Anomalous 304 Stainless Steel Mechanical Properties in Medical Guide Wires

A Senior Project presented to the Faculty of the Materials Engineering Department,
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In Partial Fulfillment of the Requirements for the Degree Bachelor of Science

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Abstract

Stainless steel medical guide wire cores, processed by Abbott Vascular, are returning anomalous mechanical properties upon strain hardening and heat treatment. As theory dictates, mechanical strength properties increase with strain hardening, and decrease with an annealing treatment. The opposite response is being observed. This is counter intuitive to fundamental materials knowledge, and a perfect materials engineering paradox. This project was designed to characterize these behaviors, and attempt to determine causation. To accomplish this, tensile testing of all processing steps mapped the mechanical property evolution of the wire. Published literature research revealed the potential of nitrogen and chromium solid state diffusion at the annealing temperature. This would result in the precipitation of chromium nitrides, which would increase mechanical strength properties by impeding dislocation movement. X-ray diffraction (XRD) was utilized for chemical composition analysis to investigate this hypothesis, looking for CrN intensity peaks, amongst the austenite and ferrite matrix. Scanning electron microscopy (SEM) and metallography was utilized for fracture analysis. A denser coalescence of microvoids after the annealing step, would dictate an increased concentration of sites to initiate fracture. CrN precipitates act as sites for fracture, therefore if the denser coalescence is observed, it will reinforce the CrN hypothesis as well. Change in response to the Adler’s Reagent etchant after the annealing processing step may indicate a change in corrosion resistance, indicating chromium depletion that occurs with CrN precipitation. Further analysis is recommended utilizing transmission electron microscopy to definitively conclude that the precipitation of the CrN phase is occurring.

Keywords: 304 Stainless Steel, Guide Wires, X-Ray Diffraction, Scanning Electron Microscopy, Heat Treatment, Tensile Test, Ductile Fracture, Materials Engineering, Anomalous Mechanical Properties
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1 Introduction

1.1 Problem Statement

Stainless steel medical guide wires, processed by Abbott Vascular, are returning anomalous mechanical properties upon strain hardening and heat treatment. As theory dictates, mechanical strength properties increase with strain hardening, and decrease with an annealing treatment. The opposite response is being observed. No published literature currently addresses a decrease in strength from the rotary, strain hardening process that Abbott Vascular uses to straighten and section the wire to net shape. However, there is peer-reviewed literature on chromium nitrides that precipitate below the 480°C “burn” temperature that Abbott Vascular anneals with, resulting in an increase in mechanical strength properties.

This project is designed to reveal causality for this anomalous behavior, and suggest a change in processing that might revert or at least mitigate the undesired effects. Abbott Vascular will receive insight to improve the next generation of stainless steel medical guide wires. To investigate, duplicated tensile testing will occur at every step of processing, in order to establish a precise timeline for changes in tensile test output properties. X-ray diffraction will be implemented to detect changes in phase across each stage of processing. A scanning electron microscope will be implemented for fracture analysis, to determine either ductile or brittle fractures. Two medical guide wires were under inspection, Abbott Vascular’s “Hyten” and “Triple Spring” models.

1.2 Abbott Vascular Inc.

Abbott Vascular Inc. (parent company, Abbott), is a world leader (Top Ten, 10.11$ Billion [1]) in medical device manufacturing and distribution, with a distribution pipeline spanning over 150 countries. Diagnostic products, vascular products, diabetes care and medical optics are the four foremost divisions of Abbott Vascular. Their core company value is to not only elongate life, but to substantially increase the quality of life of its customers. This core belief is realized by the allocation of resources towards the research and development of pharmaceuticals, medical devices, diagnostics, and nutritional products. Abbott has also invested in the acquisition of the St. Jude Medical Foundation, which embodies a high standard of health care that Abbott wishes for its clientele. Miles D. White, chairman and chief executive officer of Abbott Laboratories, noted in a press release, “Abbott has a strong track record of successfully integrating dozens of businesses on a global scale and accelerating growth. The addition of St. Jude Medical strengthens our global medical device leadership while offering innovative products to address more areas of care, in more physicians’ offices and hospitals around the world.” [2]

Abbott Vascular Inc., the sponsor of this project, is located in Temecula, CA and is one of seven subdivisions of Abbott Laboratories, with global headquarters in Chicago, Ill. The recent acquisition of
St. Jude’s will enrich Abbott’s cardiovascular division by absorbing the medical foundation’s notable portfolio in atrial fibrillation, heart failure, structural heart, and chronic pain. This will complement Abbott’s strong position in coronary interventions and mitral valve disease. Current cardiovascular products include; guide wires, coronary stent and scaffolding platforms, minimally invasive structural heart technologies, carotid stent and embolic protection systems, balloon dilation catheters, and vessel closure technology. Their flagship vascular product releases include the Supera peripheral stent system to treat people with blocked blood vessels in the upper leg caused by peripheral artery disease (PAD), and the catheter-based Mitraclip therapy, a treatment option for high-risk mitral regurgitation (MR) [1].

1.3 Medical Guide Wires

Medical guide wires are noninvasive blood vessel navigation devices for therapeutic and diagnostic procedures. For the specialization of this treatment, various types of guide wires are in circulation, hence the four models in which Abbott Vascular is witnessing anomalous properties. There are three components of guide wires. There is a core wire with a tapered tip (304 stainless steel composition for this project), surrounding wire coil or braid, and a final coating (Figure 1). The core material, the primary focus of this project, provides the main support of the guide wire. Surrounding wire coil or sheath improves flexibility, push-ability, and kink resistance of the core wire [3]. The behavior of the guide wire in practice is manipulated by adjusting the taper. A taper confined to a shorter distance becomes more rigid, steerable, and torque-able, whereas when the wire tapers more proximally, resulting in a longer guide wire tip, the tip is less prone to prolapse, where the body of the wire does not follow the tip’s bearing around bends. The coating is added to facilitate either a hydrophobic or hydrophilic finish, which dictates how the guide wire travels through the vasculature, primarily by tactile sensation properties opposing smooth delivery properties [4].

Figure 1: Medical guide wire with core, tip, and coil / sheath components [5].
The stepwise installation (Figure 2a-f) in which these guide wires are utilized is known as the Seldinger technique. A hollow needle accesses a strategic blood vessel and is oriented along the artery axis (Figure 2a). The guide wire is funneled through the needle and is maneuvered through the patient’s vasculature to the objective treatment site (Figure 2b). The needle is then removed and the artery is compressed, pinning the guide wire placement (Figure 2c). A catheter device is then threaded by the guide wire and follows the predefined path to the treatment site (Figure 2d-e). Guide wire is then removed, leaving the catheter in place to allow the delivery of stents, balloons, etc. through the catheter’s hollow passageway (Figure 2f) [5].

![Figure 2: Seldinger technique for intravenous catheter delivery. There are variations in this technique dependent on the treatment and its specializations [6].](image)

Guide wire visibility under fluoroscopy during operation has a positive direct relationship with material density, therefore increasing density increases the degree of fluoroscopy visibility, i.e. radiopaque. Stainless Steel AISI 304 $\rho = 7.95$ g/cm³, therefore insufficiently radiopaque [4]. The coated guide wires have a thin film of polytetrafluoroethylene (PTFE, Teflon). PTFE is a synthetic fluoropolymer of tetrafluoroethylene and a fluorocarbon solid as it is a high molecular weight compound consisting wholly of carbon and fluorine. This finish is hydrophobic: neither H₂O nor H₂O-containing substances wet PTFE, due to the fact that PTFE has the third lowest coefficient of static friction of any solid. This low coefficient is derived from the fluorocarbons demonstrating mitigated London dispersion forces. London dispersion forces are exhibited by nonpolar molecules due to the correlated movements of the electrons in interacting molecules. Electrons in adjacent molecules shift away from each other, therefore electron density in a molecule becomes redistributed in proximity to another molecule, forming instantaneous dipoles. These dipoles act as forces of attraction. Fluorine’s high electronegativity in PTFE mitigates these electron redistributions, ceasing the formation of instantaneous dipoles. This facilitates non-polarity and therefore a hydrophobic nature. PTFE melting/curing temperature is 327°C [7].

1.4 Abbott Vascular Processing

Abbott Vascular receives coiled, wire-drawn stainless steel from an external vendor. The wire is then coated in Teflon (PTFE) via a rapid reel-to-reel 460°C immersion process. The short immersion intentionally prohibits a full-cure of the Teflon coating, which would otherwise be sloughed off by the...
downstream wire straightening processing. Wire straightening involves the wire being fed into a rotary device where the wire is torsionally plastically deformed at a high rate. Pitch marks result along the periphery of the wire every 0.4 – 0.6 cm. The nitinol tip for these guide wires is then resistance welded for a seamless fusion. The relatively large diameter, orthogonal disk that results at the fusion point is ground off. A final grind then takes places to tune the diameter to net shape, 0.013”. The product is then assembled with metal coil or polymer jacket. Sterilization and labeling follow.

For nitinol guide wire tips, where superelastic behavior is warranted, swaging is utilized to reduce the diameter to near net shape. Swaging imparts a percent reduction in area, which accounts for the primary amount of cold work the wires receive. However, there is a secondary work factor that branches from the swaging process, known as redundant cold work. Rotary swaging involves two opposing dies plastically deforming the periphery of the wire at a rapid succession. The initial compressions result in an oval-shaped cross section. The dies then rotate in sixty degree intervals, therefore forcing the ovals to become progressively circular, in addition to decreasing the diameter of the wire (Figure 3). Each successive strike produces permanent deformation within the wire, resulting in a zone of shear strain. The rotation of the dies causes overlapping shear zones in the center of the circular cross-section, therefore a secondary cold working mechanism is imparted, known as “redundant work” (Figure 4). A cold work gradient is then instilled across the cross section of the wire, so that higher strength is present in the center of the as-swaged wires [8]. The redundant work factor results in a larger strength than was to be expected from solely a percent reduction in area.

![Figure 3: Rotary (60°) swaging die, cross section with offset, opposite shearing force directions. [8]](image)

![Figure 4: Cold work gradient as a result of redundant cold work across guide wire cross section. [8]](image)

A final grind is then utilized to acquire the tip’s net shape (Ø 0.007”). This negates the cold work gradient by sectioning off the lower relative-strength surface material. Post-grinding, the core wire is given a twenty-minute temperature (460°C) heat treatment (known within Abbott Vascular as a “burn
in”). The intention of this heat treatment is to reduce the dislocation density from the downstream manufacturing processes, therefore increasing ductility.

### 1.5 304 Stainless Steel

AISI 304 is the most-used grade of stainless steels. The alloying element composition of which is primarily chromium and nickel (Table I). AISI 304 is solution heat treated above 1050 °C to ensure the diffusion-dependent homogenization of all alloying elements, which removes thermal history from prior fabrication. The alloy is then quenched to room temperature to mitigate both the segregation of impurities to grain boundaries, and precipitation of equilibrium phases. Face-centered-cubic (FCC) austenite has twelve slip systems, which accounts for its relatively higher ductility [9].

<table>
<thead>
<tr>
<th>Alloying Element</th>
<th>Weight Percent</th>
<th>Chromium</th>
<th>Nickel</th>
<th>Manganese</th>
<th>Silicon</th>
<th>Carbon</th>
<th>Nitrogen</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>18.0-20.0</td>
<td>8.0-10.5</td>
<td>2.0</td>
<td>1.0</td>
<td>0.08</td>
<td>&lt;0.10</td>
<td>&lt;0.030</td>
</tr>
</tbody>
</table>

Chromium is alloyed for its high affinity for oxygen, which forms an exceedingly stable intermetallic compound, Cr₂O₃, the nanoscale passivation layer between the oxygen environment and the alloy substrate (Figure 5). This passive layer is impermeable and prevents further oxidation and corrosion from occurring. As it applies to corrosion resistance, the complete solid solution of chromium is essential. Homogenization ensures that there is no gradient in electrochemical potential across the surface of the material, with a scratch which
Figure 5: Characterization of the passive layer of a mechanically polished surface layer. The Auger analysis of atomic percentage as a function of distance from surface. S denotes the mean thickness of the passivation layer = 1.1 nm. Electron spectroscopy for chemical analysis yielded a Cr/Fe atomic ratio of 1.01 at passivation layer [10].

Chromium is a body-centered-cubic crystal structure (BCC) delta-ferrite (δ) stabilizer, therefore any supplemental impurity composition of silicon, molybdenum, titanium, or niobium (additional δ-ferrite stabilizers), could result in the presence of acicular or vermicular delta ferrite precipitates. The splines of acicular and vermicular ferrite have a higher surface-area-to-volume ratio (localized grain boundary density) than the austenite matrix, therefore the majority of mechanical and corrosive issues occur in this vicinity [11]. BCC elements destabilize the FCC crystal structure of austenite, therefore supplemental FCC elements are alloyed. These include nickel, nitrogen, manganese, and carbon, with nickel being the primary austenite-stabilizer. Nickel also forms a passive nickel oxide film and hinders the electrochemical reactions of corrosion along the surface, specifically in caustic environments [12]. (Fe,Cr)23C6 is the most observed carbide in austenitic stainless steels and precipitates in the 500-950°C range. These precipitates absorb large amounts of chromium that would otherwise contribute to corrosion resistance [9].

Manganese has an allotropic Bravais lattice morphology. In the context of austenitic stainless steels, γ-Manganese is FCC at 1095°C, and therefore stable at the solution annealing temperature. Room temperature α-phase crystal structure, which is loosely a BCC with a basis of 29 atoms, and β-phase simple cubic unique Bravais lattice, containing 20 atoms in 2 groups, existing at 727°C [13]. Manganese additionally increases the solubility of nitrogen, which is a solid solution strengthener, and the primary reason for alloying 304 SS with nitrogen [14]. Due to manganese’s higher affinity for sulfur than iron, manganese sulfides (soft, non-detrimental compound) form in higher priority than iron sulfides, which would otherwise segregate and embrittle grain boundaries [15].

1.6 Nitrides and Compositional Analysis

Nitrogen interstitial diffusivity is significant at the 400°C thermal energy input level. At 450°C, chromium’s coefficient of diffusivity also becomes significant. Therefore, the formation of chromium nitride (CrN) precipitates in the Fe–Ni matrix becomes thermally possible. This has a beneficial effect on the material strength (increase in incoherent precipitate grain boundary density) but a detrimental effect on its corrosion resistance due to the depletion of Cr from the austenite matrix, that would otherwise form a passivating oxide layer. Nitriding is effectively a coherent to incoherent precipitate transition.

Conventional techniques such as X-Ray Diffraction/Crystallography (XRD, XRC), scanning electron microscope (SEM), or transmission electron microscope (TEM) investigate precipitation in metals to an extent. Field ion microscopy (FIM) or atom probe tomography (APT) allow identification of small coherent precipitates or clustering. The CrN precipitates have irregular, sphere-like shapes. X-ray
spectroscopic investigation reveals three different intermetallic distances and different chemical environments for Fe, Cr and Ni, accompanied by a large static disorder. This suggests that the presence of the interstitial N destabilizes the homogeneous element distribution in 304 SS at 400°C. This leads to N segregating into Cr rich zones that are coherent with the Fe,Ni matrix.

At the later stages of precipitation, when particle size becomes fully incoherent and is on the micro scale, XRD becomes a viable technique to detect chromium nitrides. EDS is used concurrently with the SEM, for elemental analysis or chemical characterization. With EDS, a high-energy beam of charged particles (electrons, protons) transmits a ground state electron to discrete energy levels or electron shells to form an electron hole. A higher energy, outer shell electron then transmits to that hole to stabilize. Upon transmission, the energy difference between those shells is made apparent by the ejection of an X-ray. The specific wavelength of those X-Rays, is measured by an energy dispersive spectrometer, and counted. The emitting element’s difference in energy shells can therefore be differentiated to tell an elemental composition. XRD is utilized as well for compositional analysis. A beam of X-rays is projected onto a crystalline surface at a specific angle. The bond length and crystal structure then dictate the angle of diffraction. From, Bragg’s Law, when the path length of the electromagnetic wave within the lattice equals an integer multiple of the radiation’s wavelength, constructive interference will occur. This constructive interference occurs with those X-Rays that diffracted from the top layer of atoms, therefore resulting in intensity peaks. The characteristic intensity peak 2-theta angles are cross referenced with a database of atomic or molecular structure diffraction behavior to determine composition.

Thermochemical treatment, i.e. diffusive saturation of metal near-surface layers with additional elements (in this case, N), is widely used to improve the surface properties of metals such as hardness, wear or corrosion resistance. During the nitriding of iron or steels, two layers are usually observed, which consist of a compound layer (with nitrides) close to the surface, and a diffusion layer deeper in the material. That layer contains a N solid solution and possibly small nitride precipitates. The double-layer structure, phase composition and depth distribution depends on the local phase equilibria and atomic mobility during the treatment or post-treatment annealing, and is determined by the local N amount and temperature [16].

2 Experimental Procedure

2.1 Safety

General lab safety procedures were followed. This included wearing proper PPE attire: long pants, closed toed shoes, safety glasses/goggles, hair tied back. While in lab, an additional person, also wearing the proper PPE, was kept in close proximity. Additional safety procedures were followed during the etchant process which utilized Adler’s Reagent. A Standard Operating Procedure (SOP), referencing
MSDS was compiled for the use of this highly caustic chemical mixture. This SOP included spill, disposal, storage, and potential hazards protocols. For all equipment, training was completed prior to use, by authorized personnel, and the respective SOPs were followed to ensure safe operation.

2.2 Tensile Testing

A Mini 55 Instron, in conjunction with a 500 Newton load cell, was utilized for the tensile testing of wire (Figure 6). Bluehill 3 software outputted stress-strain curves with respective tensile mechanical property measurements. Yield and tensile strength were measured and recorded in Newtons, which were equivalent across all testing, due to fracture upon yielding. Percent elongation was also measured and recorded, yielding elastic information, as the use of an extensometer was impossible. There were some initial issues pertaining to the jaws/vice mount mechanics. Specifically, with too smooth of a jaw surface, the wire slipped gradually throughout the test and no maximum load could be drawn. With too abrasive a jaw, the high grit imposed localized stresses (Figure 7). 15-cm sample of wire was sectioned to allow ample length for a 9-cm testing gage length. The two, right jaws on the Mini Instron were set equidistant and locked, with only the left two jaws being manipulated to move the sample in and out, this ensured the wire samples were parallel to the load direction. The samples were centered in the jaws via a tick-mark feature. The left grips were tightened to a point that was not excessive (in order to mitigate premature ingrip fracture) for a proper hold.
Every processing step diameter was measured using a micrometer, measuring to the fourth decimal point, in millimeters. The tensile testing drawing rate was set to 4mm per minute. The most abrasive grip grits were being utilized, therefore grinding off the PTFE coating was not necessary, where applicable, as no degree of slippage was occurring. A 500 Newton Load cell was being utilized, based off of experimental results (~200 N) and the ASTM Standard theoretical maximum load calculations for 0.013-inch diameter geometry [17]. Over 150 tensile tests were performed in this fashion between the Triple Spring and Hyten Abbott Vascular models at California Polytechnic State University.

High abrasion jaws impose localized stresses on the periphery of the wire. This causes fracture outside of the testing gage length. Instead, fracturing occurred within the jaw, and on the jaw’s edges. To correct this misrepresentation of the wire’s tensile properties, Abbott Vascular, Temecula performed a new series of tensile testing utilizing Lloyd Bollard grips (Figure 8). To grip the wire samples, Lloyd Bollard grips wrap the wire around a duo of coils before pinning the ends. This cultivates a more representative tensile fracture system, that mimics the plastic deformation that occurs upon application. Other than the replacement of grips, the methodology from the California Polytechnic State University, San Luis Obispo samples was replicated.

2.3 Scanning Electron Microscopy

Scanning Electron Microscopy was utilized to inspect the fracture surfaces of the tensile tested wires. An FEI Phillips Quanta 200 Environmental SEM was used at high vacuum, backfilled with nitrogen gas. The Everhart Throne Detector was used to process the secondary electrons into topographical information. The fracture of the wires cleaved diagonally, such that an ellipsoid fracture surface cross sections were under inspection. The wire was bent in order to orient a section of the wire that could be adhered to the sample holder while maintaining the surface plane orthogonal to the electron beam. Samples were cleaned with acetone to remove any debris or contaminates. Samples were placed 10-mm from the aperture, an ideal initial distance for high vacuum. Upon initiating microscopy, a voltage
of 10-kV was used in order to mitigate the amount of charging and therefore, sputtering that occurs when the PTFE is within the electron beams rastering spot size diameter. Once the magnification was increased, such that only the electrically conductive 304 SS was under inspection, the voltage was increased. The samples were focused, where the working distance is changed, at twice the magnification as target magnification, to maximize clarity. Upon changes in spot size or voltage, the system was Degaussed and refocused.

2.4 X-Ray Diffraction

An XRD Siemens D5000 was utilized, with the thin film attachment, in order to implement grazing incidence x-ray diffraction detection scans (GIXRD). The copper filament was replaced with a cobalt filament in order to reduce the iron Kα fluorescence that occurs with the relatively high energy Cu Kα and Kβ radiation. For the x-ray diffraction wire samples, the PTFE coating was ground off, and sectioned into ~1 cm lengths. The ~1 cm sections were then placed longitudinally in close-packed succession. This maximized the amount of 304 SS metal exposed in the cross section of the high-hardness diallyl phthalate mount (Figure 9). The mounts were then ground from 240 to 600 grit, to remove ~0.006-inches, half the diameter of the wire, to once again maximize 304 SS metal surface area. For the grazing incidence, thin film scan, the increment was set to 0.008, with a scan speed of 5 second per increment, for a 30 to 90 degree 2θ scan sweep. Total scan time was approximately 10 hours per sample.

Figure 9: Mount of the sectioned samples, ~1 cm, in close-packed succession, to maximize surface area for the thin film grazing incidence x-ray diffraction detection scan.
2.5 Metallography and Etchant Treatment

For the etchant treatment wire samples, the PTFE coating was ground off, and sectioned into ~1 cm lengths. The ~1 cm sections were then placed longitudinally in close-packed succession. This maximized the amount of 304 SS metal exposed in the cross section of the high-hardness diallyl phthalate. The post wire straightened and post burn in processing steps were adjacent in the sample, such that they received the same scratch and etchant treatment. The mounts were then ground from 240 to 600 grit, and polished to 6-μm diamond suspension mirror finish, to remove ~0.006-inches, half the diameter of the wire, to once again maximize 304 SS metal surface area. Adler’s reagent was synthesized from 4.5 grams Cu ammonium chloride, 75 mL Hydrochloric acid, 22.5 grams ferric (III) chloride, and 37.5 mL deionized water [19]. A cotton swab was used to uniformly etch the sample for approximately 10 seconds. Methanol was used to rinse, in order to avoid oxide spots, with a heated fan to evaporate the methanol rapidly. Digital microscopy was then implemented, normal to the cross-sectional plane, and images were captured in greyscale 8 with μm-scale markers attached. All photographs underwent the same brightness and contrast editing, and multiple pictures were taken, to capture a representative etchant response across the samples.

3 Results

3.1 Tensile Testing – California Polytechnic, San Luis Obispo Materials Engineering Dept.

Tensile testing with the abrasive vice-jaw grips delivered lower than expected maximum loads. This is likely due to the inherent error involved with the abrasive jaw’s stress localization, causing premature fracture. The basis of the project, an increase in mechanical properties upon annealing, and a decrease in mechanical properties upon strain hardening, is not shown in these results: Upon strain hardening for the Hyten model of wire, there is an average increase of 6 Newtons. After annealing, there is an average decrease of 57 Newtons (Table II). Upon strain hardening for the Triple Spring model of wire, there is an average decrease of 4 Newtons, conforming to the anomalous basis of the project. However, similar to the Hyten, after annealing, there is an average decrease of 33 Newtons (Table III). Representative Stress Strain curves for the Triple Spring (Figures 10-12) and Hyten (Figures 13-15) models show tensile behavior. Poor precision is shown in the two wire models across the respective processing steps, with large standard deviations at the processing steps of interest: Hyten, 26.6 Newtons post Wire Straightening, and 22.3 Newtons post Burn In. Triple Spring, 15.1 Newtons post Wire Straightening, and 23.1 Newtons post Burn In. Due to the high standard deviations across processing steps, the small differences between means are inconclusive, being lost in the noise of the deviations. The remaining stress strain curves have been logged in the appendix of this report.
Table II: Maximum Load between the Hyten Processing Steps with Abrasive Vice Jaw Grips

<table>
<thead>
<tr>
<th>Hyten Processing Step</th>
<th>Maximum Load (N)</th>
<th>Average Tensile Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Standard Deviation</td>
</tr>
<tr>
<td>As Received 152</td>
<td>15.6</td>
<td>1817</td>
</tr>
<tr>
<td>Reel to Reel 155</td>
<td>19.7</td>
<td>1719</td>
</tr>
<tr>
<td>Post Wire Straightening 161</td>
<td>26.6</td>
<td>1802</td>
</tr>
<tr>
<td>Post Burn In 104</td>
<td>22.3</td>
<td>1178</td>
</tr>
<tr>
<td>Stress Relieve 128</td>
<td>23.6</td>
<td>1438</td>
</tr>
</tbody>
</table>

Table III: Maximum Load between the Triple Spring Processing Steps with Abrasive Vice Jaw Grips

<table>
<thead>
<tr>
<th>Triple Spring Processing Step</th>
<th>Maximum Load (N)</th>
<th>Average Tensile Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Standard Deviation</td>
</tr>
<tr>
<td>As Received 171</td>
<td>7.2</td>
<td>1976</td>
</tr>
<tr>
<td>Reel to Reel 198</td>
<td>6.4</td>
<td>2166</td>
</tr>
<tr>
<td>Post Wire Straightening 202</td>
<td>15.1</td>
<td>2147</td>
</tr>
<tr>
<td>Post Burn In 169</td>
<td>23.1</td>
<td>1793</td>
</tr>
</tbody>
</table>

Figure 10: Stress-Strain curves for Triple Spring Reel to Reel.
Figure 11: Stress-Strain curves for Triple Spring Post Wire Straightened.

Figure 12: Stress-Strain curves for Triple Spring Post Burn In. Specimens 1-15.

Figure 13: Stress-Strain curves for Hyten Post Reel to Reel.
Figure 14: Stress-Strain curves for Hyten Post Wire Straightened.

Figure 15: Stress-Strain curves for Hyten Post Burn In.

### 3.2 Tensile Testing – Abbott Vascular, Temecula Samples

The Tensile testing utilizing Lloyd Bollard grips showed higher accuracy, correlating with the calculated maximum load from the ASTM Standard theoretical maximum. The basis of the project is represented: Upon strain hardening the Triple Spring model of wire, there was an average decrease of 15 Newtons. After annealing, there was an average increase of 12 Newtons (Table IV). Precision substantially increased with the Lloyd Bollard grips relative to the abrasive vice jaw grips, with a standard deviation of 0.12 for the post Wire Straightening processing step and a standard deviation of 0.30 for the post Burn In processing step. The same anomalous trend was seen with the Hyten samples: Upon strain hardening, there was an average decrease of 18 Newtons. After annealing, there was an average increase of 13 Newtons (Table V). Similar precision was observed with the Hyten, with a standard deviation of 0.38 for the post Wire Straightening processing step and a standard deviation of 0.17 for the post Burn In processing step. The stress strain curves have been logged in the appendix of this report.

Table IV: Maximum Load between the Triple Spring Processing Steps with Lloyd Bollard Grips
### 3.3 Grazing Incidence XRD Detector Scans

The GIXRD detector scans utilizing Co Kα and Kβ electromagnetic radiation have been reduced to a 30 to 56 degree 2θ range for both the Hyten post Wire Straightening (Figure 16) and Burn In (Figure 17) processing steps. The Bragg’s law calculation accounting for the radiation energy difference, resulted in higher 2θ values being undefined upon an inverse sinusoidal conversion. The outputted intensity peaks (arbitrary units) with respect to 2θ (degrees), returned characteristic 304 phases, with the austenitic (γ) and ferritic (α) (111) crystallographic orientations occurring in both scans. The characteristic chromium nitride 20 positions are indicated, with the (111) crystallographic orientation occurring at 45.0 degrees and the (200) crystallographic orientation occurring at 53.3 degrees. The three leftmost peaks in both scans, occurring at 32, 34.3, and 37.5 degrees, are undefined, possibly characteristic of the aggregate crystals in the diallyl phthalate mounting agent.
3.4 Scanning Electron Microscopy Fracture Analysis

SEM utilized a voltage range of 10 to 30 kV, and a spot diameter from 2.5 to 4. Ductile fracture was universal across the samples, with few, non-representative exceptions of brittle, granular fractures (Figure 20D). The full ellipsoidal cross-sectional areas of the fracture surfaces can be seen in the ~230 times magnification microscopy images (Figures 18C, 19C, 20C, and 21D). The surrounding white, shredded-texture feature is the PTFE coating. Microvoids for the Hyten and Triple Spring Wire
Straightened samples (Figures 18 and 20) are on the microscale while the Burn In fractures have a denser coalescence of voids on the nanoscale (Figures 19 and 21). The ASTM Standard for measuring average grain size was referenced in order to determine an average void diameter [20]. Since the void dispersion can be assumed as uniform and randomly oriented, the linear intercept method of sampling was appropriate, as opposed to the circular intercept procedure. For the Hyten post Wire Straightened micrographs, an average diameter of 1.8 μm was calculated. For the Hyten post Burn In micrographs, an average diameter of 670 nm was calculated. For the Triple Spring post Wire Straightened micrographs, an average diameter of 1.1 μm was calculated. For the Triple Spring post Burn In micrographs, an average diameter of 430 nm was calculated.
Figure 18: Representative fracture surfaces of the Hyten post Wire Straightening processing step. An overall ductile fracture response is observed, with the majority of microvoids on the scale of 1-2 microns and above. Average void diameter of 1.8 μm was calculated.

Figure 19: Representative fracture surfaces of the Hyten post Burn In processing step. An overall ductile fracture response is observed, with the majority of voids on the nanoscale. Average void diameter of 670 nm was calculated.
Figure 20: Representative fracture surfaces of the Triple Spring post Wire Straightening processing step. An overall ductile fracture response is observed, with the majority of microvoids on the scale of 1 microns and above. Average void diameter of 1.1 μm was calculated.
Figure 21: Representative fracture surfaces of the Triple Spring post Burn In processing step. An overall ductile fracture response is observed, with the majority of voids on the nanoscale. Average void diameter of 430 nm was calculated.

### 3.5 Etchant Response

Upon equal grinding and polishing, etching, and microscopy treatment, there is a definitive difference in response to Adler’s Reagent between the Hyten post Wire Straightened (Figures 22-23) and Burn In (Figures 24-25) processing steps. Different magnifications of the longitudinal wire samples are shown and denoted with respective micron bars. The post Wire Straightened samples have a lighter tint relative to the post Burn In, indicating a heightened etchant attack on susceptible scratches. Pitting corrosion is apparent with the post Burn In processing step as well, indicating a sharp contrast in behavior between the two samples.
4 Analysis

Utilizing Co Kα and Kβ electromagnetic radiation in GIXRD detector scans has shown no definitive characteristic differences between the Hyten post Wire Straightening (Figure 16) and Burn In (Figure 17) processing steps. The most prominent crystallographic orientation intensity peak for the chromium nitride phase, the (200), occurs at the same 2θ value as the ferrite (α) (111), overshadowing any detection (Figure 26): The 2θ value for the CrN (200) with Cu Kα radiation is 43.7 degrees. Converted with Bragg’s law for the Co Kα radiation, the 2θ value for the CrN (200) is 53.3 degrees. The
20 value for the $\alpha$ Ferrite (111) with Cu K$\alpha$ radiation is 44.6 degrees. With Co K$\alpha$ radiation, the 20 value for the $\alpha$ Ferrite (111) is 54.6 degrees. The 20 value for the CrN (111), the next most prominent CrN intensity peak, with Cu K$\alpha$ radiation is 37.5 degrees. With Co K$\alpha$ radiation, the 20 value for the CrN (111) is 45.0 degrees. At the 20 45-degree point for the post annealing processing step, a small uptick of intensity is seen, but is not definitive enough to be conclusive. The intensity peaks and their magnitudes are essentially indicators of the volume fraction of each respective phases’ crystallographic orientation. Theoretically, precipitation would therefore decrease the magnitude of one pre-annealing intensity peak, having lost a volume percentage within the sample, in exchange for a new intensity peak denoting a newly-precipitated CrN volume. These results are intuitive, 0.1wt% N is a limiting factor to produce a large enough volume fraction of CrN phase, and therefore a challenge to be represented in a GIXRD detector scan.

![Intensity peaks](image)

**Figure 26:** CrN characteristic intensity peaks. Cu K$\alpha$ radiation 20 values. [21]

Fracture analysis has supported the hypothesis of chromium nitrides precipitating during the burn in processing step. For the Triple Spring post wire straightened processing step, representative microvoids are on the microscale (Figure 27). Post 480°C annealing treatment, there is a change in fracture behavior, with a denser coalescence of microvoids occurring on the nanoscale (Figure 28). Individual voids initiate on three possible sites: impurities, dislocation clusters, or preexisting surfaces. Preexisting surfaces include precipitated phases, such as the intermetallic chromium nitride. Considering impurities, the two processing steps are of the same stock of 304 SS, therefore the elemental compositions are equivalent. Additionally, no introduction of impurities into the wire occurred during the annealing step. Considering
dislocation clusters, while the burn in step is indeed anomalous, the fundamental stress relieve mechanisms are intact. Therefore, dislocation density is decreasing, not increasing. With the Triple Spring model of wire, the average void diameter underwent a 61% reduction after the annealing step. With the Hyten model of wire, the average void diameter underwent a 63% reduction after the annealing step. Consequently, a fine dispersion of a new phase being precipitated is the remaining possibility accounting for the increased fracture initiation-site density.

Adler’s Reagent has shown a drastic difference between the Hyten post Wire Straightened (Figures 22 and 23) and Burn In (Figures 24 and 25) processing steps in response to an etchant treatment. Considering the stoichiometric reaction for chromium nitriding: \(2\text{Cr} + \text{N}_2 \rightarrow 2\text{CrN}\). Upon precipitation of the intermetallic, chromium depletion is occurring. Less chromium in solid solution translates to less chromium to reform the low energy state chromium oxide passivation layer that makes stainless steel corrosion resistant. Due to the unorthodox 0.013-inch diameter geometry, traditional galvanic corrosion testing was not possible. An etchant response is not perfectly representative of an application’s corrosive environment. However, considering the extreme corrosive pitting occurring with the post Burn In processing step, such a contrasting response to a chlorine etchant to a scratched surface may be indicative of chromium depletion.
5 Conclusions

1. Tensile testing that utilized Lloyd Bollard grips confirmed the anomalous response to processing that Abbott Vascular has been witnessing. Mechanical properties decreased upon strain hardening, and increased upon annealing.

2. Fracture analysis of the 304 SS guidewires support chromium nitride precipitation due to a denser microvoid coalescence during the “Burn-In” processing step, indicating that new CrN precipitate surfaces are serving as fracture initiation sites.

3. Change in response to etchant after the “Burn-In” processing step may indicate a change in corrosion resistance, indicating chromium depletion that occurs with CrN precipitation.
6 References


7 Appendix

**Triple Spring Specifications and Tensile Testing Results**

Implant Type: Hi-Torque Guide wire

Material: SS 304V – Triple Spring/ASTM A313

Mechanical Properties:

- Tensile Strength: 360 - 390 ksi
- Elongation: 2% minimum based on a 10 inch gage length
- Sample Size: 190 cm long wire from each step (can be cut as desired for testing)

Processing steps to be investigated:

- As-received
- Reel To Reel: 860°F
- Wire Straightening/Swaging: Pitch marks, 0.4 – 0.6 cm
- Burn-In: ~860 – 900°F

![Stress-Strain curves for Triple Spring As Received. Displaced curve of specimen #1 is because the jaws were not zeroed, same gage length was used.](image_url)
Figure 30: Stress-Strain curves for Triple Spring Post Wire Straightened.

Figure 31: Stress-Strain curves for Triple Spring Post Burn In.

Figure 32: Stress-Strain curves for Triple Spring Post Burn In. Specimens 16-21.
Figure 33: Stress-Strain curves for Triple Spring post Reel to Reel. Abbott Vascular tested samples utilizing Lloyd Bollard Grips.

Figure 34: Stress-Strain curves for Triple Spring As Received. Abbott Vascular tested samples utilizing Lloyd Bollard Grips.

Figure 35: Stress-Strain curves for Triple Spring post Wire Straightened. Abbott Vascular tested samples utilizing Lloyd Bollard Grips.
Figure 36: Stress-Strain curves for Triple Spring post Burn In. Abbott Vascular tested samples utilizing Lloyd Bollard Grips.

**Hyten Specifications and Tensile Testing Results**

Implant Type: Hi-Torque Guide Wire  
Material: SS 304V – Hyten/ASTM A313  
Mechanical Properties:  
Tensile Strength: 400 - 435 ksi  
Elongation: 2% minimum based on a 10 inch gage length  
Sample Size: 190 cm long wire from each step (can be cut as desired for testing)  
Processing steps to be investigated:  
- As-received  
- Reel To Reel: 860°F  
- Wire Straightening/Swaging: Single pitch distance 0.4 - 0.6 cm  
- Burn-In: ~860 – 900°F  
- Stress Relieve: 800°F
Figure 37: Stress-Strain curves for Hyten As Received.

Figure 38: Stress-Strain curves for Hyten Post Wire Straightened.

Figure 39: Stress-Strain curves for Hyten Post Stress Relieve. Displaced curve of specimen #4 is because the jaws were not zeroed, same gage length was used.

Figure 40: Stress-Strain curves for Hyten As Received. Abbott Vascular tested samples utilizing Lloyd Bollard Grips.

Figure 41: Stress-Strain curves for Hyten post Reel to Reel. Abbott Vascular tested samples utilizing Lloyd Bollard Grips.
Figure 42: Stress-Strain curves for Hyten post Wire Straightened. Abbott Vascular tested samples utilizing Lloyd Bollard Grips.

Figure 43: Stress-Strain curves for Hyten post Burn In. Abbott Vascular tested samples utilizing Lloyd Bollard Grips.