THERMOMECHANICAL CHARACTERIZATION OF ONE-WAY SHAPE MEMORY NITINOL AS AN ACTUATOR FOR ACTIVE SURGICAL NEEDLE

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ABSTRACT

Needle-based intervention insertion is one of the common surgical techniques used in many diagnostic and therapeutic percutaneous procedures. The success of such procedures highly depends on the accuracy of needle placement at target locations. An active needle has the potential to enhance the accuracy of needle placement as well as to improve clinical outcome. Bending forces provided by the attached actuators can assist the maneuverability in order to reach the targets following a desired trajectory.

There are three major research parts in the development of active needle project in the Composites Laboratory of Temple University. They are thermomechanical characterization of shape memory alloy (SMA) or Nitinol as an actuator for smart needle, mechanical modeling and design of smart needles, and study of tissue needle interaction. The characterization of SMA is the focus of this dissertation.

Unique thermomechanical properties of Nitinol known as shape memory effect and superelasticity make it applicable for different fields such as biomedical, structural and aerospace engineering. These unique behaviors are due to the comparatively large amount of recoverable strain which is being produced in a martensitic phase transformation. However, under certain ranges of stresses and temperatures, Nitinol wires exhibit unrecovered strain (also known as residual strain); which limits their applicability. Therefore, for applications that rely on the strain response in repetitive loading and unloading cycles, it is important to understand the generation of the unrecovered strain in the Nitinol wires. In this study, the unrecovered strain of Nitinol wires with various diameters was investigated, using two experimental approaches: constant stress and uniaxial tensile tests. Moreover, a critical range of stress was found beyond which the
unrecovered strain was negligible at temperatures of 70 to 80°C depending on the wire diameter. Wire diameters varied from 0.10 to 0.29 mm were tested and different ranges of critical stress were found for different wire diameters. The transformation temperatures of different wire diameters at zero stress have been achieved by performing the Differential Scanning Calorimetry (DSC) test. The actuation force created by Nitinol wire is measured through constant strain experiment. X-Ray Diffraction (XRD) study was also performed to investigate the phase of Nitinol wires under various thermomechanical loading conditions.

In summary, the effect of wire diameter on the required critical stresses to avoid the unrecovered strain between first and second cycle of heating and cooling are presented and the results of both mechanical tests are justified by the results obtained from the XRD study.
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CHAPTER 1

INTRODUCTION

1.1. Smart Needle for Prostate Brachytherapy

Prostate cancer is the most common non-cutaneous cancer in American men. In 2009, the American Cancer Society (ASC) has estimated 192,280 new prostate cancer cases and prostate cancer is one of the leading causes of cancer death [1]. A large and increasing number of prostate cancer interventions such as brachytherapy, photodynamic therapy, RF-based thermal ablation, biopsy, and gene therapy involve accurate placement of needles percutaneously. Guiding needle to a precise location inside the prostate is a difficult task. Radiation dose sculpting results determined, 70% tumor foci are located in peripheral zone. This emphasis the importance of constructing the smart active needle[2, 3]. It is an outpatient procedure and in many cases has been contributed to lower long term risks of urinary incontinence and impotence when compared to radical prostatectomy or cryotherapy. Moreover, the procedure is better tolerated by patients with serious comorbidities [4]. It is a non-surgical procedure that, unlike external beam radiation therapy, does not require multiple treatments. The implantation of seeds is also less technically challenging for the surgeon as compared to radical prostatectomy [5].

In brachytherapy (Figure 1.1), radioactive seeds are permanently implanted in the prostate for delivering a tumorocidal dose to the prostate tissues. The challenge in most of the existing needle based procedures is the safe and accurate navigation of the needle through tissue to the desired target. The seeds provide a significant radiation dose to a
relatively small volume, requiring the seeds to be placed accurately to ensure complete treatment. Sensitivity of the urethra and rectal mucosa to radiation are other factors that heighten the need for careful placement of seeds. The design of most needles used clinically today is several decades old. There is an urgent need for development of image- and/or sensor-guided smart needling system for improving this approach.

Figure 1.1. Prostate Brachytherapy – transperineal approach (left), Brachytherapy needle (cannula & stylet) and radioactive seeds (right) [8].

The challenge in most of the existing needle-based procedures is the safe and accurate navigation of the needle through tissue to the desired target. Once the target is reached, the subsequent steps are relatively simple and usually consist of using the needle’s lumen to deliver agents (e.g., drugs or radioactive seeds, or gene), or to capture materials (e.g., biopsy samples), or to place analytical probes. The major challenge in placing the needle at a desired location is due to the needle geometry, and the lack of proper actuation of the needle (the needle is actuated from the proximal end only, about 20 cm away from the tip).

More than 70% of the tumor foci are located in the peripheral zone of the prostate [6, 7]. However, insertion of a needle in the peripheral zone is challenging due to the difficulty in puncturing prostate capsule away from the central axis (Figure 1.2),
inadequacy/non-rigidity in supporting tissue of the prostate, and single point proximal-end actuation of a long slender needle. Additionally, the anterior base of the prostate is inadequately analyzed and treated because of the difficulty in placing conventional needles at the desired location. However, once the suspicious lesions are localized, a self-actuation (active/smart) needle can be steered to the tumor targets and then through the lumen of needle chemicals or therapeutic agents (i.e., drugs, genes, radioactive seeds) can be delivered or a biopsy tool, or an analytical probe can conveniently inserted.

This study focused on the NiTi material characterization which will help the development of smart needle. Needle having distributed actuators and sensors along the needle’s body/shaft for accurate and flexible percutaneous intervention facilitating the precise placement of any therapeutic agents (e.g. radioactive seeds, genes, drugs).

Figure 1.2. Accessing peripheral parts of the prostate with – (a) conventional straight needles, (b) proposed smart needles [8].

Needle-based intervention insertion is one of the common surgical techniques used in many diagnostic and therapeutic percutaneous procedures. An active needle as illustrated in Figure 1.3 has the potential to enhance the accuracy of needle placement as
well as to improve clinical outcome [8]. As can be seen in Figure 1.3, bending forces provided by the attached Nitinol actuators can assist the maneuverability in order to reach the target following a desired trajectory. Avoiding critical organs during insertion and minimizing trauma to patient by decreasing number of needle insertions are among many privileges of using the active needle [8, 9].

![Smart needle design](image)

**Figure 1.3. Smart needle design.**

### 1.2. Research Goals

There are three major research parts in the development of smart needle project in the Composites Laboratory [10-14]. They are: thermomechanical characterization of shape memory alloy (SMA) or Nitinol as an actuator for smart needle, mechanical modeling and design of smart needle, and study of tissue-smart needle interaction. Characterization of NiTi based SMA is the fundamental part of this dissertation and is the main focus of the proposed work. Mechanical modeling and design were performed by using both experimental and numerical approaches. The mechanical behavior of SMA wires is modeled using Brinson model [15]. This behavior has been integrated with the finite element software (ANSYS) as the material properties to predict the active needle deflection by the SMAs’ actuators [11]. Study of tissue-smart needle interaction has
been performed by Datla et al. [12, 13]. Polacrylamide (PA) gel has been used as a prostate phantom material because its stiffness can be tailored to mimic prostate tissue by changing the acrylamide concentration. Tissue damage due to high temperatures of the active needle can be replicated in gel by adding proteins that change color beyond a certain temperature. The prototype model using SMA wire actuators was proposed as shown in Figure 1.4. Using this prototype, the behavior of smart needle inside tissue was investigated.

![Smart needle prototype](image.png)

**Figure 1.4. Smart needle prototype**

Characterizing the thermomechanical properties of Nitinol is an critical part of the needle project, since the strain and stress generated by the Nitinol wires are critical parameters for designing the actuator part of smart needle. Nitinol is a good alternative for various applications such as actuators for biomedical devices (such as orthodontic wires and steerable catheters), aerospace, and structural engineering [16]. As in the case of the research performed by Hutapea and his collaborators [10, 14], Nitinol wire was used as an actuator for a smart brachytherapy needle because of its smaller size and higher power density; i.e. it can produce high amounts of elastic strain and actuating force with smaller wire diameters. It has been shown that a smart needle device has great potential to enhance the accuracy of needle placement and improve clinical outcomes [8, 11]. However, to achieve these improvements it is important to have a reliable and
consistent strain response from Nitinol wires by possibly minimizing the unrecovered strain between actuation cycles [14].
CHAPTER 2
BACKGROUND

2.1. Nitinol Actuator

The term nitinol is derived from its composition and its place of discovery: (Nickel Titanium-Naval Ordnance Laboratory). William J. Buehler [15] along with Frederick Wang [16] discovered its properties during research at the Naval Ordnance Laboratory in 1959 [17]. William Buehler was attempting to make a better missile nose cone, which could resist fatigue, heat and the force of impact. Having found that a 1:1 alloy of nickel and titanium did the job, he took a sample, folded up like an accordion, and showed it to his colleagues. One of them, presumably tested its heat-resistant properties, held a lighter to it. While the potential applications for nitinol were realized immediately, practical efforts to commercialize the alloy did not take place until a decade later. This delay was largely because of the extraordinary difficulty of melting, processing and machining the alloy. Even these efforts encountered financial challenges that were not really overcome until the 1990s, when these practical difficulties finally began to be resolved. The discovery of the shape-memory effect in general dates back to 1932, when Swedish chemist Arne Ölander first observed the property in gold-cadmium alloys. Nitinol has good biocompatibility [18, 19] and good magnetic resonance imaging opacity [20, 21]. Coupled with unique superelasticity and shape memory effect, Nitinol have been widely studied for medical applications such as orthodontic wire, biomedical stents, and steerable catheter [20, 22].
Nitinol wire is one of the most common types of shape memory alloys (SMAs) used in several applications where the wire diameters range from a few microns to a few millimeters. The change in wire diameter can influence thermomechanical properties of Nitinol wires, namely, transformation temperatures and stresses [23]. The amount of unrecovered strain and the required critical stress, which avoid the generation of unrecovered strain in wires, can vary with their diameter. The maximum temperature which wires experience through the heating cycle can influence the amount of unrecovered strain and critical stresses observed due to the change in the state of internal stresses in the wires [24]. Usually the Nitinol wires are Joule-heated by applying an electrical current to induce a martensite phase transformation in the wire that can produce up to 6% recoverable strain in an unconstrained condition or up to 35 N for actuating the needle on constraint situation [25]. Martensite transformation is a reversible solid phase transformation that occurs without diffusion or plasticity.

2.1.1. Nitinol Characteristic Parameters

Nitinol is an equiatomic intermetallic compound of binary alloy of Nickel and Titanium with approximate composition of 50 at. % Ni and 50 at. % Ti. Nitinol has two distinct crystal phases. One is Austenite which exists at high temperature with high symmetric crystal structure (two intermediate single cubic), also is known as parent phase. The other phase is Martensite with lower symmetric crystal structure (orthorhombic or monoclinic) and exists at low temperature. An intermediate R-phase with rhombohedral crystal structure also can exist during cooling from Austenite before
formation of Martensite [26]. Figure 2.1. shows schematic crystal structure of 3 different phases in Nitinol.

![Crystal structures of different Nitinol phases](image)

Figure 2.1. Crystal structures of different Nitinol phases [27].

Martensite phase can be existed in two configurations. Twinned or detwinned Martensite can form based on the state of stress during phase transformation [27, 28]. Figure 2.2 shows schematic orientation of Twinned and Detwinned Martensite. A minor change in chemical composition of Nitinol can cause a noticeable variation in mechanical behavior, transformation temperatures and transformation stresses of Nitinol [29]. Transformation temperatures are the temperatures at which transformation between two phases (Austenite and Martensite) starts and finishes, namely as $A_s$ and $A_f$ (Austenite start and finish respectively), $M_s$ and $M_f$ (Martensite start and finish, respectively). Figure 2.3 shows the characteristic transition temperatures of Nitinol achieved from DSC test. It noticeable that transition temperatures obtained from DSC test are evaluated at 0 stress.
Figure 2.2. Different phases of Nitinol: (a) Austenite (b) low temperature martensite (Twinned Martensite), and (c) stress induced martensite (Detwinned Martensite)[83].

It is applicable to determine the transition temperatures of Nitinol from other methods such as Constant Stress Experiment, which presents the variation of these characteristic temperatures with applied stress as illustrated in Figure 2.4 (a) and the variation of transition temperatures with stress which represents the Nitinol phase diagram is displayed in Figure 2.4. (b). These subjects will be discussed more in detail in Chapters 3 and 4. Also it should be mentioned that the transition temperatures are very dependent on chemical composition, heat treatment and manufacturing process. Minor changes in the mentioned parameters change the transition temperatures drastically.
Figure 2.3. Nitinol transition temperatures ($A_s$, $A_f$, $R_s$, $R_f$, $M_s$ and $M_f$) obtained at zero stress via DSC experiment [27].

Figure 2.4. Determination of transition temperature from (a) constant stress results and (b) variation of transition temperatures with stress [83].
Phase transformation between different phases of Nitinol is also possible by applying stress to Austenite and transform it to Martensite. This process can be performed in isothermal condition which cause the superelastic behavior of Nitinol. Transformation stresses are the starting ($\sigma_{Ms}$) and finishing stresses ($\sigma_{Mf}$) at which the phase transformation occurs between Austenite to Martensite and vise versa ($\sigma_{As}$, $\sigma_{Af}$) in the superelastic behavior. This concept will be discussed in the next section of this chapter. The same as transition temperatures, subscripts $s$ and $f$ represent the start and finish of transformation and $M$ and $A$ represent Martensite and Austenite, respectively [30]. Critical stress are the amount of stress which transform the twinned Martensite to detwinned Martensite. This transformation emerged as strain plateau and has been showed in Figure 2.5. Figure 2.5. shows the schematic for determination of critical stresses in Nitinol phase transformation.

![Figure 2.5. Measuring the critical transformation stresses of Nitinol from isothermal tensile test [84].](image)

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In regards to the imposed thermomechanical conditions such as, state of biased stress (constant stress during thermal cycle) and maximum temperature experienced during thermal cycle, different strain behaviors from Nitinol alloys have been observed. Martensitic phase transformation in Nitinol can produce up to 6% recoverable strain [31,32]. This strain response is influenced by several factors such as transformation temperatures, transformation stresses, the generated strain during phase transformation, the biased stress during thermal cycle, and the maximum temperature of wires during heating cycle.

2.1.2. Shape memory, Superelasticity and Unrecovered Strains

Shape Memory Alloy has its name from its most special characteristic: Shape Memory Effect. The phenomenon of the shape memory effect governed by the thermoelastic behavior of the Martensite phase was widely reported by Kurdjumov and Khandros [33] and also by Chang and Read [34]. Since then, shape memory alloys with various materials composition have been widely used. Wuttig et. al. [35] explored $\text{CO}_2\text{Ni}_{1-x}\text{Ga}_{1+x}$ as possible ferromagnetic shape memory alloys. Oikawa et.al. [36] studied Ni-Co-Al alloy as a promising ferromagnetic shape memory alloy system, while Murray et.al [37] investigated large field induced strain in Ni-Mn-Ga alloys for magnetic application. Among them, Nitinol is the most popular and extensively studied. Nitinol is an alloy of roughly 50% Nickel and 50% Titanium. Phase transformation in Nitinol between Austenite and Martensite and vise versa causes shape memory effect and
superelasticity. Change of temperature and application of stress are two driving forces which can cause phase transformation in Nitinol alloy [38].

2.1.2.1. One-way and Two-way Shape Memory Effects

In one-way shape memory behavior, a temperature change induces high recoverable strain at a certain level of the biased stress. However, when the biased stress is lower than a specific stress level (i.e., the critical stress, \(\sigma_{crs}, \sigma_{crf}\)), a small recovered strain is observed and high unrecovered strain is produced between first and second thermal cycles in one-way Nitinol shape memory wires [39, 10]. The formation of Austenite from detwinned Martensite during a heating cycle causes up to 6% strain in the wire. If the amount of biased stress during thermal cycle is sufficient (higher than \(\sigma_{crf}\)) the detwinned Martensite forms during cooling cycle and complete strain recovery happens. On the other hand, if the amount of biased stress is lower than \(\sigma_{crs}\) then, twinned Martensite forms during cooling cycle and some unrecovered strain appears in the wires. The effect of wire diameters and maximum heating temperature on the strain behavior of one-way shape memory Nitinol have been discussed in detail by Honarvar et.al. [10]. In other terms an SMA exhibits the shape memory effect (SME) when it is deformed, while in the twinned Martensitic phase, and then unloaded, while at a temperature below \(A_s\). When it is subsequently heated above \(A_f\), the SMA will regain its original shape by transforming back into the parent Austenitic phase. The nature of the SME can be better understood by following the thermomechanical loading and thermal cycle as shown in Figure 2.6.
Figure 2.6. Stress-strain-temperature data exhibiting the shape memory effect for a typical NiTi SMA [40].

As demonstrated in Figure 2.6, the thermal cycle on the one way shape memory Nitinol is started from point D. The process of detwinning (mechanical cycle from point B to D) has been performed by manufacturing process. So as-received wires provided by manufacture have initial 5% prestrain. During thermal cycle and by increasing the wires temperature to more than $A_f$, transformation from detwinned Martensite to Austenite occurs. The thermal path from point D to F shows this step of transformation. By cooling the wire to room temperature the wire transforms back to twinned Martensite and unrecovered strain about 5% is generated in the wire. In order to avoid the formation of unrecovered strain due to creation of twinned Martensite the amount of stress has to be sufficient enough to perform the detwinnig process in One-way shape memory Nitinol. This part is simulated in Figure 2.6 from point B to D.
Sometimes a SMA can exhibit repeatable shape changes under no applied mechanical load when subjected to a cyclic thermal load. This behavior is termed two-way shape memory effect (TWSME). The TWSME can be observed in a SMA material which has undergone repeated thermomechanical cycling along a specific loading path (training). Repetition along a loading path for a large number of cycles can induce changes in the microstructure, which causes macroscopically observable permanent changes in the material behavior. Training a SMA refers to a process of repeatedly loading the material following a cyclic thermomechanical loading path until the hysteretic response of the material stabilizes and the inelastic strain saturates two-way shape memory effect which concerns with the existence of large recoverable strains due to the temperature change. In wires treated to show two-way shape memory effect, application of thermal cycle along with negligible amount of stress (about 0 MPa) can cause about 6% recoverable strain in the wires. So a structure using the two-way shape memory effect (TWSME) returns to its initial shape by applying thermal cycle under initial residual stress. This residual stress is applied to the wire during training procedure. Figure 2.7. shows the training procedure for two-way shape memory behavior of Nitinol wire [40]. During the first thermal cycle, only a partial recovery of the strain generated during cooling is observed upon heating with some permanent (unrecoverable or plastic) strain generated during the cycle. A small permanent strain remains after each thermal cycle is completed. The additional permanent strain associated with each consecutive cycle begins to gradually decrease until it practically ceases to further accumulate the TWSME.
The TWSME behavior can also be achieved by adopting different training sequences. A more recent technique that leads to TWSME deals with aging the material under stress in the martensitic state [40]. TWSME is a result of defects introduced during training. These permanent defects create a residual internal stress state, thereby facilitating the formation of preferred martensitic variants when the SMA is cooled in the absence of external loads. If the internal stress state is modified for any reason (e.g., aging at high temperature or mechanical overload), the TWSME will be disturbed.

2.1.2.2. Superelasticity

The superelastic behavior of SMAs is associated with stress-induced transformation, which leads to strain generation during loading and subsequent strain recovery upon unloading at temperatures above $A_f$. A pseudoelastic thermomechanical
loading path generally starts at a sufficiently high temperature where stable Austenite exists, then develops under an applied load to a state at which detwinned Martensite is stable, and finally returns to the Austenitic phase when returned to zero stress state. The typical superelastic behavior of Nitinol is illustrated in figure 2.8.

![Figure 2.8. Typical SMA superelastic loading cycle [40].](image)

Figure 2.8 demonstrates while the amount of stress reaches to the sufficient amount, \( \sigma_{Ms} \), at the temperature higher than \( A_f \), the transformation from Austenite to detwinned Martensite starts and continues up to the point C by reaching to \( \sigma_{Mf} \). The 5% strain is generated in the Nitinol which is observed as smooth slope plateau from points B to C. The process is accompanied by the recovery of the strain due to phase transformation at the end of unloading. The end of the transformation back to Austenite is denoted by the point at which the \( \sigma-\varepsilon \) unloading curve rejoins the elastic region of
Austenite (point F corresponding to stress $\sigma_{Af}$). The material then elastically unloads to A. The forward and reverse phase transformation during a complete superelastic cycle results in a hysteresis, which, in the $\sigma$-$\varepsilon$ space, represents the energy dissipated in the transformation cycle. The transformation stress levels and the size of the hysteresis vary depending on the SMA material and testing conditions. The superelastic behavior in Nitinol alloys makes it very good candidate for catheters, orthodontic wires and aerospace applications. Sometimes this behavior called pseudoelasticity in other references.

### 2.1.2.3. Martensite Detwinning and Critical Stresses

Martensite phase has two crystal configurations. Upon cooling in the absence of an applied load, the crystal structure changes from Austenite to Martensite. The phase transition from Austenite to Martensite is termed the forward transformation. The transformation results in the formation of several Martensitic variants, up to 24 for NiTi. The arrangement of variants occurs such that the average macroscopic shape change is negligible, resulting in twinned Martensite. When the material is heated from the Martensitic phase, the crystal structure transforms back to Austenite, and this transition is called reverse transformation, during which there is no associated shape change. If the cooling cycle from Austenite to Martensite is along with sufficient biased stress, detwinned Martensite forms which cause a significant shape change and recoverable strain. The schematic pattern of crystal change from Austenite to twinned Martensite and twinned Martensite to detwinned Martensite has been illustrated in Figures 2.9. and 2.10 respectively.
Figure 2.9. Temperature-induced phase transformation of an SMA without mechanical loading [40].

Figure 2.10. Formation of detwinned Martensite from Austenite and vise versa by application of thermal cycle at sufficient biased stress [40].

If twinned Martensite forms during cooling cycle in the absence of a sufficient biased stress, a high value of unrecovered strain forms between initial thermal cycles [41, 42]. Based on the biased stress levels, the formation of twinned or detwinned Martensite
can be achieved. Formation of active Martensite variants during detwinning process can influence the unrecovered strain during Martensitic transformation [43, 44]. To prevent the unrecovered strain, the biased stress should be beyond certain critical stress ranges. This range of critical stress refers to the range of stress where detwinning process in Martensite phase occurs [45] which has been shown in Figure 2.10. There are different Martensite variants (twins) in twinned Martensite crystal structure in different directions. These twins are transformed along the imposed stress direction and form the detwinned martensite crystal structure. This alignment can induce Nitinol wires to undergo a large or a small shape recovery strain due to occurrence of partial or complete detwinning [46]. If the biased stress is below a certain value, the detwinning process cannot be completed and the unrecovered strain of up to 10% remains in the wires [47].

Elahinia et al. [48] claimed some unrecovered strain can be developed due to dislocation motion and glide during loading, since inelastic deformation caused by Martensite variant reorientation/detwinning can be released through reverse transformation (detwinned Martensite to Austenite). Shape recovery can be affected by factors such as temperature, annealing condition, grain size, stress mode, and microstructure. The shape memory strain response is impacted by a unique detwinning deformation mechanism in solid crystalline structures. The maximum shape recovery strain is basically determined by two factors: lattice geometry and twinning mode. The magnitude of shape recovery is related to competition between the detwinning process and dislocation generation, which are two different mechanisms responsible for strain behavior of Nitinol wires occur in different wire diameters [49]. The role of stress in
selection of appropriate Martensite variant which can accommodate well with imposed stress is so significant and this can induce Ni-Ti wires to undergo large or small shape recovery strain [46]. There is a critical range of stress for each wire diameter that reorientation process (detwinning) takes place between twinned Martensite to detwinned Martensite [45].

2.1.3. Effect of Wire Diameter on the Thermomechanical Properties of Nitinol Wire

It has been shown that changes in wire diameters affect the thermomechanical properties of Nitinol wires such as transformation temperatures and stresses [24]. In addition, the maximum temperature that wires experienced through the heating cycle influence the unrecovered strain generated in the first and second thermal cycles [25]. Other studies [50-57] have shown that the decrease in the wire diameter causes a decrease in the transformation temperatures and an increase in the transformation stresses. Therefore the decrease in wire diameter could prevent the formation of Martesite from Austenite. Waitz et al. [50] showed that reducing the wire diameter to less than 50 nm decreases the transformation temperatures in nanocrystalline NiTi. Similarly, Fu et al. [51] discovered that by decreasing the Nitinol film size, transformation temperatures (especially $M_s$) decrease and transformation stresses ($\sigma_{ms}$) increase. They argued that decreasing the size prohibits the formation of Martensite from Austenite. In contrast, Frick et al. [52] showed that for Nitinol pillars decrease in wire diameter decreased the critical stresses for both forward (Austenite to Martensite) and reversed transformation (Martensite to Austenite) in superelastic behavior. In other studies, Chen and Schuh [53]
discussed the effect of size on transformation temperatures and stresses of Cu-Al-Ni. They discussed that by decreasing the wire diameter to less than 100 µm, the transformation temperatures, Austenite transformation stresses, stress hysteresis in a mechanical cycle and temperature hysteresis in a thermal cycle are increasing. San Juan et al. [54] claimed that Cu-Al-Ni with diameters of 1.7 µm and 0.9 µm exhibit better superelastic recovery strain compared to Nitinol pillars of the same diameters. They achieved superelastic recoverable strain up to 5% for more than 100 cycles in micro compression test. Liu and Mishnaevsky [55] showed that the formation of Martensite was less probable by decreasing the grain size of Nitinol alloys in nanoscale wire diameters. An et al. [56] showed the effect of wire diameter on the required power to obtain an actuation response, reported in terms of power consumption and response time for force generation. They showed that by increasing the wire diameter, the required power to reach the same temperature in Nitinol wires was increasing. Norwich and Fasching [57] showed the dependency of Nitinol strain response on the wire diameters, wherein decreasing the wire diameter from 0.762 to 0.254 mm significantly improved the consistency (getting the unique total strain in multiple cycles).

It should be noted that most of the studies discussed above, focused on the effect of Nitinol wire diameters on thermomechanical properties, in this case, transformation temperatures and stresses. Moreover, the work done in literatures used relatively small diameters in the range of micrometer to nanometer diameters. However, there is a great need in different applications to study the thermomechanical behavior of Nitinol wire at a relatively larger scale, 0.1 to 1.0 mm in diameter. This range of diameters is critical for a
number of engineering applications, such as actuators in biomedical devices, surgical implants, stents, rivets, couplings, circuit breakers, electronic chart recorder and orthodontic wires [20, 58]. In addition, the effect of wire diameter on transformation temperatures and stresses have been discussed, but very limited number of studies investigated the effect of wire diameter on the unrecovered strain and the range of critical stresses. In summary, the goal of this study is to seek fundamental understanding of the effect of Nitinol wire diameter on the unrecovered strain as well as the critical stresses. Understanding of these parameters would help in determining the required biased stress on the wire during thermal cycle and the maximum heating temperature for a consistent strain response.

2.1.4. Microstructural Investigation of Nitinol Wires

Microstructural analysis also can show the appearance of different crystal orientation of martensite at different conditions based on the thermomechanical history of the wires. The generated crystal phase after thermomechanical cycle can be investigated using various analytical tools.

2.1.4.1. Microscopy Methods

Liu et al. [57] showed how twins behave under stresses and how the microscopic behavior of twins can be correlated to the macroscopic behavior of the materials, like stress-strain curve. They discussed the different ways for controlling or modifying the formation of twins to obtain the desired mechanical behavior from Nitinol. They
performed in-situ TEM (Transmission Electron Microscope) observation during uniaxial tensile test at different strain levels, which accompanied with detwinning process in martensite. Lopez et al. [60] investigated the formation of twinned and detwinned Martensite via TEM analysis. They captured the formation of twinned Martensite plate morphology in the as received alloys via TEM. As received alloy substructure may contain twinned microstructure as well as dislocations within twins. Gall et al. [61] examined the structure and properties of cold drawn Ti-50.1 at% Ni and Ti-50.9 at% Ni shape memory alloy wires through TEM, X-ray pole figure analysis. Except the micro structural analysis, they have done DSC (Differential Scanning Calorimetry) and uniaxial tensile test to capture the mechanical behavior of the Nitinol alloy and correlate the micro structure to its macro mechanical properties. An experimental investigation of the micro and macro-mechanical transformation behavior of polycrystalline NiTi shape memory alloy has been done by Brinson et al. [62]. They investigated the formation of macroscopic twin bands and variant microstructure, effect of cyclic loading, strain rate and temperature in the polycrystalline NiTi shape memory alloy. By use of interference filter on the microscope, they enabled to observe the grain boundaries and Martensite plate formation and growth without needing especial etching or chemical surface preparation. As mentioned in the work of Brinson [62] the surface condition of Nitinol samples can influence the qualitative analysis of different crystal structure. Using strong acidic solution for etching the sample and remove any kinds of oxide layers have been proposed as a part of sample preparation prior to TEM observation or any kind of process which needs shiny and mirror like surfaces [60]. Shabalovskaya et al. [63] have used the
same acidic solution for etching the surface of Nitinol wires and tubes, to evaluate the surface condition of As-cast alloys. The concentration of Ni at the surface through different condition (Aging in boiling water, chemical etching and heat treatment) has been discussed via different methods such as X-ray photoelectron spectroscopy (XPS), Auger electron spectrometry (AES) and SEM. Wagoner et al. [64] used SEM (Secondary Electron Microscope) to highlight the defects present in the single crystal 50.1 atomic percent Ni in Nitinol alloy with the use of a backscatter detector. They have showed an array of low-angle tilt boundaries (twin boundaries) formed in thermal Martensite with different contrast in SEM images. They recognized the formation of twin boundaries in formed self-accommodated Martensite by the contrast between different parts in SEM images. Sehitoglu et al. [65] discussed the potential role of detwinning on the recoverable strain by the theory and also temperature cycling experiment in tension and compression mode. They have captured the image of twin boundaries in Martensite by the use of TEM and evaluate the transformational strain map obtained by x-ray pole figure method. Nam et al. [66] discussed the detection of twinned structure in YBa$_2$Cu$_3$O$_{7-\delta}$ thin films by the use of laser scanning microscopy technique.

### 2.1.4.2. X-Ray Diffractometry (XRD)

X-ray diffraction is a valuable tool for determination of the crystallographic structure of material. The wavelength of X-rays is similar and in the range of the d spacing between planes of atoms in materials. As result, planes of atoms constructively interfere with X-rays and diffraction occurs. Bragg’s law, $n\lambda = 2d \sin \theta$, allows the
calculation of interplanar spacing or d-spacing from the angular location of XRD peaks, \( \theta \). By knowing the wavelength of X-ray source (Cu k\( \alpha \)), the d-spacing is determined and different phases can be introduced based on their XRD patterns.

Conventional X-ray diffraction and micro XRD methods have been used advantageously to study phases in Nitinol wires at room temperature [67-70]. When transformation between Austenite to Martensite or vise versa occurs, XRD pattern shows different peaks occur at different 2\( \theta \) angles and different intensity. New peaks appear, whereas others may disappear or split. Changes will be dependent on the percent of Austenite transforming, the resolution of XRD data and the orientation of the Martensite to the diffractometer. Kheir et al. [71, 72] used x-ray diffraction to identify phases before and after heat treatment of super elastic Nitinol. Thayer et al. [68] used Rigaku X-ray diffractometer with Cu K\( \alpha \) radiation at 40 kV and 20 mA to capture the phase transformation between Austenite and Martensite in superelastic Nitinol used for orthodontics arch wires. They ranked the degree of transformation between Austenite and Martensite based on the intensity of Austenite and Martensite peaks. Iijima et al. [70] have used the micro-XRD technique to determine the phases in two superelastic Nitinol orthodontic wires demonstrate shape memory in the oral environment and super elastic behavior in vivo applications. For analyzing very small areas on orthodontic wires, micro-XRD is a highly convenient technique although XRD is an appropriate technique to identify the phases in nickel-titanium alloy [69, 70] since the diameter of analysis area is limited to about 50 \( \mu \)m.
A conventional XRD is an appropriate technique to identify the phases in Nitinol where a bigger sample surface area is going to be analyzed. Cai et al. [73] have used XRD technique to perform texture evolution during Nitinol Martensite detwinning and phase transformation. In their study, they reported the texture evaluation of a thermally Martensitic wire and an Austenitic wire during deformation by in situ synchrotron X-ray diffraction. Their results reveal information about wire orientation distribution and texture evolution. They demonstrated the Martensite detwinning process with change in intensity of XRD patterns. Shen et al. [74] used X-ray diffraction method to identify phases in the Nitinol wires used for rotary instrument. They have used CuKα monochromatic radiation at 40 kV and tube current of 100 mA. They achieved 3 major peaks for the (110), (200) and (211) atomic planes in Austenite and couple of peaks can be associated to Martensite while they scanned their samples at between 20º -100º, 2θ angles.

Iijima et al. [75] investigated the mechanical properties and phase transformation of commercial superelastic Nitinol orthodontic wires with different transformation temperatures using DSC, three point bending test and micro X-ray diffraction. They have demonstrated the phase transformation between Austenite to Martensite when the temperature is decreased from 37ºC to 2ºC using micro XRD method. They have observed the major peak of (110) for Austenite At the angle of 42.3º in non-loading condition. The (002) and (111) peaks for Martensite phase appeared when the wires bent and the (110) peak for Austenite was shifted about 0.3º to the high-angle side with
decrease in the density. Similar findings were also observed in this study, which will be discussed in the result section.

Iijima et al. [75] have detected the phase changes in Nitinol wires by change in intensity and locations of major Austenite and Martensite peaks and their conversion to each other. Iijima et al. [67] have used XRD to study low temperature phase transformation in Nickel-Titanium orthodontic wires. In their study the XRD measurements were performed in a Bragg-Brentano system employing CuKα radiation at 40 kV and tube current of 50 mA. They attached 20 straight segments of wire lying side by side to create the surface for X-ray scan and then analyzed over the 2θ range from 30 to 130° using a step size of 0.02° with a counting time of 3 s at each step. They have obtained major characteristic peaks of different phases as (110) for Austenite at the 2θ angle of 42.8. They obtained (002) peak for Martensite at the 2θ of 43.92°. The (112) and (300) for R-phase at the 2θ angles of 42.2° and 42.7°, respectively. These peaks can be used as references for interpreting our XRD results in the current study. Kheir, Brantley and Fournelle have used XRD method for analyzing the metallurgical structures of as-received and heat treated stainless steel orthodontic wires [76].

In summary, this study investigates the relationship between macroscopic strain behavior of Nitinol wires and their crystal structures. The correlation of macroscopic strain response with microstructure of wires in each thermomechanical condition has been presented in result and discussion sections.
CHAPTER 3
EXPERIMENTAL METHODS

In this chapter experimental set up for understanding the mechanical responses of the Nitinol wires is discussed in details. These tests are Differential Scanning Calorimetry (DSC), Constant Stress, Uniaxial Tensile Test, and microstructural test tools such as SEM and XRD.

3.1. Differential Scanning Calorimetry (DSC) Test

In order to have the range of transformation temperatures for Nitinol before performing the constant stress experiment and uniaxial tensile test, the DSC tests were performed. Transformation temperatures of Nitinol wires at zero stress were determined with DSC 2920CE machine (TA Instrument, New Castle, DE). Samples were heated to 120ºC at a constant rate of 10ºC/min and then cooled down to -100 ºC. Liquid Nitrogen was used as both the cover and purge gas. Figure 3.1 shows the DSC equipment.
3.2. Constant Stress Experiment

The strain-temperature responses of Nitinol wires were obtained from the constant stress experiment. This test was performed to show the one-way shape memory behavior of Nitinol wires. From this experiment the amount of the unrecovered strain and the total strain were measured for each wire diameter and then the effect of size on the amount of unrecovered strain and critical stresses was investigated.

Figure 3.2 shows the schematic and real pictures of the test setup where Nitinol wire was loaded at constant stress using a weight hanger. The strain response of Nitinol wire during thermal cycle was measured by connecting the weight hanger to a Linear Variable Differential Transducer (LVDT). The LVDT model is, HSD 750-500 manufactured by Macro Sensors (Pennsauken, NJ) with a nominal range of ±12 mm and a scale factor of 0.8 V/mm. The temperature of Nitinol wire was measured with a Omega K-type thermocouple with diameter of 0.076 mm (Omega Engineering, Stamford, CT),
which was attached to the top portion of the Nitinol wire. The contact point between thermocouple and Nitinol wire can influence the reading of the temperature. In order to ensure a proper contact, a conductive paste (Omegatherm 201, Stanford, CT 06907) was applied at the contacts between the Nitinol wire and thermocouple. The output signal of both the thermocouple and the LVDT was collected using SCXI-1321 terminal block (National Instrument, Austin, TX). Please note that the test described is similar to the experimental procedure performed by Churchill and Shaw [27] where they examined the thermo-electro-mechanical response of shape memory alloy (Flexinol wires) during cyclic thermomechanical loading.

Figure 3.2. Constant Stress Test setup (a) Schematic (b) Actual picture
Six different wire diameters ranging from 0.10 mm to 0.29 mm were tested using this method at different biased stresses. Nitinol wires were activated by applying an electrical current produced by a programmable power supply (BK Precision 1696, Yorba Linda, CA) in a step function mode. The electrical current was applied to the wire in a step function for 15 seconds. In the first 3 seconds, the temperature on the wire reached the maximum value of 75ºC and for the next 12 seconds, the wire was kept at this temperature. Due to momentarily disconnection between the tip of thermocoupler and the activated Nitinol wire, the temperature had a fluctuation of ±7ºC during the 12-seconds of heating. The maximum temperature was determined by calculating the average temperature value during this heating period. The wire was then air-cooled to room temperature, around 24ºC for 45 s. The applied current was applied so that the temperature of the wires reached to 70 to 80ºC, please see Table 1. Four cycles of heating and cooling were performed for each wire at each individual biased stress.

3.3. Uniaxial Tensile Test

The stress-strain response of Nitinol wires was obtained by performing tensile test at room temperature in order to determine the range of critical stress of the detwinning process. An Instron Mini-55 (manufactured by Artisan Technology Group, Champaign, IL) tensile test machine was used with a 10 N load cell and a strain rate of 4x10⁻⁵ mm/s (displacement control). Figure 3.3 shows the Uniaxial Tensile test set up.
Figure 3.3. Uniaxial Tensile Test set up

The test was performed in an isothermal condition at room temperature. The Nitinol wires with the same length of 100 mm were preconditioned and then tested. The preconditioning temperature performed prior to the tensile test had a significant role on the appearance of stress plateau occurs during the Martensite detwinning process [77, 50].

The following steps were followed in the preconditioning procedure to ensure the formation of twinned Martensite in Nitinol wires. First, the wires were heated in a range of 70 to 80°C. This range of temperature is the same range of heating temperature in the constant stress experiment. Please note that for 0.24 mm wire, a stress plateau at higher strains during the tensile test was not observed when the preheating range of 70 to 80°C was applied. For this reason, a preheating range of 120 to 130°C was used only for the 0.24 mm wire. The constant stress during the preheating procedure was kept at a low level, i.e., the weight of LVDT rod and hanger. The constant stress level is 48.15 MPa for 0.10 mm wires and 9.10 MPa for 0.24 mm wires. The heating time was 15 s. At this
point, the detwinned Martensite crystal structure changes to the Austenite crystal structure. The wires were then cooled to the room temperature (24°C) at a negligible biased stress level. After this process, the Austenite structure transforms to a mixture of R-phase and twinned Martensite structure. In order to ensure the formation of fully twinned Martensite crystal structure prior to the tensile test, the wires were placed in an environmental chamber at -40°C for an hour at zero stress.

Finally, in the tensile test, it was possible to change the twinned Martensite (formed after preconditioning procedure) into the detwinned Martensite using an external load. The ranges of stress plateau ($\sigma_{crs T}$ and $\sigma_{crf T}$) were determined by drawing tangential lines at the linear parts of loading and unloading curve, following the procedure described in [50].

### 3.4. Microstructural Investigation Methods

#### 3.4.1. SEM and EDS

Nitinol wires with different treatment conditions (heat treated, mechanically treated) are prepared to be analyzed with backscatter and secondary SEM detectors in terms of surface morphology and detection of twinned and detwinned Martensite. There are different kinds of detectors available in the SEM equipment in the College of Engineering Nano Instrumentation Center such as secondary detector (SED), backscatter detector (BSD), or energy dispersive spectroscopy (EDS) detector. SED reveals information about the surface of material (topography of surface). Surface Morphology such as, shape and size of precipitations, voids, inclusions, cracks and surface roughness
can be observed using SED detector in SEM. BSD demonstrates information about the bulk of a sample. For example, BSD can recognize different phases of the material based on the difference in atomic density. EDS is used to conduct elemental analysis and provide a compositional map of the sample. These detectors have been used in this research. Figure 3.4. shows the Scanning Electron Microscopes (FEI Quanta 450FEG SEM) equipped with the latest Energy Dispersive Spectrometer (Oxford Aztec Energy Advanced EDS System) used for surface study of Nitinol wires.

The following steps have been performed to prepare each sample. Nitinol wire with diameter of 0.19 mm were heated to 75 °C in the constant stress experiment set up with constant stress of 13.33 MPa and cooled down to room temperature by convection cooling. They were then cooled to -40 °C in a separate cooling chamber to assure the formation of 100% twinned Martensite. For mechanically treated samples, the wire were loaded in uniaxial tensile test machine up to 400 MPa to transform from twinned Martensite to detwinned Martensite and then unloaded. Similar to the works of Lopez and Shabalovskaya et al. [78, 79], an acidic solution with the composition of 1HF + 4HNO₃ + 5H₂O has been used to etch the samples and remove oxide layers on the surface of the wires before placing them in the SEM chamber. Table 3.1 shows the multiple steps of sample preparation and consequent formed phase after each step for As-received, heat treated and mechanically treated samples.
Figure 3.4. Scanning Electron Microscopes equipped with the latest Energy Dispersive Spectrometer.

Table 3.1. Multiple sample preparation steps and consequent formed phase after each step

<table>
<thead>
<tr>
<th>Sample condition</th>
<th>Step 1</th>
<th>Step 2</th>
<th>Step 3</th>
<th>Step 4</th>
<th>Step 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>Etched in the acidic solution</td>
</tr>
<tr>
<td>Heat treated</td>
<td>Heat up to 75 °C</td>
<td>Cooled to room temperature</td>
<td>Cooled to -40 °C Fully twinned martensite</td>
<td>NA</td>
<td>Etched in the acidic solution</td>
</tr>
<tr>
<td></td>
<td>Austenite</td>
<td>Mixture of twinned and R-Phase</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mechanically</td>
<td>Heat up to 75 °C</td>
<td>Cooled to room temperature</td>
<td>Cooled to -40 °C Fully twinned martensite</td>
<td>Apply uniaxial tensile load up to 400 MPa</td>
<td>Etched in the acidic solution</td>
</tr>
<tr>
<td>treated</td>
<td>Austenite</td>
<td>Mixture of twinned and R-Phase</td>
<td></td>
<td>and unload Detwinned martensite</td>
<td></td>
</tr>
</tbody>
</table>


3.4.2. XRD Method

For studying the effect of microstructure on the strain response of Nitinol wires, the Nitinol wires are thermally and mechanically treated to generate different thermomechanical wire conditions and crystal structures. For this purpose, Constant stress (Figure 3.2) and Tensile test (Figure 3.3) setups along with an environmental chamber have been used to create the desired thermomechanical preconditions. Table 3.2 and Figure 3.5 shows the different thermomechanical preconditions performed on all Nitinol wires with four different diameters. It should be mentioned that in all wires, the amount of biased stress during heating cycle is negligible and lower than the range of critical stress for formation of detwinned Martensite. After preconditioning the wires they are cut with sharp pliers to the length of 3-4 cm and placed to the sample holder of XRD Bruker APEX II DUO X-ray diffractometer (Figure 3.6).

Table 3.2. Wire preconditioning procedure and generated crystal structure prior to XRD test. The crystal structure before conditioning is Detwinned Martensite.

<table>
<thead>
<tr>
<th>Case No.</th>
<th>Wire Diameter (mm)</th>
<th>Heating Cycle (°C)</th>
<th>Cooling Cycle (°C)</th>
<th>Mechanical Treatment</th>
<th>Crystal Structure after Conditioning</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Received</td>
<td>0.15, 0.19&lt;br&gt;0.24, 0.29</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>Detwinned Martensite</td>
</tr>
<tr>
<td>1</td>
<td>0.15, 0.19&lt;br&gt;0.24, 0.29</td>
<td>70-80ºC in CS</td>
<td>RT, CS</td>
<td>N.A</td>
<td>R-Phase</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Detwinned Martensite</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.15, 0.19&lt;br&gt;0.24, 0.29</td>
<td>120-130ºC in CS</td>
<td>RT, CS</td>
<td>NA</td>
<td>R-Phase</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Detwinned Martensite</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.15, 0.19&lt;br&gt;0.24, 0.29</td>
<td>70-80ºC in CS</td>
<td>RT in CS / -40ºC in CC</td>
<td>NA</td>
<td>Twinned Martensite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Detwinned Martensite</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.15, 0.19&lt;br&gt;0.24, 0.29</td>
<td>70-80ºC in CS</td>
<td>R.T in CS / -40ºC in CC</td>
<td>5% Strain in UTT Negligible Strain</td>
<td>Detwinned Martensite</td>
</tr>
</tbody>
</table>

RT: Room Temperature, CS: Constant Stress, CC: Cooling Chamber, UTT: Uniaxial Tensile test
Figure 3.5. Nitinol wires preconditioning flow chart (more details in Table 3.2).

Figure 3.6. XRD Bruker APEX II DUO
The XRD equipment is designed for structural determination of single crystals of small molecules. The diffractometer combines a molybdenum X-ray source for high throughput and charge density experiments, and a copper source for absolute configuration and protein screening. The APEX 2 software has a graphical user interface that guides the user through the complete experiment and analysis, from data acquisition through data collection, integration and scaling to structure solution and refinement and report generation. The wires are scanned between 25º to 105º, 2θ angle. The duration of test for scanning the 80º is about 20 minutes with scanning speed of 4 angle/min. The size of X-ray beam is about 0.12 mm diameter which cause some difficulties in scanning the wires with diameter of less than 0.15 mm. To avoid the strain hardening effect at the cutting locations of the wires, the midpoint of cut wire segment is set to be scanned by x-ray beam. The CuKα, of 100KV and 10mA has been used as X-ray source in this study. Figure 3.6 demonstrate the XRD equipment exist in the Department of Chemistry at Temple University.

To analyze the XRD results, they have been plotted with Matlab. Guassian distribution \( f(x) = a \exp\left(\frac{-(x-b)^2}{2\sigma^2}\right) + d \) has been used to curve fit the XRD results and the exact position and intensity of outstanding peaks in XRD pattern are achieved. The parameters a, b and c demonstrate the peak’s height, position and the width of the peak respectively. The noises have been eliminated by subtracting the background peaks of X-ray chamber from the samples peaks. Since in this study the detection of phases is based on large, outstanding peak occurs around the 2θ angle of 40-45, the portion of each
XRD pattern between 2θ angle of 35-50º have been plotted separately in each case study for comparison of crystal structure in different wire diameters.
4.1. DSC Results

By performing the DSC test, all transition temperatures of Nitinol wires consist of $M_f$, $M_s$, $R_f$, $R_s$, $A_s$ and $A_f$ have been determined. The DSC results of 0.10 and 0.19 mm diameters of Nitinol wires have been demonstrated in Figure 4.1. The transformation temperatures achieved from DSC method for all 5 diameters from (0.10 to 0.29 mm) have been expressed in Table 4.1.
Figure 4.1. DSC results of (a) 0.10 mm and (b) 0.19 mm Nitinol wires

Table 4.1. Stress free transformation temperatures determined from the DSC test for various wire diameters in as received condition.

<table>
<thead>
<tr>
<th>Wire Diameter (mm)</th>
<th>$M_f$ (°C)</th>
<th>$M_s$ (°C)</th>
<th>$A_s$ (°C)</th>
<th>$A_f$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>4</td>
<td>31</td>
<td>58</td>
<td>67</td>
</tr>
<tr>
<td>0.12</td>
<td>-11</td>
<td>29</td>
<td>54</td>
<td>65</td>
</tr>
<tr>
<td>0.15</td>
<td>-18</td>
<td>26</td>
<td>52</td>
<td>64</td>
</tr>
<tr>
<td>0.19</td>
<td>-33</td>
<td>15</td>
<td>42</td>
<td>75</td>
</tr>
<tr>
<td>0.24</td>
<td>-30</td>
<td>12</td>
<td>42</td>
<td>64</td>
</tr>
<tr>
<td>0.29</td>
<td>-32</td>
<td>15</td>
<td>37</td>
<td>67</td>
</tr>
</tbody>
</table>
It can be seen that for the wires heated above 75°C, a complete transformation to Austenite occurs; \( A_f \) is less than 75°C. For the wires cooled to -40°C transforms into a complete Martensite phase; \( M_f \) is higher than -40°C. These observations were used to choose the preconditioning temperature prior to the tensile test.

### 4.2. Constant Stress Experiment Results

The purpose of constant stress experiment was to obtain strain-temperature response of Nitinol wires under a constant biased stress. Transformation temperatures were determined by drawing tangential line to the plateau parts of the strain-temperature response at each of the constant stresses of each wire. The typical result of constant stress experiment and the method to extract 4 transition temperatures has been shown in Figure 4.2.

![Figure 4.2. Obtaining transition temperatures from strain vs. temperature plot](image-url)
By changing the biased stress in each wire diameter, the phase diagram of Nitinol wires was obtained, as shown in Figure 4.3. This figure shows the phase diagram of Nitinol wire diameters from 0.10 to 0.19 mm.

Figures 4.4 and 4.5 shows a typical strain-temperature response of Nitinol wires with 0.19 and 0.29 mm diameter under various biased stresses, and heated to the temperature range of 70 to 80°C. For 0.19 mm wire diameter under a biased stress of 48.15 MPa as in Figure 4.4(a), a large value of unrecovered strain was observed between the first and second thermal cycles. It was concluded that the biased stress was below the range of critical stress. When the biased stress was increased to 202.60 MPa as in Figure 4.4(b), a negligible unrecovered strain was observed indicating that the biased stress was higher than the range of critical stress. Similar trends were observed in smaller diameters of 0.10, 0.12 and 0.15 mm. For larger diameter of 0.29 mm under low biased stress of 13.6 MPa as in Figure 4.5(a), a small unrecovered strain (about 0.5%) was observed. By increasing the biased stress to 240.50 MPa, this small amount of unrecovered strain became negligible as shown in Figure 4.5(b).

Based on the constant stress experiment, within the heating range of 70 to 80°C, two categories of wires were defined and discussed as below. First category was the wire diameters in which the unrecovered strain was dependent on the biased stress (i.e., 0.10, 0.12, 0.15 and 0.19 mm) at the temperature range of 70 to 80°C. In these wire increasing the applied stress decreased the unrecovered strain after passing the starting critical stress. Figure 4.6 shows the relationship between the unrecovered strain and the biased stress. Based on the amount of the unrecovered strain shown in Figure 4.6 (a), the stress
value at which unrecovered strain begins to drop can be considered as the starting critical stress ($\sigma_{crsC}$) and the value of stress which causes a negligible unrecovered strain can be considered as the finishing critical stress ($\sigma_{crfC}$).

The critical stress ranges achieved from constant stress experiment are summarized in Table 4.2.

Table 4.2. The critical stresses for detwinning process in Martensite phase determined from constant stress experiment at the heating range of 70 to 80°C.

<table>
<thead>
<tr>
<th>Diameter (mm)</th>
<th>$\sigma_{crs}$ (MPa)</th>
<th>$\sigma_{crf}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>86.40</td>
<td>99.10</td>
</tr>
<tr>
<td>0.12</td>
<td>100.62</td>
<td>121.84</td>
</tr>
<tr>
<td>0.15</td>
<td>108.60</td>
<td>124.20</td>
</tr>
<tr>
<td>0.19</td>
<td>120.00</td>
<td>140.80</td>
</tr>
<tr>
<td>0.24</td>
<td>N.A</td>
<td>N.A</td>
</tr>
<tr>
<td>0.29</td>
<td>N.A</td>
<td>N.A</td>
</tr>
</tbody>
</table>
Figure 4.3. Variation in transformation temperatures with applied constant stress for Nitinol wires with diameters of (a) 0.10 mm, (b) 0.12 mm, (c) 0.15 mm, (d) 0.19 mm.
Figure 4.4. Strain response of 0.19 mm wire diameter under constant stress of (a) 48.15 MPa and (b) 202.60 MPa.
Figure 4.5. Strain response of 0.29 mm wire diameter under constant stress of (a) 13.60 MPa and (b) 240.50 MPa.
Figure 4.6. Variation in unrecovered strain with applied constant stress for Nitinol wires with diameters of (a) 0.10, 0.12, 0.15, 0.19 mm and (b) 0.24 and 0.29 mm.
It can be observed in Table 4.2 and Figure 6 (a) that by decreasing the diameter of Nitinol wires the starting and finishing critical stress was decreased. In the second category of wires, the unrecovered strain was independent from biased stress (0.24 mm and 0.29 mm) at temperature range of 70 to 80°C. In these wires, the unrecovered strain with respect to the total strain was much smaller than the values observed in the other diameters discussed in the previous sentences. As can be seen in Figure 4.6(b) the amount of unrecovered strain was relatively small. By increasing the amount of biased stress there was no sharp drop in the amount of unrecovered strain. This was an indirect method of measuring the critical stresses of different diameters.

It should be mentioned that there were differences between transition temperatures obtained from the DSC and the constant stress experiments. In the DSC test, the transformation temperatures were obtained from the change in the rate of heat flow of the sample during heating and cooling at zero stress, while the stress free transition temperatures from the constant stress experiment were achieved by a linear extrapolation to zero stress which can contain errors and inaccuracy due to the reading of temperature in constant stress experiment and experimental errors.

Standard deviation of ±15 MPa was included in the critical stress results (Table 3) due to the variation of weight of hanger and LVDT rod as a constant minimum load. By increasing the amount of constant stress in each wire diameter with application of the same amount of current (similar heating temperature, same diameter at different stress level), different strain-temperature responses were achieved. According to the phase diagrams of Nitinol (Figure 4.3), achieved from constant stress experiment and DSC test
for each wire diameter (Table 4.1), the whole cycle of transformation from Martensite to Austenite in heating has been performed since the wires were heated higher than 70°C which was beyond the Austenite finish temperature achieved from both methods. During cooling from high temperature to room temperature (22°C), based on the constant stress (biased stress), the transformation from Austenite to Martensite at very low stress was completed (see Figure 4.3). During cooling, Austenite reverts back to Martensite and based on the amount of biased stress twinned or detwinned Martensite could be formed [80, 81].

By increasing the range of the maximum temperature in the heating cycle from 70 -80°C to 120 -130°C range, a high unrecovered strain was observed in wire diameter of 0.24 mm. Figure 4.7 demonstrates the high unrecovered strain for 0.24 mm wire at a low biased stress (9.1 MPa) while heated to a high temperature (about 120±5°C).

Figure 4.7. Strain vs. temperature response for 0.24 mm diameter Nitinol wire at 9.1 MPa constant stress heated to high temperature range between 120 to 130°C.
4.3. Uniaxial Tensile Test

When Nitinol wire was loaded with the initial crystal structure of twinned Martensite, beyond elastic deformation, a plateau was observed in stress-strain plot due to the reorientation of twinned to detwinned Marteniste. A complete Martensite reorientation can produce up to 6% shape memory strain in Nitinol wires. The starting and finishing stresses ($\sigma_{crsT}$, $\sigma_{crfT}$) of small slope plateau are the range of critical stresses. Length of plateau was also affected by the amount of reorientation process, which was related to the maximum preconditioning temperature. Comparison within each range of temperature, between different diameters, and between different preconditioning temperatures in the same diameter, was performed. It has been observed that by increasing the wire diameter the critical stresses due to Martensite detwinning were increased. By increasing, the preheating temperature to 120 to 130°C, the critical stress and the length of strain plateau have been increased in each wire diameter. Table 4.3 shows the $\sigma_{crsT}$ and $\sigma_{crfT}$ achieved from uniaxial tensile test (the ranges of stress plateau) for two different preconditioning temperatures.
Table 4.3. Starting and finishing critical stresses determined from isothermal tensile test for the five different wire diameters (0.10 to 0.24mm) at two preconditioning procedure

<table>
<thead>
<tr>
<th>Diameter (mm)</th>
<th>Preconditioning Temperature (70 ºC -90ºC)</th>
<th>Preconditioning Temperature (120 ºC -140ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma_{crs}$</td>
<td>$\sigma_{crf}$</td>
</tr>
<tr>
<td>0.10</td>
<td>100</td>
<td>140</td>
</tr>
<tr>
<td>0.12</td>
<td>115</td>
<td>150</td>
</tr>
<tr>
<td>0.15</td>
<td>120</td>
<td>130</td>
</tr>
<tr>
<td>0.19</td>
<td>125</td>
<td>135</td>
</tr>
<tr>
<td>0.24</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

Results of the tensile tests are presented in Figures 4.8 and 4.9. As shown in Figure 4.8, a stress plateau was observed for 0.10 to 0.19 mm wires. Please note the wires were preconditioned at 70°C to 80°C. It could be seen in this figure that the ranges of critical stress increased as the diameter increased. However the stress plateau was not noticeable in 0.24 mm wire. This could be the effect of heating temperature on the Martensite reorientation process. Interestingly, as shown in Figure 4.9, when the preconditioned temperature at 120 to 130°C, the stress plateau was observed for all wire diameters.
Figure 4.8. Stress vs. strain response of Nitinol wires preconditioned between 70 to 80°C.

Figure 4.9. Stress vs. strain response of Nitinol wires preconditioned between 120 to 130°C.
In short, for all wires except the 0.24 mm wires that were preconditioned at 70 to 80°C range, the critical stresses were at about the same value. The difference between the maximum and the minimum reported values for both starting and finishing critical stress ($\sigma_{crsT}$ and $\sigma_{crfT}$) was between 5 to 25 MPa. It was also observed that as the wire diameter increased, the starting critical stress ($\sigma_{crsT}$) increased. However, a similar conclusion cannot be taken for the finishing critical stress ($\sigma_{crfT}$).

4.4. Comparison of Constant Stress and Uniaxial Tensile Test Results

The comparison between the critical stresses ($\sigma_{crsC}$ and $\sigma_{crfC}$) achieved from the constant stress experiment and the uniaxial tensile test ($\sigma_{crsT}$ and $\sigma_{crfT}$) both at heating range of 70-80°C is presented in Figures 4.10 and 4.11. Please note that 70-80°C was the heating range in the constant stress experiment while it was the preconditioning heating range in the uniaxial tensile test.

In Figure 4.10 the starting critical stresses ($\sigma_{crsC}$ and $\sigma_{crsT}$) obtained from constant stress experiment and uniaxial tensile test were found to be similar in most wires; the largest difference was 16 MPa for 0.12 mm wire. The comparison of 0.24 mm and 0.29 mm wires was not plotted in Figures 4.10 and 4.11 because the plateau was not observed in the preconditioning temperature for those diameters. It was observed from Figure 4.11 that there was a slight difference in the finishing critical stress ($\sigma_{crfC}$ and $\sigma_{crfT}$) obtained from both test methods for 0.10 mm. The inaccuracy of reading where the unrecovered strain merge to zero in the constant stress experiment may contribute to this difference.
Figure 4.10. Comparison of starting critical stress determined from constant stress experiment and uniaxial tensile test for Nitinol wire diameters of 0.10, 0.12, 0.15 and 0.19 mm.

Figure 4.11. Comparison of finishing critical stress determined from constant stress experiment and tensile test for Nitinol wire diameters of 0.10, 0.12, 0.15 and 0.19 mm.
and so the standard deviation of ±15 MPa can be considered for critical stresses
were achieved from constant stress experiment.

In constant stress experiment for 0.10 mm to 0.19 mm wires at the heating range
of 70°C to 80°C, the strain response is due to the transformation from the detwinned
Martensite (initial phase) to the Austenite during heating cycle and transformation of
Austenite to twinned Martensite and then detwinning process during cooling cycle [48,
80]. This cyclic phase transformation can produced up to 5% recoverable strain at stress
levels higher than or equal to the critical stress which accommodate the detwinning
process during cooling cycle to the room temperature. For 0.24 mm and 0.29 mm wires,
the detwinning process did not take place at 70 to 80°C due to an incomplete
transformation from detwinned Martensite to Austenite. Neither the stress plateau in
tensile test nor the sharp drop in the amount of the unrecovered strain was observed.

4.5. Effect of Heating Temperature on Strain Response of Nitinol Wires

It is evident from the above discussion in Table 4.3 that temperature has a
significant effect on the strain response of Nitinol alloy (Table 4.3). This effect of
temperature was different for different wires due to the difference in the heat transfer rate
of each wire. It is observed in this work that increased the temperature increased the
material transformed from the detwinned Martensite phase to the Austenite phase at 120
to 130°C.
The reorientation process in Martensite phase occurs due to the movement of twin boundaries towards the direction of the applied stress, which form detwinned Martensite [57, 82]. If this process is incomplete, unrecovered strain will be generated in the wires since the final phase of the material is not detwinned Martensite [82, 40]. It appears that in the heating cycle of wire diameters of 0.10 to 0.19 mm in the range of 70 to 80ºC the whole portion or approximately large volume amount of material were transformed from detwinned Martensite to Austenite. Consequently during cooling the material was transformed from Austenite to twin Martensite due to the absence of large amount of stress. High amount of unrecovered strain was generated since there were different phases before heating the wire and after cooling back to the room temperature.

On the other hand, it was observed that for 0.24 and 0.29 mm wires, the transformation of detwinned Martensite to Austenite was not complete at the heating range of 70 to 80ºC. Consequently some volumes of detwinned Martensite are not transforming to Austenite during the first heating cycle and will remain as detwinned Martensite after cooling to the room temperature. While the portion of initial detwinned Martensite transformed to twinned Martensite after a cooling cycle to the room temperature. Lower unrecovered strains were generated due to the small differences between the initial and final phases.

By increasing the heating range to 120 to130ºC, the residual fraction of detwinned Martensite transformed completely to Austenite during heating. Therefore, similar to smaller diameter (0.10 to 0.19 mm) at lower heating range, high values of unrecovered
strain were observed between the first and second thermal cycles for all wire diameters since no untransformed detwinned Martensite remained in the wires.

The presence of stress plateau in uniaxial tensile test depends on the amount of twinned Martensite in the wires before loading. Since the purpose of preheating in tensile test was to ensure complete formation of twinned Martensite in the wires, the preheating temperature plays an important role. Based on the above discussion for 0.10 to 0.19 mm wires at the heating range of 70 to 80°C, considerable fraction of twinned Martensite were formed after cooling cycle. Therefore the stress plateau was observed in these wires during the tensile test. In contrast, for larger wire diameter at a lower heating range the stress plateau was not observed. It is conjectured that the non existence of stress plateau is due to a negligible fraction of twinned Martensite but a high fraction of residual detwinned Martensite. In summary, increasing the heating temperature to the range of 120 to 130°C generated a high fraction of twinned Martensite after cooling resulting in distinctive stress during the tensile test.

4.6. Microstructural Results

4.6.1. SEM and EDS

Since the EDS results have been used as complementary information to confirm the chemical composition of Nitinol wires and is not directly related to the theory followed in this work (the effect of wire diameter on thermomechanical behavior of Nitinol wires), these results have been presented in Appendix 2.
The primary goal of using SEM was to detect twinned and detwinned bands in Martensite phase. As two kinds of detectors, SED (secondary electron detector) and BSD (Back scatter detector) were existed in nano-instrumentation center of Temple university, analysis of free surfaces of 0.19 mm wire diameter prepared and preconditioned according to table 3.1. have been demonstrated in figure 4.12 to 4.14.

As discussed in Section 4.3., the reorientation process takes place between twinned Martensite and detwinned Martensite by applying uniaxial tensile stress. The orientation of martensite variant from twin to detwin emerge as a plateau in the tensile test results. As mentioned in part 4.3 the Nitinol wires are heated from as-received condition (detwinned Martensite) to Austenite and cooled back to room temperature (mostly twinned Martensite) in constant stress set up. To assure the whole crystal structure was twinned Martensite before performing the tensile test, the wires were cooled to -40 °C in a separate cooling chamber under zero stress. For observing the detwinning process in these wires, they were loaded in uniaxial tensile test machine up to around 350 MPa. The stress plateaus have emerged around 100 - 120 MPa for both wires with the length of about 1.5% strain. By comparing these results with Figures 4.8 and 4.9, it can be concluded that the complete detwinning process have not been performed in these wires.
This can be due to the fact that wires have been heated up to just 75°C in a heating cycle and a whole transformation between detwinned Martensite to Austenite has not happened. Since the $A_f$ temperature of these wires are reported to be less than 75°C based on DSC results (Table 4.1) and constant stress experiment (Figure 4.3), incomplete
transformation from detwinned Martensite to Austenite can be due to insufficient heating, so some part of the Nitinol wire dose not transform from detwinned Martensite to Austenite in heating cycle and consequently not converted to twined Martensite in cooling. The result of uniaxial tensile test for two mentioned wire have been shown in Figure 4.15, along with SEM images of the beginning and the end of tensile test.

![Figure 4.15. Tensile test results of first and second wire.](image)

As it is clear from the figures 4.12 to 4.15, detection of twinned and detwinned band from two kinds of existed detectors were not possible and XRD as an alternative method to detect the type of crystal structure has been implemented.

### 4.6.2. XRD Results

XRD is a valuable tool for determination of the crystallographic structure of material. The wavelength of X-rays is similar and in the range of the spacing between planes of atoms in materials. As result, planes of atoms constructively interfere with X-
rays and diffraction occurs. Bragg’s law (Equation 1) allows the calculation of interplanar spacing or d-spacing from the angular location of XRD peaks, θ. By knowing the wavelength of X-ray source (Cu kα), the d-spacing is determined and different phases can be introduced based on their XRD patterns. \[ n\lambda = 2dsin\theta \quad (1) \]

The transformation temperatures of the wires were measured using DSC. The results are presented in Table 4.1, which was used to predict the generated crystal structure after each conditioning step. According to Table 4.1, heating the wire in the range of 70-80ºC has to be high enough to transform the detwinned Martensite crystal structure (as-received condition) to Austenite. A cooling cycle to room temperature between 22 to 25ºC causes the formation of R-phase, i.e., intermediate phase between Austenite and Martensite, from Austenite since the temperature does not go low enough to reach \( M_s \). Definitely cooling the wires in cooling chamber to -40ºC transforms the R-phase to Martensite phase in Nitinol wire. Table 3.1 shows the preconditioning steps before performing the XRD test. The XRD results have confirmed the formation of expected phases after each thermomechanical conditions described in each case in Table 3.1.

Figure 4.16 (a) shows the whole XRD pattern of 4 diameters as-received wires between 25º to 105º (2θ). The XRD patterns of as-received wires show that these wires have the same crystal structure of Detwinned Martensite. Figure 4.16 (b) shows characteristic peaks in the range of 35 to 50º (2θ) since detection of different phases occurs between 40º to 45º (2θ).
Table 4.4 illustrates the values for $a$, $b$, and $c$ parameters of Gaussian curve fitting for Figure 4.16 (b). The decrease in intensity of peak (a values) in 0.15 mm can be related to small diameter of the wire in regard to the size of X-ray beam (0.12 mm) which caused lower reflection due to smaller contact area. From Figure 4.16 and Table 4.4, it can be concluded that all four as-received diameters have the same crystal structure of detwinned Martensite. With comparison to the other studies [67-76], it can be concluded that the major part of initial existed phase in all four wire diameters are detwinned Martensite with peaks at the 2$\theta$ angle of 43.5°, which is the characteristic peak of Martensite phase.

Table 4.4. Gaussian’s height, position, and width of outstanding peaks for XRD patterns of as-received Nitinol wires.

<table>
<thead>
<tr>
<th>Wire Diameter (mm)</th>
<th>Height (a)</th>
<th>Position (b)</th>
<th>Width (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>505.7</td>
<td>43.59</td>
<td>0.21</td>
</tr>
<tr>
<td>0.19</td>
<td>615.318</td>
<td>43.53</td>
<td>0.231</td>
</tr>
<tr>
<td>0.24</td>
<td>652.053</td>
<td>43.65</td>
<td>0.217</td>
</tr>
<tr>
<td>0.29</td>
<td>684.090</td>
<td>43.65</td>
<td>0.22</td>
</tr>
</tbody>
</table>
Figure 4.16. (a) Complete XRD pattern of as-received wires; (b) XRD patterns of 0.15, 0.19, 0.24 and 0.29 mm wires.
Case 1 preconditioning was applied in investigating the strain behavior of Nitinol wires of various sizes subjected to thermal cycle of 70-80°C (heating cycle). As mentioned in section 4.2, the macroscopic strain response of all wires divided into two categories (wire diameters smaller and larger than 0.19). Figure 4.17 shows the XRD patterns of the Nitinol wires after preconditioning using Case 1. Figure 4.17 (a) shows the whole XRD pattern of four diameters between 25 to 105° (2θ). Figures 4.17(b) demonstrate the XRD patterns between 35 to 50 (2θ) of 0.15, 0.19, 0.24 and 0.29 mm wire diameters, respectively. Table 4.5 illustrates the values for \(a\), \(b\), and \(c\) parameters of Gaussian curve fitting for Figure 4.17(b).

<table>
<thead>
<tr>
<th>Wire Diameter (mm)</th>
<th>Height (a)</th>
<th>Position (b)</th>
<th>Width (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>573.549</td>
<td>42.41</td>
<td>0.2</td>
</tr>
<tr>
<td>0.19</td>
<td>1140</td>
<td>42.33</td>
<td>0.176</td>
</tr>
<tr>
<td>0.24</td>
<td>599.117</td>
<td>43.63</td>
<td>0.219</td>
</tr>
<tr>
<td>0.29</td>
<td>689.865</td>
<td>43.65</td>
<td>0.228</td>
</tr>
</tbody>
</table>

As it is presented in Figure 4.17 and Table 4.5, there are different XRD patterns for diameters of 0.15 and 0.19 mm and diameters of 0.24 and 0.29 mm. The generated crystal structure for the diameters less than 0.19 mm after Case 1 treating condition is R-phase with outstanding peak occurring at the 2θ angle around 42.3° while the detwinned Martensite occurs at 2θ angle of 43.6° for diameters of 0.24 mm and 0.29 mm [67]. This difference in crystal structures can justify the difference in strain response and the amount of unrecovered strain demonstrated in Figure 4.6. The reason for such behavior can be insufficient heating for transforming the crystal structure from detwinned Martensite to Austenite during heating in diameters of 0.24 mm and 0.29 mm at the
Figure 4.17. (a) Complete XRD pattern of Case 1 wires; (b) XRD patterns of 0.15, 0.19, 0.24 and 0.29 mm wires
heating range of 70 to 80°C. Consequently the major portion of crystal structure for these diameters is untransformed and intact detwinned Martensite.

It has been discussed by Honarvar et al [10] while for wires that have diameter larger than 0.19 mm that is heated in the range of 120 -130°C, they show a large amount of unrecovered strain after being cooled to room temperature. It was observed that they have the same strain behavior as that of wire diameters less than 0.19 mm. To investigate the effect of maximum heating temperature on the strain response of various wire diameters, Nitinol wires were treated in Case 2 thermomechanical condition.

The XRD patterns between 25° to 105° (2θ) of Nitinol wires treated in this condition are illustrated in Figure 4.18. Figures 4.18 (b) demonstrate the XRD patterns between 35° to 50° (2θ). Table 4.6 illustrates the values for a, b, and c parameters of Gaussian curve fitting for Figure 4.18 (b). Figure 4.18 shows the uniform XRD patterns for all wire diameters while treated in Case 2.

Table 4.6. Gaussian’s height, position, and width of outstanding peaks for XRD patterns of Case 2 Nitinol wires

<table>
<thead>
<tr>
<th>Wire Diameter (mm)</th>
<th>Height (a)</th>
<th>Position (b)</th>
<th>Width (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>770.029</td>
<td>42.29</td>
<td>0.181</td>
</tr>
<tr>
<td>0.19</td>
<td>1130</td>
<td>42.33</td>
<td>0.178</td>
</tr>
<tr>
<td>0.24</td>
<td>1090</td>
<td>42.41</td>
<td>0.175</td>
</tr>
<tr>
<td>0.29</td>
<td>892.167</td>
<td>42.47</td>
<td>0.192</td>
</tr>
</tbody>
</table>

From Figs. 4.18(b), it can be observed that R-phase crystal structure with characteristic peak occurring at 2θ about 42.3° has been generated in all four Nitinol wire diameters when they were heated to 120-130°C and then cooled back to room
temperature. R-phase crystal structure confirms the reason for the formation of high unrecovered strains in all wires where initial phase for all as-received wires are detwinned Martensite. The Nitinol wire behavior particularly the transformation of twinned Martensite to detwinned Martensite has been discussed in [9]. In investigating the difference in the crystal structures of twinned and detwinned Martensite, the Nitinol wires were treated in Cases 3 and 4 respectively.

In Case 3, the Nitinol wires that have been treated in Case 1 have R-phase crystal structure at room temperature. They were cooled in an environmental chamber at -40°C at zero stress to achieve a Twinned Martensite phase. In Case 4, after the wires were subjected to thermomechanical condition of Case 3, they were subjected to tensile tests to 5% strain. This process will transform twinned Martensite to detwinned Martensite.

The XRD patterns of these wires are determined are shown in Figures 4.19 and 4.20. The XRD pattern illustrated in Figure 4.19 shows the twinned Martensite crystal structure with outstanding peak occurring around 43.5° (2θ). Table 4.7 illustrates a, b and c parameters of Gaussian curve fitting of Figures 4.19 (b).

<table>
<thead>
<tr>
<th>Wire Diameter (mm)</th>
<th>Height (a)</th>
<th>Position (b)</th>
<th>Width (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>507.683</td>
<td>43.61</td>
<td>0.239</td>
</tr>
<tr>
<td>0.19</td>
<td>477.399</td>
<td>43.49</td>
<td>0.181</td>
</tr>
<tr>
<td>0.24</td>
<td>525.424</td>
<td>43.63</td>
<td>0.228</td>
</tr>
<tr>
<td>0.29</td>
<td>668.76</td>
<td>43.65</td>
<td>0.215</td>
</tr>
</tbody>
</table>
Figure 4.18. (a) Complete XRD pattern of Case 2 wires; (b - e) XRD patterns of 0.15, 0.19, 0.24 and 0.29 mm wires.
Figure 4.20 (a) shows the XRD pattern of Nitinol wires with different diameters treated in Case 4. Figures 4.20 (b) demonstrate the characteristic peak occurring between 35-50° (2θ). Table 4.8 shows a, b, and c parameters of Gaussian curve fitting of Figure 4.16 (b).

Table 4.8. Gaussian’s height, position, and width of outstanding peaks for XRD patterns of Case 4 Nitinol wires

<table>
<thead>
<tr>
<th>Wire Diameter (mm)</th>
<th>Height (a)</th>
<th>Position (b)</th>
<th>Width (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>588.014</td>
<td>43.55</td>
<td>0.216</td>
</tr>
<tr>
<td>0.19</td>
<td>526.271</td>
<td>43.47</td>
<td>0.202</td>
</tr>
<tr>
<td>0.24</td>
<td>687.196</td>
<td>43.61</td>
<td>0.210</td>
</tr>
<tr>
<td>0.29</td>
<td>737.68</td>
<td>43.63</td>
<td>0.214</td>
</tr>
</tbody>
</table>

The difference between crystal structure of Twinned and Detwinned Martensite in XRD patterns can be emphasized by the difference in intensity of characteristic peak of Martensite that occurs at 43.5° (2θ). Detwinned Martensite has higher XRD peaks intensity. Twin boundaries and uninformed surface crystal structure in Twinned Martensite reduce the number of reflected X-ray counts accumulating by X-ray detector from the surface of material.
Figure 4.19. (a) Complete XRD pattern of Case 3 wires; (b - e) XRD patterns of 0.15, 0.19, 0.24 and 0.29 mm wires
Figure 4.20. (a) Complete XRD pattern of Case 4 wires; (b - e) XRD patterns of 0.15, 0.19, 0.24 and 0.29 mm wires
CHAPTER 5
CONCLUSIONS

Constructing active surgical needle by use of Nitinol actuator is a great step to overcome the brachytherapy troubles in terms of accurate needle placement, decrease the number of insertions and to reduce the pain and trauma to patients. For achieving this goal, characterizing the Nitinol wires as an needle actuators seems critical. Obtaining consistent strain response out of Nitinol wires in terms of the amount of recovered strain in each thermal cycle is a big challenge in designing the active needle. In addition, the effect of Nitinol wire diameter, maximum heating temperature during thermal cycle, the amount of biased stress while wires are under thermal load and other factors make it more complicated to understand the strain response of Nitinol wires. Therefore, Constant stress experiment and uniaxial tensile tests were performed on various Nitinol wire diameters to determine the amount of critical stresses needed to avoid unrecovered strain between first and second thermal cycles. The thermal strain response of Nitinol wires varied with the change in wire diameters.

The strain response of Nitinol wires was found different for wire diameter in range of 0.10 to 0.29 mm. For wire diameters of 0.10 to 0.19 mm, decreasing the wire diameter decreased the critical stresses. Because of the effect of preconditioning temperatures, this trend was not very obvious for critical stresses obtained from the tensile tests. For 0.24 and 0.29 mm wires heated to 70 to 80°C, the effect of critical stress on the strain response of Nitinol wires was not observed. The comparison of
critical stresses achieved from constant stress experiment and the uniaxial tensile test showed consistent results except in the 0.10 mm diameter (inconsistency in this diameter can be due to the difficulties in reading of accurate temperature of this wire in constant stress experiment). It was observed that the range of heating temperature during heating cycle of constant stress experiment and preconditioning of uniaxial tensile test, can affect the results in a great extent due to the amount of transformed initial phase (detwinned Martensite) to Austenite and consequently the amount of twinned Martensite formed after cooling back to the room temperature.

Evaluation of detwinning process which accounts for generation of unrecovered strain in cooling period of Nitinol wire has been investigated. Consequently determination of range of critical stress (range of plateau stress in detwinning process) of different sizes of Nitinol through macro-mechanical test such as constant stress experiment and uniaxial tensile test has been done.

To confirm the mechanical strain response, analyzing the Nitinol wire microstructure in regard to the existed phases prior to imposed thermo-mechanical cycle and after that has been performed. An appropriate method to analyze the microstructure of Nitinol wire in regards to generated crystal structure is XRD. So the crystal structures of the wires exposed at different thermomechanical conditions using XRD method were investigated. Using XRD patterns of different diameters, it can be determined that they show different strain responses after they were exposed to the same thermomechanical conditions.
For 0.15 mm and 0.19 mm diameter wires, after they were heated to 70 to 80ºC, the crystal structure was R-phase, which caused a large unrecovered strain. The initial crystal structure is Detwinned Martensite. For 0.24 and 0.29 mm diameter wires, the crystal structure was Detwinned Martensite after they were heated to 70 to 80ºC. Very small or negligible unrecovered strain was observed for these wires. Exposing the wires to higher temperature of 120 to 130ºC created R-phase crystal structures in all wires. Their thermomechanical response was similar and high unrecovered strain was observed. The difference between crystal structure of detwinned Martensite and twinned Martensite in XRD patterns has been distinguished by the difference in intensity of characteristics peaks. It has been observed that detwinned Martensite has higher peak intensity rather than twinned martensite since it has a better uniform reflection surface for X-ray beams.

Besides the scientific points discussed in this study, the results of constant stress experiment and uniaxial tensile test can be used for modeling algorithm of Nitinol actuator. Mentioned experiments were used to obtain materials constant inputs for the modeling purposes. It was found that constant stress experiments should be used to obtain the four Transformation Temperatures as well as the Clausius-Clayperon coefficients.

For Brinson’s model inputs, this thesis did not obtain \( \sigma^c_r \) and \( \sigma^f_r \) experimentally. These two constants can only be obtained via isothermal mechanical testing. Other types of mechanical test, such as constant strain experiment, has been performed to evaluate the amount of generated force while wires are constrained. Since this test has been performed for the sake of achieving needle design parameters, and the
effect of wire diameters haven’t been discussed in this type of experiment, this section has been discussed separately in Appendix A.

The initial microstructural investigation, such as confirmation of chemical composition and surface morphology has been performed by the use of EDS and SEM equipment. The surface preparation (Etching with acidic solution) prior to perform microscopic analysis have been expressed all together in Appendix B.

At the end the author can propose the following subjects for pursuing the goal of this study for future research.

- Temperature measurement of Nitinol wires during thermal cycle with other kinds of measurement methods and comparing the results with results of this study.
- Investigating more details about parameter achieved from Guassian curve fit of XRD results.
- Designing appropriate cooling system to harness the thermal impact of Nitinol actuator on In-vivo applications.


APPENDICES

APPENDIX A

CONSTANT STRAIN EXPERIMENT

The project’s application is to model and make a prototype of active surgical needle. Since the Nitinol wires play the actuation role of the needle, the amount of force produced by Nitinol wires is a driving force for actuation purpose. The actuation capability can be described analogously as a fixed end cantilever beam. When thermally activated, the actuator contracts to its higher temperature (shorter) shape. Since the actuator would be fixed at both ends by the plastic collet (Fig. 1.1), there would be “reaction force” at the collet, or “actuation force”. Therefore, a fixed-strain experiment was conducted to simulate the “actuation force” response of Nitinol. The schematic and real pictures of constant stress experiment have been illustrated in Fig. A.1. and A.2.

The Nitinol wires were also activated using resistance heating by applying current as a ramp function. Force response of the Nitinol wire is measured using a 5 and 50 lbs load cells dependent on the wire diameter (Futek Advance Sensor Tech, Irvine, California). The load cell signal was collected using SCXI-1314 DAQ system. Similarly to the constant stress experiment, a K-type thermocouple also was attached on the top of the wires. A linear stage (Edmund Optics, Barrington, NJ) were used to control pre-strained amount of the Nitinol wires The Nitinol wires were also activated using resistance heating by applying current as a ramp function. Typical result of constant strain experiment, including force response and temperature response of 0.29 mm has been demonstrated in Figure A.3.
Figure A.1. Schematic (a) and real picture (b) of Constant Strain Experiment

Figure A.2. Force (a) and Temperature (b) responses of 0.29 mm Nitinol wire diameter in Constant Strain experiment respectively
EDS is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray emission spectrum. The EDS analysis has been done on Nitinol wires to confirm the chemical composition of Nitinol. Figure B.1 shows the EDS results of Nitinol wires. EDS is used to conduct elemental analysis and provide a compositional map of the sample.

Figure B.1. EDS result of Nitinol wire.