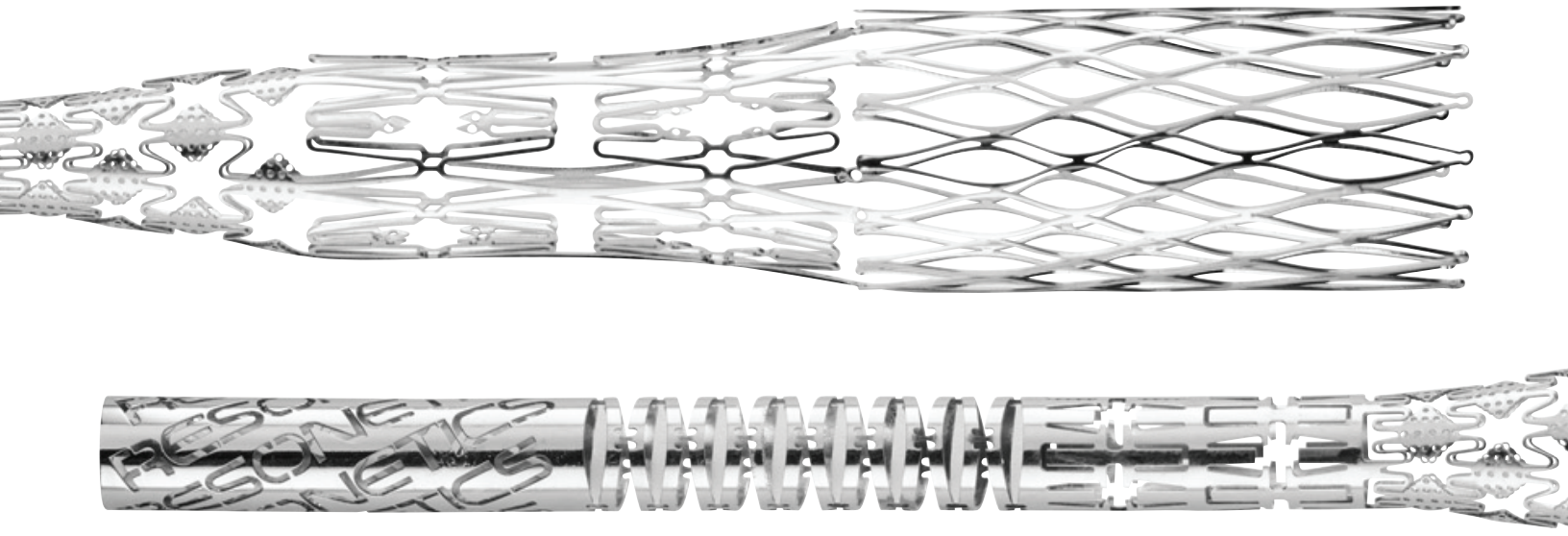
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Introduction to Nitinol



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Contents

Glossary 3

Section 1 **Key Concepts** 5

1.1 **Phase Transformations - Austenite↔Martensite** 6

1.1.1 **The R-Phase** 7

1.2 **Identifying Transformation Temperatures** 8

1.2.1 **Differential Scanning Calorimetry (DSC)** 8

1.2.2 **Bend and Free Recovery (BFR)** 9

1.3 **Functional Properties of Nitinol** 10

1.3.1 **Superelasticity** 10

1.3.2 **Shape Memory Effect** 12

1.4 **Thermal Hysteresis** 13

1.5 **Effect of Cold Work** 13

1.6 **Alloy Ratio and Ms** 14

Section 2 **The Nitinol Ingot and Wrought Material** 15

2.1 **ASTM Standard for the Nitinol Alloy** 15

2.2 **Melting of the Nitinol Ingot** 16

2.2.1 **Inclusion Content** 17

2.3 **Redox™ Nitinol Alloy** 19

2.4 **The Nickel Titanium Cobalt (NiTiCo) Alloy** 20

Section 3 **Semi-Finished Materials** 21

3.1 **Nitinol Wire** 21

3.1.1 **Nitinol Strip** 21

3.2 **Nitinol Tube** 22

3.3 **Nitinol Sheet** 22

Section 4 **Processing Nitinol** 23

4.1 **Laser Cutting** 23

4.2 **Shape Setting (Heat Treatment)** 25

4.3 Machining 26

4.3.1 **Milling, Turning, and Drilling** 26

4.3.2 **Wire EDM** 26

4.4 **Grinding** 27

4.5 **Water Jet Cutting** 27

4..6 **Stamping** 27

4.7 **Photochemical Etching** 28

4.8 **Joining** 29

4.8.1 **Welding** 30

4.8.2 **Crimping** 30

4.8.3 **Soldering and Adhesives** 30

4.9 **Finishing** 31

4.9.1 **Blasting** 31

4.9.2 **Mechanical Tumbling** 31

4.9.3 **Chemical Processing** 31

4.9.4 **Other Finishing Options** 33

Section 5 **Medical Device Design Considerations** 34

5.1 **Typical Physical and Mechanical Properties** 34

5.2 **Corrosion** 36

5.3 **Sterilization of Nitinol** 36

5.4 **Biocompatibility** 36

5.5 **Fatigue** 37

5.6 **Surface Finishes** 37

5.7 **Strain** 38

Glossary

The following technical terms and their definitions are essential for understanding nitinol and the concepts presented in this document. For an extensive list of standard terminology it is recommended to reference ***ASTM F2005 – Standard Terminology for Nickel-Titanium Shape Memory Alloys***.

Active austenite finish temperature (Active Af) – term for austenite finish temperature of raw wire, tube, sheet or semi-finished component as determined by bend and free recovery (BFR) test method described in ASTM F2082. The active Af is often preferred when specifying thermal properties of a component as it is more representative of performance in application.

Austenite – the high temperature parent phase of the nitinol alloy having a B2 crystal structure.

Austenite finish temperature (A_f) – the temperature at which martensite (or R-phase) to austenite transformation is completed on heating of the alloy.

Austenite peak temperature (A_p) – the temperature of the endothermic peak position on the differential scanning calorimetry (DSC) curve upon heating for the martensite (or R-phase) to austenite transformation.

Austenite start temperature (A_s) – the temperature at which the martensite (or R-phase) to austenite transformation begins on heating of the alloy.

Free recovery – unconstrained motion of a shape memory alloy upon heating and transformation to austenite after deformation in a lower temperature phase.

Lower plateau strength/stress (LPS) – the stress measured at 2.5 % strain during tensile unloading of the sample, after loading to 6 % strain per the method described in ASTM F2516.

Martensite – the lowest temperature phase in nitinol shape memory alloys with a B19' (B19 prime) monoclinic crystal structure.

Martensite deformation temperature (M_d) – the highest temperature at which martensite will form from the austenite phase in response to an applied stress. At temperature above Md the nitinol shape memory alloy will not exhibit superelasticity it will rather exhibit a typical elastic-plastic behavior when loaded.

Martensite finish temperature (M_f) – the temperature at which the transformation of martensite from austenite (or R-phase) is completed on cooling of the alloy.

Martensite peak temperature (M_p) – the temperature of the exothermic peak position on the DSC curve upon cooling for the austenite (or R-phase) to martensite transformation.

Martensite start temperature (M_s) – the temperature at which the transformation from austenite (or R-phase) to martensite begins on cooling of the alloy.

Pseudoelasticity – another name for superelasticity. See **superelasticity**.

R-phase – the intermediate phase which may form between austenite and martensite. The R-phase occurs in nitinol alloys under certain conditions. The R-phase has a rhombohedral crystal structure.

R-phase finish temperature (R_f) – the temperature at which the transformation from austenite to R-phase is completed on cooling; in an alloy that exhibits two-stage transformation.

R-phase peak temperature (R_p) – the temperature of the exothermic peak position on the DSC curve upon cooling for the austenite to R-phase transformation.

R-phase start temperature (R_s) – the temperature at which the transformation from austenite to R-phase begins on cooling; in an alloy that exhibits two-stage transformation.

R'-phase finish temperature (R'_f) – the temperature at which the martensite to R-phase transformation is completed on heating of an alloy that exhibits two-stage transformation.

R'-phase peak temperature (R'_p) – the temperature of the endothermic peak position on the DSC curve upon heating for the martensite to R-phase transformation.

R'-phase start temperature (R'_s) – the temperature at which the transformation from martensite to R-phase transformation begins on heating of an alloy that exhibits two-stage transformation.

Residual elongation (El_r) – the percent strain measured after tensile loading to 6 % strain and unloading to 7 MPa per ASTM 2516.

Superelasticity – nonlinear recoverable deformation behavior of nitinol shape memory alloys that occurs at temperatures above Af but below Md.

Uniform elongation (Elu) – the percent elongation (or strain) determined at the maximum force sustained by the test sample prior to necking, or fracture, or both upon tensile loading per ASTM 2516.

Upper plateau strength/stress (UPS) – the stress measured at 3 % strain during tensile loading of the sample per the method described in **ASTM F2516**.

Section 1.0 - Key Concepts

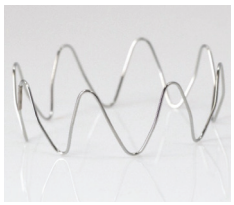
Nitinol is a special type of alloy known as a Shape Memory Alloy (SMA) that is composed of near equiatomic Nickel and Titanium (i.e. 50:50 at.% Ni and Ti). Nitinol exhibits excellent superelastic and shape memory properties as well as biocompatibility. The first medical device application was orthodontic archwires in the early 1970's. Many other devices were introduced to the market following the approval of the Mitek suture anchor device by the US Food and Drug Administration in 1989. Nitinol has since become a staple in the cardiovascular, neurovascular, endovascular, peripheralvascular, orthopedic, spinal, urology and dental arenas with applications ranging from neurovascular stents and heart valve frames to orthopedic staples and single-use suture passers.

Nitinol is an essential material in the medical device engineer's toolbox. However, traditional material properties, design concepts, and manufacturing processes are often not applicable. Much experience in working with the alloy is required before the necessary engineering-know-how is obtained to bring a device from initial conception to final release. The main purpose of this document is to provide a reference for companies and engineers new to nitinol alloys with the main goal of expediting the learning process. Many concepts used every day by our engineers at Resonetics will be introduced herein, including:

- Basic metallurgy
- Mechanical and thermal properties
- ASTM standards for the alloy and material testing
- Common manufacturing processes
- Nitinol specific design considerations



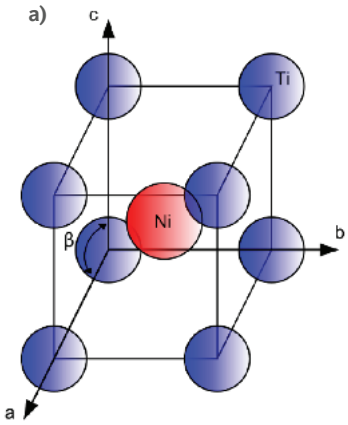




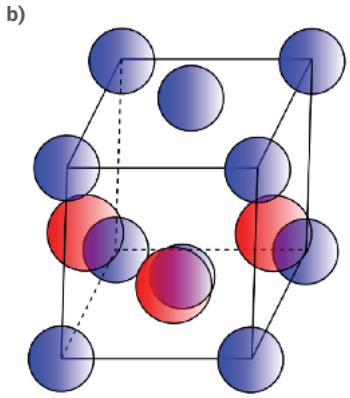


1.1 Phase Transformations - Austenite ↔ Martensite

In order to understand how shape memory alloys work you must first grasp the concept of phase transformations. The unique shape memory and superelastic properties of nitinol result from reversible solid-state phase transformations that occur when the material is subject to external stimuli such as a change in temperature or applied stress. A phase transformation induced by a change in temperature is the mechanism responsible for the shape memory property while transformation induced by stress is the mechanism responsible for the superelastic property (see section 1.3). This diffusionless martensitic transformation occurs between the parent B2 austenite phase and the B19' martensitic phase.



Austenite
(B2, CsCl type ordered structure)



Martensite
(B19', Monoclinic structure)

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In nitinol the diffusionless transformation is an instantaneous distortion in the crystal lattice (B2↔B19') that occurs at the speed of sound; often referred to as a military transformation.

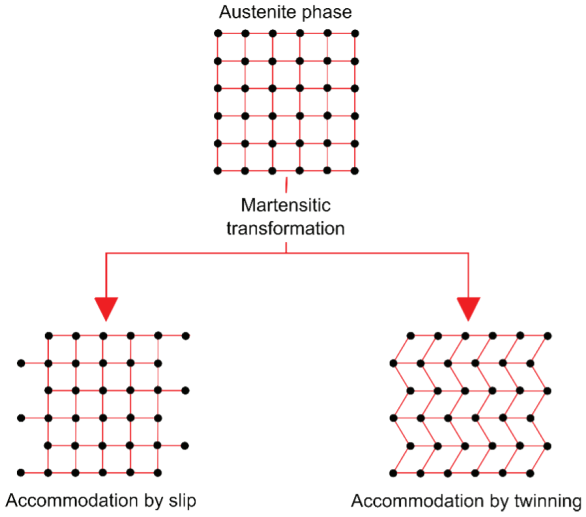
In contrast, diffusion based phase transformations, as common in steel alloys, requires the diffusion of atoms over relatively long distances. Diffusion requires heating the alloy at a high temperature for extended periods of time.

Martensitic transformation is defined as a shear/shuffle of the crystal lattice that takes place due to a change in the thermodynamic stability of the system. The reversible martensitic phase transformation that occurs in nitinol is accommodated through twinning of the crystal lattice. Unlike during martensitic transformations in steel alloys, which is accommodated by irreversible dislocation motion (i.e. slip), twinning in nitinol is reversible. This concept is visualized below where in reversible twinning, the lattice planes shift by less than one unit cell and still maintain correspondence with the parent lattice structure.

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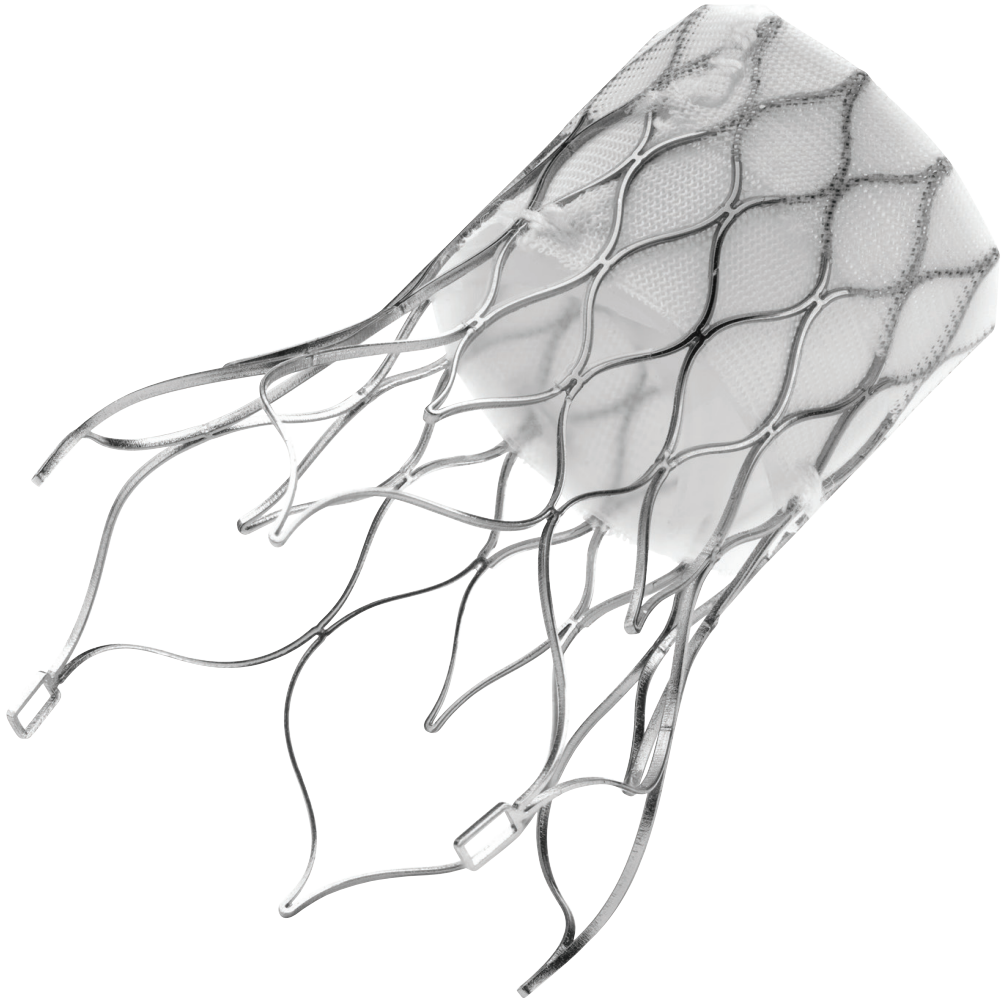
In nitinol the diffusionless transformation is an instantaneous distortion in the crystal lattice (B2↔B19') that occurs at the speed of sound; often referred to as a military transformation.

In contrast, diffusion-based phase transformations, as common in steel alloys, requires the diffusion of atoms over relatively long distances. Diffusion requires heating the alloy at a high temperature for extended periods of time.



1.1.1 The R-Phase

Intermediate phases are sometimes present that are stable at temperatures or stresses between the B2, austenite and B19', martensite phases. A phase known as R-phase, having a rhombohedral crystal structure, is the most common of these phases; especially when considering traditional binary NiTi nitinol alloys. The R-phase is an intermediate martensitic phase that competes with the B19' martensite phase transformation that occurs in nitinol materials that have high dislocation density (i.e. cold worked), Ni-rich precipitates (i.e. heat treated), or in some ternary alloys. Dislocations in the crystal structure as well as Ni-rich precipitates all resist large strains in the crystal lattice (see section 1.5). Since the R-phase transformation requires much less straining of the crystal structure it is therefore thermodynamically favorable to occur between the austenite and martensite phases in these cases.

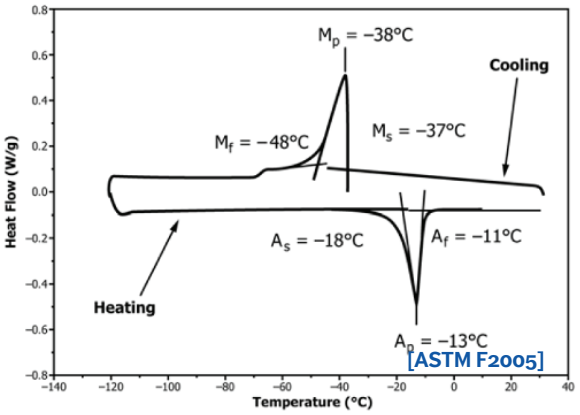


1.2 Identifying Transformation Temperatures

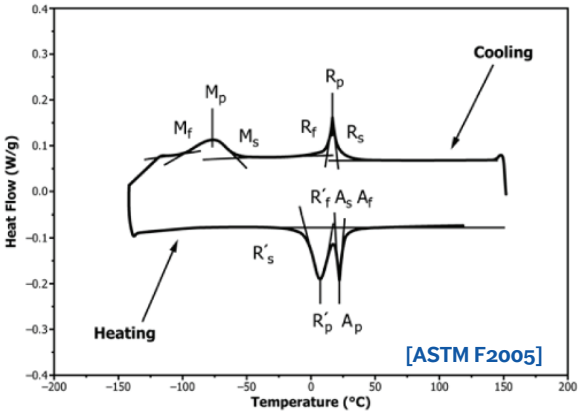
1.2.1 Differential Scanning Calorimetry (DSC)

ASTM F2004
Standard Test Method for Transformation Temperature of Nickel-Titanium Alloys by Thermal Analysis

Differential scanning calorimetry (DSC) is the thermoanalytical technique used to characterize the phase transformation behavior of nitinol shape memory alloys. The DSC method produces a curve through measuring the amount of heat given off (i.e. exothermic) or absorbed (i.e. endothermic) by a sample as it is cooled and heated through its phase transformations. The DSC test yields extremely repeatable curves where tangents are used to identify the start, finish, and peak temperatures of each of the phases present in a particular component/alloy.



The DSC technique is most commonly used to characterize wrought nitinol materials or ingot per ASTM F2063. When nitinol is in the fully annealed state, the Ni:Ti ratio of the alloy can be confirmed based on the transformation temperatures as a form of quality control. In the fully annealed state Nitinol will exhibit single-stage transformations between austenite and martensite. If the material is however processed further, for example, cold worked and aged to produce Ni-rich precipitates (i.e. heat treated) a two-stage transformation will be identified through DSC where R-phase is present.



Design Considerations

- The DSC test is a destructive test.
- The A_s temperature provided on certificate of conformance for a wrought nitinol product will have been determined using DSC testing
- The DSC technique can also be used to test raw materials or finished components where BFR is not feasible or practical; for example, a complex braided device
- Due to the thermomechanical processing necessary to manufacture superelastic net-shape raw materials and/or final components, R-phase is usually present (i.e. two-stage transformation)

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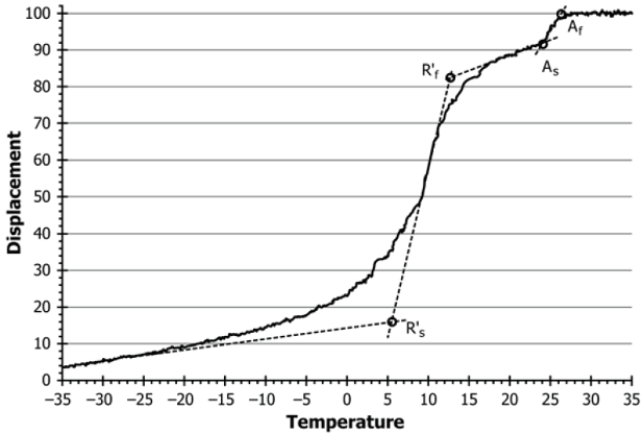
The DSC curve is very useful when developing thermomechanical manufacturing processes. Much can be learned from the curves, for example:

- Shallow wider peaks indicates more cold work in the material.
- Aging heat treatments used to tune the A_f temperature and superelastic plateau stresses can be optimized through visualizing changes in A_p.
- The area under a peak is the heat of transformation and is related to the volume of material changing phases.

1.2.2 Bend and Free Recovery (BFR)

ASTM F2004
Standard Test Method for Transformation Temperature of Nickel-Titanium Alloys by Thermal Analysis

The bend and free recovery (BFR) test is used to determine the Active Af temperature of a net-shape raw material product (i.e. wire, tube, sheet, rod, etc.) or finished component. In this test the nitinol sample is cooled to below the Mf temperature and then deformed in a controlled fashion. Upon heating the sample through the austenite (and R-phase) transformation temperatures the sample will recover its original shape (i.e. free recovery). The displacement measured by means of a linear or rotary variable differential transducer (LVDT/RVDT) is then plotted against temperature. Tangents are then taken from the curve to determine the active transformation temperatures.

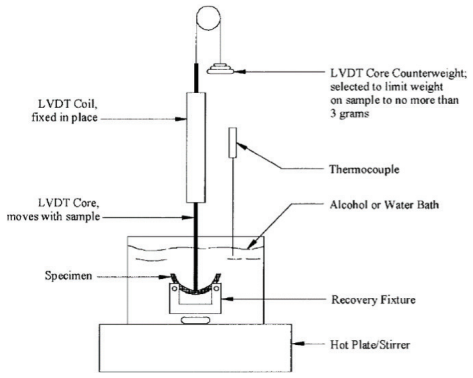


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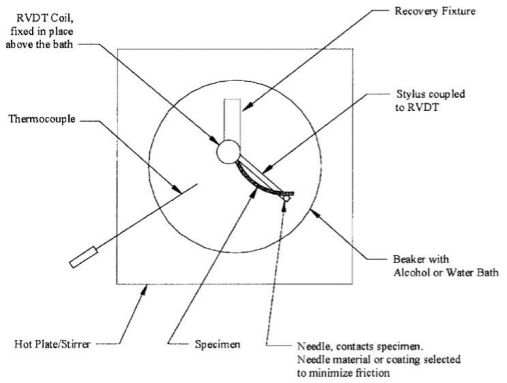
Depending on previous processing history stress on the sample/component can shift the transformation temperatures to lower temperatures. For this reason BFR is considered to better represent the transformation temperatures experienced in application.

The active Af temperature measured via BFR testing is usually found to be lower than the Af determined through DSC testing. The active Af can be up to 15 °C lower.

Schematics of the vertically mounted LVDT and rotary RVDT BFR methods are provided below as presented in **ASTM F2082**. Non-contact methods can also be used where a vision system tracks strain, but these systems are less common. BFR testing is typically used to characterize the austenite finish temperature, Af of net-shape raw materials and finished components wherever possible and will appear on the certificates of compliance. However, drawbacks to this type of test include lack of martensite phase characterization and difficulty accommodating complex geometries. DSC testing is therefore sometimes still necessary



Vertically mounted LVDT set-up



Top view of RVDT set-up

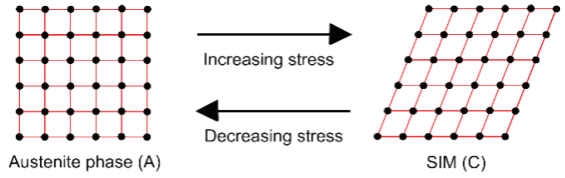
1.3 Functional Properties of Nitinol

The functional properties of nitinol originate from the thermomechanical response of the material. The thermomechanical response can be differentiated into two different functional properties depending on whether the austenite ↔ martensite phase transformation is induced thermally or by applied stress. Thermally induced transformation enables the shape memory effect while the stress induced transformation leads to superelasticity.

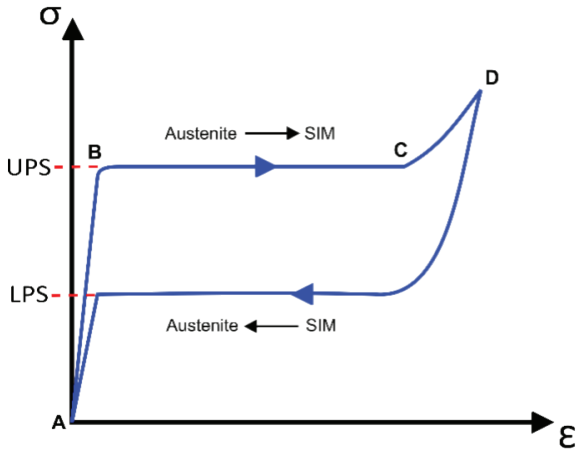
A common misconception is that superelastic and shape memory responses are unrelated. In fact, the response simply depends on the transformation temperature of the nitinol component coupled with the application (or test) temperature. Below the Mf temperature the nitinol alloy will exhibit shape memory while above the Af temperature the nitinol material will exhibit superelasticity. This concept is critical when designing a nitinol device and further highlights the importance of identifying the final phase transformation temperatures of a component through DSC and/or BFR testing, described in the prevision section.

1.3.1 Superelasticity

If a stress is applied to a nitinol component, at a temperature above Af, the austenite phase will be converted to stress induced martensite (SIM) resulting in a superelastic response. Superelastic behavior of nitinol is usually characterized through cyclic tensile testing per **ASTM F2516**.



A typical cyclic tensile curve for superelastic nitinol can be broken into several different segments. During initial loading the austenite phase exhibits typical elastic deformation (A → B) up until the Upper Plateau Stress (UPS) is reached. Once the UPS has been reached an isostress condition is observed (B → C) as the cubic austenite structure shears into detwinned SIM, followed by the elastic deformation of the detwinned SIM structure (C → D). Just as for the thermally induced phase transformation, the formation of SIM is reversible. During unloading (D → A) elastic strain is recovered and the SIM transforms back into the parent austenite phase. Note that the recovery stress (or Lower Plateau Stress, LPS) is lower than UPS. The hysteresis observed arises from internal friction and defects in the crystal structure.



A typical nitinol alloy will exhibit superelasticity up to 8% strain before permanent deformation begins. However, there is always some % of permanent-set or residual elongation, El_r. The magnitude of El_r depends on the past thermomechanical processing of the material and also the percentage strain the component was subject to before unloading.

Design Considerations

The difference between the UPS and LPS is called mechanical hysteresis. It is important to understand which plateau stress is more important for the specific application. To illustrate this point two examples are given:

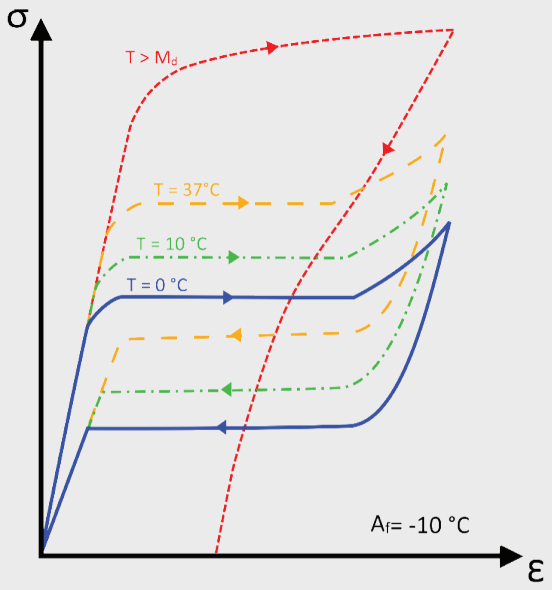
i) Guidewire – The "stiffness" of a guidewire during loading is important for both navigating through the anatomy and also for guiding devices through complex anatomy. The UPS is therefore critical in this case.

ii) Cardiovascular Stent – The force it takes to compress a stent is related to the UPS, however upon deployment inside a vessel, the radial force exerted is related to the LPS. Both the UPS and LPS are important in this case.

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The UPS and LPS are not fixed for all temperatures. The superelastic plateaus will increase with application (or test) temperature following a Clausius-Clapeyron relation. For every °C the plateaus can change by 3 – 20 MPa/°C (0.4 – 3 ksi/°C); depending on the alloy and processing history. It is therefore important to test the superelastic properties of the final device at the application temperature (ex. 37 °C for implantable devices).

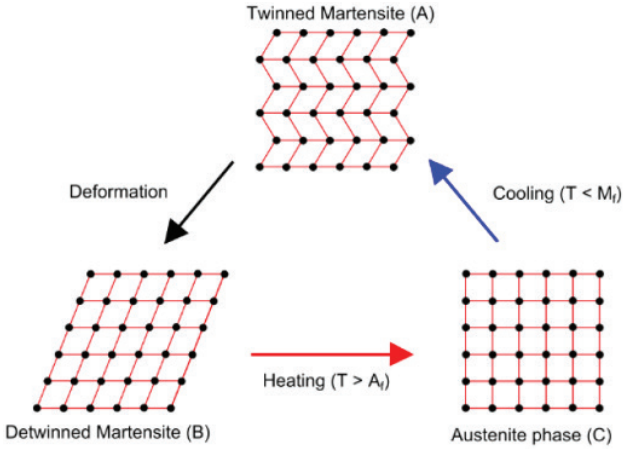
This increase in plateau stresses is due to increasing thermodynamic stability of the high temperature austenite phase the further the temperature of the nitinol material is increased above the Af temperature. In fact, the UPS will continue to increase until the yield stress of the alloy is reached and the material will yield and behave again like an elastic plastic material. Superelasticity therefore cannot occur above this critical temperature termed "martensite deformation temperature" or Md (~ 80 °C > Af).

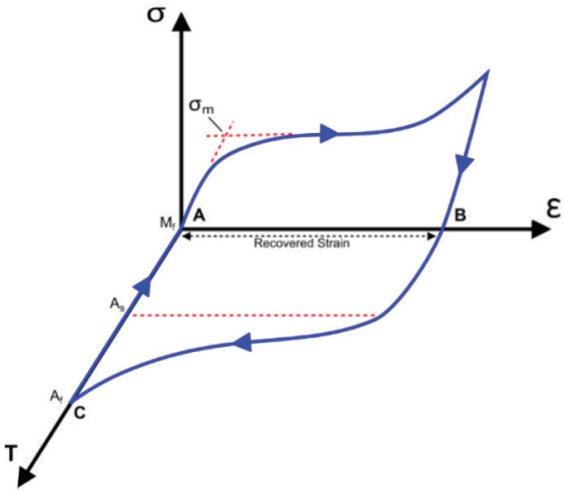


1.3.2 Shape Memory Effect

Thermally induced phase transformations between martensite and austenite result in the shape memory response of nitinol. The shape memory effect is utilized for creating actuators as well as for the deployment of medical devices such as cardiovascular stents as they reach body temperature.

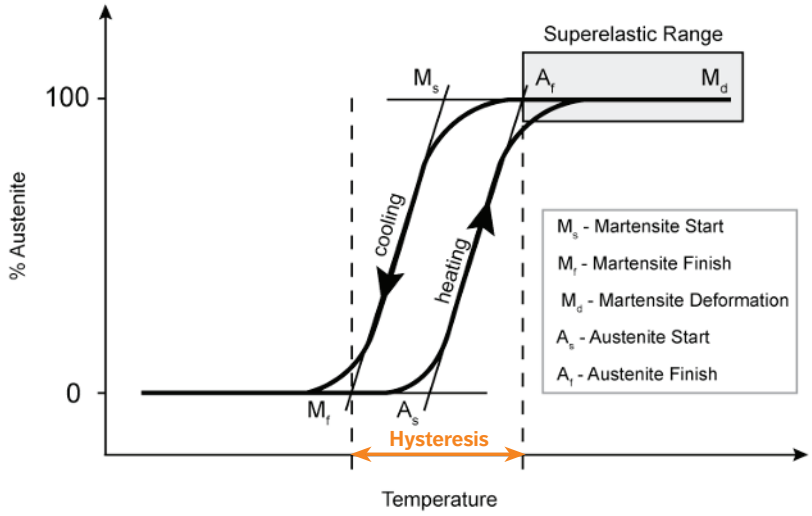
The shape memory effect is best illustrated using a stress-strain-temperature plot. To exhibit shape memory behavior the nitinol alloy must first be cooled below Mf. Deformation of martensite is visualized moving from point A to point B on the stress-strain-temperature plot. In the early stages of the deformation an elastic region is observed before the martensite detwinning stress (σm) is reached where the stress remains almost constant. This constant stress region is followed by the elastic straining of the fully detwinned structure. Once the material is in the deformed state and the stress has been unloaded, heating to a temperature above As will cause the detwinned martensite to begin transforming into austenite. This transformation of the crystal structure translates into the recovery of the original trained shape of the component on the macroscopic scale once the temperature reaches above Af (B → C). The deformed crystal structure remembers its original orientation because of the lattice correspondence. When the temperature is returned to below Mf the austenite structure changes back to martensite (A → B), with no macroscopic shape change, and the cycle can be repeated.





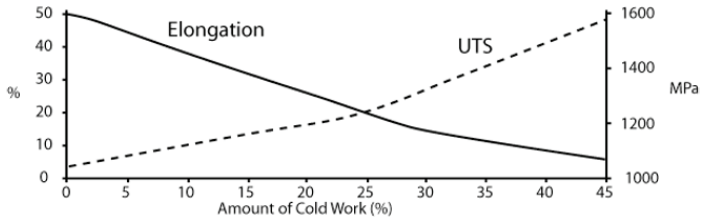
1.4 Thermal Hysteresis

Thermal hysteresis is the difference in phase transformation temperatures when the alloy is heated versus when it is cooled. This hysteresis is typically around 20 – 30 ºC (i.e. Af – Mf) for a fully annealed nitinol alloy used in medical device applications. The thermal hysteresis is related to mechanical hysteresis of the UPS and LPS during the superelastic response of the alloy at temperatures above Af. A greater thermal hysteresis will yield a greater mechanical hysteresis.



1.5 Effect of Cold Work

Also known as work or strain hardening, cold work is the strengthening of a material through plastic deformation. This strengthening occurs due to dislocation movement (i.e. creation of defects) within the crystal structure of the material. Cold working is critical in the thermomechanical processing of net-shape raw materials to obtain the desired mechanical and functional properties of the final nitinol component. The physical act of plastic deformation occurs in reducing the wrought nitinol material into the final net-shape through processes such as wire drawing, tube drawing, or sheet rolling. The typical final amount of cold work resulting from the final drawing/rolling process step ranges from 30 – 50 %; calculated in terms of reduction of cross sectional area.



In nitinol, the amount of cold work affects both the mechanical and functional properties of the alloy. For example, mechanical properties such as the yield stress and ultimate tensile strength (UTS) of the material increase with the percentage of cold work. This increase in strength however comes at the expense of a reduction in elongation (or ductility). It is important to note that a final heat treatment is required to allow the nitinol material to exhibit the shape memory and

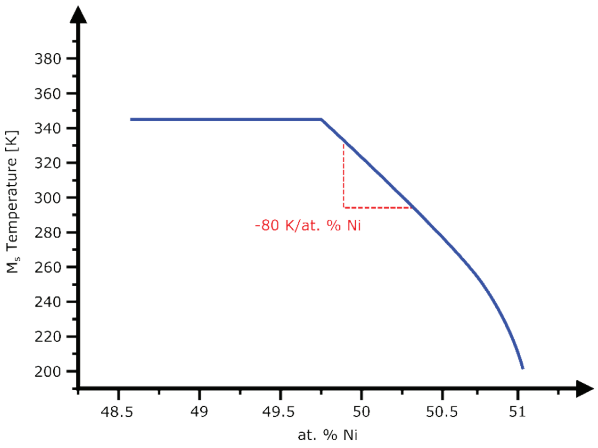
superelastic properties. A material with 30% cold work for example has too high of a dislocation density within the crystal lattice and does not allow the necessary straining to occur for phase transformation. On the contrary, if the amount of cold work imparted into the material is not high enough, for example in fully annealed material, the yield stress can be too low where the material plastically deforms below the UPS or martensite detwinning stress, σm. The material will therefore not exhibit shape memory or superelasticity in this case.

Design Considerations

- Increased cold work leads to a decrease in transformation temperatures. This translates to a slightly increased UPS and LPS when considering superelasticity.
- It is recommended to start with a cold worked net-shape material to obtain the highest possible UPS and LPS post shape-setting. This is common practice for example in manufacturing wire-form type nitinol devices.
- Due to reduced ductility of cold worked material, multiple shape setting steps are often required to obtain the final component shape without facture/cracking of the nitinol material. Using a raw material with less cold work can allow for larger shape setting strains and fewer process steps, however this comes with the expense of lower UPS, LPS and UTS of the final component.

1.6 Alloy Ratio and M_S

Nitinol is typically composed of approximately 50 to 51% Nickel by atomic percent (i.e. 55 to 56 wt. %). For example, Resonetics' Alloy BB manufactured at the Resonetics melt facility in New Hartford, NY, is specifically cast with 55.8 wt. % Ni. As can be seen by the following graph, the Ms of the material is highly sensitive to the alloying ratio. The smallest change in Ni content has a large effect on the transformation temperatures. This is important to understand when considering different wrought nitinol materials and aging heat treatments which will be discussed in subsequent sections.



Nitinol IQ

The M_S temperature changes by approximately 80 degrees Kelvin for every atomic percent change in Ni content. For this reason, great control of the alloy content is required during the casting process at our melt facility.

For alloys with Ni content below approximately 49.75 at. %, Ti becomes saturated in the matrix and precipitates out in the form of Ti rich precipitates. The matrix composition remains the same in this region and the M_S Temperature is therefore unchanged. Ti saturation limits the maximum transformation temperatures of the nitinol alloys typically used for shape memory applications.

Since the transformation temperatures are extremely sensitive to thermomechanical processes used in downstream processing, the transformation temperature of the raw net-shape material or finished component will differ greatly from those of the ingot or wrought nitinol material.

Section 2 - The Nitinol Ingot and Wrought Material

2.1 ASTM Standard for the Nitinol Alloy

ASTM F2063-18 is the standard specification for wrought nickel-titanium shape memory alloys for medical devices and surgical implants. This standard specifies allowable chemical compositions, transformation temperature tolerances, basic microstructure (i.e. grains size and inclusion/void content) and annealed mechanical properties. For reference, the chemical composition requirement for an ASTM F2063-18 compliant nitinol material is outlined in the table below.

Chemical Requirements & Product Analysis Tolerance①

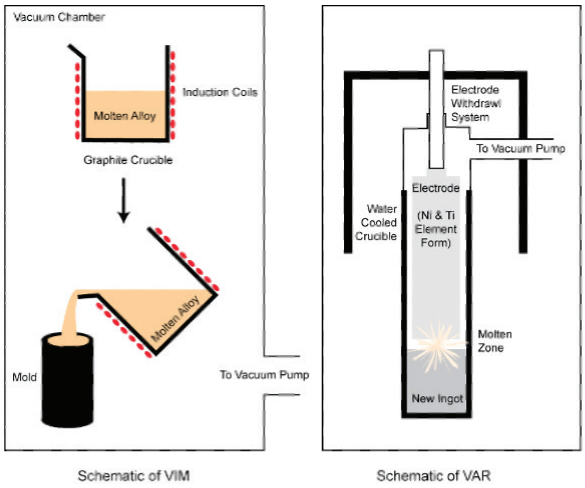
Element	% (mass/mass)	Tolerance % (mass/mass)
Nickel	54.5 TO 57.0	0.2 under min; 0.2 over max
Carbon, maximum	0.050	0.002
Cobalt, maximum	0.050	0.001
Copper, maximum	0.010	0.001
Chromium, maximum	0.010	0.001
Hydrogen, maximum	0.005	0.0005
Iron, maximum	0.050	0.01
Niobium, maximum	0.025	0.004
Nitrogen plus oxygen, maximum	0.050	0.004 for each
Titanium②	Balance	n/a

Notes: ① Product analysis tolerance limits are based on analytical capabilities that have been demonstrated for this composition.

② Approximately equal to the difference between 100% and the sum percentage of the other specified elements. The percentage titanium content by difference is not required to be reported per ASTM F2063-18.

2.2 Melting of the Nitinol Ingot

Nitinol phase transformation temperatures and mechanical properties are extremely sensitive to alloy composition and impurities. For ingot production, the alloy melting process and elemental raw material must be selected to not only ensure homogeneity of the melt, but also to ensure highest purity for consistent properties both within a single melt and between melts. The two common commercial melting methods for nitinol materials are vacuum-induction melting (VIM) and vacuum-arc melting (VAR).



For VIM ingot production, the Nickel and Titanium are placed in an electrically conductive graphite crucible. The crucible is heated and stirred by electrically induced alternating magnetic fields.

VAR ingot production involves a water-cooled copper crucible. Inside the crucible, elemental Nickel and Titanium are used as consumable electrodes. An electrical arc is struck between the electrode and the bottom of the copper crucible. The electrode melts to form molten material at the base of the crucible. This refining process is repeated using the ingot created from the previous melt as the new electrode to promote mixing and homogeneity of the ingot.

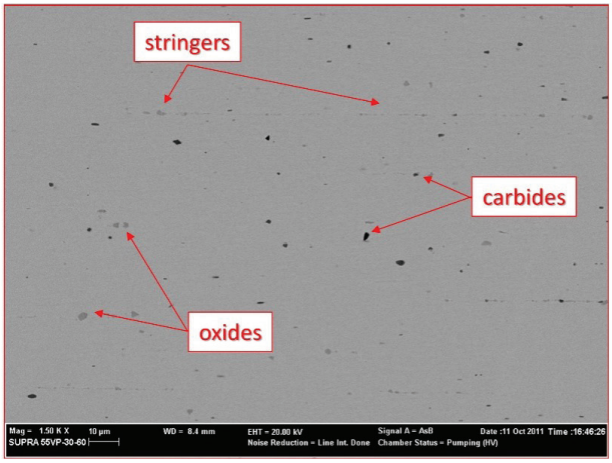
The Resonetics melt facility uses a VIM/VAR process. The raw materials are first melted in a VIM furnace and then subjected to the VAR process, yielding a very clean, consistent melt. This has since established Resonetics as a leader in nitinol material and processing, such as laser cutting, shape setting, electropolishing, and braiding.

Nitinol IQ

Some properties can be enhanced by a ternary alloying element. The most popular ternary alloys include NiTiNb, NiTiCu, NiTiCr, NiTiFe, and NiTiCo. Exception to the ASTM F2063 chemical composition requirement must however be made when using these alloys.

2.2.1 Inclusion Content

Theoretically, binary nitinol contains only the elements Nickel and Titanium. However, impurities, most commonly carbon and oxygen, are found in the raw materials. The impurities are dissolved in the alloy during melting and form second-phase particles during solidification. These particles include carbides and oxides having different chemical composition and crystal structure from the base metal and are therefore classified as inclusions.



Research has shown that inclusions can act as initiation sites for fatigue cracks and can even promote corrosion. Moreover, large inclusions or high volume fraction within the melt will result in significant degradation in mechanical properties. Therefore the goal is always to limit the volume, size and quantity of inclusions. The control of impurities largely depends on the casting of the ingot. However, subsequent thermomechanical processing of the material can also have an effect on the inclusion size, geometry and distribution. A common example of the effects of thermomechanical processing on inclusion morphology is the formation of stringers, which are inclusions that are broken up and displaced linearly in the drawing/rolling direction.

ASTM F2063 is the standard that governs inclusion size and measurement in nitinol alloys. Prior to 2005, the maximum acceptable inclusion size was 12 µm. As inclusion detection methods became more sophisticated, it was determined that none of the nitinol manufacturers could actually meet this 12 µm maximum. The ASTM standard was rewritten in 2005 to accurately reflect the state of the industry.

Currently **ASTM F2063** stipulates that inclusions or voids must be < 39 µm in size and take up < 2.8 % area fraction for alloys with a fully annealed A_s of less than or equal to 30 °C. Alloys with a fully annealed A_s greater than 30 °C are to have maximum inclusion size and area fraction as agreed upon between purchaser and supplier.

Nitinol IQ

The scientific community has taken an interest in low inclusion NiTi to improve both the fatigue and corrosion resistance properties of finished components. The number of papers on inclusions at the various Shape Memory and Superelastic Technologies (SMST) conferences has been steadily increasing.

Several articles have been published investigating whether or not material with lower inclusions actually performs better than material with higher inclusion content. Questions still remain as to which characteristics of low inclusion materials are more important; their size, quantity or location in the material. Other factors such as sample preparation, overall cross-section of the material being tested, the probability of inclusions residing at points of high stress concentration, and the type of strain being applied are all still up for debate. Resonetics Redox™ and Euduro™ alloys both offer a decreased number and decreased size of inclusions in an effort to improve nitinol's performance.

The ASTM committees have reviewed inclusion requirements in the past and will most likely continue to do so as research progresses.

Method Used by Resonetics for Characterizing Inclusion Content

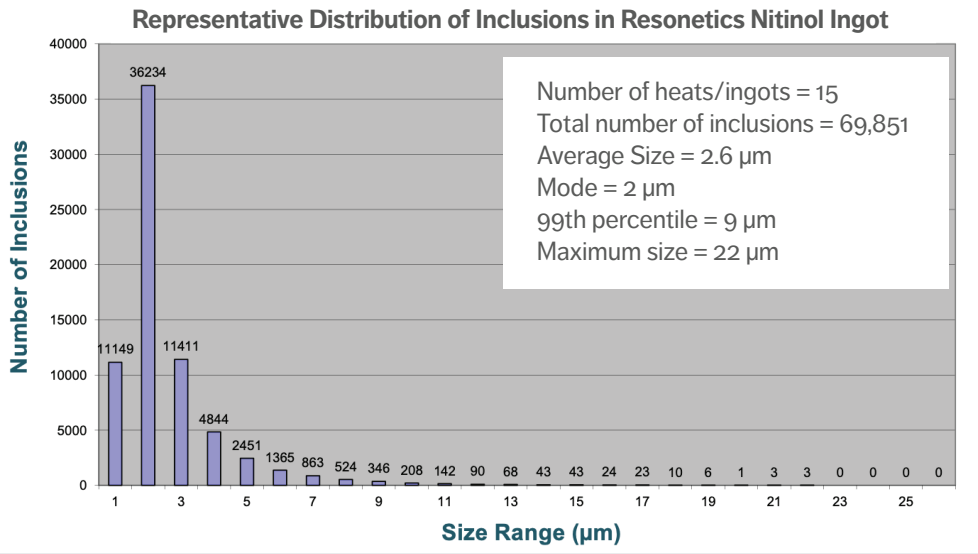
- ASTM F2063 compliant method
- Wire products are sampled at ¼" hot worked coil
- Bar products are sampled at 2" hot worked round cornered square (RCS)
- Optical microscopy performed at 500x magnification
- Three locations per ingot tested (i.e. Top, Middle and Bottom). Ingot top and bottom have highest probability for non-steady state solidification and are potential worst-case regions.
- Inclusion content is evaluated by looking for the largest inclusion and/or the largest area density of inclusions in three regions - the centerline, the mid-radius line, and the edge of the product cross section.
- Certify largest inclusion and largest area fraction observed.

*Complete description of method used available on the Resonetics website

Typical Inclusion Profile - Standard Resonetics Nitinol Material

- Most inclusions below 3 µm in size
- 99% below 9 µm
- Median size = 2 µm
- No inclusions above 30 µm (ASTM max. 39 µm) and no area fraction above 1.92 % (ASTM max. 2.8 %) in all material tested to-date
- Resonetics material inclusions significantly lower than ASTM 2063 standard

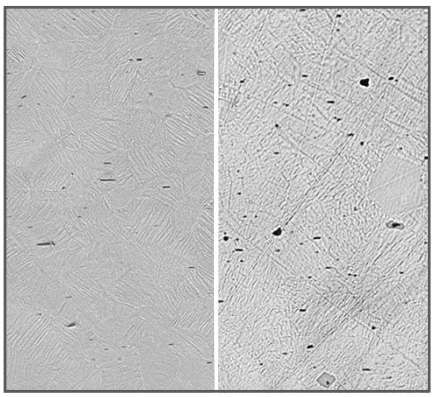
Note: per ASTM F2063, this data is from As ≥ 30 °C alloys



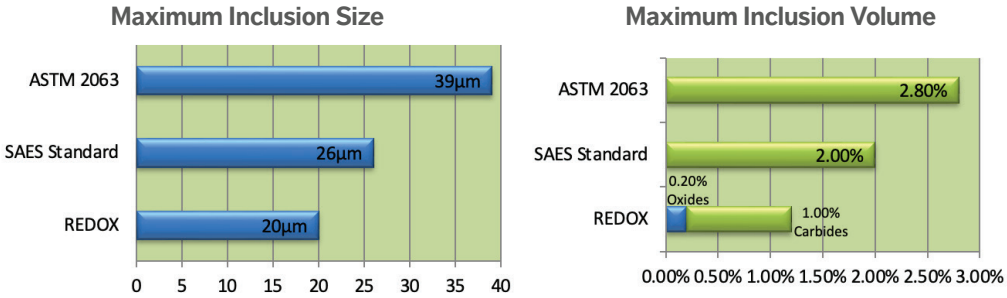
2.3 Redox™ Nitinol Alloy

Redox™ is an alloy exclusive to Resonetics that addresses the industry's ever-increasing design challenges pertaining to microcleanliness. It exhibits reduced oxide volume as well as inclusion particle size. Redox™ offers significant improvements over the standard Resonetics nitinol alloys and is fully compliant to **ASTM F2063**.

Redox™ is available in all forms of raw nitinol including tube, wire, strip, and sheet as well as in fully finished components. Due to Resonetics' exclusive melting and processing technologies, Redox™ is able to maintain the high integrity and strength found in standard nitinol alloys.



Redox™ (left) has 80% fewer oxides than standard material (right).



Design Considerations

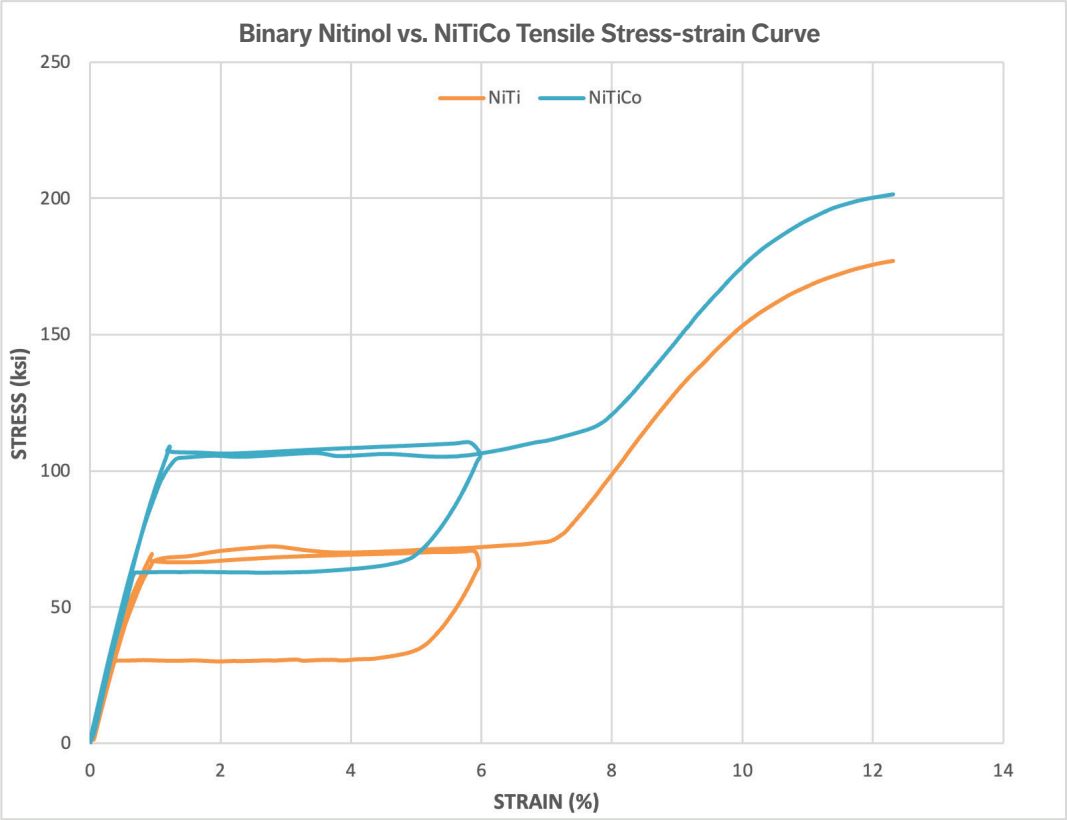
High-purity nitinol materials are certainly not necessary for all medical device applications. In low-risk applications or single-use/deployment devices, low inclusion material would not benefit the end performance of the device and wouldn't make economic sense.

Customers that benefit the most from low inclusion nitinol are ones developing long-term implants that are subjected to a very high number of loading/unloading cycles during their lifetime (ex. heart valve frame).

2.4 The Nickel Titanium Cobalt (NiTiCo) Alloy

NiTiCo is a relatively new shape memory alloy with “stiffness” properties that exceed that of standard nitinol. From an application perspective, there are significant advantages for certain medical devices in utilizing an alloy that exhibits the superelasticity of standard nitinol in combination with an increase in modulus of elasticity and UPS/LPS. For example, the higher elastic modulus, UPS and LPS will allow for smaller device profiles, thus enabling new opportunities for device development.

It is however important to note that the chemical composition of NiTiCo is not in accordance with ASTM F2063, which allows a maximum trace quantity of 0.05% Co. NiTiCo alloys contains 1.2-1.5 wt. % Cobalt.

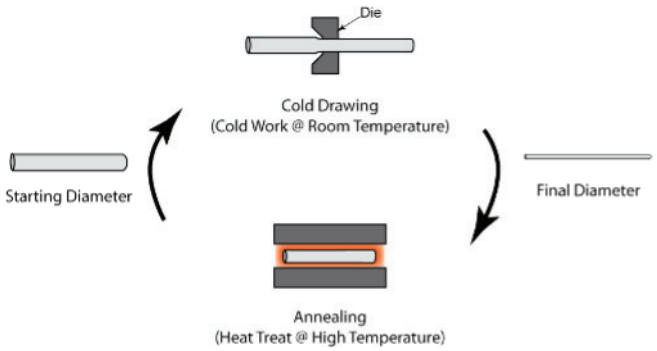


Section 3.0 - Semi-Finished Materials

3.1 Nitinol Wire

The wire form is one of the most common uses for nitinol and has proven to be very versatile. After melting and mixing, the nitinol ingot is forged and rolled into a bar at high temperatures (i.e. hot worked). The bar is then drawn down into a “Redraw” which is typically 0.085” in diameter. Resonetics then processes the redraw material through a series of cold drawing and annealing steps to fabricate the final desired wire diameter.

Drawing at room temperature adds cold work to the material. Cold working nitinol is difficult because the material work-hardens rapidly. Cold work must be done in multiple passes with an annealing step in between. Annealing heat treatments annihilate/remove dislocations within the crystal lattice and cause some degree of grain recrystallization and growth, ultimately restoring ductility of the nitinol material.



Wire is sold in both the straight annealed and cold worked (as-drawn) states. The as-drawn state is typically used for downstream shape setting as the product will take the form easier and will result in a higher strength compared to using a straight annealed nitinol material. The most common wire and strip raw materials offered by Resonetics can be found on our website. Custom surface finishes, geometries and material properties can be provided upon request.

3.2 Nitinol Strip

Strip is produced by rolling wire into a rectangular cross-section using a small rolling mill. Width to thickness ratios (W/T) are typically limited to 12. Naturally rolled (rounded) edges are standard but square edges can be produced using a turks head (i.e. rollers work on the sides along with the top/bottom surfaces). Strip is available in the same surface finishes and alloys as the wire net-shape raw materials.

3.3 Nitinol Tube



ASTM F2633 is the standard specification for wrought seamless Nickel-Titanium Shape Memory Alloy Tube for Medical Devices and Surgical Implants. Resonetics started drawing tube in 1992, and has a wealth of experience in manufacturing tube to various dimensions and surface finishes. Tubes can be manufactured to meet specific customer requirements and specifications. Critical requirements in ID, OD (or wall), mechanical properties, straightness, surface finish and visual specifications are commonly adjusted to meet application-specific needs. Unlike for raw wire materials, tubes are typically sold in the straight annealed condition due to process limitations.

For the manufacture of tubes, the ingot is first forged and rolled into a bar. This is followed by gun-drilling, where a hole is drilled through the center of the bar creating the "hollow" or initial tube form. The hollow is then processed into the desired tube dimensions using various hot work, cold work, and annealing process steps. Typical tube ratios (OD/ID) range from 1.05 – 2.50. The most common tube raw materials offered by Resonetics can be found on our website. Custom surface finishes, geometries, and material properties can be provided upon request.

3.4 Nitinol Sheet



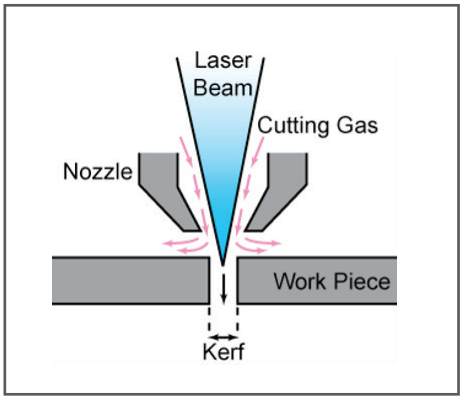
For the manufacture of nitinol sheet, the ingot is forged and rolled into a slab using hot working processes. As in tube and wire manufacturing, the wrought nitinol slab is then processed into the desired sheet dimensions using various hot work, cold work, and annealing process steps.

Nitinol sheet is available in the many different alloys offered by Resonetics. Sheets are often supplied in the flat annealed condition to ensure flatness, and as a result, they will have some degree of superelasticity or shape memory. Common surface finishes include light oxide, oxide free (pickled), or ground/polished.

The most common sheet raw materials offered by Resonetics can be found on our website. Custom surface finishes, geometries, and material properties can be provided upon request.

Section 4.0 - Processing Nitinol

4.1 Laser Cutting



intensity focused light to locally melt or ablate the material which is removed with the help of a coaxial gas nozzle.. When cutting a nitinol tube, for example during the manufacture of a cardiovascular stent, the tube is rotated and moved longitudinally under the focused laser beam to create the desired cut geometry. For sheet, either the laser head or the sheet material (or a combination of the two) is moved in relation to the other to create the desired cut geometry. Laser cutting has become one of the most commonly utilized machining technologies for the manufacture of nitinol devices mainly due to extreme precision and low thermal input characteristics. Current laser technologies at Resonetics allow for cutting of material as thin as 25 µm (0.001") to thicknesses of > 0.8 mm (0.031").



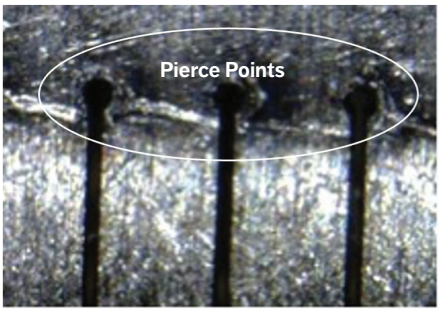
Laser cut tubes + Honing



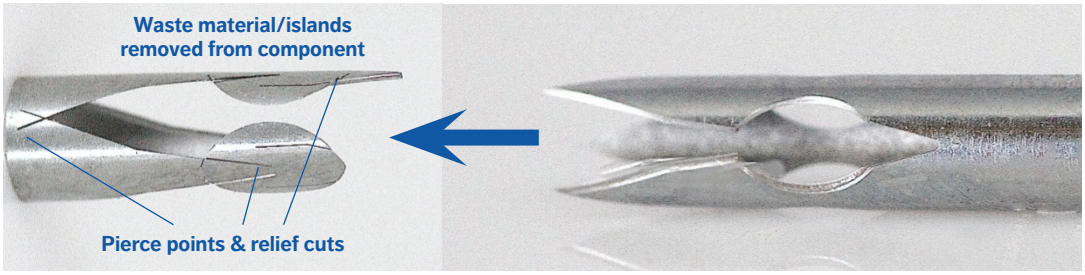
Laser cut sheet + Honing + Shape set + Chemical etch

The ability of the laser system to cut fine complex geometries largely depends on the type of laser used, motion system, and spot size of the focused laser beam. In the context of laser machining, "kerf width" means the width of material melted and removed by the laser cutting process which is dependent on the laser spot size. Smaller kerf widths allow for designs with smaller and more complex geometries and are therefore generally considered to be better. Many people believe that kerf widths are fixed for each laser system. However, in practice, kerf widths are much more dynamic. As material thickness increases so does the power needed to penetrate and cut the material and as a result the kerf width also increases. Ultra-short femtosecond lasers have the highest beam quality and can achieve kerf widths as low as 5 µm (0.0002") when cutting relatively thin (i.e. < 50 µm, 0.002") nitinol components.

Some considerations that must be made when designing a laser cut component include the cutting path, and if using a fiber laser, the heat affected zone (HAZ), recast layer, and slag. The laser path must be optimized to limit any undesirable artifacts such as spatter, notches/bites or steps as well as allow for the islands (i.e. waste material) to be easily removed. Single kerf, or single line features, will have pierce points at the end of each cut. These



pierce points will have a larger kerf and often spatter adjacent to the cut edge. Where possible pierce points are made well within the islands away from the features of the component, as shown below.



Fiber laser cutting uses a focused laser beam to melt the nitinol material which is expelled through the cut via a high pressure assist gas. It used to be the primary method to laser cut nitinol material and is still used in many applications. Advantages of the process are a fast processing speed, but the heat required to melt the material for cutting is conducted away from the kerf. This region adjacent to the cut will have compromised mechanical properties due to over aging of the nitinol material; where recrystallization and grain growth has occurred. This HAZ may have a negative effect on maximum attainable strains and fatigue life of the component. Moreover, as the laser cuts some of the molten material will be re-cast on to the wall of the component. This part of the heat affected zone is called "re-cast layer". The re-cast laser is heavily oxidized and very brittle. This layer typically contains micro-cracks that serve as fracture initiation points.

Molten material that does not re-cast to the cut wall will sometimes form as “slag” at the exit of the laser cut. If present, the slag needs to be removed via some type of mechanical or chemical process.

Design Considerations

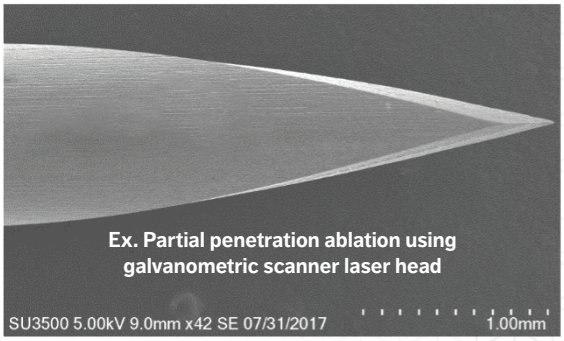
Post-processing of laser cut component must be performed to remove the heat affected zone, re-cast layer and slag in order to achieve acceptable device performance. Standard methods for doing this include honing, sand blasting, chemical etching and tumbling.

Post-processing can affect the final geometry of the component and must be designed into the process.

Femtosecond laser machining processes are the state-of-the-art in cutting nitinol. High power, ultra-short pulses can be used to cause direct solid to plasma ablation of nitinol. Since the laser-material interaction time is so short, heat is not conducted into the bulk material, eliminating past concerns with heat affected material, re-recast layers, and slag. In addition to eliminating the detrimental side effects inherent to thermal laser cutting processes, the cut quality is greatly improved, which translates directly to improved device performance.

As a general guide, tubes with a thin wall (<125 µm) and designs with thin struts or small geometrically critical features (i.e. <100µm) will benefit from such a process.

A large percentage of new products manufactured via laser processing at Resonetics are now processed with femtosecond lasers. Partial penetration ablation processes that are now possible with femtosecond lasers are also proving to be excellent for machining fine complex features.



Design Considerations

In many cases using a femtosecond laser process is advised not because of component size or precision requirements but simply to minimize or even eliminate time-consuming downstream post processes.

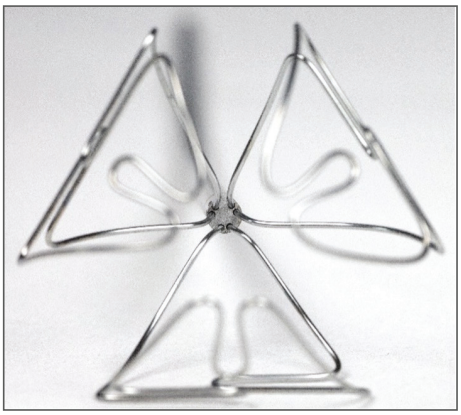
For example, tubes with small inner diameter and fine, complex features are nearly impossible to hone and consistent chemical etching and electro-polishing is challenging. Minimizing heat input and eliminating re-cast and slag through a femtosecond laser processes mitigates these common challenges.

4.2 Shape Setting (Heat Treatment)

Shape setting refers to the process used to form a nitinol wire, tube, or sheet into a specific and often complex geometric component. Whether the nitinol alloy is to be used in a superelastic or shape memory application, it is often necessary to form the material. This is done by carefully constraining the material into its new shape using a specially designed fixture or mandrel and then performing a shape set heat treatment. Multiple shaping operations may be necessary if the part is particularly complex or to prevent cracking/fracture if high strains are required.

To shape set nitinol, the heat treatment temperature should be above 475 °C with most performed above 500 °C to reduce process time and improve shape retention (i.e. reduce spring back). The actual temperatures and soak times are determined based upon the starting alloy composition and desired thermal and mechanical specifications. The shape setting process is usually finished off with a water quench to prevent further aging and reduce process variability.

Since high UPS and UTS are often desired in nitinol components, the number of heat treatments needs to be minimized and a cold worked starting material should be used whenever possible (recall section 1.5). A cold worked material will take the desired shape better and will maintain a higher UPS/LPS and UTS when compared to a straight/flat annealed material.



Shape set wire + Chemical etch + Electropolish

Design Considerations

It is important to consider the thermal mass of the fixture and heat treatment method when designing a heat treatment process (i.e. forced convection oven, fluidized bed, salt bath, joule heating, RF induction, heated die, etc.). In most cases it is preferred to use a salt bath and low mass fixture for uniform and rapid treatment of the component. Note: The transfer of heat treating parameters between heating methods is not possible due to variability in heat transfer.

The higher the strain imparted into the nitinol component during shape setting, the better it will hold the desired shape.

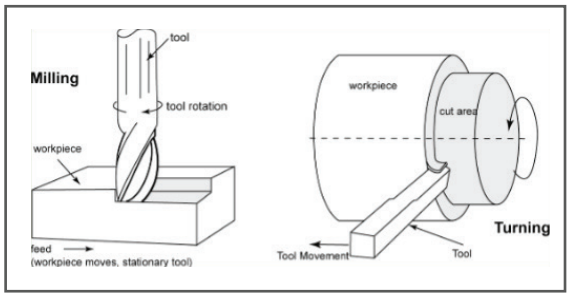
4.3 Machining

4.3.1 Milling, Turning, and Drilling

Nitinol is a hard material when in the cold worked state and is also extremely abrasive due to the tough Titanium oxide layer on its surface. Conventional machining techniques such as milling, turning or drilling are typically avoided whenever possible but can be successful in specific applications.

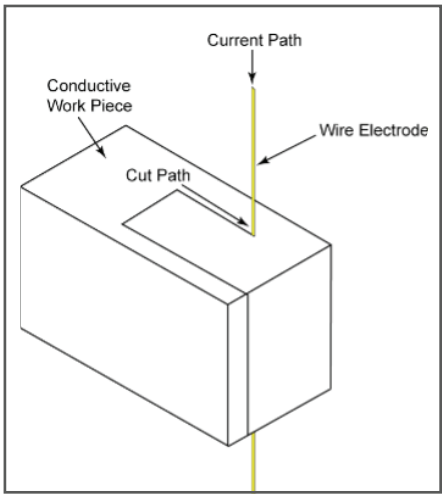
Some guidelines to consider are as follows:

- CNC controlled speeds/feeds, a strong coolant flood and carbide tools are vital;
- Expect rapid tool wear;
- Very small features (ex. drilled holes less than 1 mm) should be avoided;
- Turning can be more successful than milling due to the uninterrupted nature of the cut; and
- Tapping is strongly discouraged.



4.3.2 Wire EDM

This technique is especially attractive for cutting features into thick nitinol materials. The cutting is performed by a continuously fed, electrically charged wire that's passed through the material. As the wire nears the work piece, it spark discharges and ablates the material nearest the wire. There is no force placed on the work piece during the cutting. The recast/heat affected zone (HAZ) thickness is minimized by cutting the work piece while submerged in deionized (non-conductive) water. For implants, the EDM cut surface should be modified via mechanical or chemical means to remove the recast layer and eliminate transferred material from the EDM wire (i.e. typically brass).



When possible, work pieces are stacked during cutting to improve efficiency. Typical EDM wire sizes are 0.1 to 0.305 mm (0.004" to 0.012") in diameter. Depending on the geometry, the wire "overburns" by 50 µm (0.002") total (ex. a 255 µm/0.010" diameter wire will create a slot approximately 305 µm/0.012" wide). Larger diameter wires are typically used to increase cut speed unless the component geometry necessitates use of a smaller wire.


Wire EDM + Shape set


Wire EDM + Tumble + Chemical etch

4.4 Grinding



This abrasive technique can be an effective way to machine nitinol. Common grinding technologies used on nitinol materials include centerless, Swiss style, and conventional 3 or 4 axis CNC abrasive grinding. A strong coolant flood is generally recommended to prevent overheating of the nitinol material. Grinding of features as small as 125 – 250 µm (0.005" – 0.010") in length are possible. Resonetics is capable of grinding geometries ranging from simple guidewires to sophisticated grinds for any custom application, including flats, radii, drill points, trocars, needles, or thread-like profiles.

Electrochemical Grinding (ECG) processes are part of a less common family of grinding technologies that harness electrolytic effects imparted by an electrically charged grinding wheel. The ECG process limits physical stresses, mechanical damage, and heat affect inherent to a more conventional mechanical machining/grinding process. Resonetics successfully applies ECG technologies to overcome the challenges associated with machining fine and/or delicate features in nitinol, such as the extreme sensitivity to cold work (i.e. work hardening) and metallurgical damage associated with excessive heat input as discussed in previous sections.

4.5 Water Jet Cutting

This technique utilizes high pressure water mixed with an abrasive cutting media to cut the nitinol material via an erosion-type mechanism. This process is an excellent cutting method for thick raw materials because it is quick and does not generate high temperatures during cutting. However, this process is not as accurate as other cutting methods and the achievable tolerances are large when compared to other machining techniques. Water jet cutting is typically reserved for rough cutting of thick nitinol raw sheet materials.

4.6 Stamping

Nitinol can be stamped successfully in select applications. The process consists of very precise punch (positive cut geometry) and die (negative cut geometry) elements. The material (usually a strip or sheet) is positioned under the die set, and then the punch is rapidly driven through the material and into the die with great force. Stamping is typically only entertained for very high volume operations that can be fed continuously (ex. strip). Die clearances should be minimized to reduce burrs and improve edge quality. Carbide tooling is required and excessive die wear is to be expected when stamping nitinol.

4.7 Photochemical Machining

Photochemical machining can be an efficient method for fabricating thin (less than .020") nitinol components from sheet. The process starts with coating the material in a polymer photoresist, using UV light to transfer a pattern onto the photoresist, and then developing the resist to selectively expose bare metal. The sheet is then exposed to a chemical solution which etches away the unprotected nitinol material, leaving only the desired component. The masking material is then removed.

This technique results in a burr-free finish and is suitable for high volume production of small intricate geometries. This technique however, is limited to thin sheets and the tolerances held depend on the material thickness. It also leaves a small ridge along the wall of the part, adjacent to where the masking material was placed, that may be problematic for some applications. Resonetics is experienced in photochemical machining and can produce nitinol components with the process.

Comparison of Processing Methods

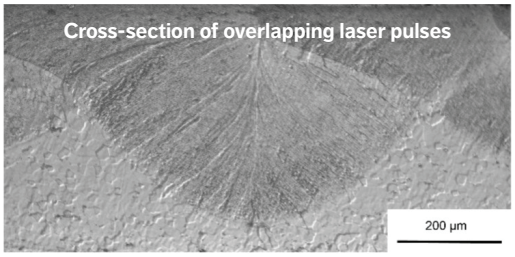
	Pros	Cons
Milling, Turning, or Drilling	• Can have up to 5 axis capability • Moderate to good tolerance control • Can make screw threads	• Rapid tool wear • Relatively slow cutting speeds • High force exerted on work piece • Especially difficult with martensitic NiTi material
Laser Cutting	• Tight tolerance features • Flexibility / low tooling cost • Femtosecond laser process is athermal • Can make screw threads	• Re-cast layer and heat affected zone needs to be removed post thermal laser cutting
Grinding	• Tight tolerance features • Flexibility / low tooling cost • Femtosecond laser process is athermal • Can make screw threads	• Relatively large axial feature tolerance • Single piece production (except thru-feed centerless) • Cannot produce off-axis shapes • Can make screw threads
Wire EDM	• Tight tolerance features • Flexibility / low tooling cost • Femtosecond laser process is athermal • Can make screw threads	• Slow cutting speed • Re-cast layer and wire transfer (typically brass) should be removed for implants • Material (and surface) needs to be electrically conductive
Waterjet Cutting	• Full 6 axis cutting/tapering/turning capability • No heat affected zone (no recast layer) • Can handle very thick work pieces • Burr-free finish	• Only moderate tolerances can be held • Significant taper from top of cut to bottom • Abrasive media may lodge into cut surface • Poor to moderate cut finish quality
Stamping	• High speed production • Relatively high precision	• Very high tooling cost • Limited to thin materials (< 0.030") • Burrs
Photo-Chemical Etching	• High volume production • Burr free finish • No HAZ	• Rather loose tolerance control • Ridge or bevel adjacent to cut • Limited to thin sheets

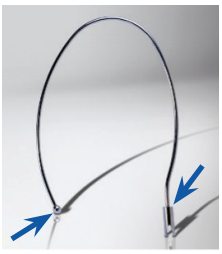
4.8 Joining

4.8.1 Welding

Laser, plasma, and resistance welding processes are all commonly used for joining nitinol components. A common design challenge for welded components is the large amount of heat input required to create the joint. The weld itself, as well as the heat affected zone (HAZ) adjacent to the joint, will have different mechanical and functional properties. In laser, plasma, and resistance welding the weld fusion zone (FZ) will have an as-cast structure and properties more similar to the nitinol ingot. The HAZ will be subject to over-aging effects such as recrystallization and grain growth leading to a decrease in mechanical strength and shifts in the transformation temperatures. When welding more Ti-rich alloys such as those used for shape memory applications, cracking can also become a challenge due to solute segregation and the formation of brittle Ti-rich intermetallic phases.

Laser - CNC pulsed laser systems are the most common welding processes used for assembling nitinol components. The high speed, non-contact, low heat input characteristics of this process make it very attractive in the manufacture of nitinol medical devices. Single spot laser processes are commonly used for tack weld type applications for example, welding of a collar or tube to the end of a wire component. Seam welds are also commonly applied where overlapping of pulses is achieved through timing stage motion with the pulsing frequency of the laser source. An overlap of > 80% is usually recommended for hermetic sealing type applications.





Plasma ball + Laser weld

Plasma welding is an arc welding process and is most commonly used at Resonetics for forming atraumatic balls on the ends of nitinol wires or tubes. Balls up to 3x the parent material diameter can be realized using this process.

Resistance welding utilizes joule heating and mechanical load to form a weld nugget, or fusion zone, between two components resulting from higher electrical resistance at the faying surface. Resistance welding processes are commonly used for butt welding the ends of large diameter nitinol wires or for lap joints, where two nitinol sheets or strips are to be joined. Since resistance welding required the mechanical contact of the electrodes (i.e. commonly Cu alloys) with the surface of the nitinol component, it is recommended to modified the surface via mechanical or chemical means to mitigate risks associated with transferred material.

Design Considerations

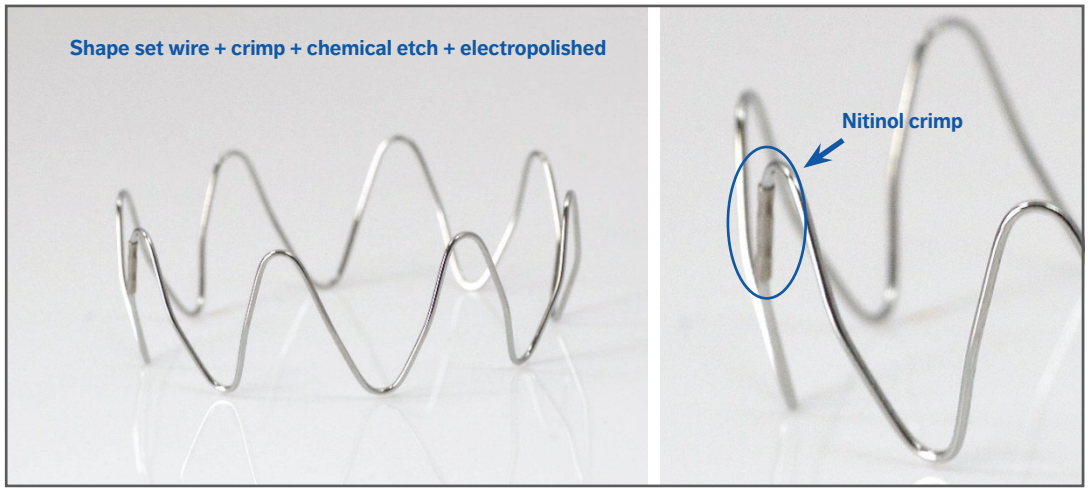
It is very challenging to weld nitinol successfully to dissimilar metals such as stainless steels. Dissimilar welded joints are often brittle due to intermetallic formation and will not withstand high stresses or strains.

Techniques such as solid-state welding or the use of interlayers in for example laser welding have shown some promise for making dissimilar joints, however these techniques are not commonly applied.

The design of the welded joint must not be overlooked when considering a nitinol component.
The joint should be designed to be positioned away from critical features and areas of highest stress/strain.
The mechanical and functional properties of both the fusion zone and HAZ will have been jeopardized by the thermal input of the welding process.

4.8.2 Crimping

Crimping is a very robust method for joining nitinol to itself or dissimilar materials. The major drawbacks include a rather bulky profile of the crimp and the process challenges associated with multi-piece construction. Crimping is typically the joining method of choice when considering the termination of the wire ends in a wire form device. Specially processed nitinol tubing is recommended for the crimp component. Important design considerations include: i) the crimp must be ductile enough to be plastically deformed around the components to be joined and ii) using a dissimilar material such as stainless steel for the crimp tube can lead to issues associated with incompatibility of material properties and galvanic corrosion. An excellent example of a crimping application is wire formed stents where the wire ends are traditionally crimped together (i.e. to complete the ring) using a length of nitinol tubing.



4.8.3 Soldering and Adhesives

Soldering and adhesives can be excellent methods for joining nitinol to dissimilar materials. In both cases, the oxide layer should be removed for best results. For soldering, silver bearing solders work well (ex: Sn95Ag5) combined with a suitable flux (we use Indalloy® #3 from Indium Corporation). When considering adhesives, both UV and heat curable options are available. Dymax®, Loctite®, and MasterBond® all have formulations that work with nitinol. It is important to note that neither soldering nor adhesives should be considered for implantable medical device applications.

4.9 Finishing

4.9.1 Blasting

Grit blasting & microblasting are methods used to remove oxides, surface marks, and processing materials/contaminants from upstream processes such as drawing, heat treatment, laser-cutting, EDM, or localized heating processes. Grit blasting is usually performed on tube or wires and is a relatively large scale process, whereas microblasting is performed on smaller scale components. Microblasting is common practice for the post-processing of laser cut or wire EDM'd components prior to chemical etching processes.

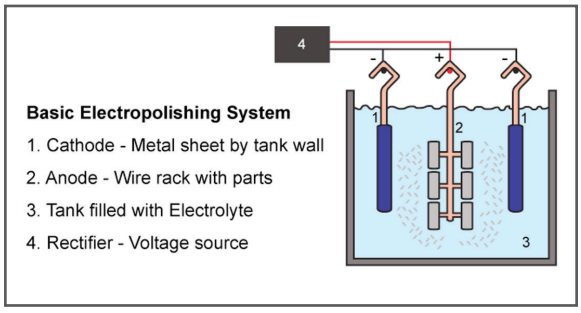
Both abrasive techniques consist of sand-like grit directed under high pressure at the nitinol component. The abrasive action is capable of removing material such as, the re-cast layer, heat affected zones, and micro-cracks found around the nitinol surface and can remove significant amounts of material. Resonetics has the capability to perform manual or automated blasting processes.

4.9.2 Mechanical Tumbling

Tumbling is an operation where components are loaded into a vessel containing abrasive media and the vessel is agitated via rotary or vibrational means. The action of the media on the parts serves to smooth the surface and round sharp edges. Tumbling is typically not effective in removing large amounts of material, it is more effective at breaking edges and rounding sharp features.

4.9.3 Chemical Processing

Etching, also known as pickling, is common practice for oxide removal and removing a relatively large volume of material from the nitinol surface. An etched part will have a light or bright surface finish. It will appear smooth to the naked eye, but will have a mildly rough surface topography if viewed at higher magnification. As a general rule, longer etch times produce a slightly smoother topography. Common examples of chemical etching processes include: i) the removal of the brittle re-cast layer from laser cut components and ii) removal of any transfer material from the wire electrode of EDM cut components. It is important that the components are burr-free prior to etching in order to mitigate risks of selective etching adjacent to artifacts.



Electropolishing is an electrochemical process that removes material from the surface of the nitinol component. As the name suggests, electropolishing is used to polish and smooth the surface of the nitinol component. In an electropolishing system, electrical potential is applied to remove metal ions from the surface of the component and

bring them into solution. Dissolution of metal occurs within the electrolytic solution.

An important process consideration is how and where the anodic contact is made to the component. The contact between the anode and the parts should be secure enough to eliminate electrical arcs. Inadequate fixturing will cause burned or melted spots around the contact points of the finished part. Witness marks from the electrical contact points are to some degree unavoidable.

During electropolishing, electrical current flows over the peaks present on a relatively rough surface and creates a high current density at these locations. This results in the preferential removal of high spots during electropolishing which makes it ideal for eliminating burrs and ultimately lowering (i.e. improving) surface roughness. By lowering the surface roughness, micro-cracks and other surface imperfections are reduced or even eliminated. A properly electropolished part will have a lustrous, mirror-like surface, that will appear as such even at higher magnification.

The main drawbacks of electropolishing are the added cost per part, witness marks where the part contacts the anode, and the difficulty of precise material removal on larger parts. However, it is important to note that the improvements in biocompatibility and fatigue resistance often makes electropolishing worth the extra cost for implantable nitinol medical device applications.

Passivation, as applied to nitinol components, is the modification of the surface chemistry to make the nitinol device less reactive or more resistant when exposed to certain environmental factors. Passivation is largely performed to ensure the surface is resistant to electrochemical corrosion reactions and hence doesn't degrade and ultimately fail or release harmful Ni-ions into the body.

Nitinol has a naturally occurring passive Titanium oxide (TiO_2) layer that forms on its surface. However, much research has shown that improper processing can lead to the creation of more volatile surface oxides that can reduce the passivity of the nitinol component. As a result different passivation techniques have been developed for nitinol medical devices such as, chemical passivation or even boiling in water. The most common passivation treatment performed by Resonetics is a HNO_3 based

Design Considerations

Customers often request passivation for implantable medical device applications. However, in many other nitinol device applications, chemical passivation may not be necessary. Resonetics' standard manufacturing processes have been optimized for example, to yield excellent corrosion performance even without final passivation.

4.9.4 Other Finishing Options



Laser Marking – Laser marking of nitinol components is common practice. Examples of laser marking applications includes visual indicators such as depth marks or labels, manufacturing lot numbers or even QR codes and company logos. There are two different modes of laser marking which include ablation and annealing. During an ablation type laser marking process a metallic (often shinny) appearance is created through melting and ablating surface material. Annealing type processes on the other hand do not cause any changes in macroscopic surface topography but instead change the color of the nitinol surface through modification of the oxide layer.

Coating & Plating - Nitinol can be coated with materials such as PTFE, FEP, Parylene, diamond like coating (DLC), etc. to improve lubricity or wear resistance. Moreover, a variety of platings, often comprised of gold, platinum, or tantalum, can also be applied to nitinol components, conferring improved radiopacity. Elevated temperatures of some coatings operations must be considered as they can affect the material properties of the nitinol component.

Some other important considerations to coating and plating processes include the selection of the best surface for coating adhesion as well as incompatibility of material properties where the coating may crack or flake off when exposed to superelastic strains.



Section 5.0 - Medical Device Design Considerations

The following section discusses different design considerations that should be considered when using nitinol in a medical device. Resonetics also offers nitinol design and development support through the AGILE Product Development team. The group can provide engineering services, brainstorming sessions, design refinement, and full-service product development.

5.1 Typical Physical and Mechanical Properties

In this section the typical material properties of nitinol are presented to aid in the initial design phases. It is important to understand that there are two values for certain properties of nitinol. The first is for the martensite phase and shape memory applications while the second is for the austenite phase and therefore superelastic applications (recall section 1). A comparison with stainless steel properties and performance is also made in this section to act as a frame of reference.

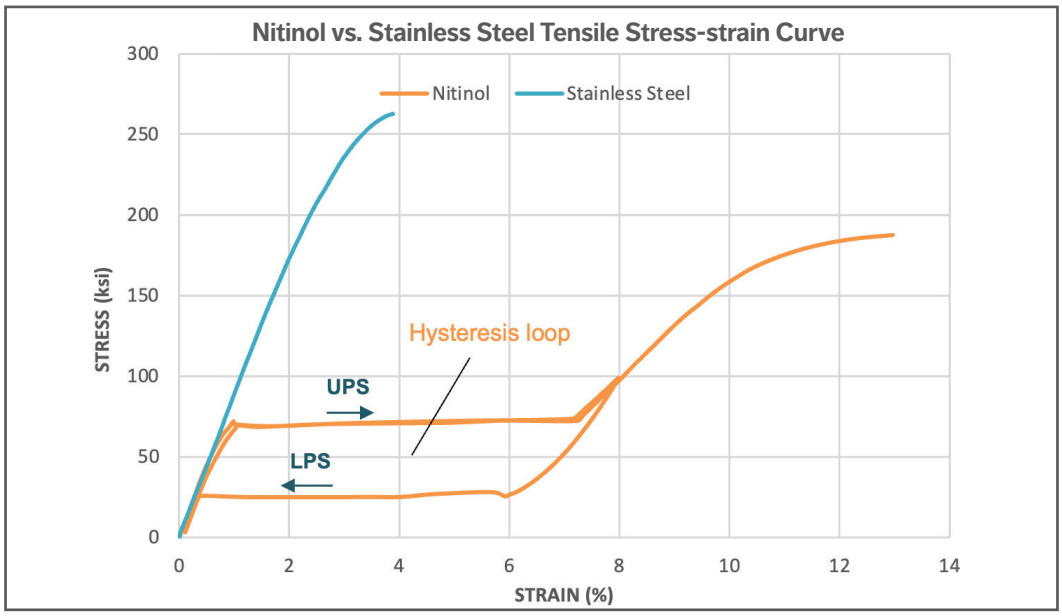
Typical Physical Properties	Units	Nitinol	Stainless Steel
Melting Point	°C *(°F)*	1310 *(2,390)*	1450 *(2,642)*
Density	g/cm^3 *(lb/in^3)*	6.5 *(0.235)*	8 *(0.289)*
Specific Electrical Resistivity	μΩcm *(μΩin)*	76 (M) / 82 (A) *(29.9 (M) / 32.3 (A))*	72 *(28.3)*
Coefficient of Thermal Expansion	10^{-6}/°C *(10^{-6}/°F)*	6.6 (M) / 11 (A) *(3.7 (M) / 6.1 (A))*	17.3 *(9.6)*
Thermal Conductivity	10 BTU/hr Ft °F	8.6 (M)/18(A)	16.3 *(0.031)*
Young's Modulus	GPa (ksi)	40 (M) / 75 (A) *(5,802 (M) / 10,878 (A))*	193 *(27,992)*
Ultimate Tensile Strength	MPa (ksi)	1100-1500① *(145-218)①*	620-2400① *(90-348)①*

Notes: ① UTS can vary greatly depending on heat treatment and alloy.
② (M) = Martensite, (A) = Austenite

Stress-Strain curves are shown below for a typical stainless steel alloy and a nitinol alloy. A simple comparison of the curves illustrates the difference between elastic-plastic behavior common to engineering metals and the non-linear superelastic behavior of nitinol. The nitinol sample shown below was strained to 8%, released back to 0%, and then pulled to failure to illustrate the superelastic loop. The stainless steel sample was pulled straight to failure.

For both materials, if the strain on the material is greater than the elastic limit, the deformation caused by tensile loading the material ultimately led to failure. The elastic limit of the stainless steel alloy is around 0.2% before permanent straining occurs whereas nitinol can be strained up to 8% before

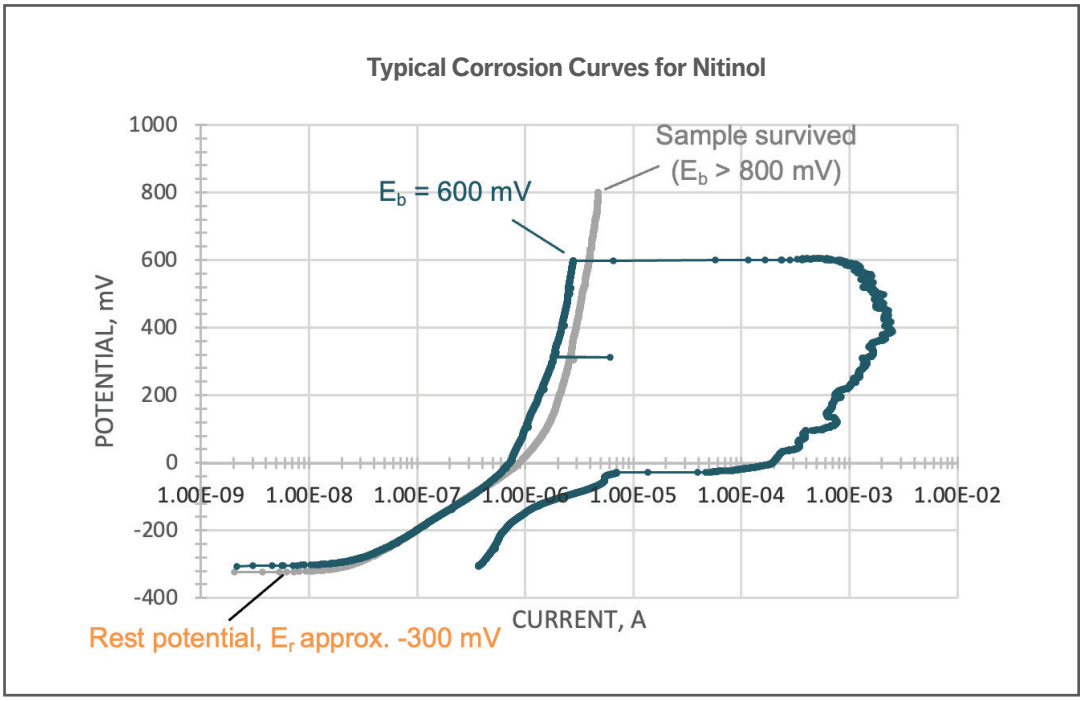
permanently straining. When designing a superelastic nitinol component the non-linear strain is a critical design input and should be selected with the superelastic UPS and LPS of the material in mind. Moreover, the non-linear behavior of the nitinol component is different depending on whether you are loading or unloading (i.e. UPS vs. LPS) and the hysteresis loop will also change slightly with the application of less than 8 % strain cycles. In contrast, the yield stress and elastic modulus of a stainless steel component are paramount for designing a stainless steel device. Hence, there are many more variables to consider when designing a nitinol device.



5.2 Corrosion

The unique combination of shape memory and superelasticity properties coupled with its biocompatibility response has made nitinol an excellent material for medical device applications. On the surface of nitinol, Titanium ions interact with oxygen to form an extremely tenacious and passive Titanium oxide layer (TiO_2). This oxide layer protects the nitinol material beneath from the external environment which typically gives the nitinol excellent corrosion resistance and biocompatibility. The thickness and quality (i.e. homogeneity, defect free, etc.) of the oxide layer is closely related to the corrosion resistance and biocompatibility of the nitinol.

ASTM F2129 is the standard test method for conducting cyclic potentiodynamic polarization measurements to determine the corrosion susceptibility of small implant devices. This standard is recognized as the accepted test method for determining the corrosion resistance of nitinol implant devices and is commonly used by Resonetics to evaluate corrosion susceptibility of nitinol components. During cyclic polarization testing, voltage is applied to the nitinol device until the passive layer breaks down (i.e. much like an electrical capacitor) and pitting type corrosion occurs due to progression of electrochemical corrosion reactions. The voltage at which this breakdown occurs and pitting begins on the surface of the component is termed the breakdown potential, Eb. Although there is no pass/fail criterion listed in the ASTM standard, Eb > 300 mV is generally deemed acceptable and Eb ≥ 600 mV demonstrates that a device has excellent corrosion resistance.



Design Considerations

- As discussed in section 4.4.3, Resonetics standard manufacturing processes have been optimized to yield excellent corrosion performance
- Nitinol devices should be tested in their final condition to get a true assessment of corrosion susceptibility
- The standard test solution is a phosphate buffered saline (PBS) with a pH of 7.4 ± 0.2. Other solutions can be used to better mimic in-vivo conditions, for example to simulate blood.
- When testing a device in PBS solution the maximum test potential of 800 mV is used due to the Oxygen evolution reaction. If the device lasts to 800 mV the device is said to have survived with no corrosion. This is the best test result possible, but by no means required to consider a device to have passed.

5.3 Sterilization of Nitinol

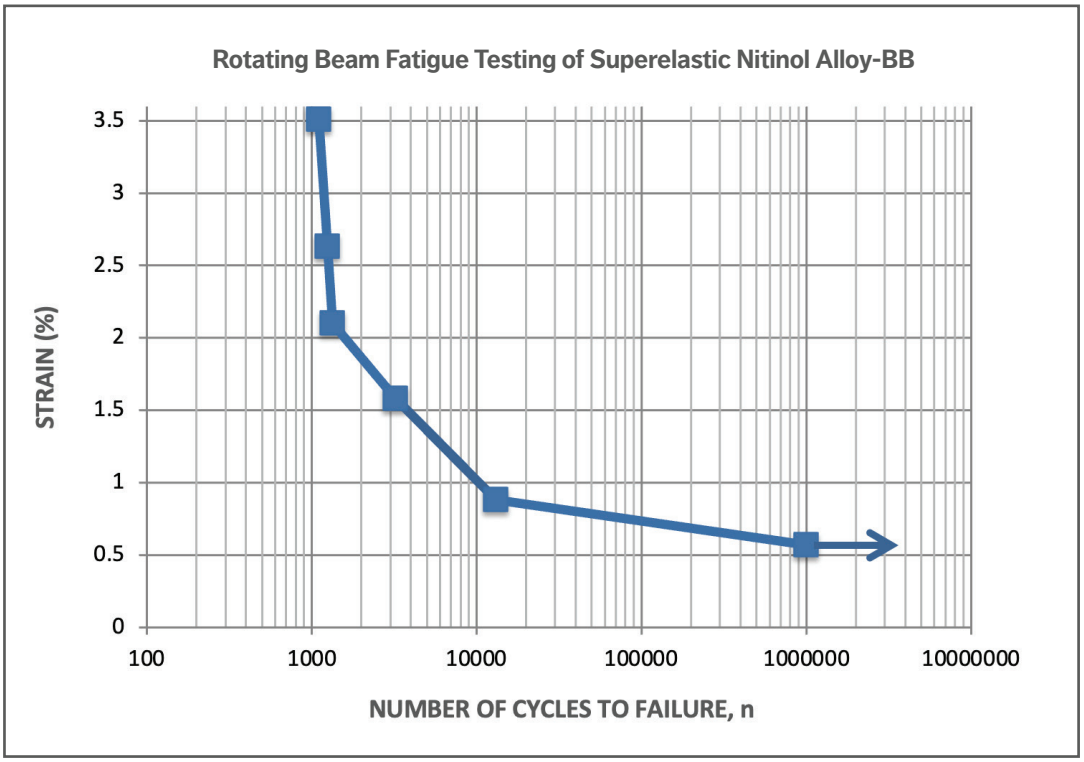
Medical devices made from nitinol can be sterilized through most typical sterilization methods including steam (autoclave), ethylene oxide (EtO), or radiation (gamma). Literature and experience has shown that nitinol devices can be sterilized without affecting the functionality. However, the temperature seen by the device must be considered and maintained below 300 °C to ensure no effects on mechanical and functional properties.

5.4 Biocompatibility

Nitinol shows a high degree of biocompatibility largely due to the robust passive Titanium oxide layer native to the surface (see sections 4.4.4 & 5.2). A long history of use has been demonstrated in many applications ranging from single-use devices to long-term implants with few complications. The most common concern with biocompatibility is Ni ion leaching from the device for implant applications. This is an interesting source of study and academic debate however, it has been shown that optimized manufacturing processes such as those developed at Resonetics limit Ni ion release to less than that of medical grade stainless steels.

5.5 Fatigue

Although nitinol has excellent mechanical properties and can recover from very high strain levels, fatigue needs to be considered for long-term, high-cycle applications. The chart shown below presents a typical dramatic decrease in fatigue life as the strain level increases. For example, at 0.57% strain testing was terminated after 1 million cycles and the wire survived. Increasing the strain to just 0.88%, the wire failed at just over 13 thousand cycles. Fatigue performance is therefore very important to consider when designing a nitinol component. If a full 6% of elasticity is required, designers need to minimize their cycles (perhaps less than 100); where single use low cycle applications may only be possible. However, if the application uses 0.5% or less strain, such as experience in many cardiovascular stent or heart valve applications, the material will likely survive millions of cycles.



5.6 Surface Finishes

The following list and general information regarding surface finishes provides insight into which finish may be best for a specific application.

Light or Amber Oxide

- Typically amber/gold in color, but can range to blue/purple depending on heat treatment method
- Standard finish for tube, but optional for wire
- Good lubricity and wear resistance
- Generally preferred for wire components that will be electropolished

Hard Black Oxide

- This is a standard finish for wire and strip
- Exhibits very good lubricity and wear resistance and generally preferred for applications in which tribological properties are critical

Oxide Free/Acid Cleaned

- Matte gray to silver surface and generally considered to have best aesthetic appearance
- Excellent for downstream EDM processing (i.e. better conductivity than oxide) and joining operations such as welding, soldering, and the use of adhesives
- Not ideal for wear resistance. Surface marks or scratches/galls more easily

Ground

- Typically a ground finish is necessitated by OD modification of a wire or tube for tightened dimensional control
- Smooth surface as grinding removes any artifacts from the upstream raw material manufacturing processes such as draw lines
- Provides best substrate for optimal upstream surface finishing processes
- Not ideal for wear resistance. Surface marks or scratches/galls more easily

Electropolished

- Provides best corrosion resistance, biocompatibility and fatigue life (see also section 4.4.3)

Passivated

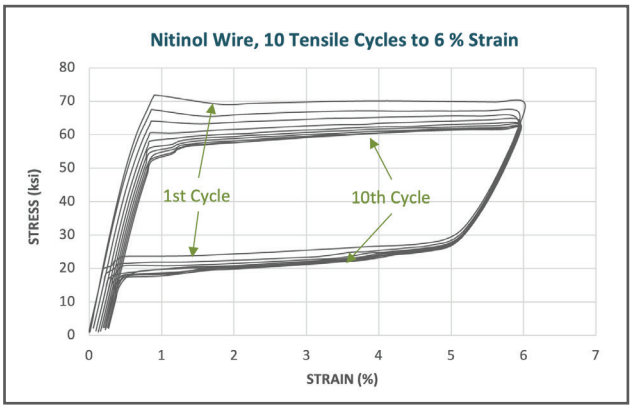
- Can help improve corrosion resistance and biocompatibility (see also section 4.4.3)

5.7 Strain

When performing feasibility reviews, it is important to consider both the forming strain and functional strain. Some common strain calculations are provided below for reference.

Forming Strain – This is the strain that the raw material is subjected to during forming (not during functional use). Examples are very tight bends on components. Bends such as these should be limited to a maximum strain of approximately 25 %. Beyond this strain, additional consideration must be taken to prevent cracking of the material such as performing pre-heat treatments and utilizing multiple shape setting steps.

Functional Strain – This is the strain level that a finished component will be subjected to during use. Examples are a guidewire being passed through a tortuous path or a hook shaped tube that is straightened for insertion into the body. For wire, this strain value should be limited to 6% maximum, while tubing should be limited to approximately 4%. It should be noted that, although the material is able to recover from these high strains, its properties can change over the first 10 – 50 cycles, and minimal fatigue life should be expected. The graph below illustrates changes in superelasticity with cycling, in particular decreases in the UPS and LPS after 10 cycles of tensile loading to 6% strain.



Example Strain Calculations

Tension / Compression

L_o: Initial Length

L_f: Final Length

$$\varepsilon = \frac{L_f - L_o}{L_o}$$

Bending

t: Thickness/diameter

R_O: Initial radius of curvature

R_f: Final radius of curvature

$$\varepsilon_{max} = \frac{t}{2R_f} \quad \text{(Straight Bar)}$$

$$\varepsilon_{max} = \frac{t}{2}\left(\frac{1}{R_f} - \frac{1}{R_o}\right) \quad \text{(Curved Bar)}$$

Torsion (Round Bar)

L: Length

θ: Angle of twist

r: radius of the bar

$$\gamma_{max} = \frac{r\theta}{L} \quad \text{(Shear Strain)}$$

$$\varepsilon_{max} = \frac{r\theta}{L\sqrt{3}} \quad \text{(Equivelent Strain)VonMises}$$

Talk to one of our experts today about nitinol.

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About Resonetics

Working at the forefront of medical technology since 1987, Resonetics comprises industry experts who excel in the most advanced engineering, micro-manufacturing, and assembly processes and capabilities, including laser processing, metal fabrication, nitinol processing, thin-wall tubing, and sensors.

24/7 operations allow us to meet even the most aggressive timelines, while our proprietary Lightspeed Lab offers end-to-end service in pre-production and production phases with flexibility and accessibility unique to the industry.

We thrive on complex challenges and supporting projects at every stage with advanced technologies, purpose-built equipment, and vertically integrated capabilities. Known for rethinking what's possible, we help you expand the accessibility and efficacy of medical technology, improving treatment options worldwide.

RESONETICS