstrates the effect of heat treatment through a shifting of the martensite start ($M_s$) temperature. This transformation shift is caused by the presence of precipitates and dislocations within the structure, which alters the energy barrier for martensite formation. Also, multiple-stage transformations appear at annealing temperatures above 500 °C with the occurrence of an R-phase. The diffuse thermal transformation in the NiTiPt alloy limits full interpretation, however it appears that the $M_s$ temperatures are lower and do not exhibit the characteristic shift shown with the creation of precipitates through annealing. However, it is very interesting to note that evidence of multiple stage transformations exist at the 600 °C heat treatment even though precipitation was not observed in TEM studies on this material. Prior work on NiTi [18, 20-23] has partially attributed the multi-step transformation to
inhomogeneous transformation at grain boundaries and precipitates. Given the lack of precipitates, the multi-step transformation in NiTiPt is likely driven by grain boundary inhomogeneity, although further work is necessary. Moreover, the introduction of ternary elements is known to influence $M_s$ and has been shown to depend on occupation sites and relative ternary element concentration. [17, 24]

When examining the microstructure of the as-received materials in Fig. 4 (a,b,e,f), a grain size difference is apparent between the ternary alloy and the NiTi. Based on this, one would expect the NiTiPt alloy to show higher strength due to the nano-scale grain size and increased grain boundary density impeding dislocation movement. However, overall stress-strain behavior is quite similar for both materials as shown in Fig. 7a, and this is likely driven by the fact that the NiTi is strengthened by nanometer scale precipitation while the NiTiPt is strengthened by nanometer scale grains. As with most metals, particularly nanocrystalline metals, heat treatment led to coarsening of the microstructure as grain boundary area reduction results in a decline of total energy. Evidence of the grain size increase for the NiTiPt alloy can be seen in Fig. 4 c, d. The low temperature heat treatments from 300 °C to 450 °C have minimal effect on loading stress-strain behavior as indicated by the similar trends seen in failure strength, failure strain, and martensite yield strength. This insensitivity is partially driven by the thermal history of the materials, which last saw a 5 minute 505 °C heat treatment.

Previous work has shown different phase distributions with varying Pt addition. X-ray diffraction measurements taken at room temperature indicated for 5 at.% Pt additions, the phases were primarily B19' martensite with some parent phase B2, while for 10 at.% additions the phases were mostly parent phase B2 with some B19' martensite.
Above 20 at.% Pt additions, the phase present was primarily B19 martensite. [13] The TEM results from the NiTiPt wires did not indicate the existence of a second phase, however it could exist. Additional work would need to be performed to determine if a second phase is present.

For heat treatments beyond 450 °C, failure strength and martensite yield strength decrease, while ductility is increased for both alloys. Compared to the ternary alloy, the NiTi becomes significantly more ductile beyond 500 °C as indicated by increased failure strains. On the other hand, the NiTiPt alloy shows a reduction in failure strength and minimal increases in failure strain at the 550 °C and 600 °C heat treatments. This result indicates that the NiTi is inherently more ductile than NiTiPt once strengthening mechanisms (small coherent precipitates and nanometer scale grains) are removed. It is also noted that the stress level at which martensitic transformation occurs in NiTi is depressed with increasing heat treatment temperature. This effect is driven by the increased impact of precipitate stress fields and also Ni depletion in the NiTi matrix. The stress-induced martensite plateau for the NiTiPt is depressed to a smaller degree even at high temperature heat treatments. In this case, stress-induced martensite formation becomes easier in the coarsened grain structure at the sacrifice of decreasing slip resistance.

When a shape memory alloy is loaded at a temperature above $A_s$, the creation of martensite is stress-induced and upon unloading the martensite will revert back to the parent phase. More stress is required to induce martensite formation upon loading than the reverse transformation upon unloading resulting in a stress hysteresis. The NiTiPt alloy has a much narrower stress hysteresis compared to the NiTi alloy. Figure 8d shows
that the lower plateau strength of the NiTiPt alloy is significantly higher than the NiTi with the difference increasing at higher heat treatment temperatures as the NiTi transitions to shape memory behavior. Quantum transformation effects (for example a different transformation product) or the fundamental difference in strengthening mechanisms could drive the inherently lower hysteresis in NiTiPt relative to NiTi. It is possible that precipitation hardening may more effectively block reverse transformation relative to hardening through grain size reduction. However, this assumption would not be fully supported by the low hysteresis in the NiTiPt heat treated at 600 °C that had relatively larger grains and still a low hysteresis compared to NiTi across all heat treatments. Further work is needed to understand the low hysteresis in the NiTiPt alloys, an effect that is likely driven by quantum effect on the transformation behavior. It is worth noting that increased stress hysteresis has been shown to occur with the addition of other ternary elements into NiTi such as Cu.[25]

It has been demonstrated previously that the creation of precipitates in Ni-rich NiTi alloys through heat treatment increases slip resistance and recoverable strains.[3] Investigation of the recoverable strain properties of the as-received wire shown in Figure 9, indicate that the recovery properties of NiTi and NiTiPt are similar at strains below 12% due to the equally effective strengthening mechanisms. Above 12% applied strain, both materials begin to show non-recoverable strain due to plastic flow facilitated by breakdown of their strengthening mechanisms. At heat treatment temperatures above 500 °C, these superior recovery properties are lost in the NiTi alloy due to coarsening of the precipitates and in NiTiPt due to coarsening of the grains.
It is well known that the stress needed to induce martensite transformation increases linearly with temperatures above $M_s$. This linear relationship is governed by the Clausius-Clapeyron equation usually written as:

$$\frac{d\sigma}{dM_s} = -\frac{\Delta H}{T\varepsilon_o}$$

where $\Delta H$ is the transformation latent heat, $T$ is the temperature, $\sigma$ is the applied stress, $M_s$ is the martensitic start temperature, and $\varepsilon_o$ is the transformational strain.[2] Figure 11 shows the relationship between the critical stress for inducing martensite as a function of test temperature ($\frac{d\sigma}{dT}$) for both alloys. It has been previously shown that $\frac{d\sigma}{dT}$ decreases with decreasing Ti content.[26] This holds true with the alloys investigated here in which the NiTi wire (43.93wt% Ti) shows higher stress-induced martensite temperature sensitivity compared to the NiTiPt wire (37.56 wt% Ti). This difference indicates that the thermodynamics of the phase change are different in the NiTi and NiTiPt, which supports the need to further understand the quantum effect that Pt addition has on the transformation and transformation products in NiTiPt.

Lower stress hysteresis has practical application in many products including medical devices. For stent applications, with as-received materials, the radial resistive force (RRF) or the force that resists compression upon loading could be similar for both materials if the upper plateau strengths were matched. However, once deployed inside a blood vessel, stents exert a small force on the vessel wall as they attempt to return to their initial pre-set state. This force is known as a chronic outward force (COF) and could be higher for a NiTiPt alloy stent compared to Nitinol at similar temperatures based on the
varied stress hysteresis behavior seen with the wires. Further work would be necessary to extend the results observed with the wires to more complex geometries in superelastic stents. However benefits of higher COF relative to RRF may include decreased stent migration rates if COF is increased and also capacity to lower RRF for a desired COF. Use of increased COF should be used with caution since it can contribute to increased pressure necrosis and atrophy of the smooth muscle layer leading to vessel perforation.[4, 9]

Linquist et al. found that only slight changes in Pt content greatly affected transformation temperatures, therefore one could readily reduce Pt content in the alloy to obtain appropriate physical properties at desired temperatures.[17] In summary, similar design criteria should be applied when designing a deployable stent from NiTiPt, with some consideration of the difference in stress hysteresis.

As indicated by the discussion above, the general thermo-mechanical behavior of the NiTi and NiTiPt alloys are very similar in nature. Low temperature heat treatments below 450 °C do not drastically differentiate stress-strain behavior between the two alloys. Above 500 °C, the NiTi becomes highly ductile and loses pseudoelasticity driven by second phase precipitate coarsening. The mechanical properties of the NiTiPt alloy after heat treatment are not governed by the creation of a second phase precipitate but rather through the nanometer scale grain size. One distinct difference is the reduction in stress hysteresis during recovery of the NiTiPt alloy. This has practical application by improving response force during unloading. In wire form, the NiTiPt wires do not show major thermo-mechanical property differences compared to Ni-rich NiTi wires. However to truly determine behavior in stent applications, one would have to investigate more
complicated tube structures and stents with advanced strut designs, and also explore cyclic loading effects.
CHAPTER 5
CONCLUSIONS

This work supports the following conclusions:

(1) Within the range of conditions considered here, NiTiPt alloys demonstrate thermo-mechanical recovery behavior nearly identical to Ni-rich NiTi shape memory alloys.

(2) The texture of NiTiPt alloys is similar to NiTi alloys with a <111> fiber texture along the wire drawing axis. The grain size of NiTiPt alloys is on the order of 10 nm’s and is slightly smaller than the grain size in drawn Ni-rich NiTi wires.

(3) The strength and ductility of NiTiPt and NiTi shape memory alloy wires are basically identical when both are given appropriate aging/heat treatments.

(4) The outstanding mechanical properties of NiTiPt alloys are derived in part due to their nanometer scale grain structure. High temperature annealing coarsens the grains in NiTiPt and diminishes the material strength. In contrast to Ni-rich NiTi shape memory alloys, the NiTiPt shape memory alloy studied is not strengthened by precipitation of a second phase.

(5) The recoverable strain limit in textured polycrystalline NiTi and NiTiPt alloys deformed in tension are both close to 6% when elastic strains are removed from recoverable strain calculations.

(6) NiTiPt alloys demonstrate a much smaller stress hysteresis and smaller temperature dependence of the transformation stress compared to NiTi alloys.
REFERENCES


