

THESIS

A NOVEL DESIGN METHODOLOGY FOR OSSEOINTEGRATED IMPLANTS AND THE EFFECTS OF HEAT-TREATMENT ON SHAPE SETTING NITINOL FOIL

Submitted by

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ABSTRACT

A NOVEL DESIGN METHODOLOGY FOR OSSEOINTEGRATED IMPLANTS AND THE EFFECTS OF HEAT-TREATMENT ON SHAPE SETTING NITINOL FOIL

Nitinol, approximately equiatomic nickel and titanium and a popular shape memory alloy, has been used extensively in modern, implantable medical devices due to its natural biocompatibility, remarkable shape memory properties, and superelasticity. Much of the current literature on processing and handling this material focuses on thin wires, as this is what has historically been of most interest (e.g. for orthopedics, orthodontia, and orthognathics); however, as this technology advances, there are emerging applications of nitinol that require other form factors such as films and foils. In addition, although many manufacturers can produce three-dimensional nitinol structures, much of the information on shaping techniques is still proprietary. In an effort to fill these gaps in the literature and add to the knowledge of nitinol shaping techniques, this study compares the effects of various heat-treatments on the shape-setting of nitinol foil. Foils of two different NiTi compositions (50.2 and 50.8 percent Ni by atomic mole fraction) were rigidly fixed into a cylindrical shape and heat-treated at five different temperatures (400, 450, 500, 550, and 600 degrees C) and for five different durations (5, 10, 15, 20, and 25 minutes). The morphological rebound of these samples was evaluated, and a model was developed to described this shape setting behavior. In addition, the Austenite finishing temperature (A_f), and fatigue effects of all samples were evaluated to further quantify the effects of heat-treatment. The results from this materials study were then used in part to develop a novel design methodology for osseointegrated implants. Devices using this methodology have anchors that deploy from the main body to lock the implant in place. The contact points act as "active sacrificial zones" which can experience bone resorption without losing rigidity, while the remainder of the implant body undergoes normal loading conditions. This methodology aims to improve the quality and speed of bone ingrowth.

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DEDICATION

Dedicated to my Harbour, Shelter, and Family.

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Part I: The Effects of Heat-Treatment on Shape Setting Nitinol Foil

Chapter 1

Introduction

This thesis is comprised of two parts: an exploration of heat-treatment effects of nitinol, and the development of a novel design methodology for bone implants using nitinol foil. The former is presented in its entirety here in Part I (chapters 1 – 6), and the latter will be presented separately in Part II (chapters 7 – 11). The two parts are related such that the information presented in Part I was developed to enable further exploration of the concepts presented in Part II. Portions of Part I have been previously submitted to the Journal of Biomedical Materials Research Part B: Applied Biomaterials [1].

Nitinol, an approximately equiatomic mix of Ni and Ti, exhibits nearly unique shape memory and superelastic effects and has well-known biocompatibility. These properties make NiTi of much interest in biomedical, aerospace, and other industries [2, 3]. Much of the current literature on nitinol processing and handling focuses on thin wires, which have historically been the focus of use; however, as technology advances, there are emerging applications of nitinol that require other form factors, such as films and foils. In addition, although several manufacturers can produce three-dimensional nitinol structures, much of the information on shaping techniques is still proprietary. In an effort to fill these gaps in the literature and add to the knowledge of nitinol shaping techniques, this study compares the effects of various heat-treatments on the shape-setting of nitinol foil. Foils of two different NiTi compositions (50.2 and 50.8 percent Ni by atomic mole fraction) are rigidly fixed into a cylindrical shape and heat-treated at five different temperatures (400, 450, 500, 550, and 600 degrees C) and for five different durations (5, 10, 15, 20, and 25 minutes). These samples are then evaluated based on how closely the final shapes matched that of the cylindrical fixture, a term called morphological rebound (MR), which is an aspect of shape memory. In addition, the Austenite finishing temperature (A_f) and fatigue effects of all samples are evaluated to further

quantify the effects of heat-treatment. Finally, to assess the process variability, three sets of time and temperature settings are chosen at which three identical NiTi samples are made.

Chapter 2

Background

2.1 Properties of Nitinol

Nitinol, as the first part of its name suggests, is an alloy made of approximately equiatomic nickel and titanium; typical compositions range from about 50:50 to 52:48 Ni:Ti by atomic mole fraction. The "-nol" suffix stands for the Naval Ordnance Laboratory, to whom this unique material owes its discovery [4]. The basic working principle of nitinol has to do with the crystallographic structure of its main austenite and martensite phases. The austenite phase, which is typically considered the "parent" phase, occurs when the material is above a certain phase-transition temperature denoted as A_f , which stands for the austenite finishing temperature. The high-temperature, austenite phase has a simple cubic atomic structure. The unique properties of nitinol arise from how this parent phase transitions into the lower temperature martensite phase [5–9].

2.1.1 Martensite Transition

There are two ways to induce martensite structure in nitinol: one method is to cool the metal below the martensite finishing temperature (M_f), and the other is to stress-induce the transition while the temperature is still above A_f . In either case, the formally cubic atomic structure switches to a rhomboidal structure. Notably, the adjacent atoms do not "slip" with respect to one another, but rather form associated sets of lattices called "twins" in a process called "twinning" and crystalline plane zig-zag over one another (see Figure 2.2) [10]. Notably, this transition is able to occur without any diffusion, meaning it can happen effectively instantaneously [11]. When heated again, or unstressed, the material rebounds and returns to its cuboidal austenite phase [12]. A diagram of this phase change behavior is presented in Figure 2.1.

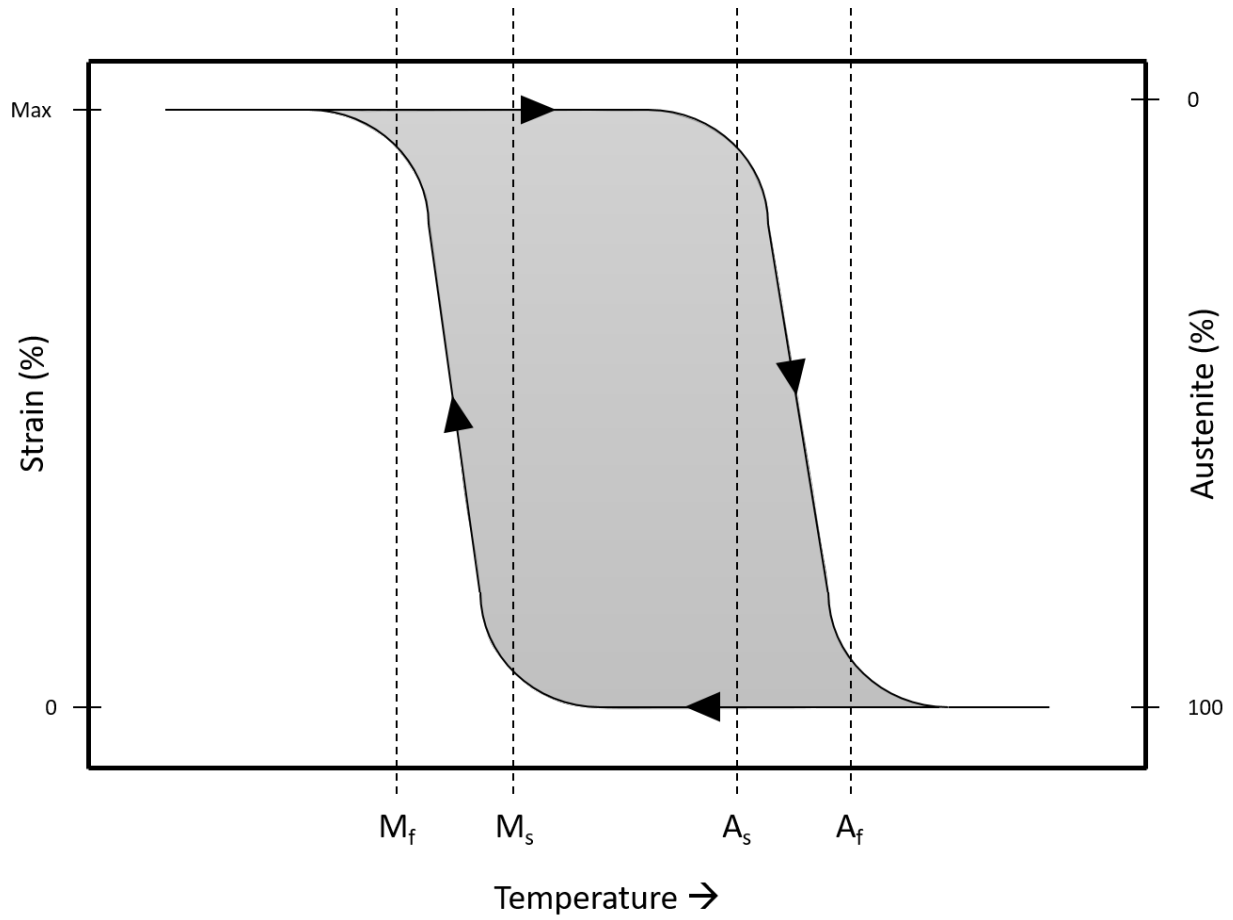


Figure 2.1: Heat-induced transitions between phases of a constantly loaded piece of nitinol. The approximate locations where austenite starts (A_s), and finishes (A_f) forming as temperature increases, as well as where martensite starts (M_s), and finishes (M_f) forming as temperature decreases are shown. The shaded middle region represented an area of hysteresis, and is equivalent to the amount of thermomechanical energy expended in one cycle of loaded phase transitions.

2.1.2 Shape Memory Effect (SME)

The shape memory effect is responsible for much of the fame of nitinol and is the namesake of the class of metals called "shape memory alloys." It occurs when a phase transition between martensite and austenite causes a change in bulk shape. Figure 2.3 shows the atomic arrangements during the SME.

One-Way SME

Most well-known, the one-way SME occurs when the material is first plastically deformed in the martensite phase, which causes a preferential arrangement of the rhomboidal structure in the direction of deformation. This process is called "detwinning," as the twin planes are rearranged [10]. When heated above A_f , the structure reverts to cuboidal austenite, and the sum motion of lattices with respect to each other results in a macro-deformation back to the original, undeformed shape. Any resistance to this change of shape is likewise a physical barrier to the phase transition, and it can thus generate a large amount of force. Typically, after re-heating and rebounding to the original, austenite shape, the material can again be cooled below M_f without any subsequent shape change. The rhomboidal structure will again be non-preferential, and the aggregate of twinned pairs will cancel out any potential bulk shape change. Thus, this memory effect is only "one-way."

Two-Way SME

There does, however, exist a second form of shape memory known as the two-way SME. Here it is important to note that there are several variants of the martensite phase, each with a slightly different crystal structure. If a piece of nitinol is "trained" into a specific shape transition by mechanically cycling through the deformation or by holding the deformation constant and thermally cycling, certain martensite variants with biases towards that particular deformation begin to dominate. After training, a transition from cubic austenite to the non-neutral, dominant martensite phase will cause a preferential shape change in the direction of the trained deformation. This means that small shape changes can be repeated in two directions by a heat-induced phase change without any external mechanical deformation [13, 14].

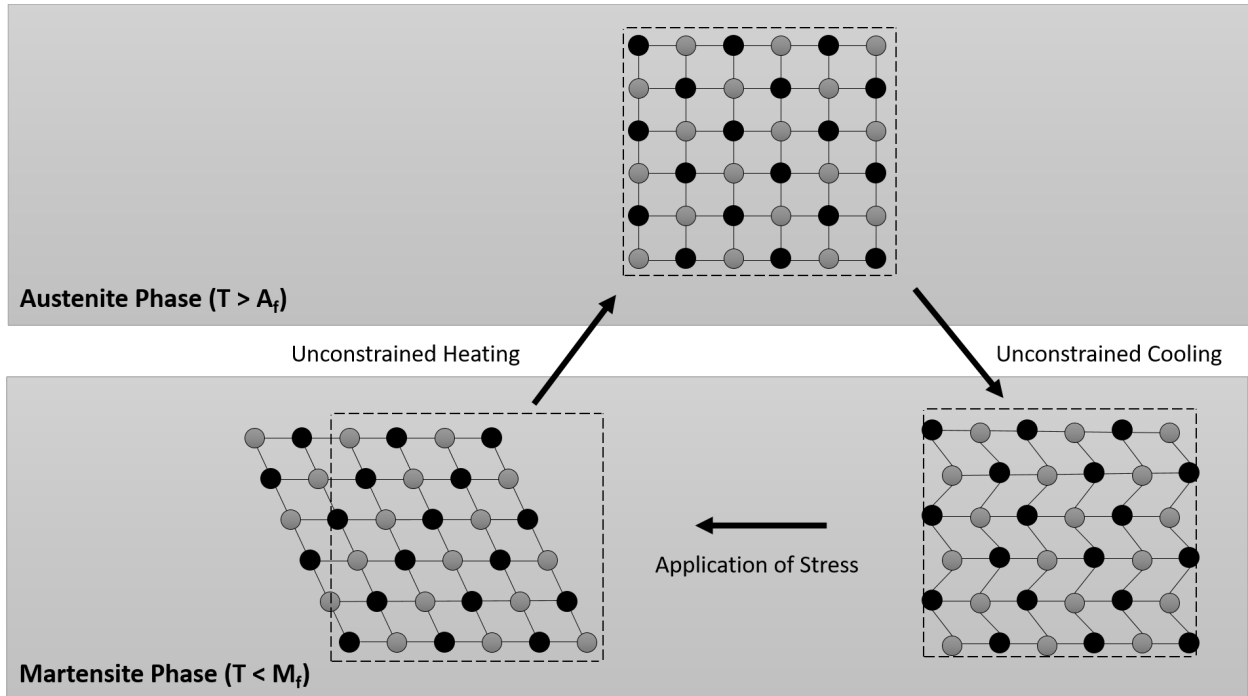


Figure 2.2: Atomic movement and relationships during the shape memory effect. The dashed boxes represent the original bulk shape.

2.1.3 Pseudoelastic Effect (PE)

Finally, the pseudoelastic effect, sometimes known as "rubber-like behavior" or the "superelastic effect", describes the ability of austenitic nitinol to be elastically deformed to strains of up to 10%. Unlike typical metals where the elastic region occurs by atoms essentially stretching apart before they plastically slip with respect to each other, the pseudoelastic effect is "pseudo" because it arises not from a stretching of atoms, but rather from a stress-induced phase transition. This effect occurs when the material is held above A_f , and the martensite phase is induced mechanically. On an atomic scale, this state of affairs is essentially identical to plastically deformed nitinol below M_f , such that there is a preferential rhomboidal structure. When unstressed, the material rebounds immediately into the original shape. This mechanism is effectively the same as that which causes the SME, the only difference being that the material never left austenite temperature range, so it snaps back to its original shape immediately when unstressed, as opposed to needing to be re-heated [12]. Figure 2.3 shows the atomic arrangements during the PE.

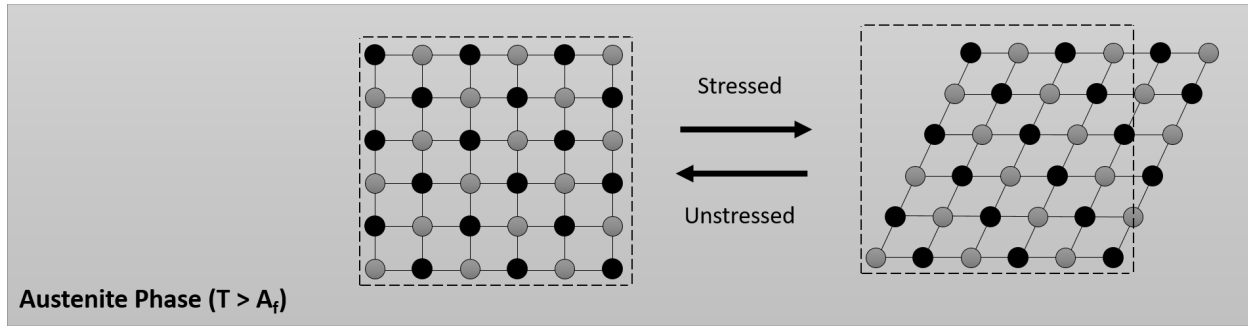


Figure 2.3: Atomic movement and relationships during the pseudoelastic effect. The dashed boxes represent the original bulk shape.

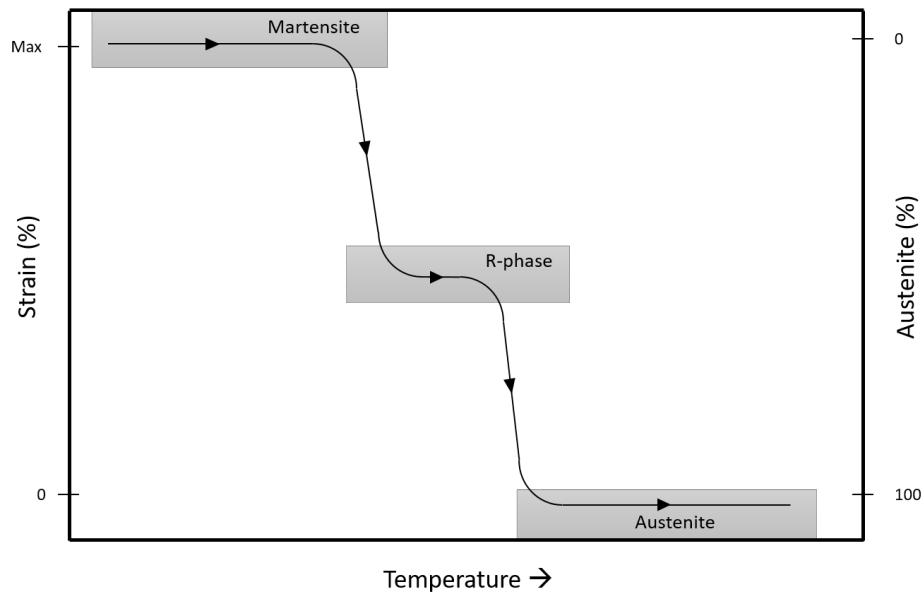


Figure 2.4: R-phase plateau occurring between martensite and austenite phases.

2.1.4 R-Phase Transition

Though not commonly discussed with respect to the SME or PE, there exists a third common phase in between austenite and martensite called the R-phase. This phase is technically martensitic, but it is a distinct phase from the martensite phase responsible for the effects being discussed here. An intermediate transition into the R-phase can cause a plateau to form midway through a phase transition, and thus through a shape transition as well [15, 16]. The appearance of an R-phase region is shown in Figure 2.4.

2.2 Heat-Treatment and Shape Setting of Nitinol

2.2.1 Theory of Heat-Treatment

Heat-treatment, whether quenched for a defined time or through a slowly-cooled annealing process, can have significant effects on both the traditional mechanical properties as well as the shape memory and pseudoelastic properties. Importantly, it is also the main method by which the austenite (parent phase) shape can be set or reset. The heat-treatment process affects the properties of nitinol in two main ways: by changing the amount of dislocations present in the material, and by causing nickel-rich precipitation phases to form.

Reduction of Cold Work Effects

Most manufactured nitinol is pressed, drawn, or rolled into its final shape at near-room temperature conditions in a process called cold working. The magnitude of cold work is measured as a percent reduction in cross-sectional area, and typical values for nitinol are between 30% and 50%. This process causes dislocations within the crystal structure to interfere in such a way that the tensile strength of the material increases due to an increase in internal stresses, which resist movement of the bulk material [17].

Cold work present in the material causes resistance to movement, and thus more cold work is correlated with higher tensile strength and lower elasticity. Likewise, more cold work is associated with a higher A_f temperature. In order to transition phases, especially if that involves a bulk movement of the material via the SME, internal stresses need to be overcome: thus, this results in a higher temperature needed to finish transitioning into austenite. Finally, heat-treatment of cold-worked materials causes higher rates of diffusion, which in turn can actually undo some of the dislocations that cause the effects of cold working. Therefore, higher temperatures and longer heat-treatments are associated with lower tensile strength, higher elasticity, and lower A_f temperatures for cold-worked nitinol [18].

Precipitation of Nickle

The superelastic and shape memory properties of nitinol ultimately derive from the elements that comprise it. Nickle and titanium are not readily compatible in a homogeneous alloy, and it thus takes manufacturing expertise (and great expense) to manufacture the consistent matrix of Ni and Ti atoms from which arise our properties of interest. Any changes to the composition of this matrix, then, can have dramatic effects on its properties. Even a few tenths of a percent more or less Ni in the alloy can change the A_f temperature several dozen degrees Celsius.

Because the Ti and Ni atoms are such different sizes and not readily compatible, additions of heat can cause the Ni atoms to diffuse through the matrix and link up to form pockets of nickel-rich phases because this is ultimately the lower energy state [17]. This process is call precipitation, and, for our purposes can be thought of as nickel atoms diffusing out of the nitinol matrix, and thus lowering the percent of available nickel in the matrix throughout the heat-treatment process [19]. Nishida *et al.* have documented this precipitation process as $Ti_{11}Ni_{14} \rightarrow Ti_2Ni_3 \rightarrow TiNi_3$ [20]. Since a decreased percentage of nickel is correlated with increased A_f temperatures, higher temperatures and durations of heat-treatments are associated with higher A_f temperatures. Finally, the presence of precipitates in the matrix can increase the tensile strength in a similar manner to dislocation hardening.

Sum Effects of heat-treatment

As can be seen, there is not a fairly direct correlation between heat-treating the nitinol and the strength of the material [21]. The same is true for the effects of A_f , however. The effects of relaxing cold work decrease the A_f , while the effects of nickel precipitating increase it. In other words, these two mechanisms are at odds with each other. For this reason, heat-treatment can both raise and lower the functional A_f temperature, depending on the parameters. This is less true, of course, if the nitinol is not cold worked. In general, especially at the high temperatures and long durations, heat-treatment will ultimately raise the phase transition temperatures [22]. Finally, if the method of heat-treatment used allows the material to be exposed to oxygen, there can be oxidation

of nickel precipitates on the surface thus producing a color change, similar to rust developing on the surface of iron.

2.2.2 Experimental Data on Heat-Treatment Effects

Here we focus on the effects of heat-treatments of the phase transition temperatures of nitinol. As previously discussed, there are two main factors affecting A_f , and they are adversarial. This, then, has the potential to lead to seemingly inconsistent outcomes.

In their foundational 2000 paper, Pelton, DiCello, and Miyazaki evaluate the effects of several processing parameters on the properties of 50.8 at.% Ni nitinol wire [23]. They aged the wires at temperatures between 300 and 550 °C at various times between 2 and 180 minutes. A plot of their results shows a seemingly consistent behavior of increasing A_f at temperatures between 300 and 500°C. The authors note the most significant changes in transition temperature occur at the intermediate heat-treatment temperatures, namely 350–450°C, whereas 300 and 500°C show less dramatic increases. At 550°C, the behavior seems to change altogether, with the A_f temperature initially dropping, followed but a sudden and rapid increase throughout the rest of the treatment times, ultimately surpassing all other aging temperatures. To explain this change in behavior, the authors refer to micro-structural data gathered by Miyazaki [24], and show how different precipitation reaction at different temperatures may explain this seemingly counter-intuitive phenomenon. Specifically, they refer to a $\text{Ti}_{11}\text{Ni}_{14}$ phase reaction which occurs dominantly at temperatures between 300 and 500°C, which explains the seemingly consistent behavior at these temperatures. Somewhere between 500 and 550°C, however, these precipitates will actually dissolve, thus lowering the A_f as Ni diffuses back into the matrix. At longer times, the increased driving force causes a second precipitation phase to form, Ti_2Ni_3 , which uses a higher proportion of Ni than the lower temperature precipitation phase, thus resulting in the more rapid increases in A_f .

In a 2006 thesis, Drexel repeated the Pelton experiments at two different levels of cold work [25]. His results were consistent with Pelton's, showing a similar behavior pattern at aging temperatures less than or equal to 500°C, with a notable change in behavior at 550°C. The results seem

to exactly confirm those obtained by Pelton, though it is worth noting that this study seems to have been done in the same facility and with material from the same manufacturing line as the Pelton study.

In their comprehensive 2006 study on aging treatment on nitinol stents, Liu *et al.* perform a nearly identical set of experiments to Pelton. They heat 50.7 at% Ni wire at 300, 350, 400, 500, and 550°C for 2, 10, 20, 30, 40, 120, and 180 minutes, for a total of 42 samples [26]. They found a fairly consistent log-shaped increase in A_f at treatment temperature below 500°C. At 500°C, they show a small initial dip, followed by a small increase around 20 minutes, and then a leveling off which resulted in almost no change of A_f over time. At 550°C, the only temperature above 500 they treated at, they show a significant initial drop around 2 minutes followed by a rapid increase in A_f throughout the durations of the tests. At the 180 minute mark, the 550°C treatment sample had the highest A_f of all samples. Their results are remarkably similar to Pelton's, but the behavior transition seems to occur at a slightly lower temperature; here, 500°C seems to mark a transition between heat-treatment behaviors.

Marchand *et al.*, in their 2011 paper, compare heat-treatments of four different temperatures, 460, 490, 530, and 560°C, over a period of about 30 minutes on Ti- 50 at% Ni wire used in stents [27]. They show a sigmoid-shaped increase in A_f in the temperatures below 500°C. Above this temperature, a different behavior pattern is observed in which the temperature initially drops, followed by an increase around 10 minutes, then rapidly decreases for the rest of the heat-treatment duration. The authors refer to Pelton's explanation of Ni and Ti precipitates to explain the change in behavior at higher temperature; however, though similar, these results represent a departure in two ways from the general aging model thus far upheld by Pelton, Drexel, and Liu. Firstly, at aging temperatures below 500°C, there appears to be a lag phase of about 5 minutes before A_f begins to increase, as opposed to a near-immediate increase shown previously. Secondly, the samples above 500°C show a marked difference in behavior. In Pelton's results, samples around 550°C drop in A_f immediately by about 5°C, before sharply turning upwards and then steadily increasing starting around 5 or 10 minutes. Marchand's results, on the other hand, first show a small increase of about

5°C in both the 530°C and 560°C samples before dropping. Furthermore, the drop in A_f shown by Marchand is more significant—over 20°C in one case—and the recovery seems to take much longer. At 30 minutes (where the Marchand experiments stop), both the 530°C and 560°C samples are barely increasing; in fact the 560°C sample has not even returned to its control value at this time.

Finally, also in 2011, Vojtech *et al.* heat-treated cold drawn 50.9 at.% Ni nitinol wires at 450, 510, and 600°C for 10 minutes in air [28]. Their results show a jump from the as-prepared A_f temperature of 28°C to 33°C after heating at 450°C for 10 minutes. The A_f then drops after heating at 510 and 600°C to 18 and -8°C, respectively. There is not enough data in the study to directly compare it to the competing models; however, the significant drops in transition temperature at higher temperatures seem to be in more in line with Marchand's results, and it does continue to suggest that 500°C is an appropriate marker for transition in behavioral—and thus, likely, microstructural—trends in response to heat-treatment.

These studies all show reasonably similar results at heat-treatment temperatures below 500°C, but appear to present conflicting accounts of behavior at higher temperatures. More data may be necessary to confirm which model is more accurate or to determine what other factors are at play to cause this divergence in results.

2.2.3 Theory of Shape Setting

Recalling from section 2.1.2, austenite phase nitinol has a cuboidal structure, and when cooled below M_f , alternating planes of the crystal shift in a zig-zag pattern to form twins. When deformed, the structure detwins, and the resulting SME is a result of the detwinned pairs snapping back to their cuboidal structure. To change the bulk shape of the material that this cuboidal structure takes, the material is deformed and constrained into the desired shape, and then heat-treated. The added heat allows enough diffusion for the cuboidal structure to reform in the constrained bulk shape. When cooled and unconstrained the new shape should remain. Figure 2.5 shows this process.

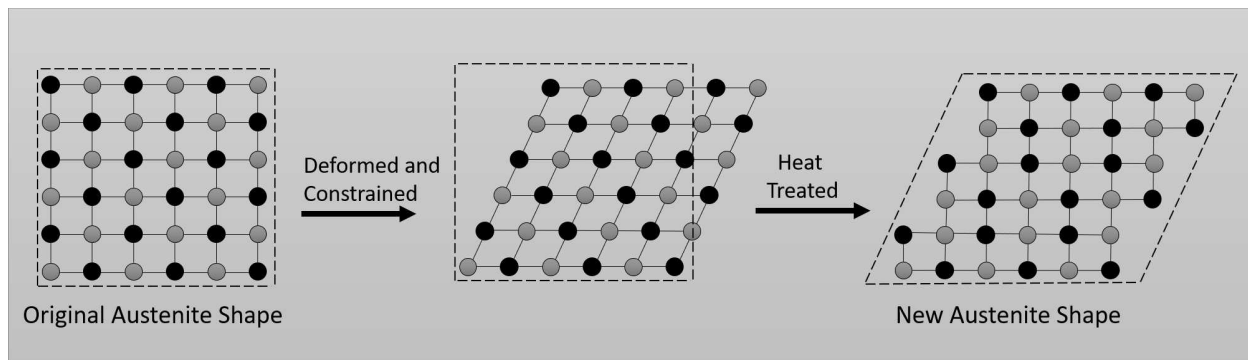


Figure 2.5: Shape setting of nitinol, showing the reformation of cubic structure under constrained conditions when heat-treated. The dashed boxes represent the austenite phase bulk shape.

It is possible, and indeed common, however, for the shape to have only partially been set, and, after removing the constraints, the final shape is an intermediate between the original shape and the desired shape. This phenomenon is termed morphological rebound (MR), and is a result of an incomplete reformation of the cubic crystal structure. In order to avoid undesirable MR, great care must be paid to the heat-treatment parameters, either to ensure sufficient treatment to completely eliminate MR or by using precompensation to achieve the desired shape after MR occurs as an intentional intermediate between the original and constrained shapes.

2.2.4 Experimental Data on Shape Setting

Besides the general ranges or the rule of thumb that every device is different, so shape setting temperatures should always be independently determined [12], there is not much publicly available information on shape setting, specifically quantitative data that directly links heat-treatment parameters to shape setting success. No studies were found that examined the shape setting of foils.

Pelton *et al.* compared heat-treatments at four different temperatures, 350, 400, 500, and 600°C, for 5 minutes each, on forming a J-hook curve on a 50.8 at.%, 0.4 mm diameter nitinol wire. They concluded that 600°C was the most accurate to its constraints, but due to a significant drop in tensile properties, 500°C, which still maintained low enough levels of MR to be acceptable, was the better option [5].

Liu *et al.* performed perhaps the most rigorous study available on the topic with medical-grade, 50.7 at.% Ni, nitinol with a 0.5 mm diameter, which is used in making stents. They heat-treated the material at 300, 350, 400, 500, and 550°C for 2, 10, 20, 30, 40, 120, and 180 minutes, for a total of 42 samples. The wires were allowed to air cool after the heat-treatment, as opposed to being quenched. Their results show reasonably complete and constant shape setting at 500 and 550°C at times greater than 10 minutes, and at 450°C at times greater than 60 minutes [26].

Finally, Marchand *et al.* did a similar experiment on medical grade, 50.8 at.% Ni, nitinol wire. Using an air furnace, they heat-treated the nitinol at 530, and 560°C for various durations between 0 and 30 minutes. Though the results are not well enumerated, it can be approximately said that successful shape setting was achieved at 530°C after 10 minutes, and at 560°C after 20 minutes [27].

Chapter 3

Materials and Methods

3.1 Preparation of Samples

Nitinol foil of two compositions, approximately 50.2%:49.8% Ni:Ti and 50.8%:49.2% Ni:Ti by mole fraction was purchased through Alfa Aesar. Both compositions have a thickness of 0.127 mm. The listed A_f temperatures of the 50.2% 50.8% Ni nitinol were 45°C and 10°C, respectively. The manufacturer was not able to disclose all of the details of the production process but confirmed that the material was annealed and cold worked. Please see Appendix A for specific product and lot information about this material.

Samples of dimension 50x15 mm $\pm 10\%$ were cut using tin shears from the original sheets of foil. These samples were then wrapped around a non-galvanized and non-zinc-plated steel rod of diameter 12.7 mm and length 304.8 mm and strapped into place with stainless steel hose clamps. The mass, and thus the thermal inertia, of this rod-and-clamp fixture is several orders of magnitude larger than the samples, so any dimensional error in cutting the samples (limited to $\pm 10\%$) is assumed not to be a significant factor affecting the outcome of the heat-treatment.

3.2 Heat-Treatment

The samples and fixtures were heated in a Lindberg/Blue M brand high-temperature air furnace with a UP150 temperature control unit. Five temperatures (400, 450, 500, 550, and 600°C) and with five durations (5, 10, 15, 20, and 25 minutes) were used for a total of 25 different heat-treatments plus a control per each composition, resulting in a total of 52 samples. The actual temperature of the furnace fluctuated cyclically over a range of $\pm 12^\circ\text{C}$ during testing. To minimize the effect of this fluctuation, the sample was placed in the furnace at the high point of the fluctuation, so that the heat lost when opening the furnace door returned the actual temperature to approximately the desired set point. The samples were quenched in a water bath of about 20°C

immediately after being removed from the furnace to stop the effects of heating at the appropriate time.

In addition to the 52 main samples, three sets of temperature and time settings were chosen to validate the variance of the heat-treatment outcomes by performing the identical heat-treatment three times for a total of nine additional samples. The three sets of parameters chosen for validation were [400°C; 10 min], [500°C; 15 min], and [600°C; 20 min].

Table 3.1: Experimental variables used in this study. Two molecular compositions were heat-treated at five temperatures and five durations each. With a control for both compositions, this led to a total of 52 samples.

50.2%:49.8% Ni:Ti by mole fraction					
50.8%:49.2% Ni:Ti by mole fraction					
Control	400°C	450°C	500°C	550°C	600°C
-	5 min	5 min	5 min	5 min	5 min
-	10 min	10 min	10 min	10 min	10 min
-	15 min	15 min	15 min	15 min	15 min
-	20 min	20 min	20 min	20 min	20 min
-	25 min	25 min	25 min	25 min	25 min

3.3 Measuring Morphological Rebound (MR)

All samples in this experiment started with a flat austenite-phase shape, meaning that the foil laid flat when above A_f and unloaded. The desired condition after heat-treatment was that the new austenite-phase shape be identical to the shape of the material when held in the fixture, which in this case was a circle with a diameter of approximately 12.7 mm. The samples used were longer than the circumference of the fixture, so there was always some overlap; the average angle of overlap was 0.45π rads. Thus, to measure how closely the final shape of the samples was to the fixture shape, each sample's length was closely measured using a standard caliper, and a calculation was used determine the distance between the two edges of the sample while in the fixture; see Equation (3.1). The distance between sample edges was used as the primary metric

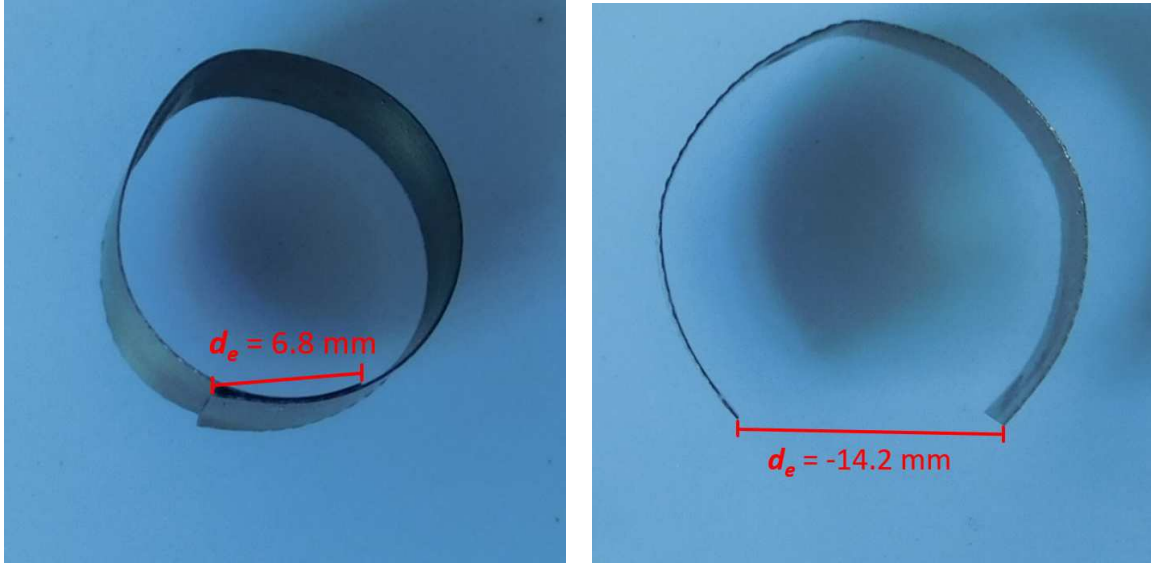
because it can be precisely measured without needing the sample to be perfectly centered on a ruler or risking compression by the measurement device like a caliper.

$$d_t(l) = 2r \left| \sin\left(\frac{l-c}{2r}\right) \right|, s.t. r < 2l \quad (3.1)$$

where $d_t(l)$ is the theoretical (i.e. desired) distance between the two ends of the sample given total sample length l , c is the constant circumference of the fixture rod, and r is the constant radius. This equation essentially converts the arc length of the overlapping material to a corresponding chord length.

To measure d_e , the experimental (i.e. measured) distance between the two ends, all samples were held at least 10°C above the highest recorded A_f temperature in a hot water bath. High-resolution digital images were taken from a calibrated overhead camera (Nikon COOLPIX B500), and the distance was measured using the Perfect Screen Ruler application [1]. The distance, measured in number of pixels, was then converted to mm based on a standard scaling factor determined during calibration. Though the desired shape, d_t always had overlapping edges, as described, some of the post-heat-treatment austenitic shapes often exhibit a considerable amount of spring back from the fixture shape and thus do not all have overlapping edges. To account for this, the d_e measurements from all non-overlapping samples were negated to better represent the divergence from the desired position, d_t . Figure 3.1 shows a series of examples illustrating this method of measuring and selectively negating d_e .

MR is measured as a percent return to the pre-heat-treated shape (flat), from the constrained fixture shape used during treatment (overlapping cylinder). Thus, a result of 0% MR represents a sample that perfectly maintained the exact shape of the fixture after heat-treatment, and a result of 100% represents a sample that sprung back completely, experiences no shape-setting whatsoever. This is shown in Figure 3.2.



(a) Sample treated at 500°C for 20 minutes.

(b) Sample treated at 450°C for 20 minutes.

Figure 3.1: Measuring d_e of post-heat-treated samples from digital images. (a) An example of overlapping edges, which yields a positive d_e . (b) An example of non-overlapping edges, which yields a negative d_e .

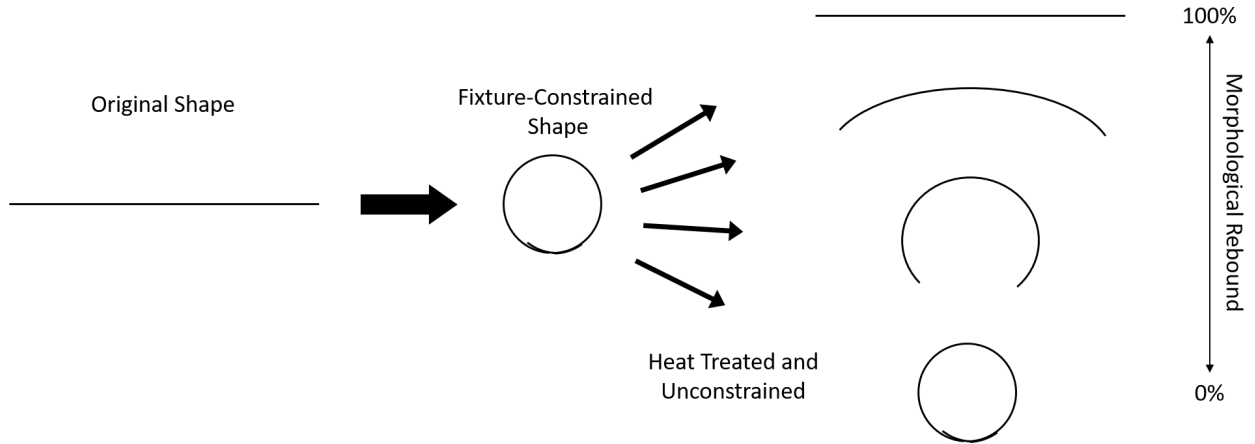


Figure 3.2: Morphological rebound is defined as the percent of return to the pre-annealed shape. 100% thus represents no noticeable shape change from the original (flat) shape, and 0% represents a complete shape change to the constrained fixture (cylindrical) shape.

3.4 Measuring A_f

A_f was measured using the ASTM F2082/F2082M-16 bend and free recovery (BFR) standard with slight modification [29]. Since this standard is for material of a uniform (i.e. straight) shape, it could not be perfectly followed in such a way as to reflect the true phase transition behavior of the samples in this study. Specifically, the ASTM standard specifies the use of a uniform mandrel to bend all samples to a uniform strain before allowing free recovery. The same was not feasible in this study due to the wide range of post-heat-treatment austenitic shapes of the samples. Instead, if the shape of the sample was straight or near-straight it was bent around the fixture rod of diameter 12.7 mm, and if the sample was round or near-round it was bent straight on a flat surface. "Near-straight" and "near-round" distinctions were based on the angle made against a flat surface by the austenite-phase; if the angle was 90° , it was considered near-straight. Figure 3.3 gives a visual representation of this bending method used for the BFR test.

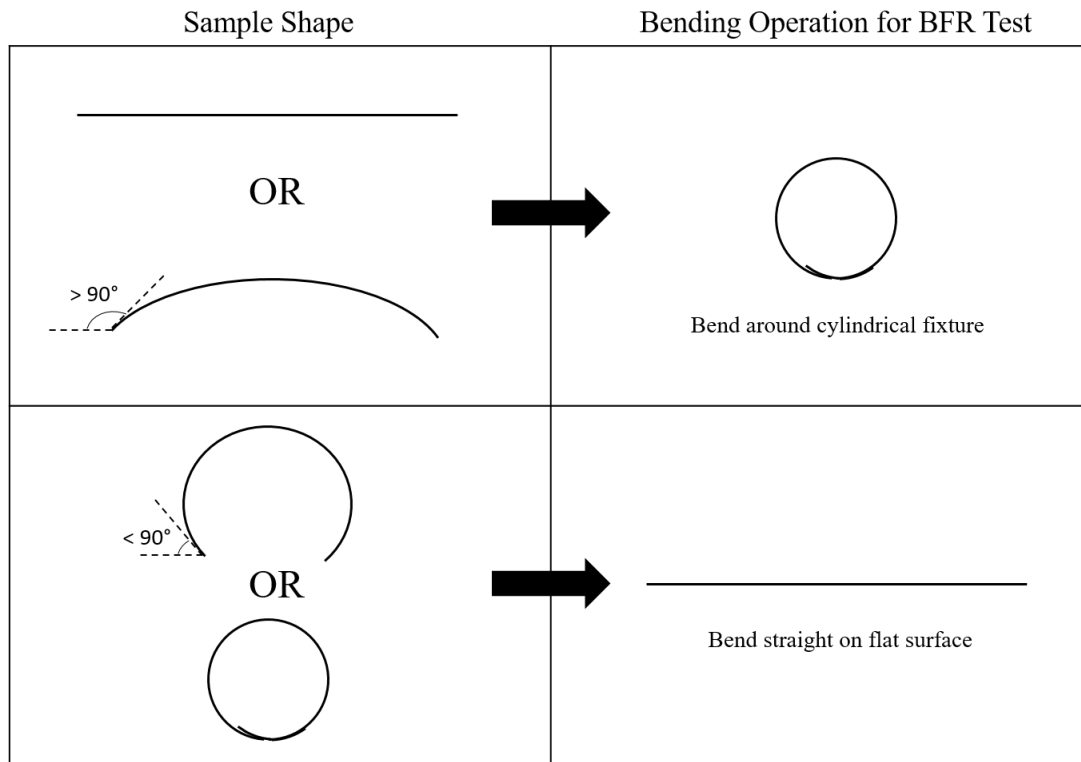


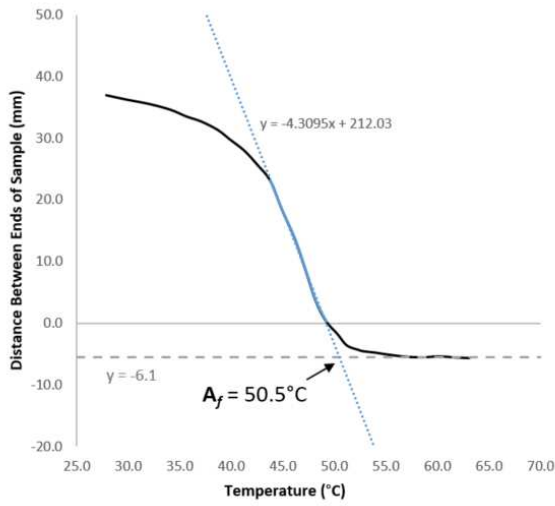
Figure 3.3: Modified bending procedure used in BFR tests. The left column represents the unloaded austenitic shape of the sample, and the right column represents the strained position used before allowing free recovery.

Using this method of initial strain, the samples were cooled below M_f in a cold water or ethanol bath, depending on the original A_f , and bent as described. The cold water or ethanol bath was then slowly heated at no more than 4°C per minute through the martensite-austenite phase transition until all motion had stopped. During the heating process, high resolution videos were taken using a calibrated overhead camera, and temperature readings of the water bath were taken with a submerged thermocouple every 30 seconds. Measurements of the distance between sample edges were taken in the same way described in section 3.3 at 30 second intervals to correlate with the periodic temperature measurements.

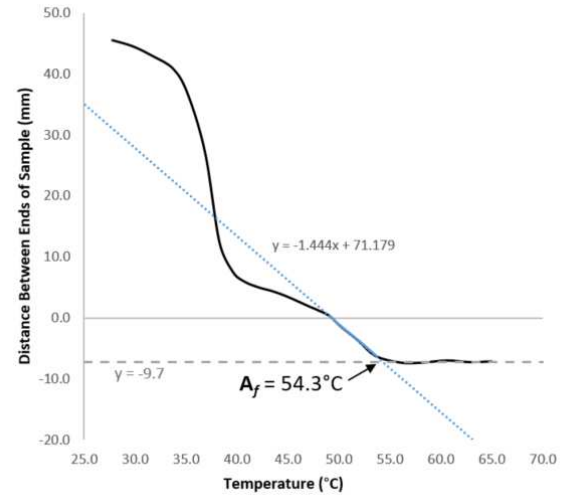
Displacement of the edges was then plotted with respect to temperature, and the A_f value was determined using the method described in ASTM F2082/F2082M-16, where a line is drawn in tangent with the steepest part of the curve, and a second line is drawn to represent the plateau value after phase transition. If the temperature-displacement curve shows a prominent R-phase development between martensite and austenite, the tangent line is drawn with respect to the R-phase-to-austenite transition. The A_f value occurs at the intersection of these two lines, as is shown in Figure 3.4.

3.5 Fatigue Testing

The fatigue behavior of heat-treated samples was evaluated to determine if a small number of mechanical and thermal cycles would significantly affect the austenite shape and phase transition behavior. Each sample was placed in a cold water or ethanol bath below M_f and deformed in the same way described in section 3.4; subsequently, the sample was transferred to a warm water bath above A_f where it returned to its austenitic shape. This process was repeated for a total of 24 cycles, and a digital image of the austenitic shape was captured on each iteration to monitor any change. The images were evaluated in the same way described in section 3.3.



(a) Sample treated at 500°C for 20 minutes.



(b) Sample treated at 550°C for 20 minutes.

Figure 3.4: Measuring A_f of post-heat-treated samples using ASTM F2082/F2082M-16 standard. (a) An example of a smooth transition from martensite to austenite. (b) An example of a prominent R-phase transition in between austenite and martensite; in this case, the tangent line is drawn with respect to the R-phase to austenite transition.

Chapter 4

Results

4.1 Shape Setting

Shape setting results are shown in Figures 4.1 through 4.2. All three figures represent the same data, but Figure 4.1 displays it in tabular form, Figure 4.1 displays it in a plot using heat-treatment duration as the x-axis parameter, and Figure 4.2 shows a plot with heat-treatment temperature as the x-axis.

Table 4.1: Shape setting results presented in the form of morphological rebound. Shaded area contains results below 5%.

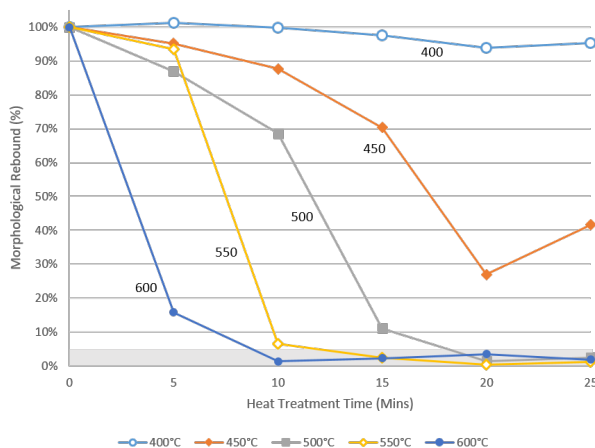
	400°C	450°C	500°C	550°C	600°C		400°C	450°C	500°C	550°C	600°C
5 min	101%	95%	87%	94%	16%	5 min	97%	95%	95%	92%	23%
10 min	100%	88%	69%	6%	1%	10 min	96%	91%	21%	9%	3%
15 min	98%	70%	11%	2%	2%	15 min	95%	69%	6%	4%	2%
20 min	94%	27%	1%	0%	3%	20 min	91%	34%	11%	4%	3%
25 min	95%	42%	2%	1%	2%	25 min	83%	31%	3%	2%	3%

(a) 50.2 at% Ni

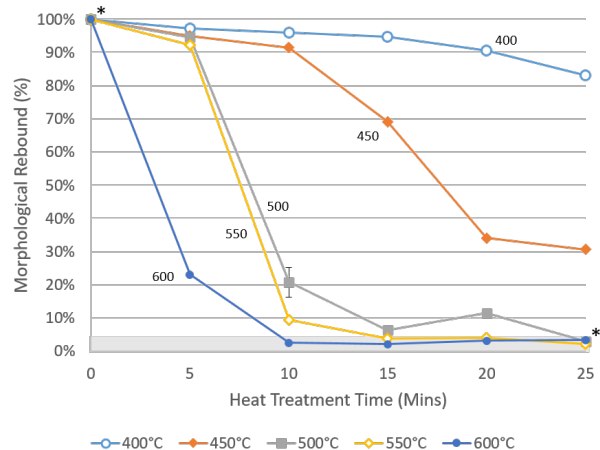
(b) 50.8 at% Ni

To establish an idea of what can be considered satisfactory, or "complete", shape setting, two considerations are taken into account: (1) within reasonable heat-treatment regiments, there may always be a small amount of morphological rebound, and (2), due to the relatively small standard deviations, precompensation may be a feasible design consideration. With these two consideration in mind, this study defines "complete" shape setting as a morphological rebound below 5%. Using this definition, Figure 4.1 shows, in shaded cells, that sufficient shape setting never occurs below 500°C for either material composition. At or above 500°C, successful shape setting occurs in a staggered pattern, with higher temperatures needing less time to drop below the 5% threshold.

The settings at which complete shape setting takes place are almost identical between the two material compositions, with the one exception being that 50.8 at% Ni nitinol needed an extra 5 minutes compared to the 50.2 at% Ni samples. When viewed graphically in Figure 4.1b, this

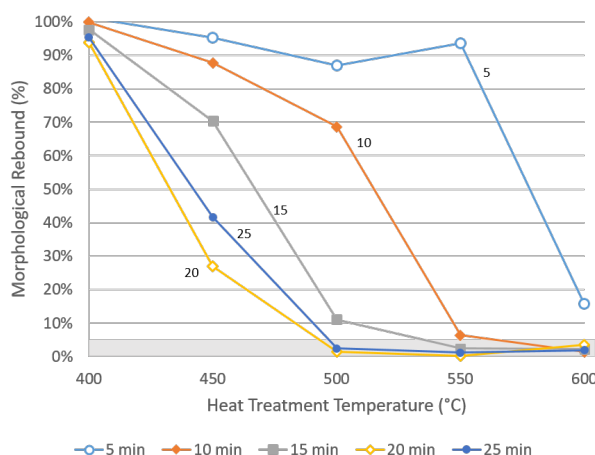


(a) 50.2 at% Ni

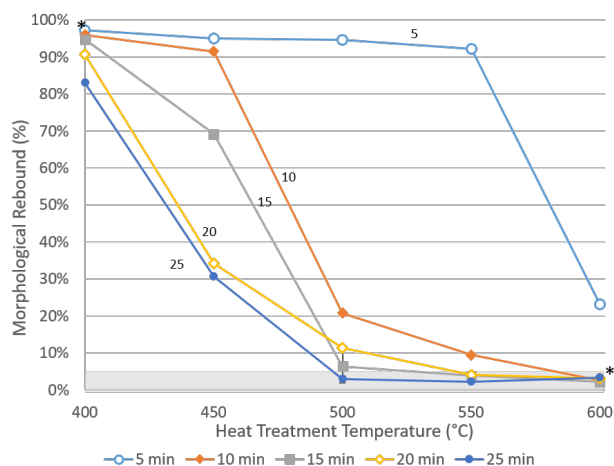


(b) 50.8 at% Ni

Figure 4.1: Shape setting results by heat-treatment time. Shaded area contains results below 5%. Error bars on the 50.8 at% Ni plot represent plus and minus one standard deviation. *Error bars at points for 400°C at 10 minutes and 600°C at 20 minutes were too small to be shown on the graph.



(a) 50.2 at% Ni



(b) 50.8 at% Ni

Figure 4.2: Shape setting results by heat-treatment temperature. Shaded area contains results below 5%. Error bars on the 50.8 at% Ni plot represent plus and minus one standard deviation. *Error bars at points for 400°C at 10 minutes and 600°C at 20 minutes were too small to be shown on the graph.

500°C, 20 minute point can be seen to exhibit unusual behavior, increasing compared to the 15 minute sample. This may be evidence of an outlier, but, in general, the trend is clear between both materials. Notable features, also exhibited in both compositions, are the apparent slowing or plateauing of the 450°C samples after 20 minutes (Figure 4.1), and the sudden drop in the 5 minutes samples at 600°C (Figure 4.2).

4.2 Modeling Shape Setting Behavior

Two types of models were developed in an attempt to characterize the shape setting behavior of nitinol. The first model was developed using heuristic methods and is a 1-term approximation. The second model was developed using multivariate regression and is a 4-term approximation. Each model is evaluated using mean squared error (MSE).

4.2.1 Heuristic Model

An analysis of Figures 4.1 and 4.2 reveals an obvious non-linear characteristic. A closer inspection of the data shows that the decrease in MR is of higher order with respect to temperature than time. Finally, since MR decreases as time and temperature increase, the model will take the form of

$$\text{MR} = C * \frac{1}{t} * \frac{1}{T^2} = \frac{C}{t * T^2} \quad (4.1)$$

where MR is the morphological rebound, C is a constant coefficient, t is time in minutes, and T is temperature in °C. A refinement of this model adds an offset factor to the temperature term, or a ΔT . This offset is due to the fact that temperature, unlike time, does not start near-zero, and, furthermore, lower temperatures are expected to have no effect on MR, regardless of time. For instance, a very short time duration (say 1 or 2 minutes) would likely be able to shape set nitinol if given a high enough temperature, but the reverse is not true. At 25°C (room temperature), shape setting will never occur. The same is likely true for practical purposes at much higher temperatures. To reflect this reality in the model, it is revised as such:

$$\text{MR} = \frac{C}{t(\mathbf{T} - \Delta T)^2} \quad (4.2)$$

To determine a reasonable value for ΔT , previous results reported by Marchand *et al.* [27] were referenced. In their study, they test temperatures as low as 300°C, and find that for times up to 180 minutes, marginal shape setting occurs. Thus, for practical purposes, it is assumed that at temperatures at or below 300°C, no shape setting occurs. Thus we say $\Delta T = 300$. To find a suitable coefficient, C , values were tuned until three conditions were met:

1. Boundary conditions are maintained such that no model-predicated MR values within the experimental time and temperature domains are above 100% or below 0%
2. All MR values are correctly predicted as being above or below the 5% threshold established in Section 4.1
3. Minimum MSE when compared with experimental results

The resulting coefficient for the 50.8 at.% Ni data set was $C_{50.8} = 45300$. The heuristic values of ΔT and C determined here were validated with an optimization algorithm, which determined the absolute combination of these two constants with the minimum resulting MSE. The ideal combination turned out to be $\Delta T = 307$ and $C = 42800$, largely confirming our heuristically determined values. To avoid artificially over-fitting the data, the heuristic results are used in the model presented here. Finally, the same process was carried out for the 50.2 at.% Ni data set, which resulted in $C_{50.2} = 40800$. The final model with constants inserted is presented below.

$$\text{MR}_{50.2} = \frac{40800}{t(\mathbf{T} - 300)^2} \quad (4.3)$$

$$\text{MR}_{50.8} = \frac{45300}{t(\mathbf{T} - 300)^2} \quad (4.4)$$

Table 4.2: Results of heuristic shape setting model. Shaded area contains results below 5%. Mean squared error compared to the experimental results in Table 4.1 are provided below the tables.

	400°C	450°C	500°C	550°C	600°C		400°C	450°C	500°C	550°C	600°C
5 min	81%	36%	20%	13%	9%	5 min	91%	40%	23%	14%	10%
10 min	40%	18%	10%	6%	4%	10 min	45%	20%	11%	7%	5%
15 min	27%	12%	7%	4%	3%	15 min	30%	13%	8%	5%	3%
20 min	20%	9%	5%	3%	2%	20 min	23%	10%	6%	4%	3%
25 min	16%	7%	4%	3%	2%	25 min	18%	8%	5%	3%	2%
Mean Squared Error:					19.4%	Mean Squared Error:					15.8%
(a) 50.2 at% Ni						(b) 50.8 at% Ni					

Table 4.2 shows the predicted MR values produced by Equations 4.3 and 4.4, as well as the MSE compared to the experimental data shown in Table 4.1. Though the MSEs of this model are relatively high (19.5% and 15.8% for the 50.2 and 50.8 at.% Ni data sets, respectively), it is still useful at least as a threshold to determine whether or not a certain time and temperature parameters will result in a complete shape setting. For instance, the equations could be reconfigured as conditional statement, shown as Equation 4.5, such that when the condition is true, the heat treatment will result in a MR less than 5%.

$$t(T - \Delta T)^2 > \frac{C}{0.05} \quad (4.5)$$

4.2.2 Regression Model

Considering the high MSEs of the 1-term model, multivariate regression was used to find a more optimum solution. Limited to the four most significant terms, the resulting model form is presented as Equation 4.6.

$$MR = \frac{C_1}{t^2 T_m} + \frac{C_2}{t^2 T_m^2} + \frac{C_3}{t T_m^3} + \frac{C_4}{t T_m^4} \quad (4.6)$$

where $T_m = T - 300$. Equation 4.7 fills in the constants.

$$MR = \frac{6,096}{t^2 T_m} - \frac{1,305,003}{t^2 T_m^2} + \frac{49,800,194}{t T_m^3} - \frac{3,110,893,101}{t T_m^4} \quad (4.7)$$

Table 4.3: Results of regression shape setting model. Mean squared error compared to the experimental results in Table 4.1 are provided below the tables.

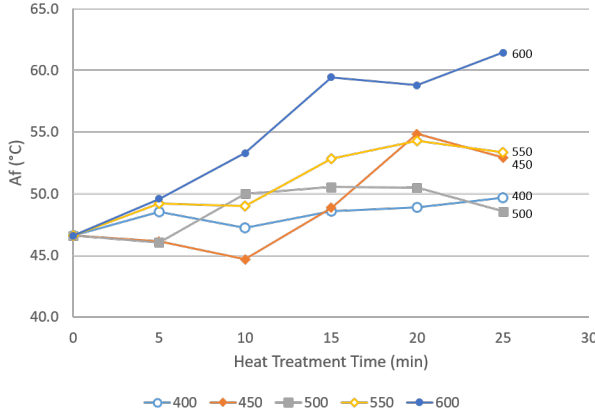
	400°C	450°C	500°C	550°C	600°C		400°C	450°C	500°C	550°C	600°C
5 min	98%	105%	75%	59%	49%	5 min	90%	103%	77%	62%	52%
10 min	124%	73%	42%	28%	20%	10 min	117%	69%	41%	27%	20%
15 min	99%	54%	29%	18%	13%	15 min	94%	50%	28%	17%	12%
20 min	81%	42%	22%	14%	9%	20 min	76%	39%	21%	13%	9%
25 min	67%	34%	18%	11%	7%	25 min	64%	32%	17%	10%	7%
Mean Squared Error:					3.2%	Mean Squared Error:					2.6%
(a) 50.2 at% Ni						(b) 50.8 at% Ni					

The results from this model are presented in Table 4.3. As can be seen, the MSE is massively reduced compared with the 1-term model, but such high order terms and massive coefficients suggest that this is an over-fitting of the data. In addition, this model does not respect boundary conditions and does not correctly predict when complete shape setting occurs. Nevertheless, the form of this model does seem to confirm the initial assertion made in Section 4.2.1 that temperature has a higher order affect than time on MR.

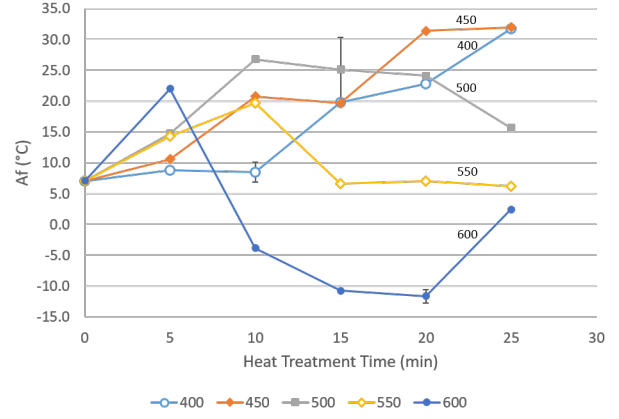
4.3 A_f Temperature

The resulting A_f temperatures of the heat-treated samples are collectively shown in Figures 4.3 and 4.4. Like with the shape setting results, these two figures represent the same data, but use heat-treatment time and temperature as the x-axis variable, respectively. The BFR curves for each individual sample are included in Appendix B.

The material data sheet for the 50.2 at% Ni nitinol (see Appendix A), rates this material as having an starting A_f of 46.5°C, and the experimental control value obtained (represented as point 0 in each plot), is 46.6°C. The same information was not provided for the 50.8 at% Ni samples, but the product in general is advertised as having an A_f of 10°C. While this is not as reliable of a figure, the experimental control results showed an A_f of 7.1°C. Overall, the results from the modified BFR measurement method described in section 3.4 seem to be reliable.

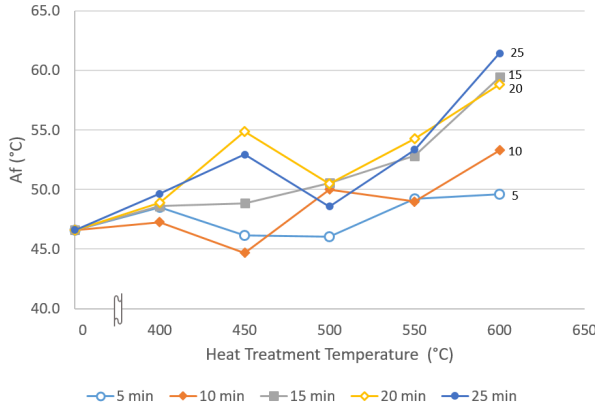


(a) 50.2 at% Ni

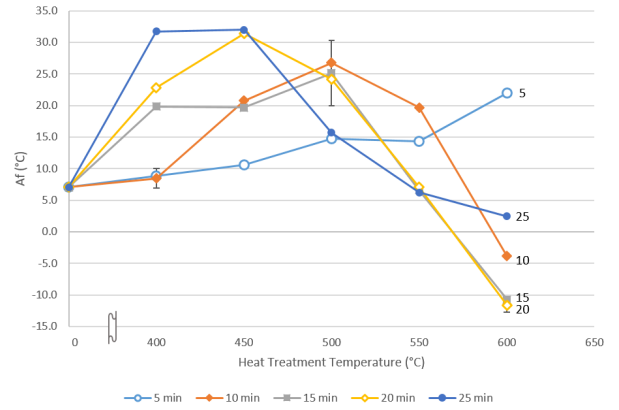


(b) 50.8 at% Ni

Figure 4.3: A_f phase transition temperature results by heat-treatment time. Error bars on the 50.8 at% Ni plot represent plus and minus one standard deviation.



(a) 50.2 at% Ni



(b) 50.8 at% Ni

Figure 4.4: A_f phase transition temperature results by heat-treatment temperature. Error bars on the 50.8 at% Ni plot represent plus and minus one standard deviation.

The same procedure described to determine standard deviation of results in section 4.1 was used here for determining A_f as well. These standard deviations are shown as error bars in the applicable figures. Notably, the standard deviation measured for the low (400°C at 10 minutes) and high (600°C for 20 minutes) setting are both below 2°C, whereas the medium (500°C for 15 minutes) was significantly higher, around 5°C. This may have been exaggerated due to an extreme outlier in the set, or it may represent a legitimate increase in sensitivity in the middle regions tested here as compared to the higher and lower temperatures. Either way, it is not so large as to invalidate the resulting trends discussed herein.

Immediately notable is the extreme difference in results between the two nitinol compositions; this stands in stark contrasts to the shape setting results where the two types of nitinol behaved very similarly. The distinction is even more pronounced when the scale is taken into account: the A_f temperatures for the 50.2 at% Ni nitinol vary over a range of about 17°C, whereas the results from the 50.8 at% Ni samples vary over a 44°C range, more than 2.5x larger.

Looking just at the results for the 50.2 at% nitinol in Figure 4.3a, it can be seen that the samples treated at 600°C stand out as increasing far above all lower temperature sets. When viewed with temperature as the x-axis in Figure 4.4a, a more recognizable pattern begins to emerge. For heat-treatment times shorter than 15 minutes, there is a dip in A_f that occurs around 450 or 500°C, higher than which it increases. At durations above 15 minutes, the A_f increases at temperature up to 450°C, and then dips back down at 500°C. At temperatures above 500, A_f again increases. Looking only at samples treated up to 500°C, the resulting curves resemble inverse behavior between longer and shorter durations. Lastly, for samples in the 15 minute set, a relatively smooth, upward curve is shown, which appears to be an intermediate between the behavior's of longer and shorter durations.

Turning now to the Figure 4.3b, there is, as expected, a notable difference in behavior above and below 500°C. The 400 and 450°C sets show a relatively steady, and seemingly linear, increase in A_f as treatment duration increases. This is contrast to the 550 and 600°C sets, which both show an initial increase in A_f , followed by a drop; in the 600°C set, the drop in A_f totals nearly 35°C. Also notable in the 600°C set is a subsequent increase again at 25 minutes. This is not shown in the 550°C samples within the timescale used in this study, though previous results would suggest that it, too, would begin to increase again at longer treatment times. The 500°C set increases in A_f over the first 20 minutes and shows a small decrease at 25 minutes; it may be the case that this temperature shows similar behavior to higher temperature treatments at longer durations.

Figure 4.4b switches to using temperature as the x-axis variable. Viewed in this way, a relatively consistent pattern is seen among sets of heat-treatment times. All durations greater than or equal to 10 minutes show an increase in A_f peaking at either 450 or 500°C, and then a subsequent

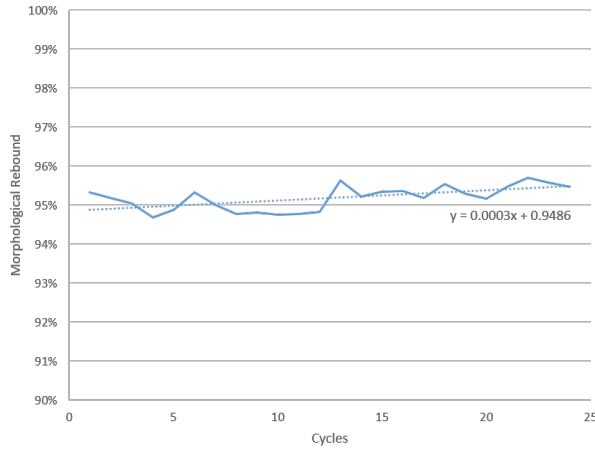
decrease in A_f , forming an inverted bowl shape. The longer duration sets generally peak at lower temperatures than the shorter durations sets. The only observed exception to this overall pattern is the 5 minutes set, which steadily increases as heat-treatment temperature rises. This behavior is not necessarily incompatible with the other time sets. It is possible that at yet higher temperatures the same inverted bowl shape curve would arise, but for the times used in this study, it still represents a break from the generally observed pattern.

4.4 Fatigue Response

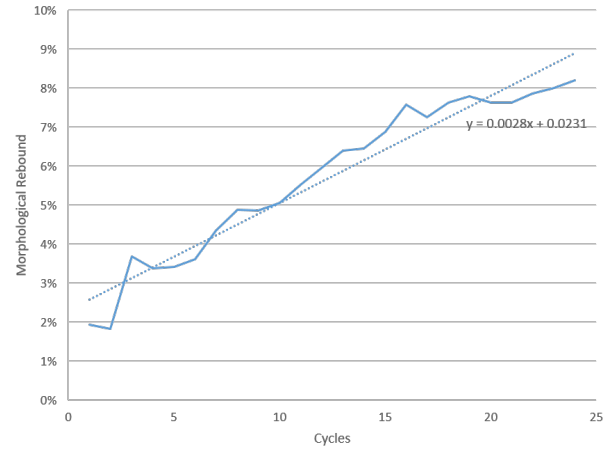
Finally, the results from the fatigue tests, described in section 3.5, are reported as morphological rebound (and thus, austenite-phase shape), measured after each fatigue cycle. Figure 4.5 shows two examples of the resulting curves generated from these tests; the rest are shown in Appendix B. As can be seen in comparing Figure 4.5a to 4.5b: some samples nearly no change outside of noise, which means the bulk shape did not change throughout the 24 cycles. Others, however, showed a steady increase in morphological rebound throughout the test, which means the austenite phase shape was slowly diverging from the fixture shape. This result is striking, as it points to the fact that some heat-treatments used for shape setting may not result in a stable shape, even after a small number of fatigue cycles. This can also be seen quantitatively by comparing the slope of the best fit lines, which are shown on the plots. The slopes shown in this figure are 0.0003 and 0.0028, nearly an order of magnitude difference.

The results from all the fatigue tests are summarized in Figure 4.6, which uses the slope of the best line as a quantitative feature. The control value, with no heat-treatment, is shown as well in these plots. Seeing as though the slope of the controls for the 50.2 and 50.8 at% Ni were about 0 and -0.0004, respectively, it seems reasonable to define significant results as those which exceed twice the control, or about ± 0.001 .

Using this definition, there appears to be no discernible pattern throughout the majority of samples, with most staying within a reasonable range of error around zero. A few notable exceptions are present: in the 50.2 at% Ni (Figure 4.6a), the samples treated at 500°C for 20 minutes appear

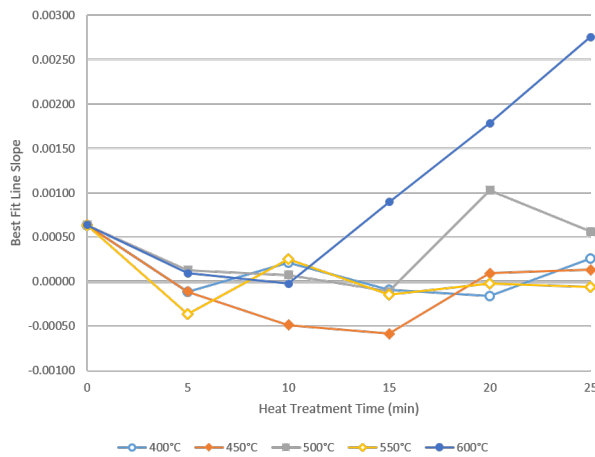


(a) 50.2 at% Ni heat-treated at 400°C for 25 minutes

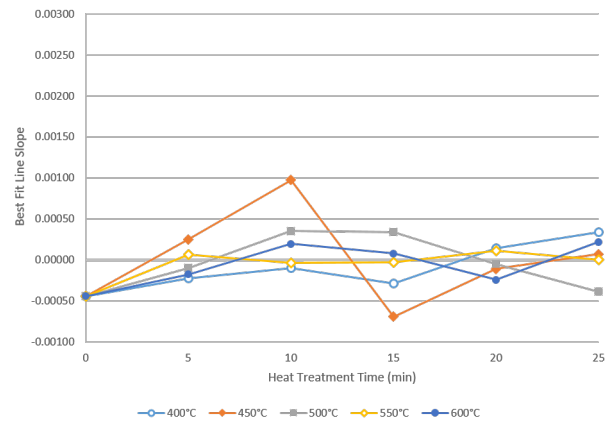


(b) 50.2 at% Ni heat-treated at 600°C for 25 minutes

Figure 4.5: Examples of fatigue test results. Results are reported as morphological rebound throughout 24 thermal and mechanical cycles. As can be seen, (a) shows no change, while (b) shows a progressive increase in morphological rebound, correlating to a loss in shape-set.



(a) 50.2 at% Ni



(b) 50.8 at% Ni

Figure 4.6: Slope of the best fit line throughout 24 cycle thermal and mechanical fatigue tests.

to show a slight loss of shape. Much more dramatically, the samples treated at 600°C, display an almost perfectly linear increase in slope for treatments between 10 and 25 minutes, with the highest slope (shown in Figure 4.5b) being about 0.0028. For the 50.8 at% Ni samples, those treated at 450°C seem to be highly variable, with the 10 minute time samples nearing 0.001, and the 15 minutes time sample nearing -0.0007. There is, however, no trend nearly as dramatic as with the 50.2 at% Ni material.

Chapter 5

Discussion

5.1 Shape Setting

The shape setting results show a clear trend: at or above 500°C, higher temperatures need less time to achieve the same morphological rebound. This implies a thermal energy threshold beyond which retwinning starts to occur. Furthermore, of all tests done in this study, the shape setting results were most similar between the two different material compositions. This may suggest that there exists a range of compositions for nitinol in which the shape setting parameters are not, or minimally, affected. This result may prove to be of significance to engineers working with nitinol, as it implies that small changes in composition choice downstream may be inert to the rest of the design parameters.

Unlike Pelton [5] and Liu [26], these results did not find that any durations under 10 minutes were suitable for shape setting regardless of the temperature. These discrepancies may be due to differences in the thermal inertial of the fixtures or in heating methods, as neither of these two authors offer much detail into their methods. It is possible that better heating methods than an air furnace, such as a molten salt bath, would decrease the time it takes to heat up the sample to the ambient furnace temperature, which may make short treatment times more viable.

Pelton's study did not have a large range of samples, but the results reported here did confirm Liu's findings that aging temperatures below 500 degrees do not result in complete shape setting with reasonable time periods (Liu did find that 450°C would eventually work for this purpose, but it would take a 2 hour heat-treatment). Both this study and Liu's support the idea that ideal heat-treatment temperatures for shape setting are between 500 and 550°C, at times above 10 minutes. The results reported here could be used as reference values for people wishing to shape set nitinol of either of these two common compositions. Finally, the heuristic model presented may add some

intuitive information on the role that time and temperature play in shape setting nitinol and may prove useful for process design considerations.

5.2 A_f Temperature

By and large, the results presented here are more in line with the Marchand's results [27] than with Pelton's [23]. Like the Marchand paper, the results of this study showed an initial increase in A_f followed by a steep and dramatic decrease ($>20^\circ\text{C}$) in samples treated above 500°C . The results for temperatures below 500 are consistent with all previously reported results.

The difference in observed behavior from Pelton's results is difficult to explain. Marchand's study states that it uses an air furnace like the present study, but Pelton does not comment on how the aging is done. It is possible that Pelton used a different method of heating, such as a molten salt bath; in this case perhaps the discrepancy could be explained by the difference in the time it would take for the samples to reach the ambient furnace temperature. The thermal inertia of the fixtures may also affect the results in a similar way.

All previous studies present and discuss these results exclusively in the format of Figure 4.3, with the data sets being grouped by heat-treatment. By switching the axes, shown in Figure 4.4, completely new patterns are able to be easily seen. These patterns cannot, perhaps, be as easily explained by temperature dependent crystallographic phenomena, which is perhaps why these results are not as often thought of in this way, but the trends presented when viewed in this way appear to be more consistent between sets than how it is traditionally presented. For this reason, thinking about heat-treatment in terms of varying temperatures instead of duration may lend itself better to the development of a working model in the future. Higher fidelity data with a larger temperature and duration range would be needed to develop such a model.

Finally, previous studies have all looked exclusively at nitinol of composition around 50.8 ± 0.1 at% Ni, as this is the typical composition used medical devices, which are a major application of the material. The inclusion in this study of a second composition, 50.2 at.% Ni, proved to be of interest, as the results were vastly different. By and large, the lower nickel composition material

showed much steadier and less dramatic changes in A_f when heat-treated as compared to the medical-grade nitinol.

Recalling Section 2.2.1, precipitation of nickel and undoing of cold work are the main factors affecting A_f . Both compositions used in this study were provided by the same manufacturer (see Appendix A), but no specifications were given on the precise amount of cold work for each. It is possible then that a difference in cold work is responsible for the different behavior. However, some studies have compared variations of cold work and not found nearly as dramatic a difference as is seen in this study [25]. Thus, it is likely that the difference in material composition is the main reason these two sets of samples behave so differently. Perhaps the lower concentration of nickel in the matrix lowers the driving force of the precipitation reaction, thus causing much slower changes. If this were the case, it would be expected that the changes in A_f temperature of the 50.2 at% Ni would exhibit similar behavior to the 50.8 at% Ni material if aged for a longer duration. Alternatively, the observed differences in response to heat treatment might be rooted in a more fundamental difference in how the Ni_xTi_y precipitates form or are distributed. If true, we would expect the difference in behavior to be present regardless of how long or at what temperature the aging is performed. Future work could examine these theories.

5.3 Fatigue Response

The fatigue tests in this study only evaluated to 24 cycles. Though this is not enough to evaluate the long-term behavior of these materials, it can show any difference in shape that might arise soon after shape setting. In some applications, such as the implant design presented in Part II of this thesis, where only a few phase-change shape memory cycles may be necessary, the ability to maintain the austenitic shape over the short-term may be important.

Nearly all samples showed minimal if any shape change over the 24 cycles. The only notable exceptions were 50.2 at% Ni samples heated at 600°C. These samples showed a significant shape change that increased with duration. For design consideration with this material, then, it would

likely be unwise to use temperatures above 550°C for shape setting heat-treatment, as the results are not stable even over a small number of cycles.

The almost perfectly linear increase in shape memory deterioration shown in Figure 4.6 implies a near-linear cause. Perhaps, at a certain point, a threshold is reached where a maximum amount of thermal energy is absorbed in the atomic reshuffling that results in austenite phase shape change (a concept explained in Section 2.2.3), and the additional thermal energy then begins to be absorbed in a deleterious way by the material. For instance, perhaps the additional heat increases the percentage of nickel-rich precipitates present in the material, and beyond a certain threshold this phase imbalance (not enough nickel in matrix, for instance, begins to work against the stability of the morphological rebound, and thus the shape memory effect, as shown here.

Interestingly, this notable result for the 600°C set was only present in the 50.2 at% Ni material. This is good news for users of medical-grade nitinol but may still act as a caution that not all heat-treatment parameters are created equal. In fact, the shape setting results were the only outcomes of this study that did not show a notable difference in behavior between the two sets of materials. Similar theories as were presented in section 5.2 may be applicable here as well. There is unfortunately no data on the cold work of these two sets of material. As has been shown by Miyazaki [24] and discussed previously here, nickel-rich precipitates form during heat treatment, so since the 50.2 at.% Ni material has less nickel in the matrix to begin with, it may be the case that the shape memory properties deteriorate at lower temperatures when compared with the 50.8 at.% Ni nitinol. This might explain why these results were only present at the highest temperatures, and why the same was not true of the 50.8 at% nitinol, since there is potentially more nickel left in the matrix after aging. If this were true, higher temperature heat treatments of 50.8 at.% Ni should show this same trend.

Chapter 6

Conclusions

In this study, the effects of heat-treatments on nitinol of two compositions were evaluated. The results presented here add reference data to the available knowledge in this field, especially with the 50.2 at% Ni, which previously has had little to no public data available in these areas. This is also the first study of its kind to use nitinol foil instead of wire; though this did not seem to have obvious effects on the behavior, it did allow a more macro-level observation. The shape setting tests helped to confirm the only other similar available results, and the A_f trends added another reference to what appears to be two schools of results from previous studies. In addition, the potential benefits of swapping axes to view A_f results in terms of time sets were presented, and promising trends based on the data when viewed this way were discussed. More data over a larger range of times and temperatures may continue to add insight to this perspective. In the future, researchers collecting similar data, or in possession of extant data, may wish to present their results in a similar way.

Ultimately, the results of this study and the shape setting models presented here may be combined to make informed design decisions when shape setting nitinol. The shape setting results showed a defined range of times and temperatures where complete setting occurs, the fatigue tests showed evidence to support avoiding treatments above 550°C, and the A_f results can be cross-referenced to ensure a parameter is chosen which does not move the phase transition temperature out of a desirable range for the application. These results will be taken into account in the design of a prototype presented in Part II of this thesis.

Part II: A Novel Design Methodology for Osseointegrated Implants

Chapter 7

Introduction

Osseointegrated implants represent a viable alternative to cementing or external fixation and have been adapted to large applications such as prosthetic limbs. Though osseointegrated solutions for amputees consistently outperform socket-style prosthesis in user comfort and ease of use [30], their adoption has been hindered by the risk of infection, prolonged recovery times, and risk of implant loosening [31]. The latter two are related to insufficient bone ingrowth. Studies have shown three main mechanical factors that are associated with successful bone ingrowth: minimal movement of the implant, sufficient space between the implant and bone to prevent resorption, and loading to encourage bone growth [32].

These factors are often mutually exclusive using current technology because applying load while leaving sufficient space to prevent resorption causes excessive movement. To reduce the trade-offs of this technology, a new design methodology is developed, based on this theory of bone ingrowth, that utilizes the unique shape memory and superelastic properties of nitinol. Devices using this methodology have anchors that deploy from the main body to lock the implant in place. The points where the anchors make contact with bone act as "active sacrificial zones", which means they can continue to expand while experiencing limited bone resorption. Therefore, these contact points can maintain rigidity throughout the bone reconstruction process, while the remainder of the implant body undergoes normal loading conditions. Following the theoretical development of this methodology, a specific implementation is proposed, and the shape setting results from the previous chapters are used to construct a prototype device.

Chapter 8

Background

Parts of the following chapter have been previously accepted as a conference paper to the Rocky Mountain Bioengineering Symposium [33].

8.1 Socket-based Prosthetic Solutions for Amputees

In the United States, approximately two million people are living with limb loss [34]. This condition, which is commonly caused by vascular disease, trauma, or cancer, is correlated with reduced physical activity and diminished health outcomes [35–37]. At present, the dominant prosthetic solution for amputees is a socket-based attachment of an artificial leg or arm. These sockets achieve load-bearing through lateral compression of the residual limb (RL) and stability by leveraging the ischial notch [38, 39].

Skin problems are common with socket-based prosthesis due to friction with the residual limb and poor temperature and humidity control. In their 2009 paper, Meulenbelt et. al surveyed a group of 805 lower limb amputees and found that 63% of participants had experienced some skin problems, and they suggest that higher activity levels may be correlated with the development of skin problems [40]. Likewise, Dudek et. al surveyed 745 lower limb amputees, 40.7% of whom reported at least one skin problem, and they similarly concluded that more active amputees are at higher risk of developing skin problems [41]. The goal using a prosthetic limb is to increase the mobility of the user, but the fact that socket attachments use soft tissue for structural support causes negative feedback between use and skin problems, which can often lead to ulceration [42]. In other words, the more successful the patient is (i.e. more active with the RL), the more likely they are to develop hindering skin complications, which then or limits their amount of activity. In addition, the soft-tissue-compression method used by these sockets often results in a trade-off between stability of the limb (related to how snug the socket is) and skin problems.

Another major issue of sockets is that the bone within the residual limb is prone to develop osteoporosis from disuse [43]. This is a consequence of Wolff's law, which states that a bone must be loaded to stimulate growth and remodeling. Again, since the socket uses soft tissue for load-bearing, the residual bone does not receive enough weight-bearing to be healthy, a process called stress shielding. These trade-offs show how the fundamental methodology of socket-based prostheses is flawed. Though there are dozen of attempts to reduce the negative effects of sockets [38], the human body simply does not use soft tissue to support weight, and this divergence from mechanical function causes numerous problems which afflict many, and have proven difficult to overcome.

8.2 Macrobiocompatibility

Here, the concept of macrobiocompatibility is introduced, which is used as a theoretical framework for understanding the shortfalls of socket-based prosthesis and the merits of alternative paradigms. On a small scale, the idea of microbiocompatibility is often used to describe a "biological inertness" of a substance with respect to human biology [44]; if we extend this concept, we might say that macrobiocompatibility is a structural inertness with respect to human biomechanics. In other words, a macrobiocompatible strategy would function without changing the basic local mechanics of its system. When viewed in this way, it might be said that the basic methodology of sockets, which use soft tissue compression instead of rigid fixation, has a fundamentally low macrobiocompatibility. This lack of macrobiocompatibility is starkly demonstrated by the prevalence of skin problems associated with socket use. A more macrobiocompatible solution is desirable, of which the field of osseointegrated prostheses (OIP) is a good candidate.

8.3 Osseointegrated Prosthetic Solutions

8.3.1 History

Osseointegrated implants were originally introduced in the field of dental surgery by Per-Ingvar Brånemark in the late 1960s [45]; he defined osseointegration as "a direct structural and functional

connection between ordered living bone and the surface of the load-covering implant" [46]. The basic principle consists of a porous, inert material, typically titanium, inserted into a bone, which, over time, allows bone ingrowth into the implant itself and creates a true, rigid bond between bone and implant. It has been shown that after successful ingrowth, it is impossible to separate bone from metal without fracturing it; in other words, they have fused together structurally [32,47].

More recently in the early 1990s, Per-Ingvar's son, Richard Brånemark, pioneered the first lower-limb osseointegrated implant for use with transfemoral amputees. This implant was inserted directly into the patient's intramedullary cavity and ingrowth was allowed for 6 months before attachment of a prosthetic leg [48]. Since then, this technology has expanded to be used in transtibial, transradial, and even transmetacarpal amputees. Two main OIP systems dominate the landscape: the Swedish Osseointegrated Prostheses for the Rehabilitation of Amputees (OPRA), and the Australian Osseointegration Group of Australia Accelerated Protocol (OGAAP) [31,49–53]. OPRA has recently been approved by the FDA as a humanitarian device exemption (HDE) to be used in the United States.

8.3.2 Methodology and Benefits

OIP methodology relies on rigid biofixation to achieve load-bearing and stability, which is the same mechanical process by which a natural skeletal system functions. In this sense, it might be said that osseointegrated fixation is more macrobiocompatible than socket fixation. Many functional outcomes support this assertion. To start, the skin of the residual limb is not covered or loaded, thus allowing natural temperature, humidity, and shear control. As a result, OIP users don't suffer from the same skin problems so prevalent with sockets. In addition, since the residual bone is naturally shouldering the load, the risk of osteoporosis is reduced, and a natural posture is easier to achieve [43,54]. Numerous studies have found up to a 44% increase in average walking speed and improved hip range of motion for patients with OIP [30,55–61]. Since the prosthetic limb itself is rigidly connected to the skeletal system, users of OIP have reported the phenomenon of "osseoperception", where a certain amount of haptic feedback is achieved through the prosthe-

sis, allowing for improved control of the artificial limb [62–65]. Furthermore, users have reported improved sitting comfort [55] and a more natural-looking limb due to the fact that OIP's abutments don't need to stick out as far, especially for patients with longer residual limbs [62]. Finally, an economic analysis performed by Haggstrom et. al found that OIP cost about the same as socket-based solutions over a lifetime of use [66].

8.3.3 Current Drawbacks

Despite the many benefits of OIP over socket fixation, some serious problems do arise. Perhaps most notably, the OIP systems have a percutaneous abutment, which results in a stoma where skin meets implant. The infection risk at the stoma is significant, affecting between 18% and 42% of patients [31, 51]. This complication disqualifies patients who have atherosclerosis from receiving OIP, a population that makes up about half of all amputees [34, 49]. Another complication results from the fact that titanium, often used in these implants, has a higher elastic modulus than bone, which can result in a stress-shielding effect and increased force translation into the upper condyles [67, 68]. In addition, recovery time can range from weeks to years. This problem arises from the fact that most patients elect to get an OIP after already healing from their original amputation surgery, which greatly extends the total recovery time. In addition, bone ingrowth is a slow process, so many OIP protocols call for no-load or light-load conditions for several months to allow satisfactory ingrowth before full weight bearing can begin. This slow build-up of loading pressure requires significant recovery time and numerous clinic visits during the early stages. Finally, though relatively infrequent (2 – 6% of cases), there is a risk of implant loosening, bone resorption, or insufficient osseointegration which requires revision surgery or the need to remove the implant altogether, extending total recovery time even further [31, 54, 60, 61, 69–76].

The latter two problems, delayed load-bearing and implant loosening, are both related to obtaining sufficient bone ingrowth. The long recovery times necessary before use ensure that bone ingrowth completes, and the problems with implant failure are what results when ingrowth does not complete or begins to reverse course. Therefore, though the methodology of OIP is an improve-

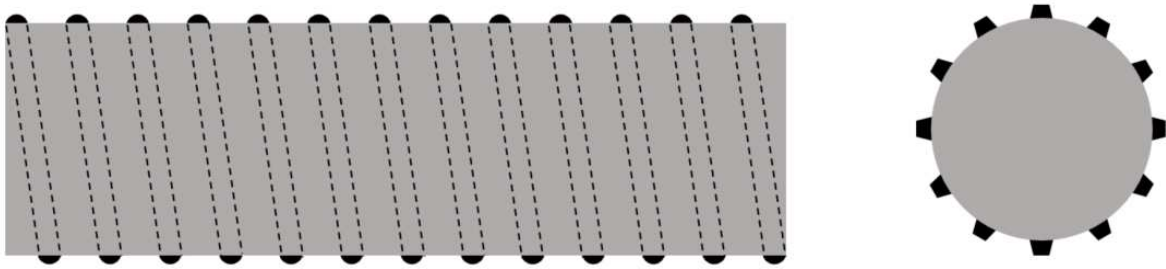


Figure 8.1: Approximate cross-sections of the Swedish (left, transverse cross-section) and Australian (right, axial cross-sections) implant models. The protrusions shown in black represent the splines or screws used to create high-pressure areas and dig into the bone, which leaves the main implant bodies, shown in gray, to be under better growth conditions.

ment over traditional socket solutions, there is still a need for improved methods to decrease the time required before loading can take place and increase the likelihood of successful implantation.

8.3.4 Conditions for Successful Osseointegration

In their 2009 article, "Biology of implant osseointegration", Mavrogenis et. al discuss three main factors that are correlated with successful bone ingrowth [32]:

- Minimal movement of the implant with respect to surrounding bone ($< 30 \mu\text{m}$) [77, 78]
- Sufficient empty space between implant and bone to prevent resorption (100 - 500 μm) [79]
- Axial loading to encourage bone growth [32, 47, 79]

These three factors are often mutually exclusive with current implant technology; for instance, applying load to the implant early on while still leaving sufficient space to prevent resorption would cause too much movement and break apart any cartilage that began to form, increasing recovery times. The most advanced implants on the market today use rigid splines or screw shapes to create alternating regions of high and low pressure between the implant and bone, essentially creating two zones of contact points which each meet part of the criterion for successful ingrowth (Figure 8.1) [49, 53].

Chapter 9

Development of Novel Implant Design Methodology

9.1 Theoretical Development of Design Methodology

Recalling the ideal growth conditions from section 8.3.4 [32], there are three main mechanical factors which are associated with successful bone ingrowth, but they are often mutually exclusive. An element placed too tightly against the bone will cause resorption, but primary stability is necessary to begin load bearing. The current solution to this paradox uses splines or screw patterns which can grab the bone for primary stability (Figure 8.1), which puts the rest of the implant in a better position to allow good ingrowth. The problem with this strategy is that it leaves a significant portion of the implant to undergo resorption. Once the resorption begins to take place, this portion becomes inherently looser with potentially negative effects on primary stability. The proposed methodology attempts to improve on this by having the "tight" portions of the implant actively expand outward to maintain constant pressure, and therefore constant primary stability, throughout a longer period of time. This idea of "actively sacrificial" anchors could, in theory, provide more time for ingrowth before the load-bearing is transferred from the anchors to the main implant body. Expanding anchors could also enable a higher gripping pressure, and thus potentially increase the primary stability and/or decrease the portion of the implant body that is used for initial gripping.

To summarize, this design paradigm uses anchors which deploy from the main body to "lock" the implant in place. The pressure applied by the anchors to the intramedullary walls provides the primary stability for the implant. Since the anchors can actively deploy, there could, in theory, be more hold strength than a typical press fit design. The high pressure at the contact points will likely experience local bone resorption over time, but they can continue to expand outward to maintain a constant pressure. The active anchors, then, with their potentially high-pressure contact points, could allow for a larger portion of the implant body to be at an ideal offset from the walls,

providing space for ingrowth without risk of resorption. In this way, all three of the mechanical factors discussed by Mavrogenis can be simultaneously satisfied.

9.2 Nitinol-Implemented Design

Though there are many ways that this basic concept could be implemented (see section 10), the proposed solution utilizes nitinol with an A_f below body temperature as the anchoring material. This material was chosen because the shape memory property allows the anchors to be compressed during insertion and then "deploy" by a phase change when the implant is positioned correctly. Furthermore, the superelastic property allows the anchors to continue to expand significantly longer than other metals using this same strategy. All this can be accomplished with a single piece of material, without any hinges, joints, pins, or springs. This solution was partially inspired by the shape memory locking device designed by Shah *et al.* for crown placement in dental implants [80].

In the proposed design, the nitinol is formed into a cylinder with slots cut out to allow the formation of bulging anchors. This then acts as an inner liner within a more traditional porous implant body. There are "windows" cut out from the main implant body to allow the shape memory anchors to deploy and adjust freely without affecting the position of the main body.

9.3 Prototype Development

A prototype of the nitinol inner liner design described in section 9.2 was developed as a proof of concept.

9.3.1 Digital Prototype

First, a computer aided design (CAD) model was created. Figure 9.1 shows the step by step production of the liner. First, a flat sheet of nitinol foil is punched to create the anchors. It is then rolled and joined together by a laser welder or similar joining technique. Finally, it is shape set so that the "deployed" position with the anchors becomes the austenitic default shape.



Figure 9.1: A CAD drawing of the nitinol insert demonstrating anchor deployment when the device is heated. (left) shows the punched sheet of nitinol, (middle) shows the device after being rolled and joined, when the internal temperature is below A_f , and (right) shows the device when the internal temperature is above A_f .



Figure 9.2: The shape memory insert fits into the larger implant body (left) and a cross-section of the insert (gray) and main body (black) together (right).

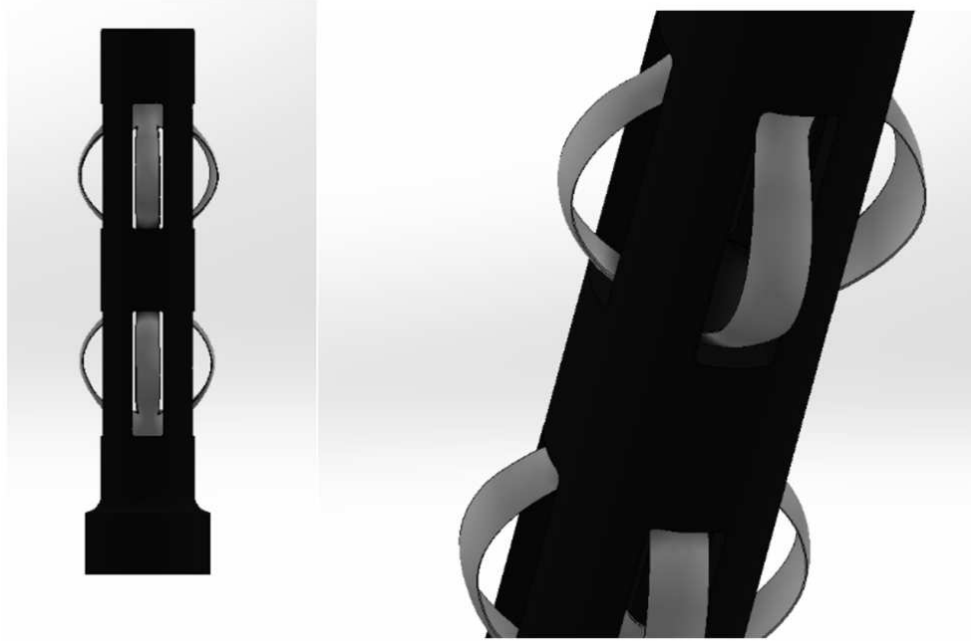


Figure 9.3: Shape memory insert (gray) inside the larger implant body (black) with anchors in the deployed state (exaggerated for demonstration).

Next, the main implant body is drawn, and the liner is added to form an assembly. Figure 9.2 shows how the liner, cooled below M_f and deformed back into a cylinder, is inserted into the main implant body. The windows cut into the implant body are lined up with the flaps of the nitinol liner to allow them to freely deploy. The liner would be fastened in the middle either by a screw or a form of fusion such that the top and bottom portion of the liner, along with the anchors, are free moving. This allows the anchors could freely deploy without any loss of symmetry. Finally, Figure 9.3 shows the fully assembled digital prototype with deployed anchors.

9.3.2 Physical Prototype

A physical prototype was then constructed from the same nitinol foil material described in section 3.1, and using the same process described in section 9.3.1. Figure 9.4 shows the constraining fixture used during heat-treatment to shape set the anchors such that they default in austenite to a deployed configuration. Essentially, thin bolts are threaded onto the 0.5 inch diameter steel rods described in section 3.2. The uncut portions of the foil are strapped directed to the rod body with



Figure 9.4: The fixture used to set the deployed anchor positions.

stainless steel hose clamps, and the bolts work to hold the anchors in a deployed position. Using the information obtained in section 3.2, a shape setting heat-treatment of 550°C for 20 minutes was used, as was shown to be suitable for this task in Part I of this thesis. The resulting device is shown in several stages of unconstrained anchor deployment in Figure 9.5.

For a general idea of the potential lateral force output generated by the anchors, a simple experiment was devised. The device was placed, below A_f and with anchors collapsed, between a fixed surface and a load cell. The load cell was then calibrated to account for the weight of the device. After calibration, the system is heated above A_f , and the anchors expand and press against the load cell, as shown in Figure 9.6. The resulting measurement represents the force output of two anchors, since one will expand upward against the fixed surface, and the other downward against the load cell. This test was repeated for each set of anchors, and at three different distances between the surface and the load cell, to capture the force generated at different points in the anchors' expansions. These tests resulted in an average of 5 N generated by each, individual anchor, as shown in Figure 9.7.



Figure 9.5: Prototype device deploying anchors during a martensite-to-austenite phase transition. (left) is in complete martensite, (middle) is intermediate, and (right) is in complete austenite.

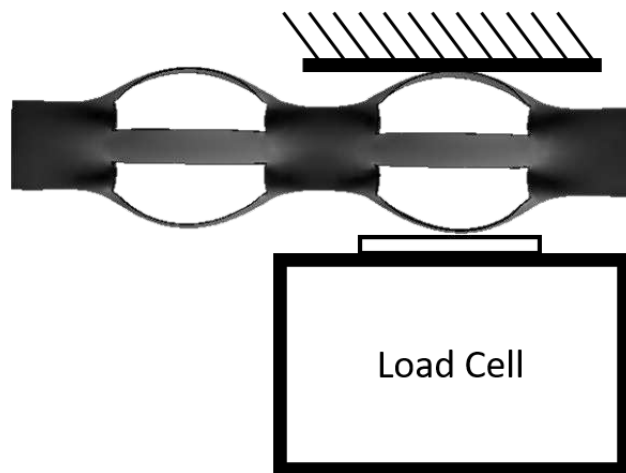


Figure 9.6: Load cell testing of device prototype. The device is pinned between a fixed object and a load cell. Since this setup has one anchor expanding upward, and one downward, the resulting force represented 2x the force delivered by an individual anchor. The load cell is calibrated to account for the weight the device itself.

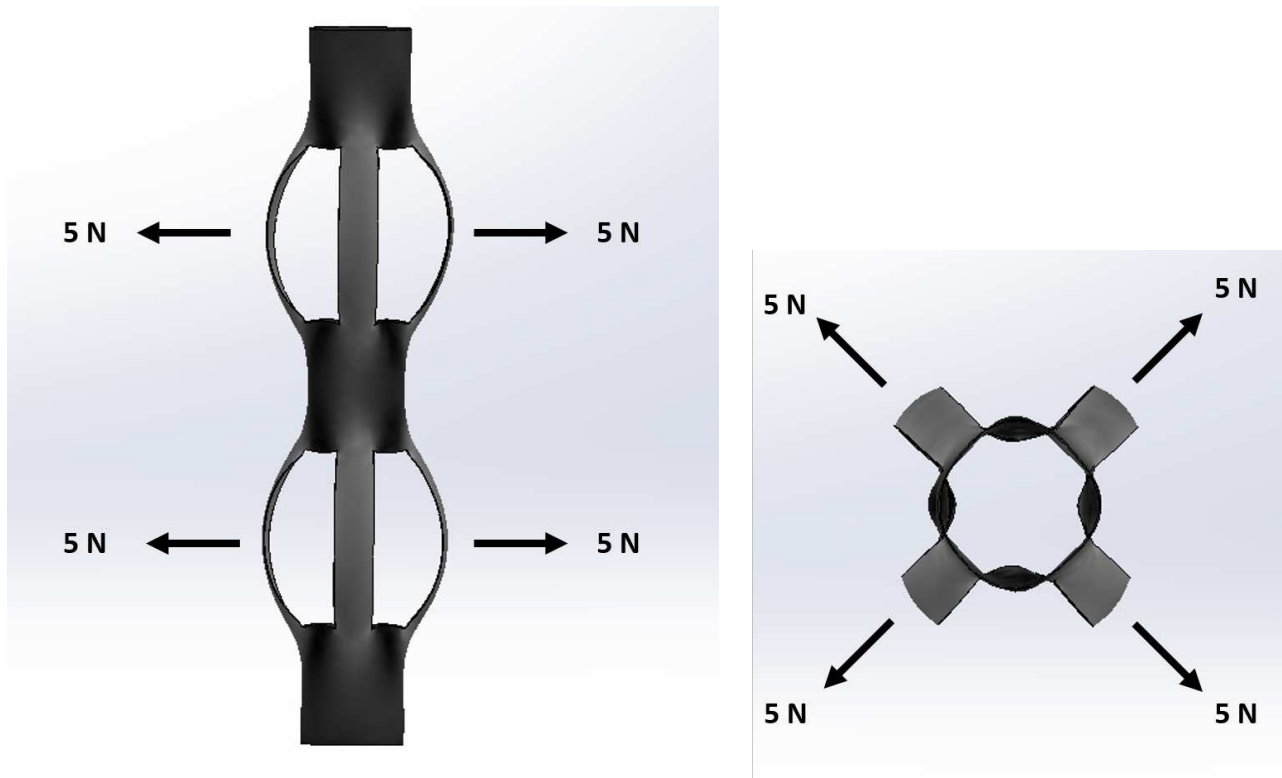


Figure 9.7: Side (left) and top (right) view force diagram of the prototype during thermal expansion.

Chapter 10

Discussion

The simple force tests discussed in Section 9.3.2 resulted in 5 N generated per anchor. Though this may not be enough for some of the potential applications presented here, it is still impressive considering that the nitinol foil used in this study has a thickness of only $0.127mm$. A thicker foil could provide higher force outputs, and, of course, more anchors could be added in parallel to increase total force output.

This lateral force should coincide with the pull-out force, or the amount of force necessary to remove the implant if "pulled" on before any bone ingrowth has occurred. To demonstrate the feasibility, consider a pullout weight of $400lbs$, which might represent the weight of an average US male times a factor of safety of 2. This would correspond to a pullout force of about $1800N$. Assuming a linear relationship between nitinol thickness and force generation, the device could easily be made of $1.27mm$ thick material, thus increasing the force generated per anchor to $50N$. It would thus take 36 anchors to achieve this, or 9 sets of 4 anchors. If we then assume the length of each anchor segment to be $1cm$, with $1cm$ of space between each anchor segment and $1cm$ at the top and bottom, then a device that supports a pullout weight of $400lbs$ would need to be at least $19cm$ long. This is by no means out of the question when considering the application of femoral implants. In addition, typical safety and rehabilitation protocols would likely make such a large pullout force unnecessary.

Finally, the proposed device presented here has theoretical improvements over the current generation of devices, but this nitinol insert style implementation is not the only way in which this design paradigm might be developed. For instance, the entire structure could be made of nitinol, with the deployable anchors built into the implant body itself. Another form might be to use nitinol wire woven through the implant body instead of large, foil anchors depicted here. This may have less stability per contact point, but the number of contact points could be massively increased. Spring steel could be used in place of nitinol, provided that some mechanism of holding it back be-

fore deployment is provided and sufficient biocompatibility is maintained. Lastly, a spring and pin mechanism could be used as the deployable anchors, with nitinol or some other latch mechanism being used to time the deployment. Finally, this design methodology, which uses actively sacrificial deployable anchors, was developed for use with osseointegrated, lower limb implants, where there appears to be the most need for improvement. However, this same methodology may find use in other osseoanchored devices, such as upper limb, finger, and toe implants, or osseointegrated dental implants.

Chapter 11

Conclusions

A new design paradigm for OIP implants is presented, and a prototype was built using the knowledge gained for the shape setting experiments. This design methodology intentionally uses actively sacrificial anchors to maximize the portion of the implant body that is under ideal or near-ideal bone ingrowth conditions and extend the efficacy of the primary stability. The proposed device has nitinol anchors that deploy from the main body to lock the implant in place. This design has the potential to improve early-stage bone ingrowth, which could allow for an accelerated weight-bearing timeline for patients, and ultimately could increase the accessibility of this slowly emerging technology. A proof of concept prototype was built and tested, and showed promising results for the feasibility of this concept. This design, however, is only in the prototype stage. Future work is needed to validate the improvements, which are largely based on the theory of how osseointegration occurs. Force testing and calculations can be performed to verify and tune the pressure conditions for the anchors, and animal model testing would be required to test the hypotheses presented here.

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Appendix A

Material Specifications

Nitinol manufacturer: Alfa Aesar

Material Composition: 50.8%:49.8% Ni:Ti by mole fraction

Product number: 44952

Lot number: R11E041

Material Composition: 50.2%:49.2% Ni:Ti by mole fraction

Product number: 45514

Lot numbers: R31F052, X02D055

Appendix B

Additional Figures

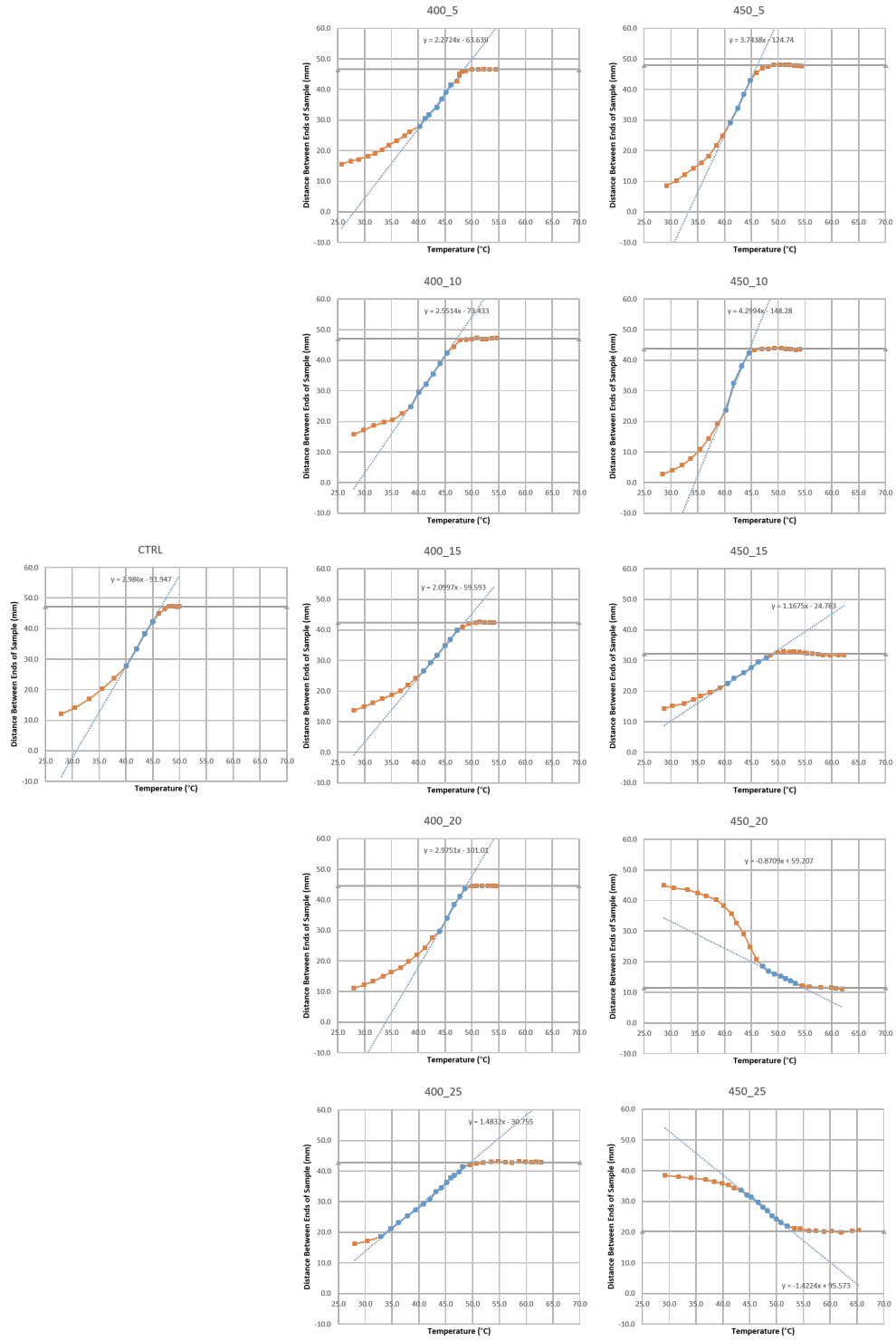


Figure B.1: Bend and free recovery (BFR) plots for 50.2 at% Ni. Control (CNTRL), 400°C, and 450°C heat-treatments. Figure titles are formatted as [heat-treatment temperature]_[heat-treatment time].

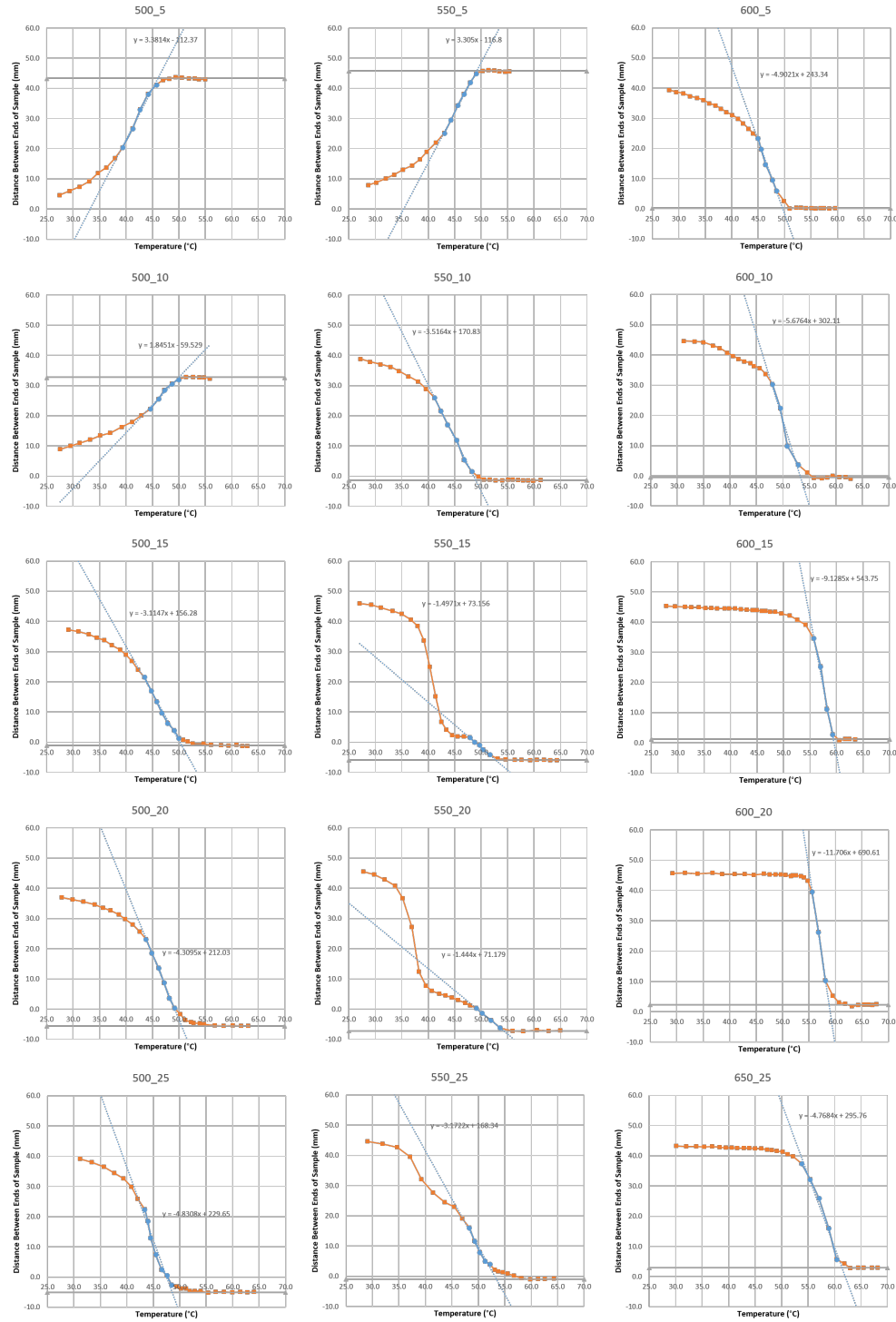


Figure B.2: Bend and free recovery (BFR) plots for 50.2 at% Ni. 500°C, 550°C, and 600°C heat-treatments. Figure titles are formatted as [heat-treatment temperature]_[heat-treatment time].

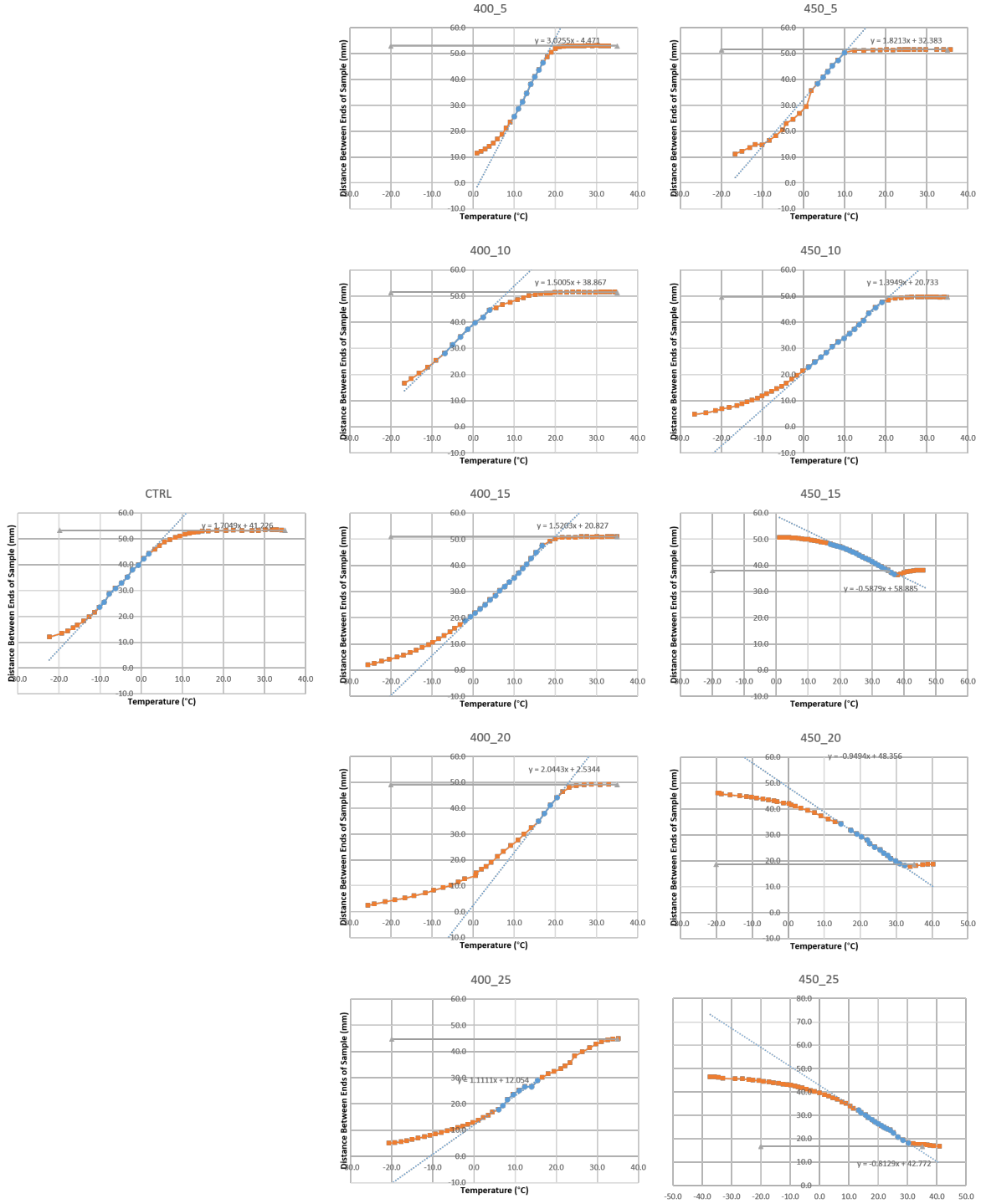


Figure B.3: Bend and free recovery (BFR) plots for 50.8 at% Ni. Control (CNTRL), 400°C, and 450°C heat-treatments. Figure titles are formatted as [heat-treatment temperature]_[heat-treatment time].

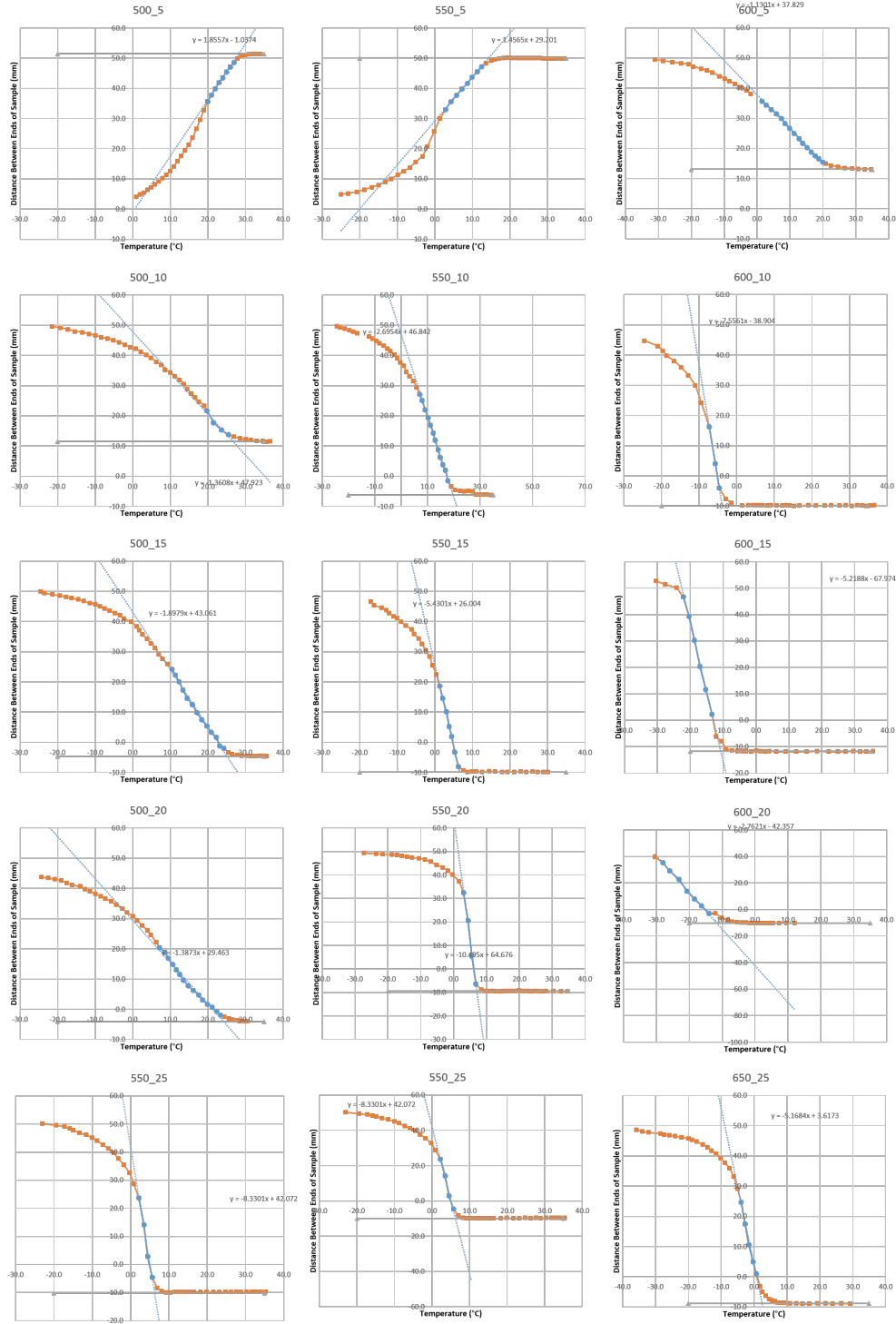


Figure B.4: Bend and free recovery (BFR) plots for 50.8 at% Ni. 500°C, 550°C, and 600°C heat-treatments. Figure titles are formatted as [heat-treatment temperature]_[heat-treatment time].

Sample	plateau (y)	slope (m)	y-intercept (b)	Af (x)
CTRL	47.2	2.9860	-91.9467	46.6
400_5	46.6	2.2724	-63.6388	48.5
400_10	47.1	2.5514	-73.4333	47.3
400_15	42.4	2.0997	-59.5933	48.6
400_20	44.5	2.9751	-101.0052	48.9
400_25	42.9	1.4832	-30.7551	49.7
450_5	48.0	3.7438	-124.7392	46.1
450_10	43.8	4.2994	-148.2787	44.7
450_15	32.2	1.1675	-24.7834	48.8
450_20	11.4	-0.8709	59.2073	54.8
450_25	20.3	-1.4224	95.5734	52.9
500_5	43.3	3.3814	-112.3730	46.1
500_10	32.7	1.8451	-59.5286	50.0
500_15	-1.1	-3.1147	156.2818	50.5
500_20	-5.5	-4.3095	212.0322	50.5
500_25	-5.0	-4.8308	229.6495	48.6
550_5	45.8	3.3050	-116.8002	49.2
550_10	-1.4	-3.5164	170.8319	49.0
550_15	-6.0	-1.4971	73.1557	52.8
550_20	-7.2	-1.4440	71.1786	54.3
550_25	-0.9	-3.1722	168.3379	53.4
600_5	0.2	-4.9021	243.3378	49.6
600_10	-0.4	-5.6764	302.1056	53.3
600_15	1.2	-9.1285	543.7464	59.4
600_20	2.3	-11.7063	690.6137	58.8
600_25	2.8	-4.7684	295.7573	61.4

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Figure B.5: A_f calculations for 50.2 at% Ni nitinol.

Sample	plateau (y)	slope (m)	y-intercept (b)	Af (x)	STD 3 samples
CTRL	53.3	1.7049	41.2260	7.1	
400_5	53.1	1.6271	38.7951	8.8	
400_10	51.6	1.5005	38.8665	8.5	1.6
400_15	50.9	1.5203	20.8274	19.8	
400_20	49.1	2.0443	2.5344	22.8	
400_25	44.7	0.9966	13.1367	31.7	
450_5	51.6	1.8213	32.3827	10.6	
450_10	49.7	1.3949	20.7332	20.8	
450_15	38.1	-0.5056	48.0046	19.7	
450_20	18.6	-0.9494	48.3560	31.4	
450_25	16.8	-0.8129	42.7724	32.0	
500_5	51.5	1.4924	29.5322	14.7	
500_10	11.5	-1.3608	47.9235	26.8	
500_15	-4.6	-1.8979	43.0614	25.1	5.2
500_20	-4.0	-1.3873	29.4633	24.1	
500_25	-10.3	-6.4653	91.0834	15.7	
550_5	50.1	1.4565	29.2009	14.3	
550_10	-6.2	-2.6954	46.8419	19.7	
550_15	-9.9	-5.4301	26.0037	6.6	
550_20	-9.5	-10.4951	64.6759	7.1	
550_25	-9.8	-8.3301	42.0723	6.2	
600_5	13.2	-1.1160	37.7193	22.0	
600_10	-9.8	-7.5561	-38.9044	-3.8	
600_15	-11.8	-5.2188	-67.9740	-10.8	
600_20	-10.3	-2.7621	-42.3574	-11.6	1.1
600_25	-8.9	-5.1684	3.6173	2.4	

Metadata
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Figure B.6: A_f calculations for 50.8 at% Ni nitinol.

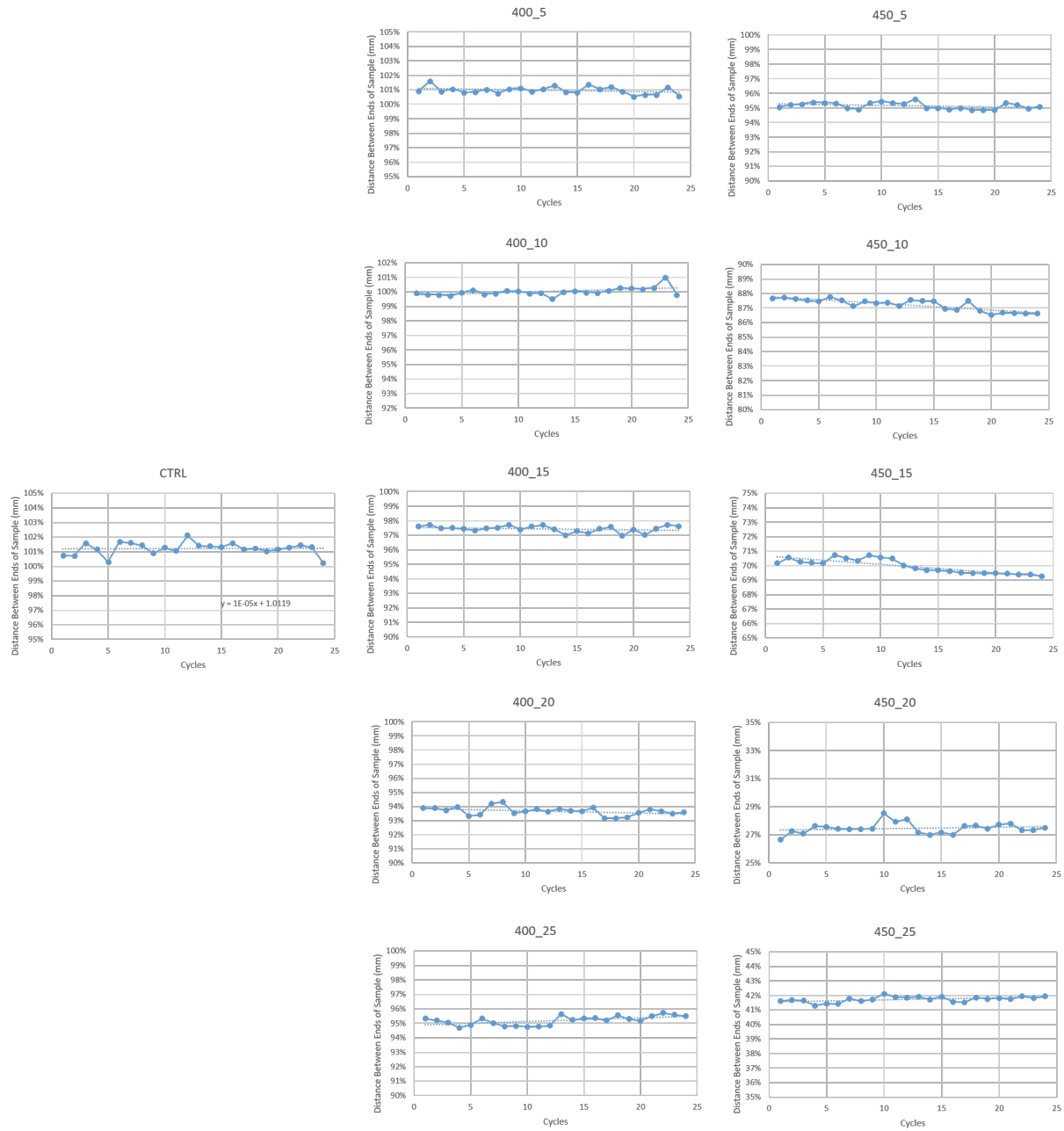


Figure B.7: Fatigue plots for 50.2 at% Ni. Control (CNTRL), 400°C, and 450°C heat-treatments. Figure titles are formatted as [heat-treatment temperature]_[heat-treatment time].

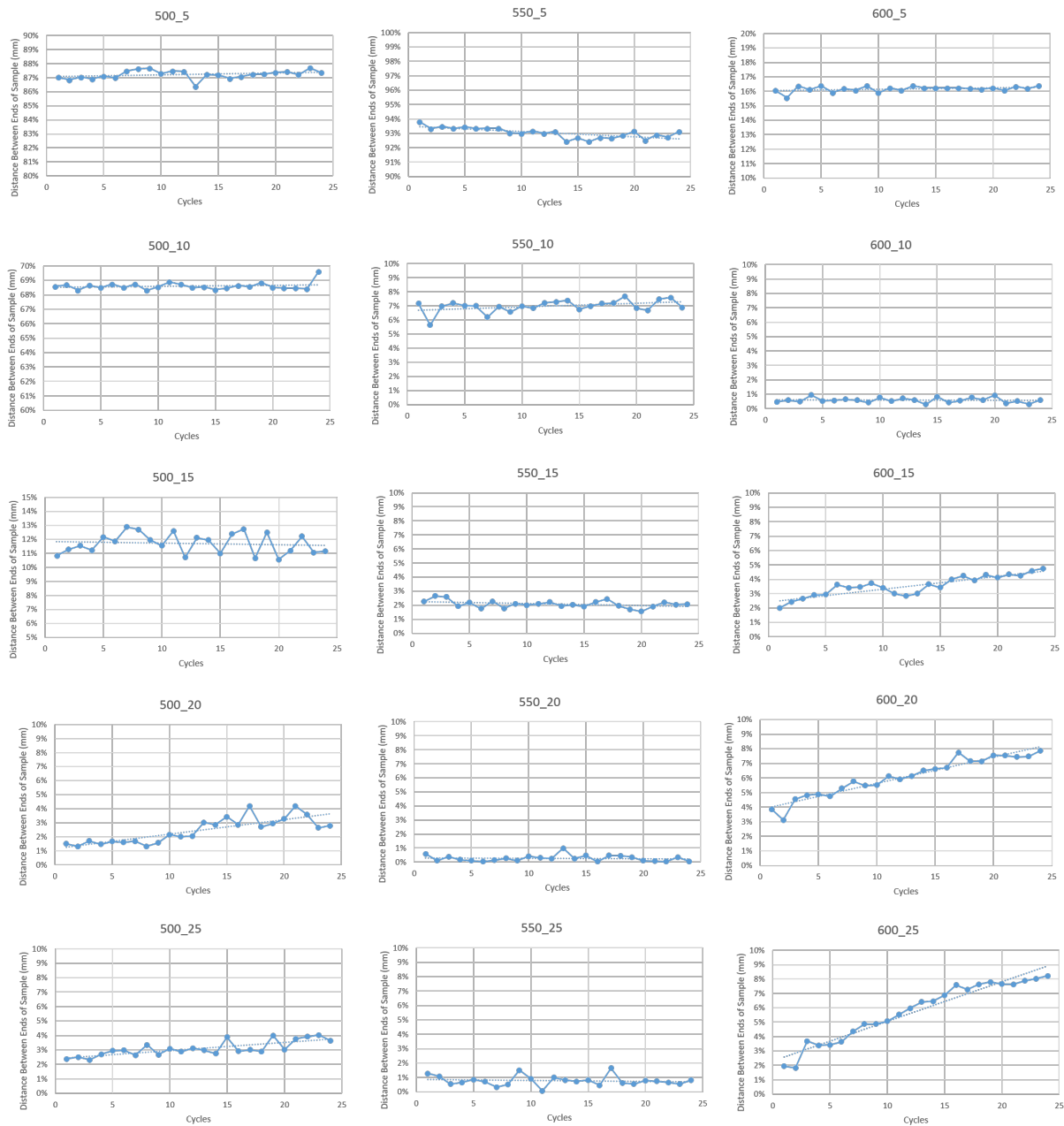


Figure B.8: Fatigue plots for 50.2 at% Ni. 500°C, 550°C, and 600°C heat-treatments. Figure titles are formatted as [heat-treatment temperature]_[heat-treatment time].

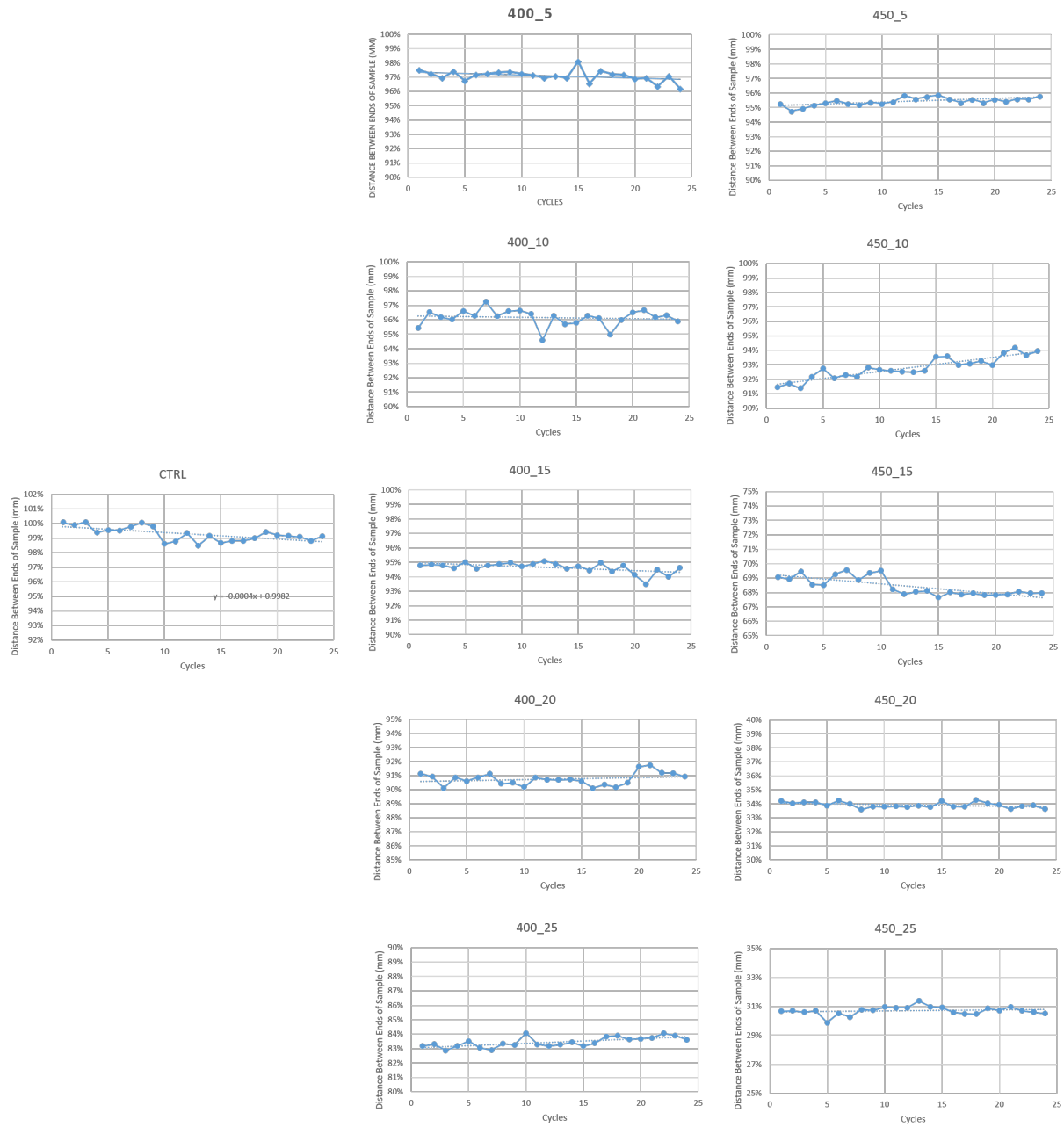


Figure B.9: Fatigue plots for 50.8 at% Ni. Control (CNTRL), 400°C, and 450°C heat-treatments. Figure titles are formatted as [heat-treatment temperature]_[heat-treatment time].

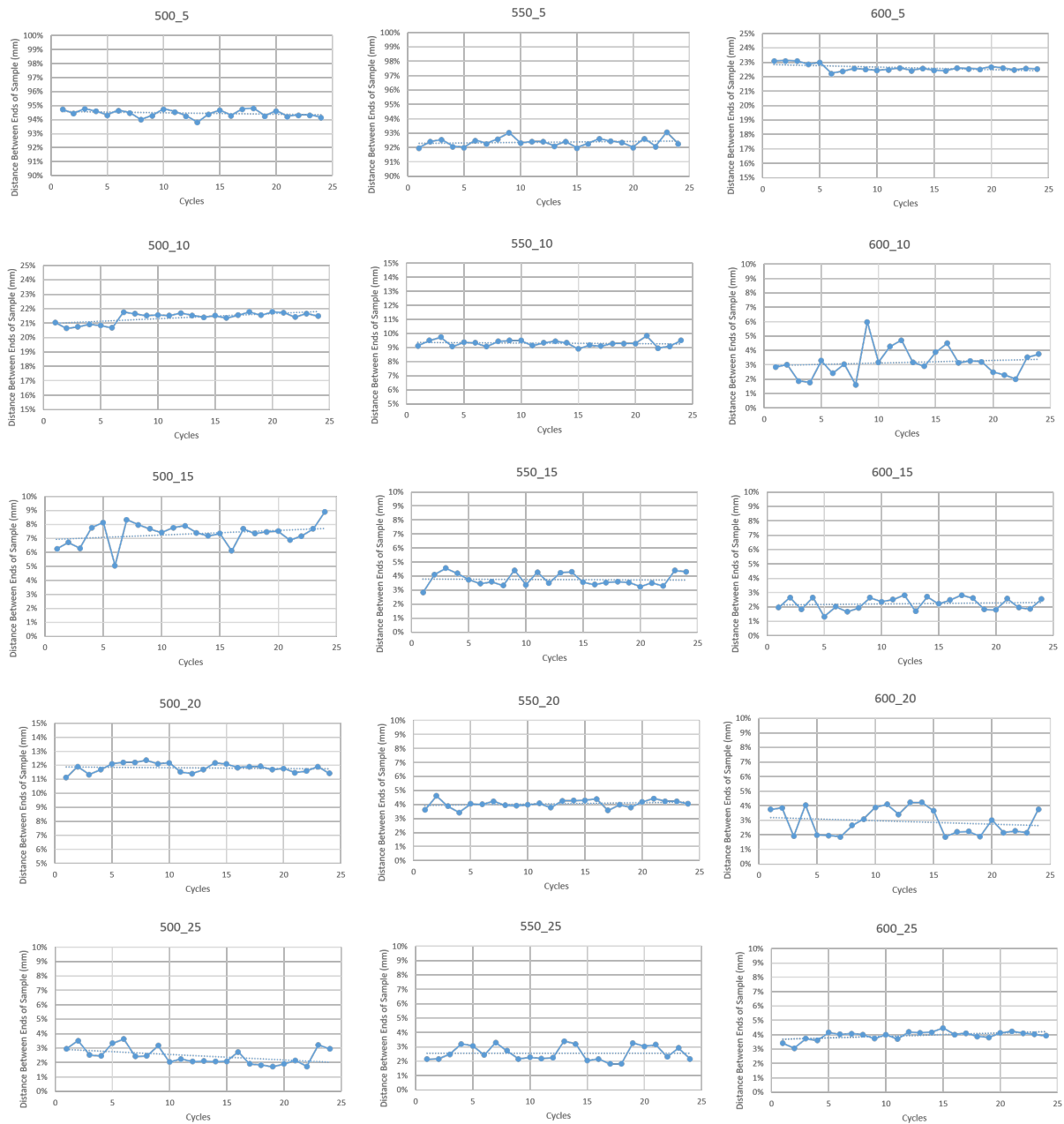


Figure B.10: Fatigue plots for 50.8 at% Ni. 500°C, 550°C, and 600°C heat-treatments. Figure titles are formatted as [heat-treatment temperature]_[heat-treatment time].