Effect of Oxidation on Weld Strength of Dissimilar Resistance Weld
Interface Between 304 Stainless Steel and Near Equiatomic
Austenitic Nitinol Guide Wire

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TITLE: Effect of Oxidation on Weld Strength of Dissimilar Resistance Weld Interface Between
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Abstract

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Abbott Vascular encountered strength and variability issues when attempting to resistively weld 304 Stainless Steel to equiatomic Nitinol. Initial observations suggested that passivation layer (Cr_2O_3 , TiO_2) formation affected the weld interface. One hundred 304 Stainless Steel/Nitinol pairs were allowed to oxidize in air at room temperature for allowed periods of time (.1, 1, 3, 5, 7, 12, 16, 24, 168, and 336 hours). Each pair was welded resistively with constant current. A Miyachi/Unitek Advanced Data Analysis Monitor (ADAM) recorded the peak resistance at the instance the weld was made. Resistances were compared to Instron 5900 tensile maximum break load (KgF). Use of optical microscopy and Scanning Electron Microscopy (SEM) revealed microstructural reduction of void size at the sample fracture surface (1-.5 μm). Literature suggested the existence of metastable precipitate forms at near equiatomic compositions within the theoretical temperature range (261.9-1425.2 $^{\circ}\text{C}$). The Instron 5900 mechanically validated presence of precipitates, while Electron Dispersive X-Ray Spectroscopy (EDS) confirmed the existence compositionally. Literature confirms B19' precipitates size increases with temperature. This suggests higher resistance samples will promote growth of precipitates due to increased heat input. Increased average particle size was observed with increased resistance (0-.3 μm). Crystal lattice inconsistencies between Nitinol parent phase (B2) and B19' promote premature fracture due to increased misfit dislocation density. Therefore increased weld resistance promotes the growth of incoherent Ti_3Ni_4 precipitates which inhibit load bearing capabilities, causing premature failure.

Keywords: Nitinol, 304 Stainless Steel, Resistance, Weld, Precipitate

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3. Introduction

3.1 Welding Process

Abbott Vascular is increasing the efficiency of guide wires. Guide wire is a delivery system used to navigate the cardiovascular system and its myriad of veins and capillaries to implement biomedical devices. Typically cardiovascular stents and catheters utilize the guide wire for implementation. The average distance from the femoral artery, the logical entry site for easiest access and minimal incision, to the heart is 2.75 ft. The guide wire has traditionally been comprised of multiple components. The first is the primary shaft, a single solid cylindrical wire with an optimal Modulus of Elasticity so the guide wire can be stiff enough to navigate the 2.75 feet, while maintaining its structural integrity around corners instead of puncturing the vein wall. The second component is the lead, an innovation that allows the guide wire to transverse extreme angles within the cardiovascular system by employing a material that has a low stiffness. The reduced stiffness allows the lead to bend around turns instead of puncturing the wall. The last piece is a mechanical clamp used to physically attach the shaft and the lead. This clasp is mechanically deformed to indent the sides of the two other components locking them into place.

In an effort to optimize guide wire performance while reducing cost, Abbott Vascular is attempting to eliminate the need for a mechanical clamp currently used to join the two materials by welding the shaft and lead together forming a metallurgical bond. A metallurgical bond will attempt to atomically join the two metals at an interface. The interface is the section at which the two metals come into contact. Through the use of heat and pressure, the two materials can be interlocked together by metallic mixing, or diffusion.

The heat input into the material is the joules (J) applied to generate sufficient heat to promote a phase change. To produce a phase change, there are four zones (Heat Affected Zone, HAZ) that are based on the amount of heat applied at a point [Figure 1]. The initial point of direct contact (zone 1) is

the weld/liquid pool. The liquid pool receives the largest amount of heat input. This amount of heat input causes the material to undergo a phase transformation to a one phase region comprised completely of liquid metal. This is generally referred to as the fusion zone. The section of material that dissipates the heat throughout the material (zone 2) is referred to as the 'mushy zone'. This is a two phase region along the interface between the melting temperature (T_L) and the solidification temperature (T_s). We see partial melting due to the heat applied by the arc. This is the region where nucleation (grain growth/coarsening) and growth occur (grain refining/recrystallizing). The area (zone 3) that receives large amounts of heat input, but not sufficient heat to reach the melting temperature (T_L) is referred to as the partially transformed region. The size of the partially transformed region depends on the materials ability to dissipate heat based on thermal conductivity, cross sectional area, and amount of heat originally applied. Depending on the amount of heat input, the material's properties could be altered. The heat from the weld is sufficient to heat treat the partially transformed region. The grain structure of the partially transformed zone will not necessarily mimic the bulk material or weld pool. The properties of the partially transformed region tend to degrade as compared to the bulk. The bulk material (zone 4) is the base metal that is completely unaffected by the arc and heat input. This material is unchanged because all heat has been dissipated by the HAZ so that there is not sufficient heat to alter the material's grain structure ^[1,2].

Figure 1- Modeling of heat transfer and fluid flow of Heat Affected Zone (HAZ) in low carbon steel using Gas Tungsten Arc welding. Zone 1 is the material that reaches the melting temperature (T_L). Zone 2 is the partially solid zone (mushy zone). Zone 3 is the partially transformed region which no melting has occurred but enough heat has been transferred to alter grain structure ^[1].

Abbott Vascular has chosen to use resistance welding due to the minimal available weld area of the wires. In resistance welding of guide wires, the relative area of the material's HAZ is reduced to a uni-axial cylinder because of the nature of the weld interface compared to the total affected area. The entire cross sectional area is considered the weld interface, so no partially transformed material is observed radially[Figure 2]. Therefore the weld transfers the majority of heat through the material into the bulk material. We still observe all four zones characterized by an arc weld, but they are throughout the entire cross section of the wire.

Figure 2- Schematic of resistance weld between dissimilar metals depicting differences in HAZ of a guide wire. . Zone 1 is the material that reaches the melting temperature (T_L). Zone 2 is the partially solid zone (mushy zone). Zone 3 is the partially transformed region which no melting has occurred but enough heat has been transferred to alter grain structure.

The resistance weld is a process of applying voltage or current across the material using the material's natural resistance to heat the weld interface. The weld interface experiences heat below the melting temperature (proprietary value) of the two materials. A pressure is applied to force the near molten materials together. The pressure deforms the two wire ends together creating a weld nugget around the interface.

Despite the differences in the welding processes (arc versus resistance), the results are similar. All four zones of the HAZ are observed. The main difference is the shape and size of each zone of the weld. As stated before, each zone will be cylindrical expanding outward from the weld interface instead of spherical layers expressed in arc welds. The size of the each zone of the HAZ is greatly reduced because of the amount of heat required to initiate welding. The surface area-to-volume leads to rapid cooling of the weld.

The two materials will be joined to optimize properties of the 304 Stainless Steel and Nitinol. 304 Stainless steel is a metallic compound comprised of Fe, <0.08% C, 17.5-20% Cr, 8-11% Ni, <2% Mn, <1% Si, <0.045% P, <0.03% S. The high elastic modulus (193 GPa) will allow sufficient force to be applied to the primary shaft to increase maximum distance travelled without failure. 304 Stainless Steel is also selected because it is biocompatible with human systems.

Biocompatibility is a material's ability to interact with an organism without adversely affecting normal function, improving biological functionality, or poisoning the host system ^[3]. 304 Stainless Steel meets the requirements of a biomaterial because it does not leech toxins into its host system. This is because of the passivation layer that forms on the surface of the material. A passivation layer is a protective oxide that forms near instantaneously. An oxide is a compound that forms as oxygen diffuses into a host material. The oxygen bonds with the host metal to form a ceramic sheath on all exposed surfaces. The passivation layer protects the 304 stainless steel from future corrosion by not allowing other elements, besides oxygen, to diffuse into the host metal and react.

3.2 Oxidation Formation

Oxidation is kinetically driven process. The initial oxidation is near instantaneous, while future growth follows a diminishing return following Equation 1-2, the Arrhenius equation. The amount of oxygen that can diffuse through the passivation oxide decreases as the oxide thickness increases.

$$k = K n e^{(-\frac{Q}{RT})} \quad (\text{Eq. 1})$$

$$\alpha(t) = 1 - e^{(-n(kt))} \quad (\text{Eq. 2})$$

Where K= pre-exponential factor, α = volume of diffusional section, k= reaction rate, n= constant experimentally determined (n=3) , Q= activation energy, and t= time ^[13]. This relationship works conversely as well. 304 Stainless steel alloying elements cannot leach through the passivation layer to diffuse out into the environment. Thermodynamically, Chromium-Oxide (Cr_2O_3) is preferred to form as the passivation layer ^[4]. The stable phase forms on the exposed area of the primary shaft.

3.3 Material Properties / Crystal Structure

Nitinol forms titanium-dioxide (TiO_2) surface as the thermodynamically stable phase. Despite ceramic structure of the biocompatible TiO_2 passivation layer, Nitinol has a super elastic property^[5]. Nitinol is super elastic because it has the ability to twin to activate a phase transformation from austenite to martensite under load, instead of plastically deforming through dislocation movement (Figure 3). This reversible process allows the material to endure load cycles a typical metal could not bear. The super elastic property depends upon the Nitinol composition, and transformation temperature range ($M_s - M_f / A_s - A_f$, depending on reaction direction). The range is the point at which Martensite or Austenite will begin and finish forming during loading. The transition temperature range of the Nitinol alters its ability to transfer loads^[6]. Below the A_s , the material can maintain the twinned Martensite state after unloading. Above the A_f , the Martensite will return to austenite upon unloading.

Figure 3- Schematic displaying the reversible twinning transformation of Nitinol during loading and unloading^[6].

The lattice parameters of the materials do not correspond. The lattice parameter is a theoretical spacing of particles based on atomic packing. The spacing assumes perfect spherical atoms arranged without vacancies or interstitial atoms. The lattice parameter and crystal structure give insight into how well materials crystal structures will correspond. 304 stainless steel has a crystal lattice parameter of

.361 nm for the FCC austenite phase (Figure 4) while the CsCl phase of Nitinol has a lattice parameter of .3015 nm (Figure 5) ^[7,8].

Figure 4- Atomic arrangement of Face Centered Cubic (FCC) of austenitic 304 Stainless steel^[9].

Figure 5- Atomic arrangement of CsCl Structure of austenitic Nitinol ^[9].

The differences in lattice parameters cause misfit strain. Incoherent interfaces induce misfit strain on the crystal lattice by forcing the atomic arrangement out of the normal atomic spacing. Coerced compression or tension on a crystal lattice will increase the interfacial strain energy ^[10]. The increased interfacial strain energy imposed in the crystal increases the probability of cleaving at the interface to reduce the total free energy of the material. The creation of a surface, due to fracture at the weld, will relieve the material of the misfit strain (Figure 6).

Figure 6- Misfit Stress caused by expansion or compression of equilibrium lattice spacing. The increased stress and strain will promote cleavage at interface to reduce energy ^[10].

Improving the contact area of the weld will reduce the probability of the weld separating at the interface. To improve the interface, the ends of the wire need to be atomically clean and close. Atomically close is a theoretical perfectly flat surface that would allow the two bulk metals to be completely in contact with each other prior to the weld. This would ensure maximum weld area, increasing the strength of the weld. Clean refers to the materials weld surface to be impervious to contaminants. The ideal weld interface is a metal surface with no contaminants, oxides, or unexpected precipitation. Therefore the weld would contain no inclusions post weld.

Perfectly clean is near impossible with 304 Stainless Steel and Nitinol, due to the passivation layer that forms. The previously stated oxidation prevents the two base metals from coming into direct contact.

3.4 Senior Project/Pilot Study

Abbott Vascular began a study to determine which factors were most influential in increasing the strength and integrity of the weld. There were six factors explored; alignment, force, heat input, surface finish, and final grind. A 6x6 partial factorial exploring 36 combinations, with ten samples per group exposed the break strength via proprietary rotational bending with each of the 6 factors

controlled at 3 levels each. Weld groups outside of two standard deviations were determined to be “above satisfactory”, while groups below two standard deviations were labeled “unsatisfactory” (Figure 7). The results showed that groups above two standard deviations (top red line) used higher weld force during welding which promoted higher strengths and integrity. Integrity is defined as reduction in variation within a group of welds.

Figure 7- Study (Senior Project) exploring 6 factors, graphing average break strength (psi) for each group. Data points are separated by red lines showing two standard deviations from the grand mean.

Images from each group, satisfactory, above satisfactory, and unsatisfactory were imaged with Scanning Electron Microscopy (SEM). The images from the ‘above satisfactory’ group showed similar trends which included large amounts of ductile fracture over the entire cross section of the weld interface (Figure 8). SEM images from the ‘satisfactory’ group showed mixed ratios of ductile and brittle fracture (Figure 9). These samples tended to have moderate break strengths. The last group showed trends which included large amounts of brittle fracture. The existence of brittle fracture suggested that

the oxide at the interface was causing differences in weld strength because metal was not able to fuse during the resistance weld process.

Figure 8- SEM image of 'above satisfactory' group displaying large amounts of ductile fracture at weld interface.

Figure 9- SEM image of 'satisfactory' group displaying ductile and brittle fracture at weld interface.

3.5 Research Question

To fully understand the difference in strength, other aspects of the welding process were assessed. Factors included incubation time prior to weld, resistance during weld, and time prepared prior to welding. Oxidation prior to welding was determined to be a main factor because of the

differences in resistance that were observed in the first study. This led researchers to question what effect time prior to welding had on the weld strength. **What effect does the thickness of oxide developed on 304 Stainless Steel and Nitinol in standard atmospheric conditions (25 °C, 50% humidity) have on resistance weld interface properties and variability?**

4. Methodology/ Experimental procedure

4.1 Pilot Study Statistical Power Analysis

Based on the Senior Project/Pilot study previously discussed, and available materials, a statistical power of .9 was achieved by comparing the variability within each group. Statistical power is a studies projected ability to make valid conclusions. The variability allocated 9 samples per group. Therefore 10 samples were selected at random to be used in the study. Each of the 10 samples was separated into 9 groups. The samples were then prepared according to the amount of time allotted for oxide growth.

4.2 Sample Wire/Group Preparation

The 90 samples were obtained from a single lot of bulk material. Each specific lot was separated out into 9 groups containing 10 samples each, as stated before. Each 304 Stainless Steel and Nitinol sample was cut to at least 9 inches in length. The largest stainless steel sample was 30 inches long. Each sample was simultaneously ground down to achieve similar flush ends. The ends were required to be clean, completely normal to all edges of the base, and have no visible abrasions. Each wire was ground using 1200 grit polishing paper. This procedure removed the native oxide without aggressively lacerating the surface. The sample aperture was rotated 90 degrees every 10 revolutions to vary scratch directions and randomize surface morphology.

Each group of 10 sample pairs received treatment at a specific date and time to allow oxides to form in standard atmospheric conditions (25 °C, 50% humidity). The groups included instantaneous, 1, 3, 5, 7, 12, 16, 21, 24 hr(s), 1 week, and 2 weeks of oxidation time. Each group was held in a similar 2 gallon plastic bag to reduce variability within groups. Each group was placed in the same air conditioned room, 68 degrees Fahrenheit/48-51% humidity, within the facility. Once required time for oxidation had been achieved, each sample pair was loaded in the proprietary welding apparatus.

Prior to welding the samples did not receive any other treatment. The samples were welded using a constant current. A Miyachi/Unitek Advanced Data Analysis Monitor (ADAM) recorded electrical resistance data at the moment of welding. The peak resistance in mOhms was manually recorded on a data sheet directly after the weld was completed. The samples were tagged with weld group and run order to correlate results.

After weld completion, each weld developed excess material, or weld mushroom, composed of material that was plastically deformed radially while the two materials were resistively heated and forced together using an air piston. Welding parameters including force, alignment, grinding, heat input, and preparation are proprietary and reserved by the manufacturer.

The weld mushroom/excess must be removed so that the weld cross section matches the parent diameter of the host wires. Each wire was ground down using a rotating belt sander at 300 rpm. The wire was draped over the belt grinder and manually rotated evenly applying light pressure until the weld excess was removed. Each wire was optically inspected and verified with a micrometer to ensure that flush diameter had been achieved around the weld interface. The typical diameter ranged from .3-.35 millimeters.

4.3 Optical Microscopy Preparation and Treatment

A sample from group 14, no allowed oxide growth time, was randomly selected, mounted and polished to reveal the longitudinal cross section of the weld interface. The sample was mounted in acrylic and allowed to set and cure for 10 minutes (Figure 10). The polymer mount was ground down using a belt sander. The sample was then prepared using grinding papers ranging from 240 to 600 grit paper. The sample was manually ground down using moderate pressure and one orientation. After 20 repetitions the sample was rotated 90 degrees and transitioned to the next finest grinding paper. After three repetitions the sample was ready to be polished.

Figure 10- Section of 304 Stainless/ Nitinol weld mounted in polymer. Ground and polished to reveal microstructure.

The sample was washed using a soap, deionized water, and ethanol series to remove any excess particles from the previous step. This reduced the chance of contaminating the finer polishing paper. The sample was polished using a 6 micron diamond polishing lubricant. Once the surface had all major scratches removed, the sample was cleaned using the previously stated method. The sample was progressed to 1 micron diamond lubricant and felt pad to remove any possible scratches left from the 6 micron polish. The sample was cleaned once again after the 1 micron polish and prepared for submicron alumina final polish. Once the weld interface had been properly polished, the sample was etched with 25 ml HNO_3 , 25 ml HF , and 5 ml Deionized water. The sample was etched for a total time of 2 seconds. This chemical corrodes the solute rich grain boundaries of Nitinol, exposing NiTi grains.

4.4 Instron 5900 Testing Parameters/ Analytical Software

The prepared samples were strained to failure using an Instron 5900 50 KN Tensile/Compressive system. Bluehill 2 analytical software was used to record and analyze the data observed from the tensile test. Wyoming Test Fixture split Capstan wire grips were used to secure the wire into the fixture to be tested in a normal field, perpendicular to the optical beam (Figure 11). The samples were loaded into the fixture allowing 20 cm of wire between the load points. The samples were allowed to have a slight amount of slack so that a biased load would not be implemented prior to fracture. This allowed each wire to be loaded identically throughout the study. The weld interface was positioned in the center of the load area to maximize chance that the weld would fail at the interface. The sample was loaded 10 mm/minute. Sample extension and load was displayed in real time using Bluehill's custom method.

Figure 11- Instron and wire grip set at 20 cm gauge length.

Maximum load prior to fracture was displayed in Bluehill's read out. Each specific maximum was recorded on the raw file, an excel spreadsheet, and within the Bluehill archives. Once samples had been

fractured, the fixture was returned to the original distance. The fractured sample was removed from the wire grips. The fracture surfaces were located and regrouped with their original identification. The samples were set aside for further inspection. The next sample was randomly selected from the specific weld group that was being tested. This reduced the chance of variation among groups due to user error. The sample was loaded using the previously stated load method. The remaining samples were tested using the same set of parameters to maintain consistency of results.

JMP Pro 9 was used to analyze the variation within groups as well as the amount of error within each group. The standard deviations, average break strength within each group, upper/lower quartiles, and standard error were obtained using an x-y fit analysis. The maximum load was plotted against peak resistance and grouped by oxide growth time. The data was also analyzed separately with respect to maximum strength, peak resistance, and oxide growth time. This gave insight into the variation and standard error of each parameter.

4.5 Scanning Electron Microscope (SEM) Imaging Parameters

As stated previously, 7 sample pairs were selected for further inspection. In every weld examined, the fracture occurred either at the interface, or in the Nitinol. Therefore, the 304 Stainless steel was the half of interest for further inspection. The fracture surfaces on the 304 stainless sections of the 7 samples were identified and prepared for Scanning Electron Microscopy (SEM).

The samples were separated into groups and cleaned using an ultrasonic cleaner. The samples each ran through a 1 minute acetone cycle immediately followed by a 15 minute methanol cycle, and finished with a 5 minute ethanol bath.

The fractured samples were loaded on a 90°/45° SEM stage mount using carbon tape to adhere the samples to the platform. 2-3 samples were loaded on the stage at once to reduce pump time. Samples were exposed to High vacuum (6×10^{-6} Torr) within the chamber. The samples were imaged

using 20 KV excitation voltage which outputted filament current of 2.7 Amps on average, and an average emission current of 100 μ Amps, with a spot size of 4.

Each sample was imaged normal to the plane of fracture at 700x magnification. This allowed for differences in diameter to be observed. The sample's cross section was also imaged at 500x magnification and 45° to give adequate examination of the fracture surface. Lastly, the samples were imaged perpendicular to the beam at 19,459x to understand surface morphologies. Void sizes were measured using the micron bar measuring each grain at a hypothetical 45° angle across the flat surface spanning from the lower left corner of the image to the top right corner. Each grain was measured from the ridge that defined it. Five images taken from the center, top left/right, and bottom left/right quadrants. The total average void size was computed and a range was established to give a quantitative measure of the size of the grains. Other points of interest were imaged at varying angles and magnifications. The SEM images gave insight into surface morphology, and also gave clues into which sections should be examined compositionally by X-Ray Photoelectron Spectroscopy (XPS).

4.6 X-Ray Photoelectron Spectroscopy (XPS) Testing Parameters

The 7 selected samples were tested using XPS to determine the relative existence, composition, oxidation state, and thickness of the oxide purposefully grown. The 7 samples were ultrasonically cleaned again using the previously stated acetone, methanol, and ethanol ultrasonic cleaning procedure.

XPS analysis was performed on a Kratos Axis Ultra Spectrometer (Kratos Analytical, Manchester UK). A monochromated, Al k-alpha x-ray beam was used. The wire tips were cantilevered from the edge of a glass slide to avoid interfering photoelectron signals from the sample bar and double-sided tape. Samples were spaced far enough apart that the approximate 300 x 700 micron data collection area would allow signal from only one sample at a time. Survey spectra were recorded at a pass energy of 160 eV and an emission current of 225 W. High-resolution scans of Ti and Cr were recorded at a pass

energy of 40 eV and an emission current of 300 W. Low-energy electrons from a neutralizer filament were used for charge compensation.

4.7 Energy Dispersive X-Ray Spectroscopy (EDS) Testing Parameters

EDS analysis was performed on a JEOL Scanning Electron Microscope running Image pro software. The system utilizes a Thermoscience Nanotrance detector running eds_in__dipstick temperature control.

Samples were imaged on a 45/90° SEM stage adhered by carbon tape. All samples were mounted on the normal plane being separated by 2 mm to avoid interference from nearest neighbors. The system ran on high vacuum (HV), bias enabled with a spot size of 7.5 at an excitation voltage of 20kV.

Each weld interface received an initial element map to scan and identify which elements were present at the surface. A cameo was constructed by overlying multiple elements over the electron image to determine relative abundance and physical location. Nickel was identified as the color yellow for the overlay cameo, and Titanium was assigned blue. Contrast and brightness of the counts collected were equalized to give a balanced idea of actual differences between samples. Four samples were tested individually for areas of interest using a point&id mode, or an area of interest. Data was output via the EDS software package. The elemental composition was tabulated in atomic % to give insight into atomic ratios and compositions.

5. Results

5.1 Peak Resistance vs. Time before welding Results and Statistical Analysis

The peak resistances (mOhms) values collected by ADAM display differences between groups. Table I can be used for all future letter correspondence. Peak resistance varied within each group (Figure 12). Statistically significant differences were observed between groups. Group A is significantly different from all other groups except for group G. Group G is significantly lower than groups B,D, and I. Lastly, Group H is significantly lower than Group I as well. Group A showed significantly lower average peak resistance (mOhms) compared to the other groups. Groups A was prepared and welded with minimal time between preparation and weld. The minimum peak resistance observed was 30.46 mOhms from Group A. The maximum resistance observed was 166.74 mOhms from Group B. This shows a difference of 5.47 times between the maximum and minimum values.

Table I- Key for letter correspondence

Time before weld	ID Letter
.1	A
1	B
3	C
5	D
7	E
16	F
24	G
168	H
336	I

Figure 12- Peak Resistance (mOhms) of each weld separated by Time before weld (Labeled A-I).

Variation of peak resistance between groups was not significant except for Group A. Group A had a standard deviation of 1.88. Group H has the closest standard deviation at 7.15. Group A (minimum) has a grouping that is 3.8 times tighter than the closest group, and 15.9 times tighter than the largest standard deviation, Group B (1 hour). No obvious trends are noticed after Group B (1 hour) - Group H (2 weeks). The upper and lower quartiles of each group (except Group A) intersect at multiple locations. This trend shows that the variation between groups is similar after the instantaneous preparation (Figure 13).

There is an interesting phenomenon happening between the variations and average peak resistance between Groups B-E. There is a substantial increase in the average peak resistance (91.67 mOhms) and decrease in variation at Group D (5 hours).

Figure 13- JMP Pro 9 Mean and Standard deviations of peak resistance (mOhms) by time before weld

Variation among groups presents an interesting observation after Group G (24 hours). The average peak R of Group G drops to 56.11 mOhms. This represents a 20.2 mOhm decrease in average peak resistance from the previous group (Group F). The groups that received extended oxidation time had resistances that increased by 12.1 mOhms (Group H), and 38.6 mOhms (Group I), respectively.

5.2 Mechanical Test: Weld Strength and Statistical Analysis

The load vs. extension of the three materials is plotted to express trends regarding fracture mechanisms between unwelded 304 Stainless Steel, unwelded Nitinol, and the welded samples (Figure 14). The 304 Stainless steel has the highest average tensile break strength at 23.91 KgF (234.5 N). Nitinol has an average break strength of 14.58 KgF (143.8 N). Welded samples strengths ranged from 4.07 KgF (40 N) - 11.31 KgF (111.07 N).

Figure 14- 304 Stainless Steel, Nitinol, and Weld load vs. extension plotted on same axis

The curve of the weld models the elastic properties of the 304 Stainless steel until 5 kgf (50 N); at this point plastic properties began to model the properties of Nitinol. The shape of the weld extension vs. load curve resembles a reduced Nitinol curve. This is speculated to be the reduced volume of available Nitinol to transfer load via martensitic transformation. The fracture is hypothesized to be in the Nitinol portion of the wire based on the load vs. extension curve. Upon optical inspection, it was determined that every sample except one fractured in the Nitinol portion of the weld, confirming that after 5 kgf the wires began to follow Nitinol fracture mechanics. Representative weld interfaces with low (green), average (red), and above average (blue) break loads were plotted to express trends in the data (Figure15). Initial observations show that elastic and plastic regions of the three welds are similar, along with the extension behavior between 5-15 mm. At this stage of loading, increased strength begins to be associated with increased extension.

Figure 15- Load (kgf) vs. extension (mm) of three representative 304 SS/Nitinol welds including peak Resistance of each weld investigated.

Secondary trends show peak resistance (mOhms) of the three welds tends to decrease as strength increases. Lastly, there is an inflection, denoted by an asterisk in figure 15, in the below average and average samples, with the below average drop in load being larger than the average load drop. No obvious cause for the inflection in load was observed.

The break load versus time to weld graph (Figure 16) shows no obvious trends in the data with respect to group oxidation. There are visible differences in the weld groups mean strength and variability between data points, but statistically the visible differences are insignificant. According to a power of .9 the only statistically significant difference in means was .1 hour vs. 168 hour delay, and 5 hour delay compared to 168 hour delay.

Figure 16- Maximum break load of welded guide wires separated by time before weld

In this study there were four outliers, one was removed due to user error and is not tabulated into the results (Figure 17). The end result is 3 values that despite proper processing still displayed break loads outside of three standard deviations, group C, E, F respectively. Despite few means being significantly different, the quartiles tend to show that increased time for oxidation increases the amount of variation between the maximum break loads within groups after 100 hours. Differences in variation were examined to verify any trends. The lowest standard deviation, and therefore variance was recorded by Group A at $\sigma = 2.52$. Groups B, D, and G had similar variances; 2.58, 2.67, and 2.65 respectively.

Figure 17- Load with respect to time before weld (JMP Pro 9) displaying error (red), quartiles (blue), and outliers (Asterisk). Outliers fall outside of 3 standard deviations from the mean.

To examine the previous theory regarding reducing effects of resistances on increasing maximum break load, the peak resistance (mOhms) was plotted against load for the 90 welded samples (Figure 18). The large cluster of data points in the center of the load vs. peak R plot contradicts the original theory that the time to oxidize before welding directly influences the characteristics of the weld interface. This is observed by the large density of data points centered between the 80-100 N break load, and 60-100 mOhms range. First observations show nonlinear, non-normal distribution of points. The only significant difference in the data is the clear separation of eight data points at the 30-35 mOhm range containing the three highest recorded break loads.

The grand mean, average of all data points, is 93.4 N and is depicted by a red line across Figure 18. The red line served as a means of determining which of the resistances had superior strengths in a

20 mOhm range. This served as an unbiased alternative to evaluate the effect of resistance on strength. The ratio at the base of the column specifies what percent of the total points within each 20 mOhm range is above the grand mean. Three ranges show all of respective points to be above the grand mean: 20-40, 100-120, and 160-180 mOhm. The limited number of data points above 100 mOhm reduces the power of conclusions for these regions. More data points are required to accurately make conclusions. The remainder of the ranges displayed between 50 – 65% of the data points being located above the grand mean. The differences between 20-40 needs to be compared to the 60-100 range to determine differences in load bearing capability.

Figure 18- Weld tensile break load vs. peak resistance of 85 samples, excluding broken and mounted samples. Ratio of samples above the grand mean and number of samples per population are depicted.

The data points across multiple 'time to weld' groups did not follow a linear curve (Figure 19). There is no immediate trend based on the location of the groups relative to peak r vs. load. Secondary trends show Group A (.1 hr), and Group E (7 hr) were the only groups to have all data points above the

grand mean. The cluster of data points that were observed to be clearly separated from the bulk was established to be group A. Overall; other groups showed varying degrees of data points above and below the grand mean. Groups C (3 hr) and H (168 hr) displayed the majority of their points below the grand mean. Overall all groups, except for Group A (.1 hr) and G (24 hr), had over 80% of the total group points located between 60-100 mOhms, also seen in Fig. 17.

Figure 19- Tensile break load vs. peak resistance with respect to time before welding for 85 samples.

Based on the data collected from the Instron tensile tests, no immediate conclusive trends have been established. The original theory suggested oxidation growth due to time before welding would promote natural log behavior in both metals by reducing diffusion of oxygen as the passivation layer thickens, which would affect the weld strength of the welds. Further examination was required to

identify mechanisms that affect the maximum tensile load 304 Stainless steel/ Nitinol welded guide wires could bear.

5.3 Optical Microscopy Images/Cross Section of HAZ

The examination of the longitudinal cross section of the mounted and etched sample (Group A-3) of the HAZ showed interesting trends (Figure 20). The first noticeable observation is the flat weld interface of the two metals, Nitinol (upper) and 304 Stainless (lower). The weld excess/mushroom has been removed prior to mounting and polishing. Two distinct phases are present in the Nitinol portion of the weld. This is the separation of the heat affected zone (dark), also known as HAZ, and the unaffected bulk material (light). The length of the HAZ is roughly 90.8 μm . The volume of the HAZ is $7.32 \times 10^{-6} \text{ cm}^3$ based on calculations for the volume of a cylinder.

Figure 20-Group A-3 (35.8 mOhms). Optical microscopy of Nitinol (upper) and 304 Stainless steel (lower) weld. Etched using 25ml HNO_3 , 25ml HF , and 5ml $\text{DI H}_2\text{O}$. 50x mag

The volume of the HAZ is directly proportional to the amount of heat input experienced at the weld. The darker region indicates that HAZ has an altered microstructure because it is not behaving the same way as the bulk material. This gives insight into the amount of heat that was experienced based on the relative size and shape of the grains in the heat affected zone compared to the bulk material. Closer examination of the weld interface (Figure 21) reveals that the microstructure of the bulk Nitinol displayed grains similar to steel acicular ferrite grains. For the duration of the paper, the grains will be referred to as 'Acicular'. Acicular grains tend to be single axis elongated grains favoring the $\langle 100 \rangle$ plane forming needle like shapes. This is due to the hot drawing process that shapes the Nitinol into wires by plastic deformation.

The grains in the HAZ are refined acicular. The single axis is exaggerated, but not as predominantly as in the typical acicular grains of the bulk. The number of grains increases compared to bulk Nitinol. This is observed in the darker regions in the weld. This means that more grain boundaries had been corroded by the etchant. More grain boundaries tend to be correlated to increased number of grains. The differences in average grain size shows that heating during the resistance weld promoted changes in the original microstructure. This leads one to believe that the material in the HAZ may possibly have different properties on the macro and micro scale. This could influence the way in which the wire responds to tensile loading.

Figure 21- Optical micrograph of displaying Nitinol grain structure and HAZ. 200x

Figure 21 clearly identifies the differences in the bulk Nitinol and the HAZ. Further inspection shows two different regions within the HAZ instead of one continuous region. The jagged nature of the heat affected zone suggests that current did not evenly flow across the material during heating. This is explained by uneven heating on a point-to-point basis due to the nature of the wire preparation process. Even using completely similar pressure, 1200 grit polishing paper, even loading, and similar time, the surfaces on an atomic level will not be flat. The size and shape of the HAZ is shown by the darker region in the optical microscopy, and outlined in red and black lines (Figure 22).

Figure 22- Optical microscopy of HAZ of Nitinol portion of weld depicting two separate regions. The two regions are separated by a black and red line to accentuate the grain boundaries. 500x

Based on the weld excess/ mushroom and grain flow at the interface we can see that material does in fact flow radially outward from the center as the two metals are heated and forced together. The grains suggest the material pushed the pre-existing oxides out into the weld excess, or weld mushroom after the initial resistance was measured. This shows that the passivation layer is not likely to have been trapped at the interface. Based on the longitudinal cross section of the weld interface we can see that there is minimal diffusion of the materials because of the clear separation between the two materials. Despite the rough nature of the HAZ, no melting was expected based on the interface and the nature of the resistance weld used.

5.4 Scanning Electron Microscope (SEM) Images/Surface Measurements

The FEI Quanta 200 was used to image six fractured sample surfaces. The samples include an unwelded Nitinol sample, four samples of varying peak resistance, and the lowest strength sample in the study. The first surface (Figure 23A, 23B) is pure unwelded Nitinol. Characteristics of this fracture include large amounts of plastic deformation in the form of necking, refer to Fig. 14. The fracture interface necked down to 60% of the initial conditions (Figure 23A). The pure Nitinol fractured in a standard cup/cone fracture. Examination of the center of the fracture interface (Figure 23B) shows a high density of ductile fracture across the interface. The voids from ductile fracture ranged from 5 - .5 μm , with the average void size being between 1-.75 μm across the unwelded Niti samples. The ductile fracture voids characteristically had indentations where material had been removed further at the bottom of the fracture. Voids in Nitinol fracture are also characterized by a meeting of two slip planes that form a ridge. The ridge is the final point of plastic deformation before fracture. This region needs to be examined further to understand the possible mechanism that affects the strength of the Nitinol.

Another characteristics of the Nitinol fracture surface is the shear wall that forms during loading. The shear walls are located at the north and south end of Figure 23A. The walls represent the area of highest ductility that resulted in large scale fracture. Ductile fracture mechanisms similar to the voids observed earlier are present on the interior of the wall, except elongated. This is typical of material deformation and fracture.

Immediately to the left of the north shear wall there is another area of plastic deformation that was characterized to understand fracture mechanisms. This mode of fracture is characterized by shear ductile fracture. For the remainder of this discussion it will be referred to as a shear incline. The ductile zone begins at the initiation site of necking and propagates to the center of the fracture interface, where the highest degree of ductile fracture exists. There is a change in elevation as the material approaches the center of the fracture.

Figure 23- A) Normal cross section of Nitinol wire fractured in tension. 700x B) Center of Nitinol fracture examined to display size and relative abundance of voids at fracture interface. 19459x

Similar fracture mechanics can be observed in 304 Stainless Steel /Nitinol welds. Fracture patterns and relative abundance of ductile fracture across the interface suggest that Group A (.1 hr. before welding) welds fractured in the Nitinol portion of the guide wire (Figure 24A, 24B). This was the sample that showed the lowest peak resistance in the study (30.46 mohm). The fracture interface in Figure 24A shows similarities and differences to the unwelded Nitinol. There is a small amount of necking during tensile loading. The 304 Stainless has a higher Young's Modulus; therefore it is less likely to plastically deform to dissipate the load, as compared to Nitinol. Typical necking deformation in Group A (.1 hr.) was 10-15 %. This results in a fracture surface that is between 85-90% of the initial diameter. Across all samples within the lowest resistance section (Group A) the entire fracture interface was characterized as plastic deformation and ductile fracture.

Further examination of the center of the weld interface depicts voids and ridges similar to the unwelded Nitinol. We can see a large dimple around 5-6 μm in width which includes large sections removed at the bottom of the void. On average, the voids were larger than unwelded Nitinol. This could be an inclusion that was removed by the tensile load. Ridges are observed on the right side of Figure 24B. On average ridges are not as pronounced or as large as previously observed in the unwelded Nitinol. But, over the weld interface at low magnification, Figure 24A, a few large ridges are observed.

These ridges tend to be multifaceted compared to typical Nitinol. The ridges observed in Group A welds have secondary ridges that extend from the primary ridge. The secondary ridges form the shallow dimples observed at high magnification. The voids of the Group A welds are shallow and do not contain removed material. The average size of the shallow voids is on the order of .75-.5 μm depending on which specific sample was being measured.

Figure 24- Group A-5. A) Low resistance (30.46 mOhm) 304 Stainless/Nitinol weld normal cross sectioned. 700x B) high magnification of center of weld interface depicting varying degree of voids. 19459x

Sample Group H (168 hrs.)-7, (Figure 25A, 25B) fractured differently than the other samples examined by the SEM. A peak Resistance of 64.71 mOhms was recorded for this sample. The sample necked to roughly 70-80% of the original parent diameter. The final fracture surface was a triangular shaped region characterized by three shear inclines showing elongated ductile fracture. The final interface comprises 2/3 of the initial fracture surface, which diminishes the available material to plastically deform during loading. This sample does not show ridges, but circular/oblong sections of raised Nitinol. An example of the raised sections is indicated by a red arrow on Figure 25. There are seven noticeably raised sections at the top left of the fracture interface.

Low magnification analysis of the surface shows morphology that resembles a combination of ductile and brittle fracture. Limited contrast at the lower right region of sample confirms that there are limited ridges as compared to the two previous samples. The sample surface seems to fracture along a flat crystallographic plane, with slight differences in elevation. At higher magnification, the surface morphology contradicts earlier beliefs. The surface is jagged and shows shallow voids similar to the previous sample. The large voids are no longer observed. Shallow voids observed in this sample are separated by regions of brittle fracture not normally associated with Nitinol's previously discussed fracture mechanisms. The presence of the extra removed materials is observed in certain cases. This removed material section is highlighted with a green box. The average void size of this sample is .4-.6 μm .

Given similar dimensions, strain/load rates, extension, and direction of loading, differences in fracture surface morphology suggest there is a microstructural difference.

Figure 25- Group H-3 A)Mid resistance weld (64.71 mOhms) 304 Stainless Steel/Nitinol Weld normally cross sectioned. 700x B) High magnification center image depicting voids and brittle fracture. 19459x. The red arrow represents a raised section of material believed to be Ti-C.

This sample from Group D (5 hrs.), (Figure 26A,26B) recorded a peak resistance of 122.49 mOhms. This sample had similar necking characteristics as the Group A sample. The fracture surface was 80-90% of the parent diameter. The fracture surface was the combination of ductile and brittle fracture similar to the Group H sample. At low magnification the sample shows a higher density of brittle fracture compared to ductile fracture. The curvature of the surface suggest that there is a level of ductile fracture across the surface, but the lack of contrast shows that if ridges or voids do exist they will be shallow and small. Multiple raised sections of Nitinol are observed similar to the previous sample. Measuring shows that the oblong raised portions in Figure 26A are larger on average than Figure 25A. This is expected given that the resistance in this sample is twice the resistance of the previous sample. This tends to increase the amount of heat available to form larger raised portions.

Ridges have begun to reappear in this sample. The ridges spawn from the shear wall that surrounds the fracture surface. The plastic deformation that is required to form ridges is promoted by the ductile properties of the materials that created the shear wall within the cup/cone fracture. The bottom of this sample contains the ductile fracture observed in the unwelded Nitinol. The shear ductile fracture on the outer wall at the edge of the necking zone suggests the wire still followed Nitinol fracture mechanics. The fracture is most likely some variant depending on the material's ability to transfer load. Based on the amount of necking, the material transferred most of the load to the Nitinol.

Higher magnification shows voids are present at the fracture interface. Despite the presence of voids the depth is almost nonexistent. Very low contrast at high magnification shows that there is contour, but overall there is not a large gradient in height. The surface shows a majority of brittle fracture. The voids that are present are the same average size as the previous size (.4-.6 μm). The number of voids is reduced to around 2/3 of number of voids from the Group H sample. The brittle fracture differs from the Group H sample as well. The reduced contour shows the difference in elevation is not as severe as the previous sample. Considering these two samples fractured at similar loads, but

have different surface morphologies and differences in amount of necking, material composition differences at the interfaces are suspected as the cause of variation.

Figure 26- Group D-7. A) Upper-mid resistance weld (122.49 mOhms) 304 Stainless Steel/Nitinol Weld normally cross sectioned. 700x B) High magnification center image depicting minimal voids and brittle fracture. 19459x.

The highest resistance sample from Group B (1 hr.) recorded a peak resistance of 166.74 mOhms. This fracture interface (Figure 27A, 27B) experienced a moderate amount of necking (20-30%). This interface consists of ductile fracture. From low magnification the interface resembles brittle fracture similar to the Group D sample. A combination of ridges and raised portions of Nitinol are present. As with the Group D sample, the ridges and raised portion stem from the shear wall that surrounds the majority of the fracture interface at the portion where necking is completed. The portion of the weld that is not surrounded by the shear wall is characterized by the shear ductile incline. Half of the weld interface perimeter is covered by the shear incline.

The fractures raised sections of Nitinol range from large 30x50 µm, down to 2x4 µm. The raised sections are more prevalent in this fracture surface than the previous samples. Ridges at the shear wall

transgress into the center of the fracture surface. Contours on the surface observed at low magnification suggest that there is more ductile fracture than Group D sample. At high magnification ductile fracture is confirmed. The shape and size of the voids are drastically smaller than any previous samples. The voids in this sample range from .45-.55 μm . The voids are widely dispersed and have no relative depth. Ridges are apparent, but not differing from the original height of the fracture surface.

Precipitates have formed on surfaces that have not been observed in all previous samples. The samples were originally believed to be contaminants because of the soft edges, but after ultrasonic cleaning, the particles were shown to be part of the fracture interface.

Figure 27-Group B- 8. A) Highest resistance weld (166.47 mOhms) 304 Stainless Steel/Nitinol Weld normally cross sectioned. 700x B) High magnification center image depicting reduced ductile fracture. 19459x.

The last fracture interface (Figure 28A, 28B) is considered an outlier in statistical terms. It failed to fall within three standard deviations of the global data of tensile strength. It is depicted because this sample shows large amounts of brittle fracture across the entire interface. Sections of Nitinol did remain

attached to the interface after separation. This fracture interface is a worst case scenario. There is no visible necking, minimal signs of cohesion, and mid resistance of 68.99 mOhms.

At high magnification the material shows few surface features besides the trace amounts of Nitinol at the edges of the interface. Resemblances of Nitinol's ductile fracture is observed at high magnification. The SEM images show the minimum amount of welding at the fracture surface. Minimal welding resulted in negligible plastic deformation in the 304 Stainless Steel section of the weld.

Figure 28- A) Brittle failure of 304 Stainless Steel/Nitinol Weld. 700x B) High magnification image of brittle fracture surface, spotted with minimum Nitinol adhesion. 19459x

5.5 Surface Chemistry : X-ray Photoelectron Spectroscopy (XPS), Electron Dispersive X-Ray Spectroscopy (EDS) Images/Material Composition

The XPS was used to characterize the oxidation state of the 304 Stainless Steel and Nitinol as passivation layers. XPS was done on samples prior to welding to get an understanding of the diffusion mechanisms of the two metal species.

Chromium (iii) Oxide (Cr_2O_3) was located on the hour sample. This is the thermodynamically preferable oxidation state for the Cr^{3+} ion typically used in 304 Stainless Steel.

Surface Chromium (iv) Oxide (CrO_2) was located on the 2 week sample. Presence of this oxidation state suggests at some point in the process a diffusion of atoms created a kinetically and thermodynamically stable reaction. The difference in chemical composition can account for a drop in resistance.

Titanium Oxide (TiO_2) was identified on Titanium samples. After further analysis it was determined that the composition of oxide formed was not crucial to the findings of the study.

Specific materials of interest were assigned a false color to highlight location when overlaid on the electron image (Figure 29). For comparison purposes, titanium was assigned the false color blue, nickel was assigned yellow. The contrast and brightness of the detector was equalized and remained constant to give an accurate representation of the relative surface composition. In unwelded Nitinol, the surface theoretically would be a unanimous shade of green across the surface due to the atomic composition of the material.

Comparing the atomic cameo of each fracture surface collectively, Figure 29A-29D, a noticeable trend emerges. The relative amount of nickel (yellow false color) at the fracture surface seems to increase proportionally as the resistance increases. For example, 29A (30.46 mOhm), shows a proportion of 44.65/49.92 Titanium (blue) to Nickel (yellow). Further examination confirms that higher resistance samples show higher densities of Nickel at the interface with 29D (166.74 mOhm) displaying the highest amount of Nickel at the surface at 43.2/53.74. The increase in Nickel content can be observed by the progression from primarily blue cameo (29A) to a primarily yellow cameo (29D).

All compositional surfaces Ti/Ni ratios did not completely encapsulate the atomic composition of the fracture surface. Each sample had a varying degree of Carbon (C), Aluminum (Al), and Silicon (Si). Al and Si are expected to show up at the interface because they are alloying elements in 304 Stainless Steel. This suggests that minimal diffusion is possible during welding. Carbon content may be attributed to contamination, but elemental analysis shows compounds of Ti-Ni-C had possibly formed during the

weld. Ti-Ni-C has also been shown to form during initial processing of Niti. These regions are characterized as white material excess on the surface of the weld. Literature suggests the formation of the Ti-Ni-C carbide is probable, but no conclusive evidence has been documented suggesting that the carbide can adversely affect the performance of the weld interface^[10]. The lattice parameter is within +/- 1% that of equiatomic Nitinol. The strength characteristics observed have not been shown to advantage or disadvantage the weld interface. The relative size and spacing of the Ti-Ni-C did not influence the strength of the weld interface. As stated before, each sample analyzed by EDS is within a tight range of strengths to observe the effects of resistance. Therefore, the differences between the Ti-Ni-C particles on separate samples of roughly equal strength does not seem to have an effect.

Figure 29- A) Group A-5 electron image and EDS elemental map overlay cameo. Nickel is artificially colored yellow, Titanium is artificially colored blue. 1400x. B) Group H-3 electron image and overlay cameo. Similar artificial coloring. Showing presence of Ti-Ni-C (white section). C) Group B-7 electron and overlay cameo. 1400x. D) Group D-8 electron and cameo of fracture weld interface. 1400x.

Figure 29A (Group A), shows a fracture surface that is predominantly composed of Ti/Ni (46.65/49.92). There are sections of the fracture interface that are uncolored; these deposits are Iron (Fe) portions. When comparing the cameo to the electron image we see that the uncolored portions of the cameo exhibit brittle fracture. Hence brittle fracture on surfaces will be characterized as a surface that is or contains large amounts of Fe. The overlay displays the largest amount of Ti (blue) compared to the other respective samples. The majority of the surface displays green mixture, $\approx 50/50$ Ti/Ni. Specifically targeted point analysis confirmed the surface comprised of nearly equiatomic Ti/Ni (47.41/51.75, 46.0/52.75, 48.36/51.46) (Figure 30). The surface of the Group A fracture interface is predominantly near equiatomic Ti/Ni.

Figure 30- EDS/SEM image of Group A-5 sample. Four locations tested to verify molecular composition. 3500x.

The Group H (29B) cameo depicts a noticeable increase in the relative amount of Nickel (yellow) on the surface. The overall composition of the cameo was measured at 44.13/50.23 Ti/Ni. The triangular surface composition remains similar to the group A sample ($\pm 1\%$ Ni). The white sections are Ti-Ni-C, discussed previously. Examination of Ni rich regions shown in the cameo overlay established points of interest (Figure 31). Five points of interest yielded three different compositions. Points 1, 3, and 4 were identified as Ti-Ni-C carbide (34.93/39.2/25.12). Optically each point showed similar surface features,

contrast, and size. Point 2 was identified as Ti_3Ni_4 (34.2/47.9). Point 5 was believed to be a form of contamination from the environment that could not be removed from under the Ti-Ni-C carbide during ultrasonic cleaning.

Figure 31- EDS/SEM image of Group H-3 sample. Five locations were identified and characterized. Ti-Ni-C (points 1,3,4) and Ti_3Ni_4 (point 2) identified. 1400x

The Group D sample surface was composed of 43.54/51.03 Ti/Ni ratio. This surface composition notes another $\approx 1\%$ increase in Ni content. Five locations were tested to explore atomic concentrations on area (Figure 32). Points 1-3 were comprised of Ti-Ni-C carbide. Point 4 was identified as Ti_3Ni_4 (20.02/27.95) at the boundary near a material excess. Point 5 was a Fe/C combination. Literature does not suggest Fe/C is commonly observed, hence this point is believed to be contamination. Continued examination showed trace amounts of Ti_3Ni_4 throughout the fracture surface located at Ni rich areas. The precipitate was located along ridges and material excess ($>3\mu\text{m}$).

Figure 32- EDS/SEM image of a Group D-7 sample. Five locations were examined consisting of Ti-Ni-C, Ti_3Ni_4 , and Fe/C compounds.

The sample surface from Group B consisted of the highest atomic concentration of nickel at a Ti/Ni ratio of 43.2/53.74. Seven points were analyzed for specific atomic concentrations (Figure 33). Point 2 had an irregular material composition (18.82/21.2/55.55 Ti-Ni-C). This composition does not resemble the previously examined carbide Ti-Ni-C. Point 4, 5, and 7 are confirmed Ti-Ni-C carbide. This seems plausible considering all three acquisitions are taken on ridges within a 20 μm radius.

Points 1, 3, and 6 have an atomic composition resembling Ti_3Ni_4 (28.96/46.09, 14.98/19.99, 15.8/23.53). Point 1 is a circular precipitate ($\approx 3 \mu\text{m}$) on the fracture interface. Point 1 surface characteristics differed from point 2 which has similar size and shape; this suggests material differences between the two particles. Point 3 is directly to the right of the ridge in the center of the image. This is likely a precipitate formed on a boundary based on its proximity to a ridge. Point 6 shows similar brightness and contrast to Point 1, but is half of the size. The possible precipitates are highlighted by red arrows. The Group B (166 mOhms) sample shows higher quantity of Ti_3Ni_4 precipitates at boundaries and on the surface as precipitates compared to previous groups. Precipitates are concentrated around interfaces between brittle and ductile fracture.

Figure 33- EDS/SEM image of Group B-8 sample. Ti_3Ni_4 precipitates are confirmed at points 1, 3, and 6. Possible Ti_3Ni_4 precipitates are highlighted with red arrows. 1600x

6. Discussion

Weld temperature directly relates to the structure of the metals after the weld. No temperature readings were taken at the time of the weld because of the proprietary nature of the weld. Therefore, theoretical temperature ranges needed to be identified to understand the possible microstructural mechanisms which could affect the weld strength of the samples.

6.1 Temperature Range Calculation/Sensitivity Analysis

Oxidation thickness was shown to not control the strength of the weld interface or the relative amount of resistance at the weld interface, except for minimal time before welding (.1 hr). Comparison of resistance measurements and break load suggest the two variables are related. Relating resistance to the amount of heat input into the interface during welding will clarify differences in heating mechanisms associated with the HAZ, given by Equation 2.

$$T = \frac{(I^2 R t)(\pi r^2 L \rho)}{c p} \quad \text{Eq 2.}$$

Where t =pulse time in seconds, I = current in amps, R = weld resistance in mOhms, r = radius of wire in cm, L = length of HAZ in cm, ρ = density of austenitic Nitinol in g/cm^3 , C_p = the specific heat of austenitic Nitinol in $\text{J/g}^\circ\text{C}$. Given current, pulse time, radius, density, and specific heat are held constant resistance and length are the remaining variables. Differences in R range from 30-166 mOhms. A high resistance sample could experience five times the potential power across the weld. That is a substantial difference in heat input. Table II displays differences in the amount of heat input. Amount of heat input across the wire diameter will have substantial effects on the final theoretical temperature reached.

Given the ADAM has specific operation currents (2, 6, 20, 80, 300, and 800 KA), the smallest current was chosen as a conservative measure of estimating final temperature. Resistance was empirically measured via the ADAM system; therefore measured values will be used. Wire diameter was averaged over all samples. The average pre-fracture diameter will be used (.32 mm). Abbott Vascular disclosed the weld operation is completed in milliseconds- seconds. Due to proprietary purposes, exact time cannot be disclosed, therefore a conservative estimate $t = .06$ sec will be utilized. The average optically measured length of the HAZ will be utilized. The density of Nitinol is 6.5 g/cm^3 [10-11]. The specific heat capacity of Nitinol is 450-620 $\text{J/Kg}^\circ\text{C}$ depending on the amount martensite formed during processing [10-11]. The composition of the as received Nitinol was not tested prior to welding. The average specific heat will be utilized, 535 $\text{J/Kg}^\circ\text{C}$.

Table II- Theoretical temperature range of four samples

Sample	I (Amp)	Peak R (mOhm)	Power @ .06 sec (J)	Temperature ($^\circ\text{C}$)
A-5	2000	30.36	7320	261.9
H-3	2000	64.71	15528	555.5
D-7	2000	122.49	29400	1051.7
H-8	2000	166.74	39840	1425.2

A hypothetical temperature range of 261.9- 1425.2 °C was calculated using measured values and conservative assumptions. Sensitivity analysis (Figure34-35) was used to verify the two assumptions (time/specific heat capacity) did not exaggerate values. The temperature range is greatly dependent on the amount of time heat is input into the weld. Since the heat is dependent on the current squared, the effects of heat input increase non-linearly at higher resistances. This is observed by the gradual spread of data points at higher resistance. The proprietary nature of the welding does not establish an exact weld time. An estimated time of $t=.06$ seconds was a valid assumption because the values give a moderate range that will not exaggerate or undermine temperature values, respectively.

Figure 34- Sensitivity analysis of Temperature range (°C) on weld time (seconds) vs. Resistance (Ohm).

Sensitivity analysis of specific heat capacity shows similar trends to weld time. This is due to the same factor previously stated; power is determined by the square current. Since the amount of martensitic transformation was not determined prior to welding, a specific heat of 535 J/Kg°C is a robust

assumption that will not over/under exaggerate the temperature range the material could be experiencing during welding.

Figure 35- Sensitivity analysis on Temperature range(C) on specific heat capacity (j/Kg°C)

6.2 Compositional Existence of Precipitate

The theoretical temperature range, 261.9- 1425.2 °C, at near equiatomic Nitinol has been shown to cause microstructural changes. Temperature and pressure alter the Nitinol's transformation tendencies ^[12]. Grain size alteration inhibits the Nitinol's ability to transfer load via austenitic twinning into martensite. Nitinol wires have been shown to have degraded microstructures after heat treatment. X. J. Yan confirmed degradation of properties in Nitinol wires by testing laser welded samples that had been annealed for 1 hour at 400°C and 500°C ^[13]. The results of the laser welded Nitinol wires (Figure 36) displayed that samples that received heat treatment transferred loads differently.

Figure 36- Fatigue cycles vs. strain curve of laser welded Nitinol joints annealed at 400/500 °C.
X.Y. Yan ^[13].

Yan's observed microstructural changes agree with the alterations observed in this study (Figure 23-26). Average fracture void size decreased from 1 μm (30.46 mOhm) to .5 μm (166.74 mOhm). The microstructural changes corresponds to a phase boundary on the Ti-Ni phase diagram (Figure 37)^[14,15]. W. Tang and K. Otsuka separately identified a Ni-rich precipitate that forms at near equiatomic concentrations of Nitinol. The precipitate forms as Nitinol is heated to above ≈ 600 °C. The solubility of nickel in the Ti-Ni parent phase increases as a function of temperature, given by Equation 3.

$$\% \text{Ni soluble} = 0.01351(t - 600) + 50 \quad \text{Eq 3.}$$

Where t = temperature from 600-1118°C. The Ti-Ni parent phase, [further referred to as B2 phase] is a CsCl interpenetrating simple cubic. Increased temperature allows additional Ni atoms to diffuse into vacancies promoting substitutional interchanges. Rapid heating and solidification cycles lock previously insoluble Ni atoms in the B2 parent structure causing substitutional strains. The substitutional

strains increase energy promoting the formation of a B2 phase variant, called B19' ^[14-16]. Otsuka found metastable B19' exists coupled with the B2 phase (Figure 38).

Figure 37- Ti-Ni Phase diagram depicting expanded view of near equiatomic Ti-Ni ^[15].

Figure 38- Enhanced portion of Ti-Ni phase diagram depicting temperature range from 300-1000 °C, and 50-57% Ni atomic % ^[15].

6.3 Validation of Precipitate Existence in Literature

B19' (Ti_3Ni_4) has been observed in the literature at temperatures within the theoretical temperature range calculated previously. W. Tang, K. Otsuka, K. Mehmet, and various authors ^[13-17] have discovered and characterized the existence of B19' EDS shows B19' forming at grain boundaries and as precipitates with a ratio of .65-.75 Ti/Ni (Figure 39). ^[16] The ratio has a tolerance due to the coupling with B2. The final composition of B19' is dependent on the parent phase composition.

Figure 39- EDS confirming existence of Ti_3Ni_4 and a second titanium rich phase. K. Memhet ^[17].

6.4 Validation of Precipitate Existence at Weld Interface

Saburi identified inflections in stress/ strain curves of Nitinol samples as evidence for the presence of Ti_3Ni_4 (Figure 40A) ^[19]. Saburi characterizes the inflection below 200 Mpa as 'Yield rhomboidal' (Y_R). This is yield at which the Rhomboidal phase hinders dislocation motion because of the incoherent orthogonal phase ^[19]. The behavior of the fractured welds (Figure 15) exhibited varying degrees of inflection early in loading cycles (Figure 40B). This is now believed to be mechanical evidence suggesting the formation of B19'. The amount of inflection increases as a function of increased resistance at the weld interface. Higher degrees of inflection suggest existence and relative abundance of B19' precipitates at the interface ^[18-20].

B19' was prevalent at resistances >64.71 mOhm. Table III summarizes the number of instances of Ti_3Ni_4 precipitates. Results from EDS are in agreement with finding from literature ^[13-17]. Following Eq. 1- Arrhenius equation, the relative abundance and size of Ti_3Ni_4 precipitates will increase with increased temperature. K. Memhet suggest that given heat input (W) and pressure, varying degrees of B19' can form. Trends suggest that increased pressure increases the abundance and size of B19' formed, as shown by XRD data ^[17].

Figure 40- A) Equiatomic Nitinol Stress Strain curve depicting inflection characterizing formation of B19'. Saburi ^[19]. B) Point of inflection (Figure 15) showing loading tendencies similar to Saburi findings.

Table III- Summary of four samples tested fracture surfaces given hypothetical temperatures. [Reference Fig 29A-29D].

Group/ Resistance	Theoretical Temp (C°)	Average void (μm)	Approximate B19' size (μm)
A/30.46	261.9	1	0
H/64.71	555.5	.75	<.1
D/122.49	1051.7	.75	<.3
B/166.74	1425.2	.5	≈. 3

6.5 Examination of Strength Degradation Due to Ti_3Ni_4 Structure

Ti_3Ni_4 precipitates have a B19' structure which results in rhomboidal crystal structure (Figure 41). During loading cycles, Austenite has the potential to dissipate load by transforming into martensite via twinning. Twinning is the re-orientation of atoms to reduce strain on a crystal lattice. The diffusionless transformation from B2 austenite to martensite gives Nitinol pseudo-elasticity, or super-elasticity^[14]. Pseudo-elasticity is a reversible material transformation of boundaries instead of introduction of defects or bond elongation. Ti_3Ni_4 is an incoherent precipitate that mitigates martensitic transformation by introducing misfit strain into the lattice. Initial strain distorts the lattice deterring the grain transformation toward martensite^[20-21].

Figure 41- Low temperature B19' structure also known as Rhomboidal. T Wang^[14].

The presence of Ti_3Ni_4 could possibly reduce the strength of welds by altering dislocation paths. B19' has a Burgers vector $\langle 111 \rangle$ and $\langle 200 \rangle$, depending on the Ti_3Ni_4 variant^[22]. Zou determined that Ti_3Ni_4 precipitates $\approx 10^{-9}$ m or less will promote coherency with the B2 phase, causing possible strengthening. Zou discovered B19' precipitates larger than 10^{-9} m have been shown to greatly degrade mechanical properties by promoting localized stress fields enclosing the coarsened B19' precipitates^[23]. The induced stress fields were caused by misfit dislocations, or semi-coherent interfaces. Inherent dislocation density will inhibit future dislocations by increasing the relative dislocation density. Inherent

mismatch dislocations along with grain boundary pinning of dislocations will cause a high stress field that will cause a material to prematurely fail by exaggerated dislocation strengthening. Localized exaggerated dislocation strengthening can possibly decrease the ductility of a specific region creating a possible crack initiation site. The increased local energy will disperse by cleaving into separate planes resulting in catastrophic failure.

The literature suggest the formation of B19' is plausible. EDS of fractured welds suggested the correct atomic composition of B19' was found at the fracture interface. Given the correct composition of the precipitate was located in our samples, and in literature, evidence suggests that the precipitate can cause localized strengthening that can create brittle zones. The brittle zones can be crack initiation sites because of the brittle nature of the precipitate and surrounding strengthened zone.

7. Conclusion

Structure of metastable Ti_3Ni_4 has been shown to be a semi-coherent interface between B2 and B19 referred to as B19'. This promotes localized stress fields that can harden areas surrounding precipitates. Hardened fields can be crack initiation sites. Therefore B19' is relatable to mechanical performance of welds

Given the phase diagram, hypothetical temperatures, EDS data, and SEM fracture images, there is strong evidence suggesting the precipitation of Ti_3Ni_4 in the heat affected zone of resistance welds

SEM images provide evidence suggesting that fracture surfaces of low strength samples exhibit brittle fracture compared to ductile fracture. High strength samples exhibit larger relative ductile fracture compared to brittle.

No obvious or statistically significant results can be drawn from the tensile break load vs. allowed time to oxidize before welding. The ambiguous data suggest that there is minimal evidence relating oxidation to the strength of welds between 304 SS and Nitinol.

8. Recommendation

Abbott Vascular should investigate reducing the time between welds to an absolute minimum. This combined with adjustable current will allow Abbott to heat the interface just above the required temperature. This will allow the weld to be fused while not inputting enough heat to adversely affect the microstructure. Depending on quantity of guide wires assembled, Abbott should consider automation to fully enhance the capabilities of the guide wire, and reduce the possibility of failure in vivo.

9. Future Work

1. Controlled precipitation of Ti_3Ni_4 in HAZ to correlate Ti_3Ni_4 characteristics to mechanical performance of welds
2. Take direct temperature measurements at weld and verify growth of Ti_3Ni_4 precipitates and their morphologies
3. Effect of Pressure and/or post weld heat treatment of Ti_3Ni_4
4. Investigate the presence, diffusion, and formation characteristics of Ti-Ni-C. Minimal research has been done on this compound, but it was prevalent at many of the fracture interfaces.
5. Controlled heat treatment of 304 Stainless steel and Nitinol to understand diffusion of steel alloying elements

10. References

1. A. Enders, Z. Brandt. Using Geographic Information System Technology to Improve Emergency Management and Disaster Response for People With Disabilities. *Journal of Disability Policy Studies* [serial online]. Spring 2007;17(4):223-229. Available from: Academic Search Premier, Ipswich, MA. Accessed December 14, 2007.
2. S. Zuniga, S. Sheppard. Determining the constitutive properties of the heat-affected zone in a resistance spot weld 1995 *Modelling Simul. Mater. Sci. Eng.* **3** 391
3. L. Griffin, Ph.D. Biomaterials Introduction, California Polytechnic State University.
4. H. Asteman, J. Svensson J, E. Johansson. KCl Induced Corrosion of a 304-type Austenitic Stainless Steel at 600°C; *Oxidation of Metals*, 2005-08-01; Springer Netherlands. Issn: 0030-770X
5. A. Pelton, L. Zhu, P. Fino. Oxidation of Nitinol; NDC, Proceedings of SMST-2003
6. G. Kuhn, L. Jordan. Fatigue and Mechanical Properties of Nickel-Titanium Endodontic Instruments, *Journal of Endodontics*, Volume 28, Issue 10, October 2002, Pages 716-720, ISSN 0099-2399, 10.1097/00004770-200210000-00009.
(<http://www.sciencedirect.com/science/article/pii/S0099239905604645>)
7. S. Thompson. An overview of nickel–titanium alloys used in dentistry. (2000) *International Endodontic Journal*, 33: 297–310. doi: 10.1046/j.1365-2591.2000.00339.x
8. K. Yeung, K. Cheung, W. Lu, C. Chung. Optimization of thermal treatment parameters to alter austenitic phase transition temperature of NiTi alloy for medical implant, *Materials Science and Engineering: A*, Volume 383, Issue 2, 15 October 2004, Pages 213-218, ISSN 0921-5093, 10.1016/j.msea.2004.05.063.
(<http://www.sciencedirect.com/science/article/pii/S0921509304007440>)
Keywords: NiTi shape memory alloy; Reverse martensitic transformation temperatures; Heat treatment; Superelasticity
9. H. Zhang, Z. Hei, G. Liu, J. Lu, K. Lu. Formation of nanostructured surface layer on AISI 304 stainless steel by means of surface mechanical attrition treatment, *Acta Materialia*, Volume 51, Issue 7, 18 April 2003, Pages 1871-1881, ISSN 1359-6454, 10.1016/S1359-6454(02)00594-3.
(<http://www.sciencedirect.com/science/article/pii/S1359645402005943>)
Keywords: Surface mechanical attrition treatment; Nanostructured material; Grain refinement mechanism; AISI 304 stainless steel; Mechanical twins
10. W. Buehler, H. Hyattsville, R. Wiley. United States Patent office 3174851, Nickel based alloys, Dec 1961; 5/19/2012

11. S. Jain, H. Harker, R. Cowley. Misfit strain and misfit dislocations in lattice mismatched epitaxial layers and other systems, *Philosophical Magazine A*. Vol. 75, Iss. 6, 1997

12. CHOI, YONG, LEE, J, MULLINS, M. Densification process of TiCx–Ni composites formed by self-propagating high-temperature synthesis reaction; *Journal of Materials Science*, Volume: 32. Issue: 7. Url: <http://dx.doi.org/10.1023/A:1018519815596>
Doi: 10.1023/A:1018519815596

13. W. Huang, On the selection of shape memory alloys for actuators, *Materials & Design*, Volume 23, Issue 1, February 2002, Pages 11-19, ISSN 0261-3069, 10.1016/S0261-3069(01)00039-5.
(<http://www.sciencedirect.com/science/article/pii/S0261306901000395>)
Keywords: Shape memory alloy; Actuator; Selection; Performance index

14. Raghavendra R. Adharapurapu, Fengchun Jiang, Kenneth S. Vecchio, George T. Gray III, Response of NiTi shape memory alloy at high strain rate: A systematic investigation of temperature effects on tension–compression asymmetry, *Acta Materialia*, Volume 54, Issue 17, October 2006, Pages 4609-4620, ISSN 1359-6454, 10.1016/j.actamat.2006.05.047.
(<http://www.sciencedirect.com/science/article/pii/S1359645406004186>)
Keywords: Shape memory alloy; Thermomechanical behavior; High strain rate; Stress-induced martensite; Compression–tension asymmetry

15. X.J. Yan, D.Z. Yang, X.P. Liu, Influence of heat treatment on the fatigue life of a laser-welded NiTi alloy wire, *Materials Characterization*, Volume 58, Issue 3, March 2007, Pages 262-266, ISSN 1044-5803, 10.1016/j.matchar.2006.05.001.
(<http://www.sciencedirect.com/science/article/pii/S1044580306001252>)
Keywords: NiTi alloy; Fatigue; Laser welding; Heat treatment; Precipitate

16. W. Tang, B. Sundman, R. Sandström, C. Qiu, New modelling of the B2 phase and its associated martensitic transformation in the Ti–Ni system, *Acta Materialia*, Volume 47, Issue 12, 29 September 1999, Pages 3457-3468, ISSN 1359-6454, 10.1016/S1359-6454(99)00193-7.
(<http://www.sciencedirect.com/science/article/pii/S1359645499001937>)
Keywords: Titanium–nickel; Shape memory; Thermodynamics; Phase diagrams; Phase equilibria

17. K. Otsuka, X. Ren, Physical metallurgy of Ti–Ni-based shape memory alloys, *Progress in Materials Science*, Volume 50, Issue 5, July 2005, Pages 511-678, ISSN 0079-6425, 10.1016/j.pmatsci.2004.10.001.
(<http://www.sciencedirect.com/science/article/pii/S0079642504000647>)

18. Mehmet Kaya, Nuri Orhan, Bulent Kurt, Tahir I. Khan, The effect of solution treatment under loading on the microstructure and phase transformation behavior of porous NiTi shape memory alloy fabricated by SHS, *Journal of Alloys and Compounds*, Volume 475, Issues 1–2, 5 May 2009, Pages 378-382, ISSN 0925-8388, 10.1016/j.jallcom.2008.07.023.
(<http://www.sciencedirect.com/science/article/pii/S0925838808011468>)
Keywords: NiTi shape memory alloy; Porous materials; Self-propagating high-temperature synthesis; Phase transformation behaviors

19. W. Huang. On the selection of shape memory alloys for actuators, *Materials & Design*, Volume 23, Issue 1, February 2002, Pages 11-19, ISSN 0261-3069, 10.1016/S0261-3069(01)00039-5.
(<http://www.sciencedirect.com/science/article/pii/S0261306901000395>)
Keywords: Shape memory alloy; Actuator; Selection; Performance index
20. T. Saburi. *Ti-Ni shape memory alloys; shape memory materials*, 2002, pg 49-63
21. T. Eliades, G. Eliades. Surface Characterization of retrieved NiTi orthodontic archwires; *Dental Biomaterials Science Unit, Manchester dental school. European journal of orthodontics* vol 22 pg 317-326. 2000
22. J. Lee, J. Park, G. Andreasen, R. Lakes. Thermomechanical study of Ni-Ti alloys. (1988), *J. Biomed. Mater. Res.*, 22: 573–588. doi: 10.1002/jbm.820220611
23. W. Zou, X. Han, R. Wang, Z. Zhang, W. Zhang, J. Lai. TEM and HREM study of the interphase interface structure of Ti₃Ni₄ precipitates and parent phase in an aged TiNi shape memory alloy, *Materials Science and Engineering: A*, Volume 219, Issues 1–2, 30 November 1996, Pages 142-147, ISSN 0921-5093, 10.1016/S0921-5093(96)10418-4.
(<http://www.sciencedirect.com/science/article/pii/S0921509396104184>)
Keywords: Transmission electron microscopy; High resolution electron microscopy; Interface structure; Ti₃Ni₄ precipitate; ; Ni shape memory alloy