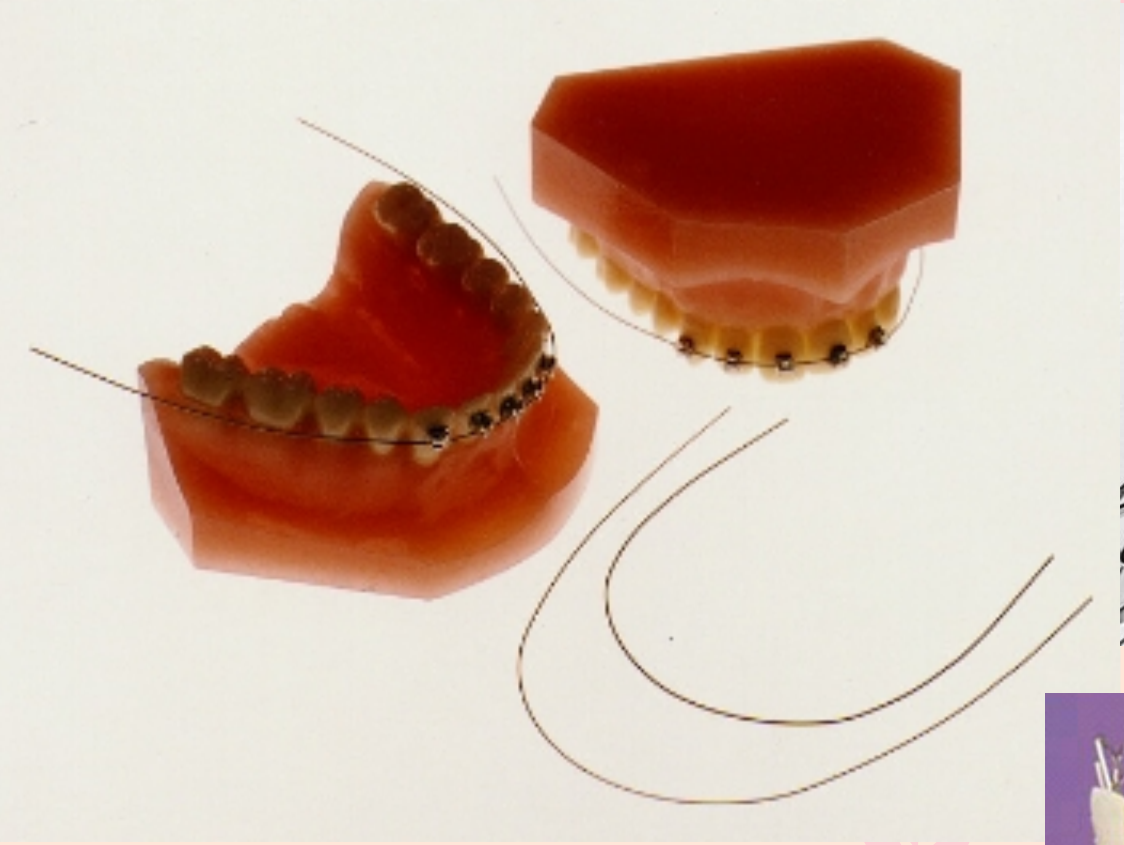
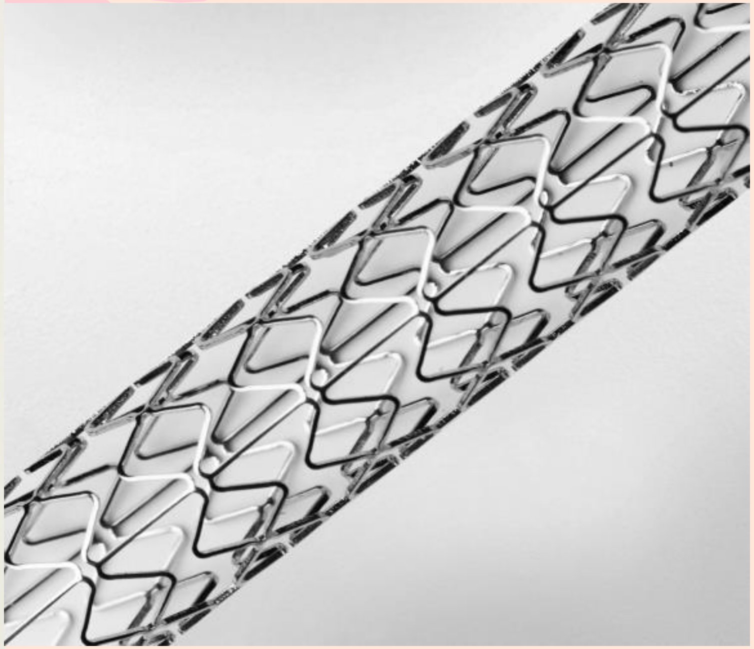
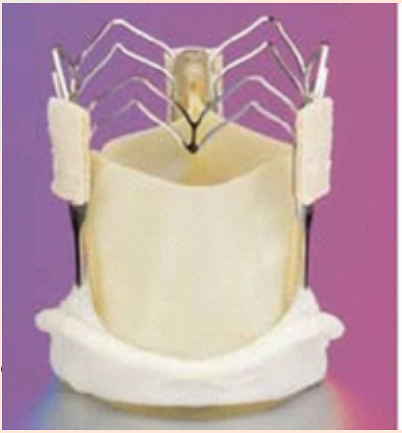
Dental Metals: Nitinol







I materiali a memoria di forma (Shape Memory Alloy - SMA) sono materiali funzionali in grado di recuperare elevate deformazioni sfruttando una **trasformazione martensitica** che avviene allo stato solido **senza diffusione**. Essa avviene mediante il passaggio, reversibile, da una struttura ad alta simmetria, detta austenite, ad una a simmetria inferiore, detta martensite. La trasformazione martensitica viene definita mediante quattro temperature caratteristiche, che indicano la temperatura di inizio e fine trasformazione diretta da austenite a martensite (Ms e Mf), e inversa da martensite ad austenite (As e Af). ***Il cambiamento di fase puo' essere provocato da una variazione di temperature del materiale nell'intervallo di trasformazione, o dall'applicazione di un carico al di sopra di un valore critico.*** La fase martensitica e quella austenitica possono coesistere in due intervalli di temperatura: (i) Mf<T<Ms quando il materiale e' sottoposto ad un raffreddamento da una temperatura superiore a Af; oppure (ii) As<T<Af quando il materiale e' sottoposto ad un riscaldamento a partire da una temperatura inferiore a Mf

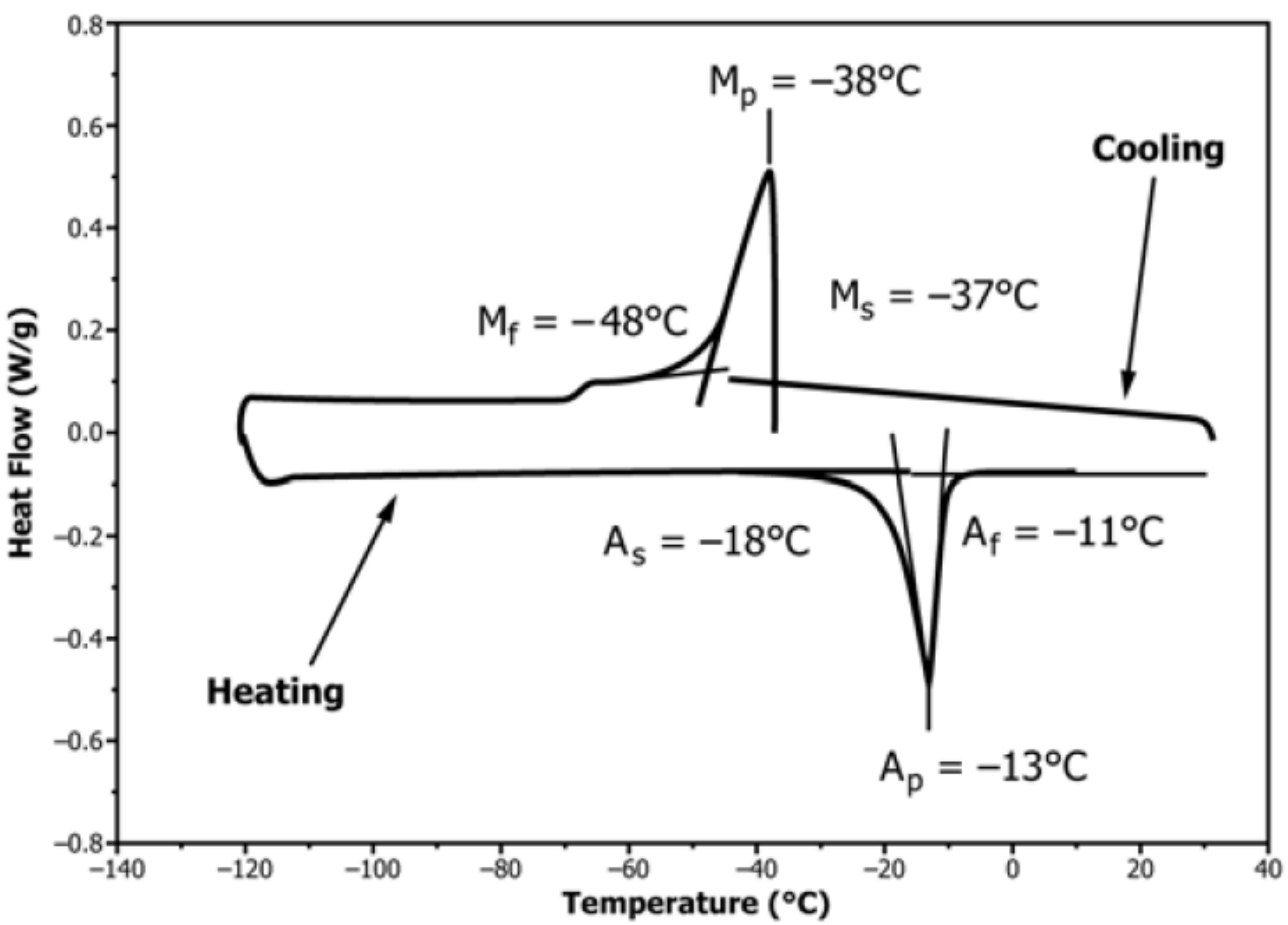
The following technical terms and their definitions are essential for understanding Nitinol and the concepts presented in this document. For an extensive list of standard terminology it is recommended to reference *ASTM F2005 – Standard Terminology for Nickel-Titanium Shape Memory Alloys*.

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

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

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



ASTM F2004 – Standard Test Method for Transformation Temperature of Ni-Ti Alloys by Thermal Analysis

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**.

Upper plateau strength/stress (UPS) – the stress measured at 3 % strain during tensile loading of the sample 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 (Md) – 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 (Mf) – the temperature at which the transformation of martensite from austenite (or R-phase) is completed on cooling of the alloy.

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

Pseudoelasticity – another name for superelasticity.

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

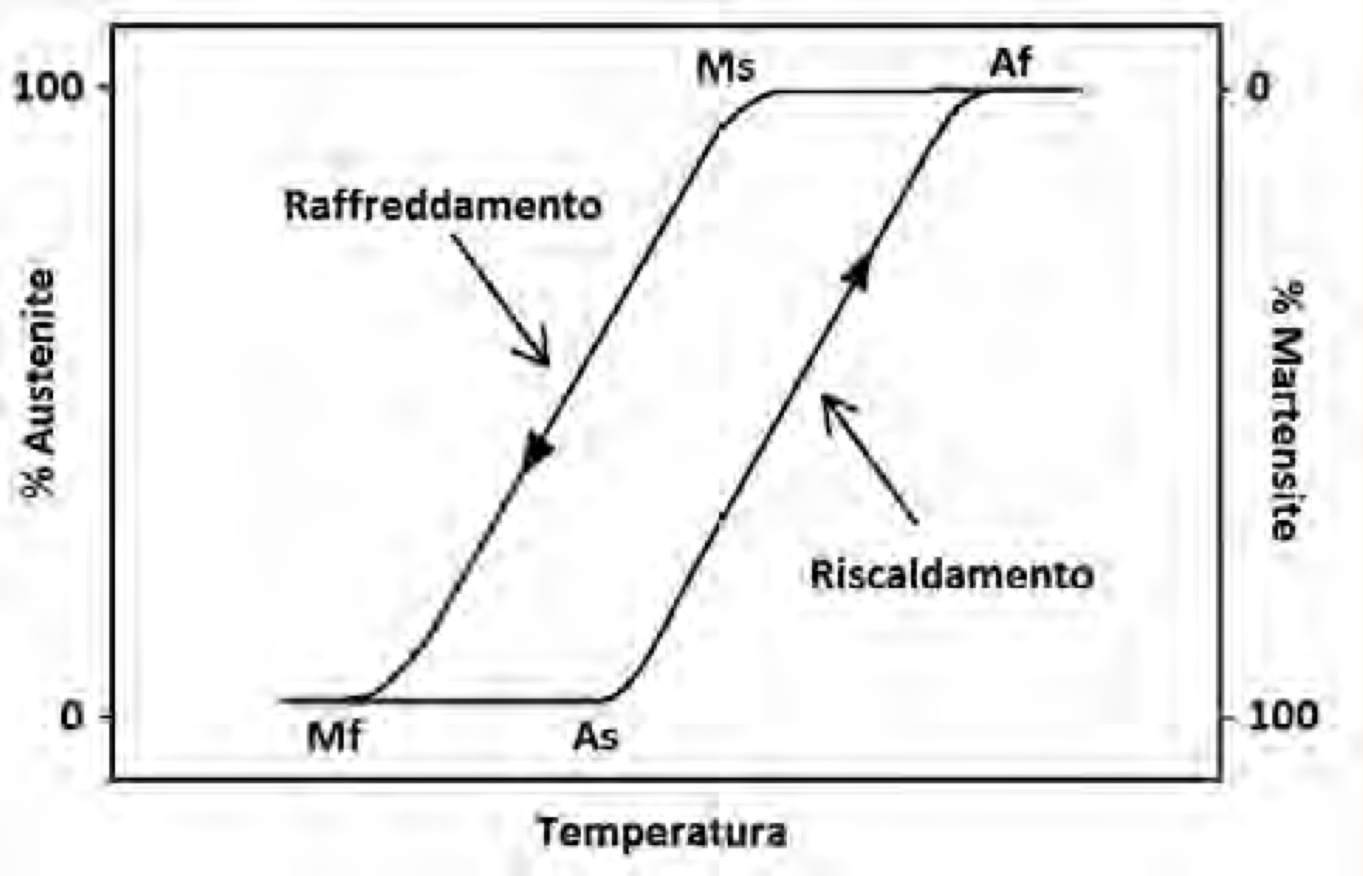
R-phase – the intermediate phase which may form between austenite and martensite. The R-phase occurs in Nitinol alloys under certain conditions. The R-phase has a rhombohedral crystal structure.

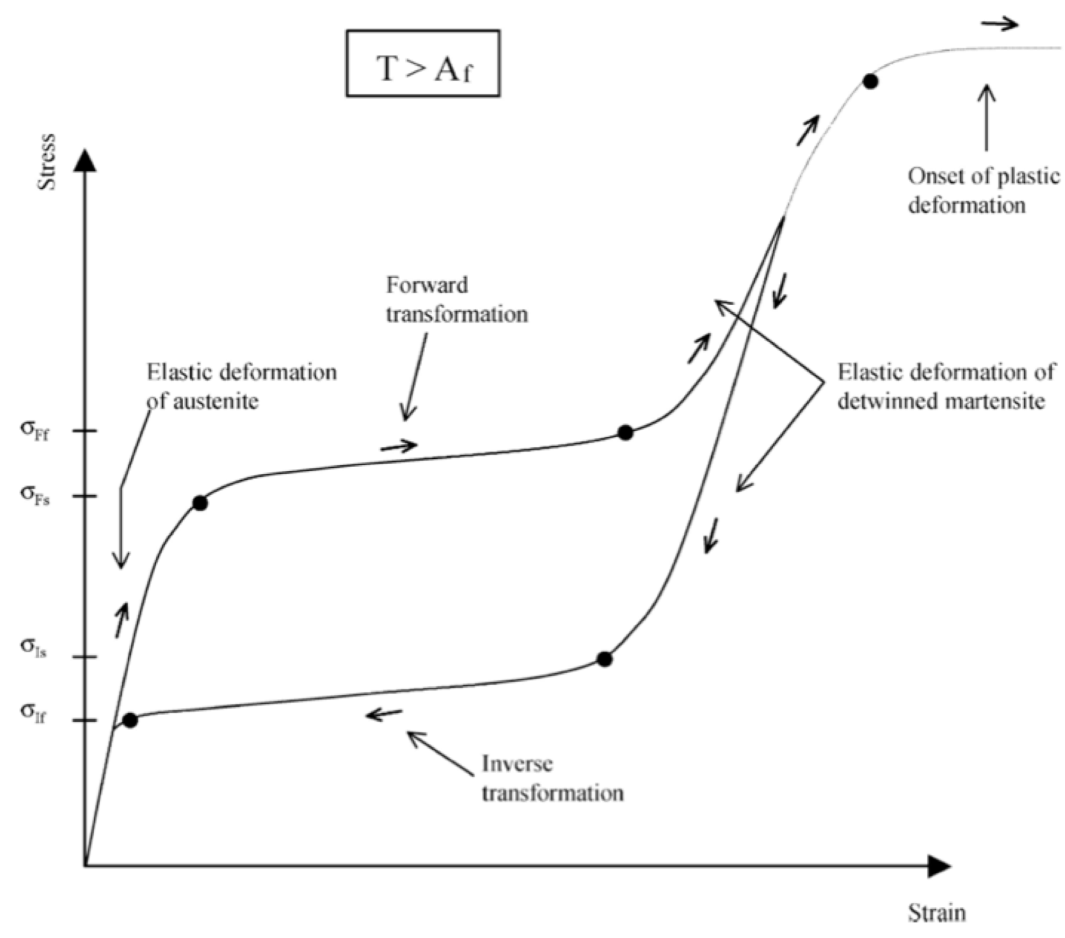
Residual elongation (Elr) – the percent strain measured after tensile loading to 6 % strain and unloading to 7 MPa per **ASTM 2516**.

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**.

The R-Phase

Intermediate phases are sometimes present that are stable at temperatures or stresses between the austenite and 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 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. ***Since the R-phase transformation requires much less straining of the lattice it is therefore thermodynamically favorable to occur between the austenite and martensite phases in these cases.***


100
0
% Austenite
Ms
Af
0
100
% Martensite
Raffreddamento
Riscaldamento
Mf
As
Temperatura



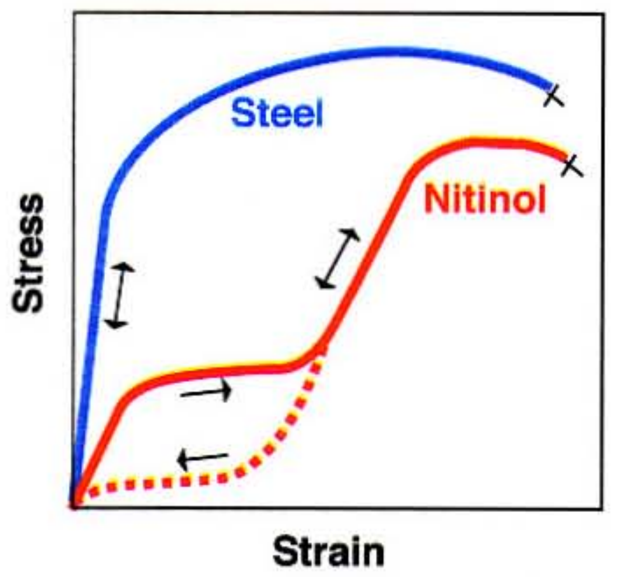


Fig. 3 Schematic stress-strain diagram for Nitinol and stainless steel

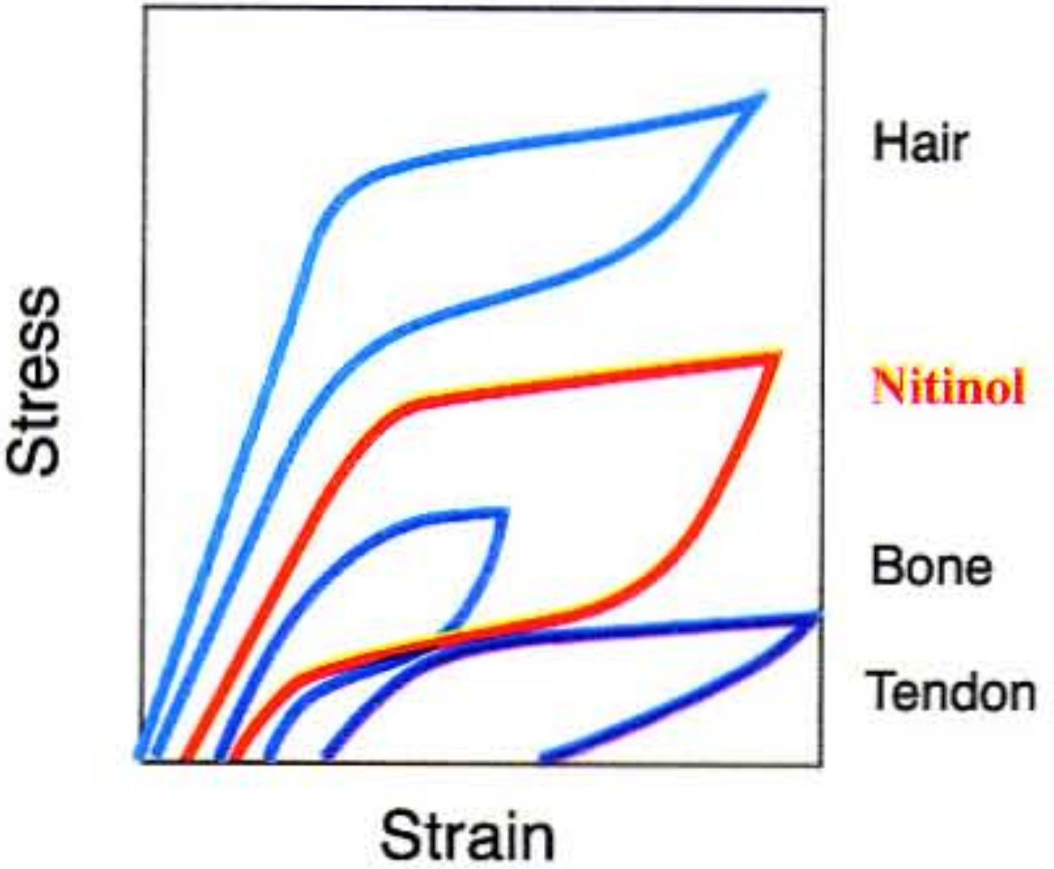
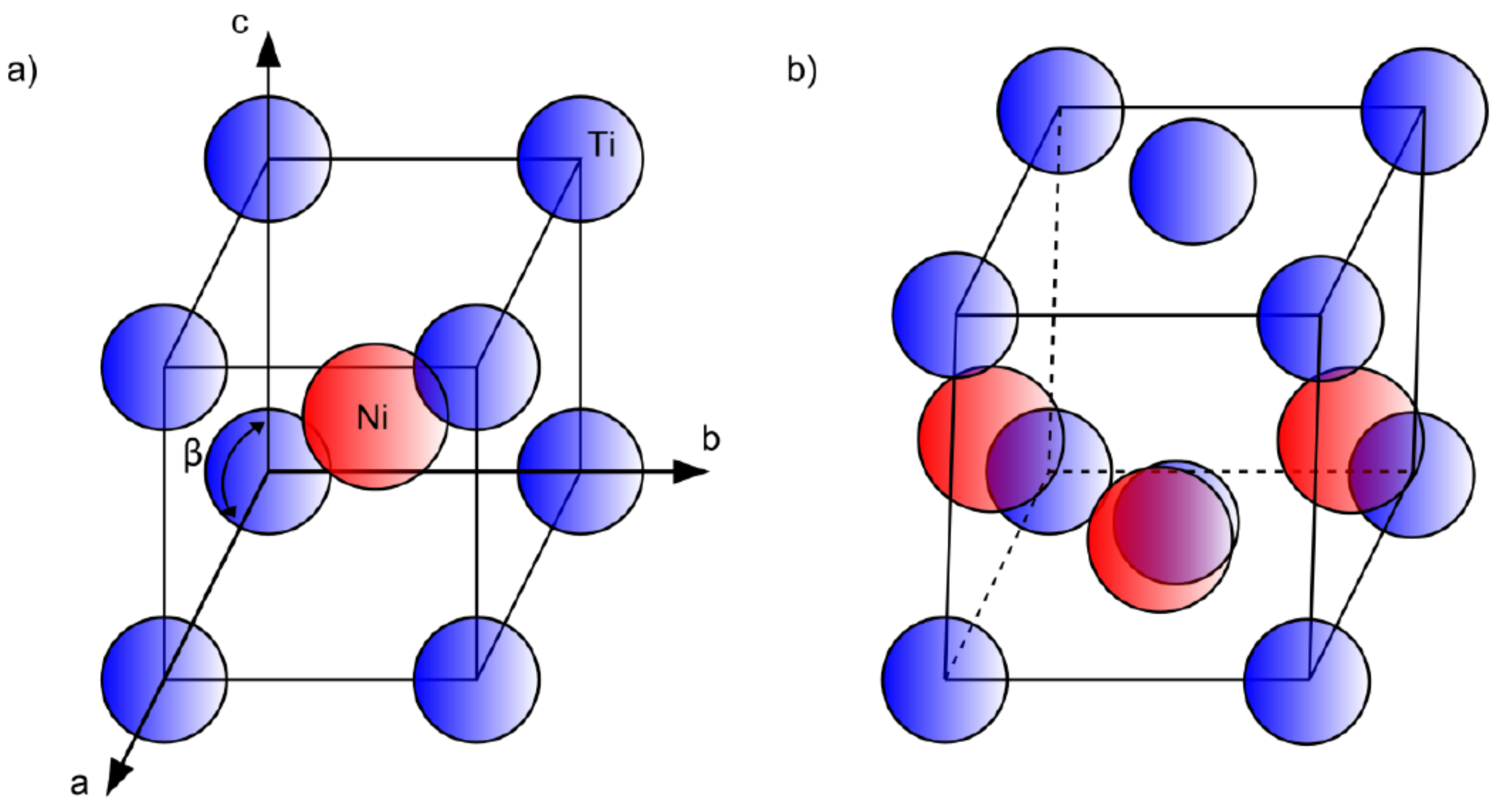


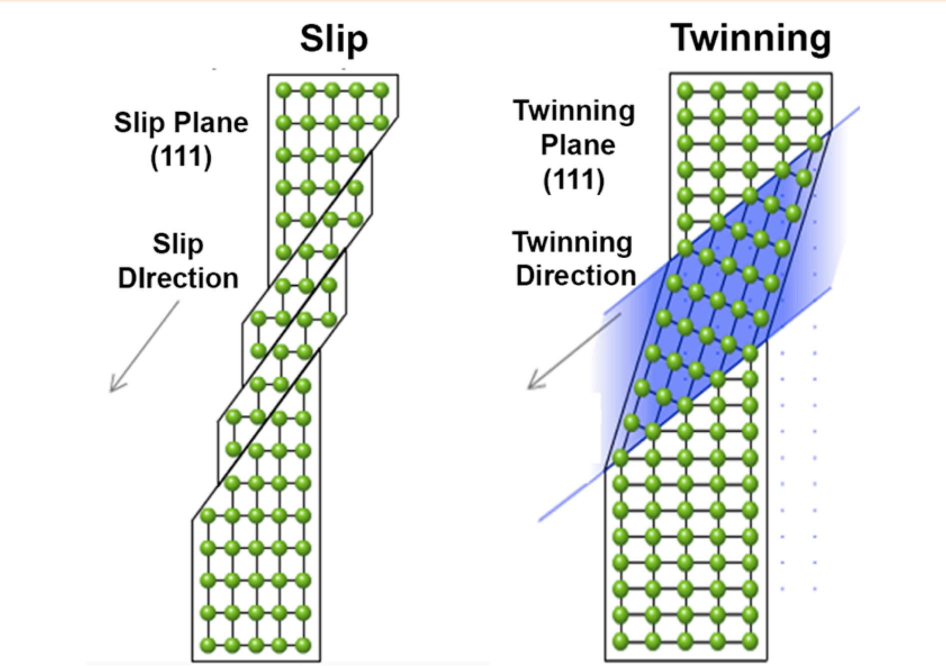
Fig. 2 Biomechanical compatibility of Nitinol: deformation characteristics of Nitinol and living tissues [2]

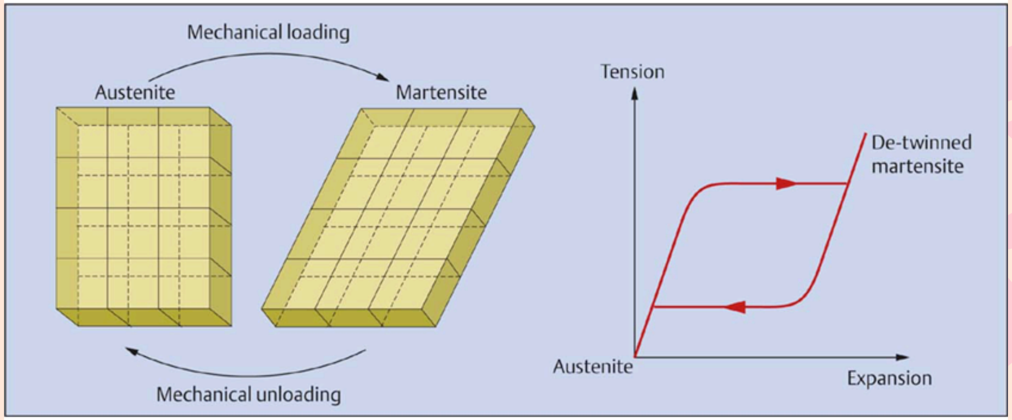


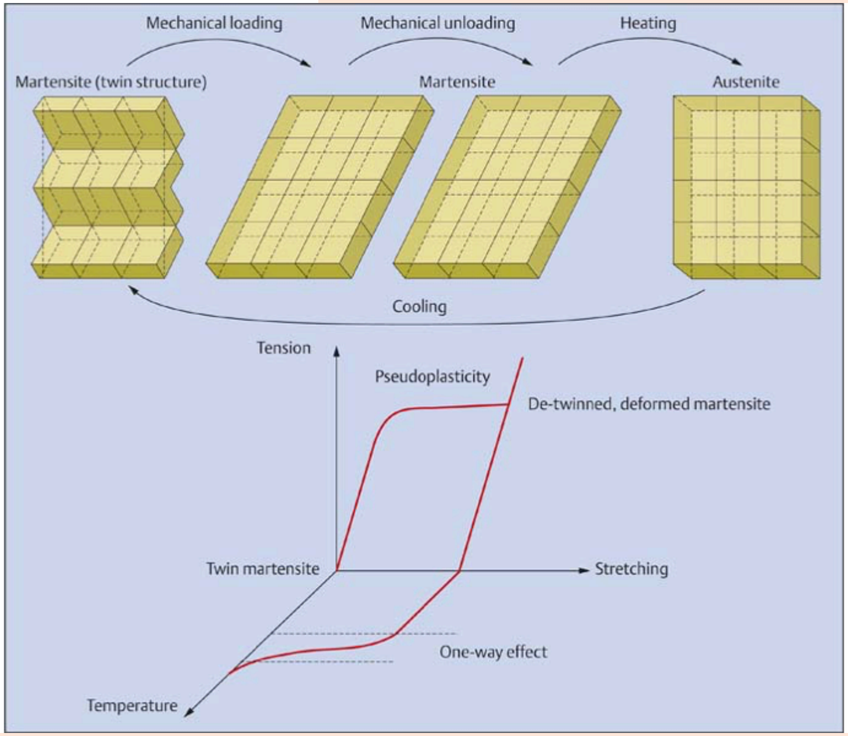
Austenite
(B2, CsCl type ordered structure)

Martensite
(B19', Monoclinic structure)

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.


Slip
Twinning
Slip Plane (111)
Slip DIrection
Twinning Plane (111)
Twinning Direction


Mechanical loading
Austenite
Martensite
Mechanical unloading
Tension
De-twinned martensite
Austenite
Expansion


Mechanical loading
Mechanical unloading
Heating
Martensite (twin structure)
Martensite
Austenite
Cooling
Tension
Pseudoplasticity
De-twinned, deformed martensite
Twin martensite
Stretching
One-way effect
Temperature

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.**

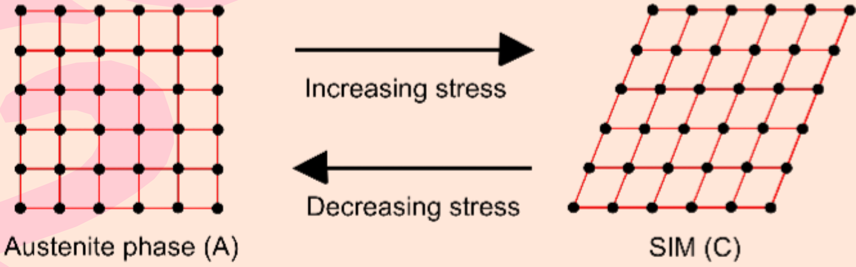
Superelastic and shape memory responses are related. In fact, the response simply depends on the transformation temperature of the Nitinol component coupled with the application temperature. ***Below the Mf temperature the Nitinol alloy will exhibit shape memory while above the Af temperature the Nitinol material will exhibit superelasticity***.

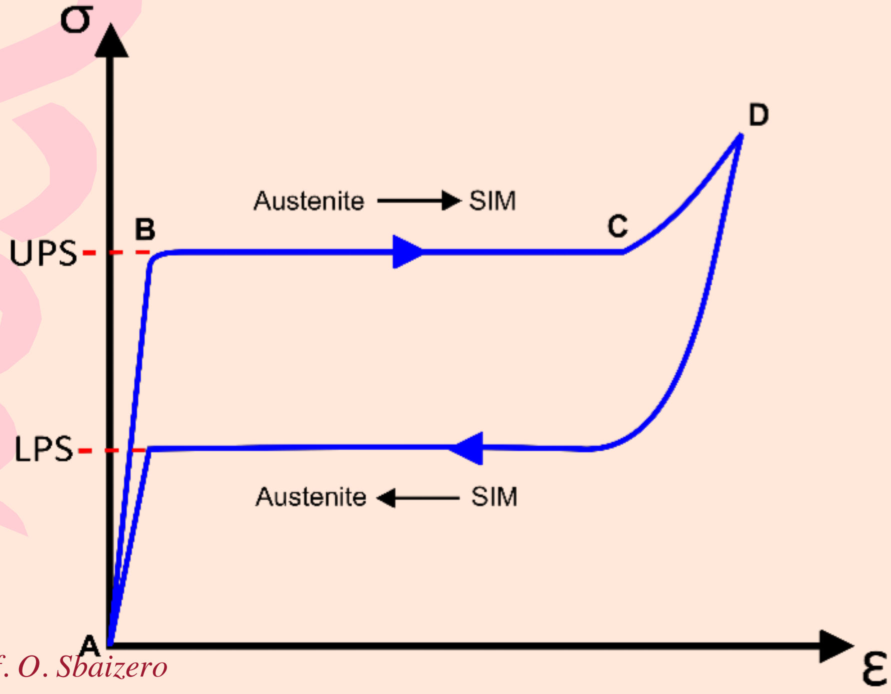
This concept is critical when designing a Nitinol device

Superelasticity

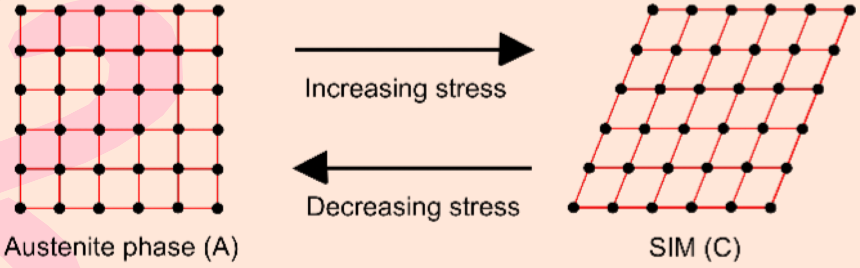
If a stress is applied to a Nitinol component, at a temperature above Af, the austenite phase will be converted to stress induced martensite (SIM-stress induced martensite) resulting in a superelastic response.

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 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.

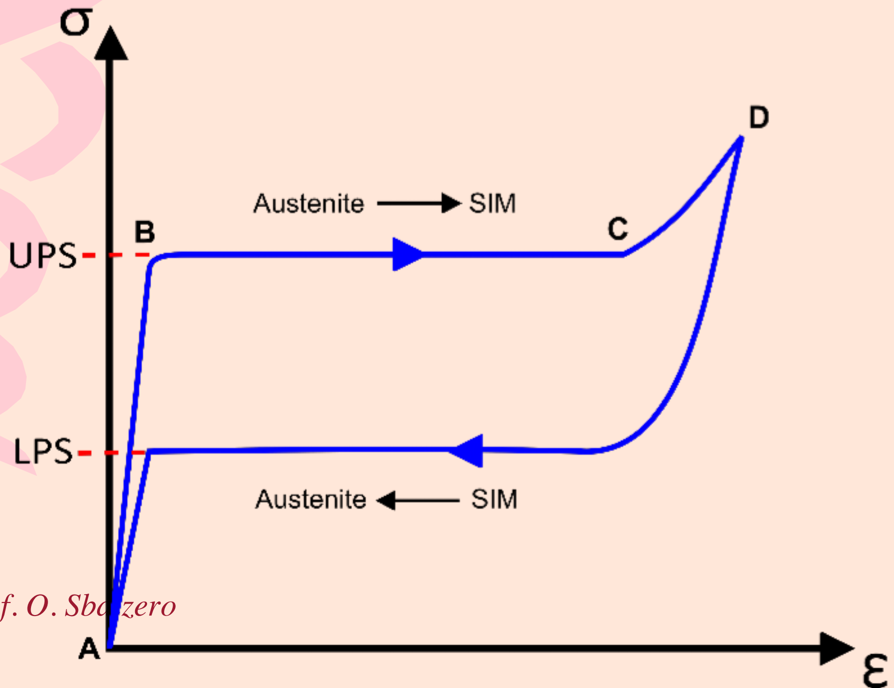




During unloading (D → A) elastic strain is recovered and the SIM transforms back into the parent austenite phase. Note that the recovery stress (or LPS) is lower than UPS. The hysteresis observed arises from internal friction and defects in the crystal structure.



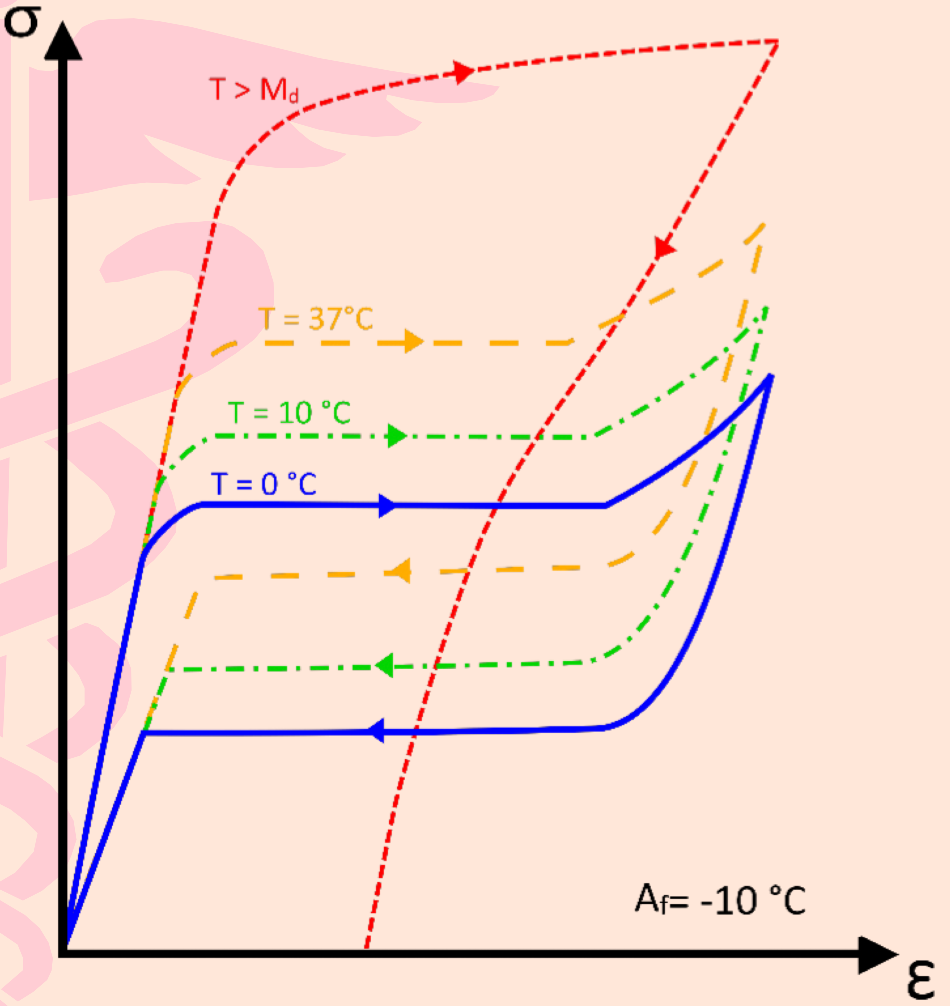
A typical Nitinol alloy will exhibit superelasticity up to **8-10 %** strain before permanent deformation begins. However, there is always some percentage of permanent-set or residual elongation, Elr. The magnitude of Elr depends on the past thermomechanical processing of the material and also the % strain the component was subject to before unloading



The UPS and LPS are not fixed for all temperatures. The superelastic plateaus will increase with application temperature

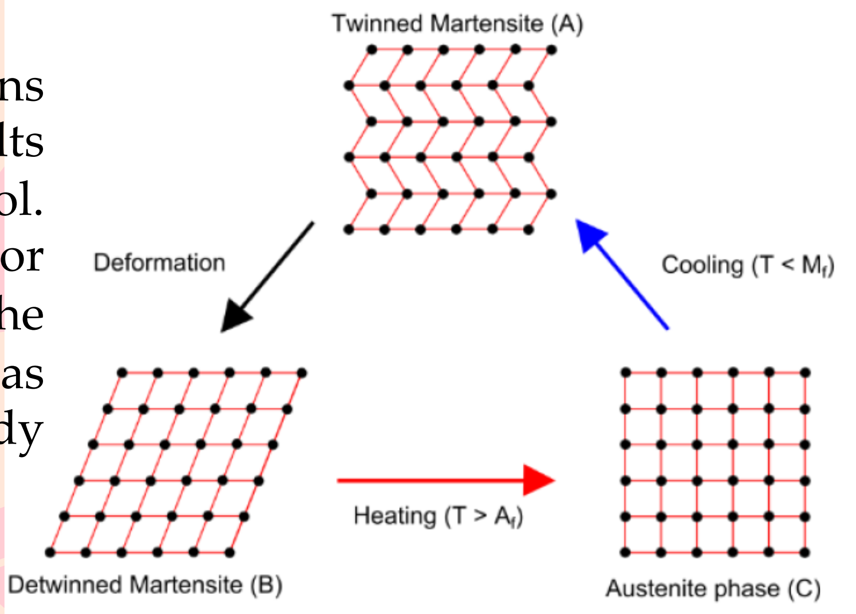
For every C the plateaus can change by 3 – 20 MPa/C; depending on the alloy and processing history. It is therefore important to test the superelastic properties of the final device at the application temperature (ex. 37 ° C for implantable devices).

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 A_f 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 M_d (~ 80 C > A_f).

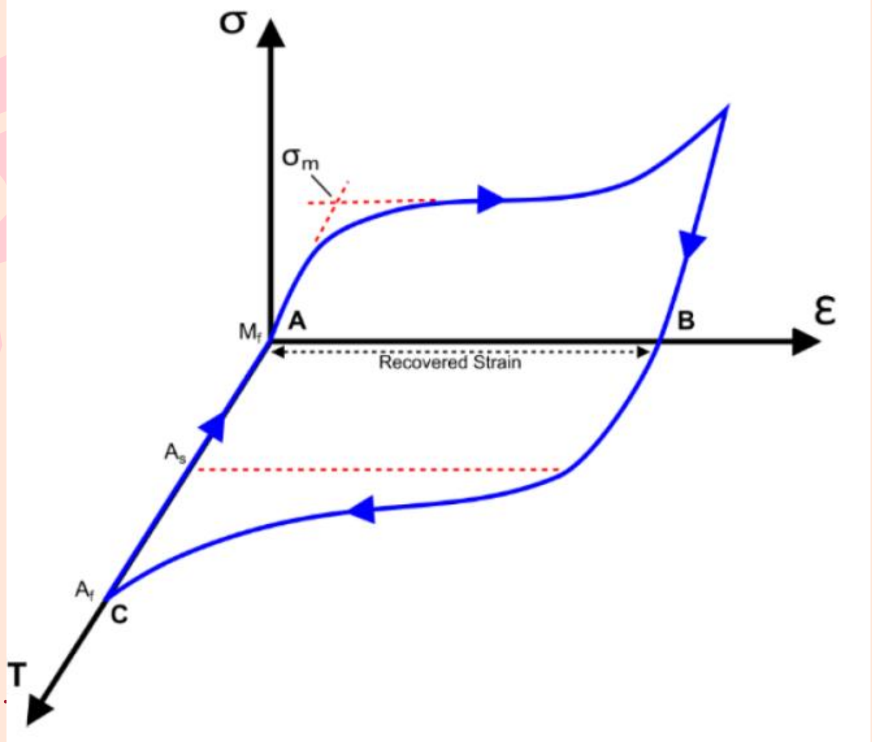


Shape Memory Effect

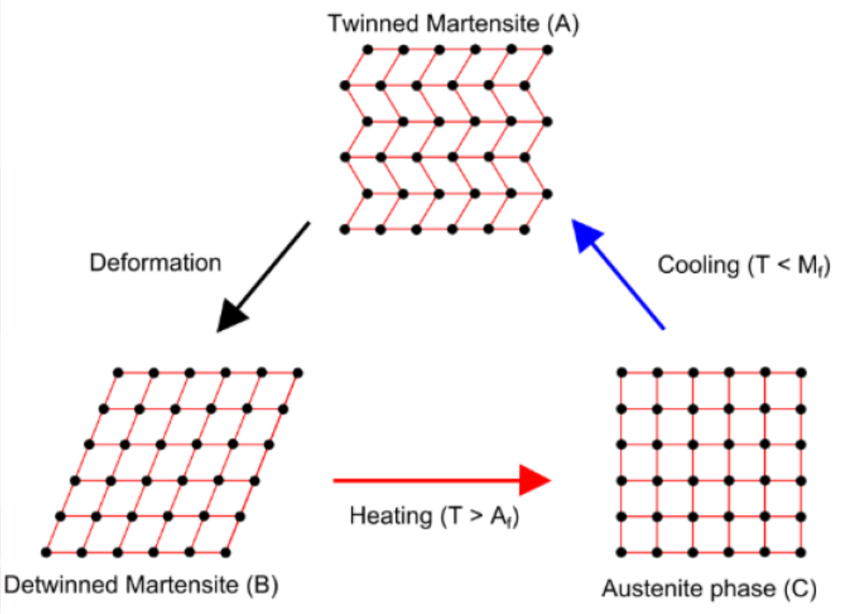
Thermally induced phase transformations between martensite and austenite results in the shape memory response of Nitinol. The shape memory effect is utilized for creating actuators as well as for the deployment of medical devices such as cardiovascular stents as they reach body temperature.

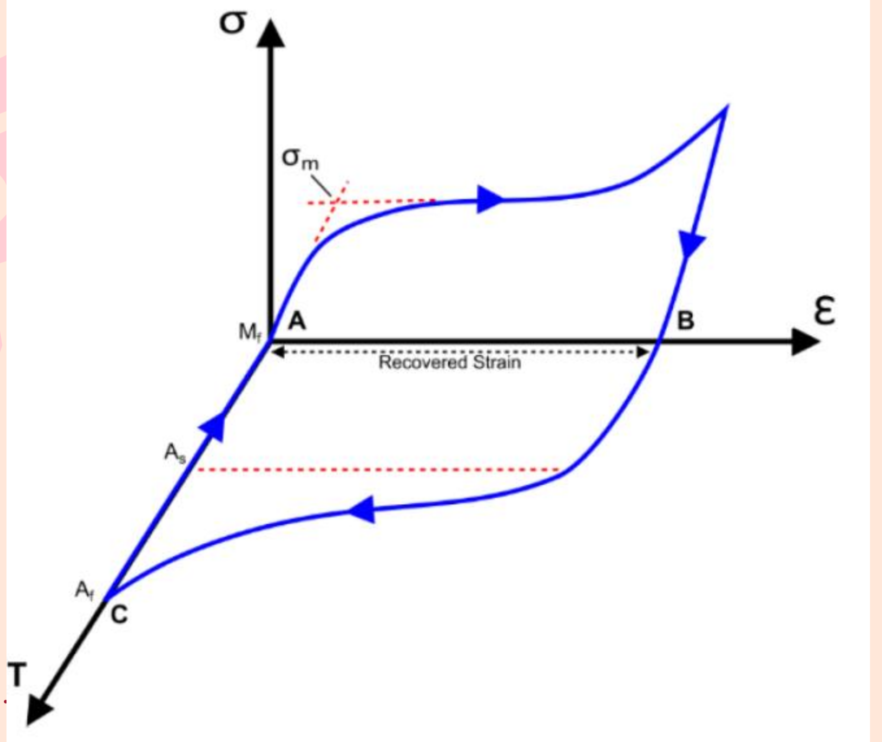


To exhibit shape memory behavior the Nitinol alloy must first be cooled below M_f. Deformation of martensite is visualized moving from point A to point B on the stress-strain-temperature plot. In the early stages of the deformation an elastic region is observed before the martensite detwinning stress (σ_m) 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 A_s will cause the detwinned martensite to begin transforming into austenite.



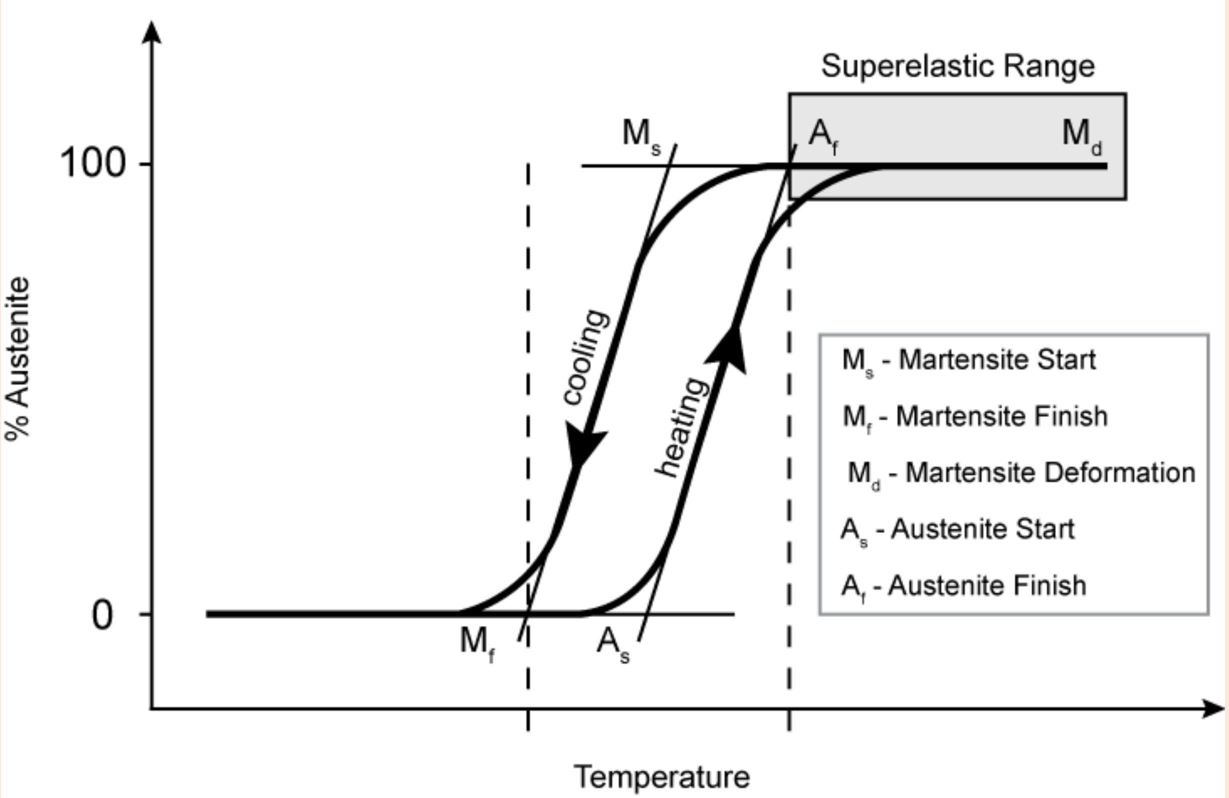
This transformation of the crystal structure translates into the recovery of the original trained shape of the component on the macroscopic scale once the temperature reaches above Af (B → C). The deformed crystal structure remembers its original orientation because of the lattice correspondence. When 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





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 C for Nitinol superelastic alloys 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.



Effect of Cold Work

Also known as work or strain hardening, cold work is the strengthening of a material through plastic deformation.

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 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.

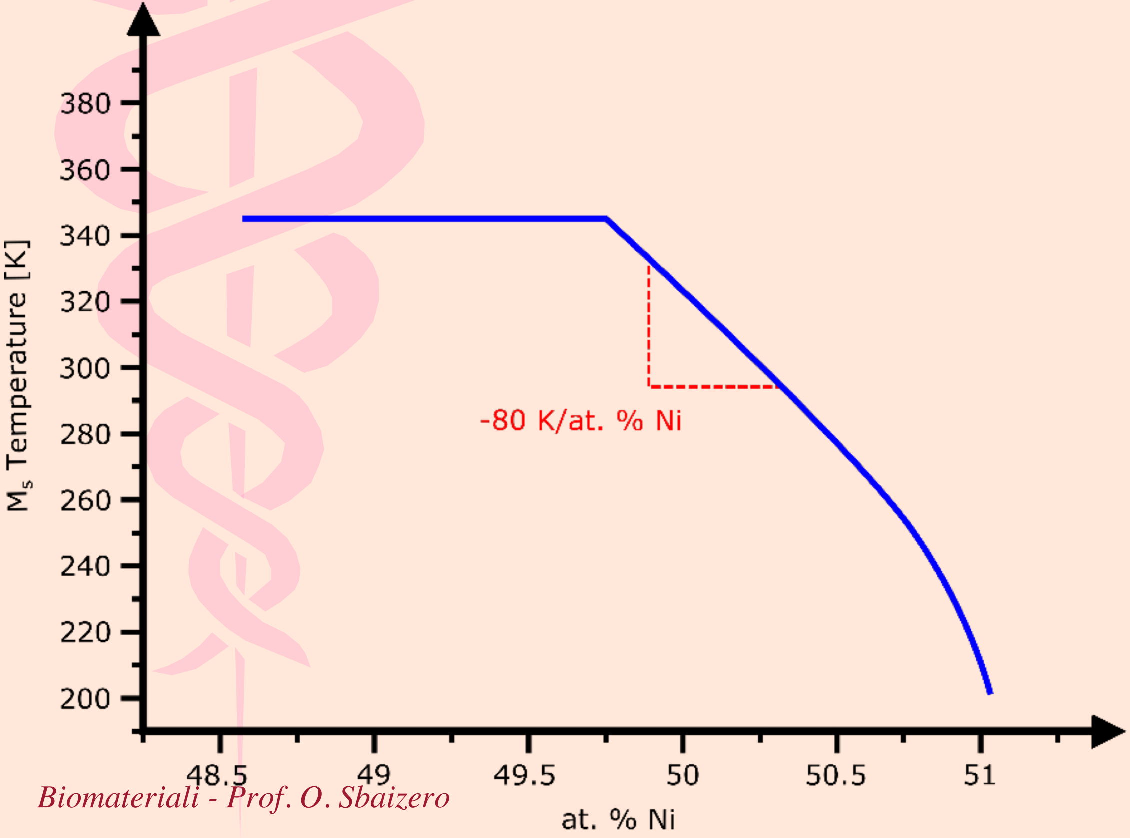
For example, mechanical properties such as the yield stress and ultimate tensile strength (UTS) of the material increase with percentage cold work. This increase in strength however comes at the expense of a reduction in elongation (or ductility).

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 dislocation density within the crystal structure 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 the yield stress can be too low where the material plastically deforms below the UPS or martensite detwinning stress, σ_m. The material will therefore not exhibit shape memory or superelasticity in this case.

Alloy Ratio and Ms

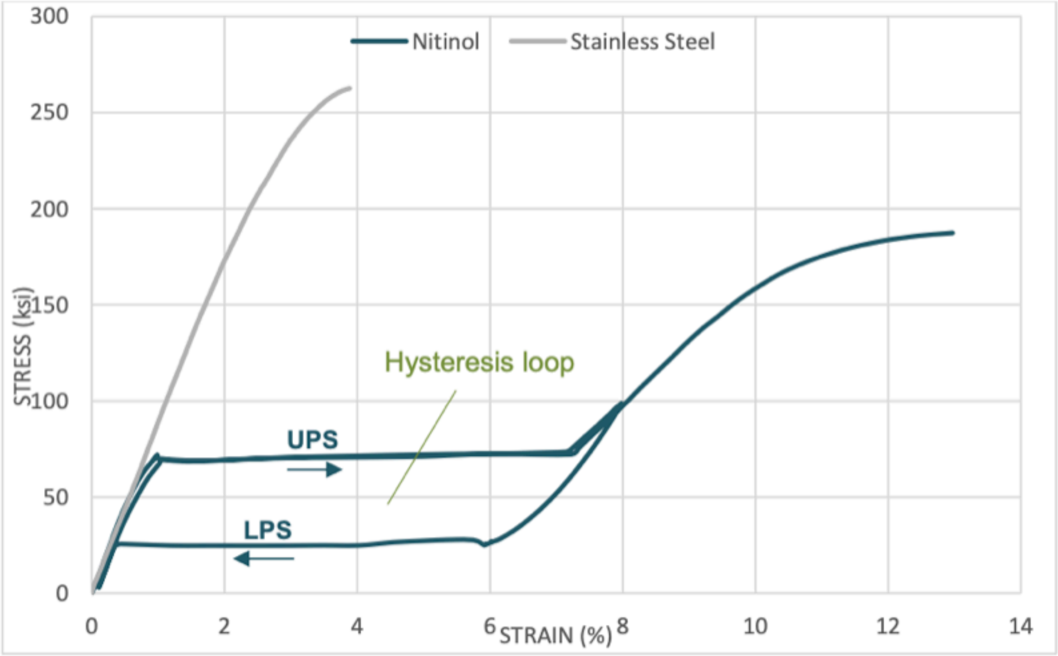
Nitinol is typically composed of approximately 50 to 51 at. % Nickel by atomic percent (i.e. 55 to 56 wt. %). **As can be seen by the following graph, the Ms of the material is highly sensitive to the alloying ratio.** The smallest change in Ni content has a large effect on the transformation temperatures. This is important to understand when considering different wrought Nitinol materials and ageing heat treatments.

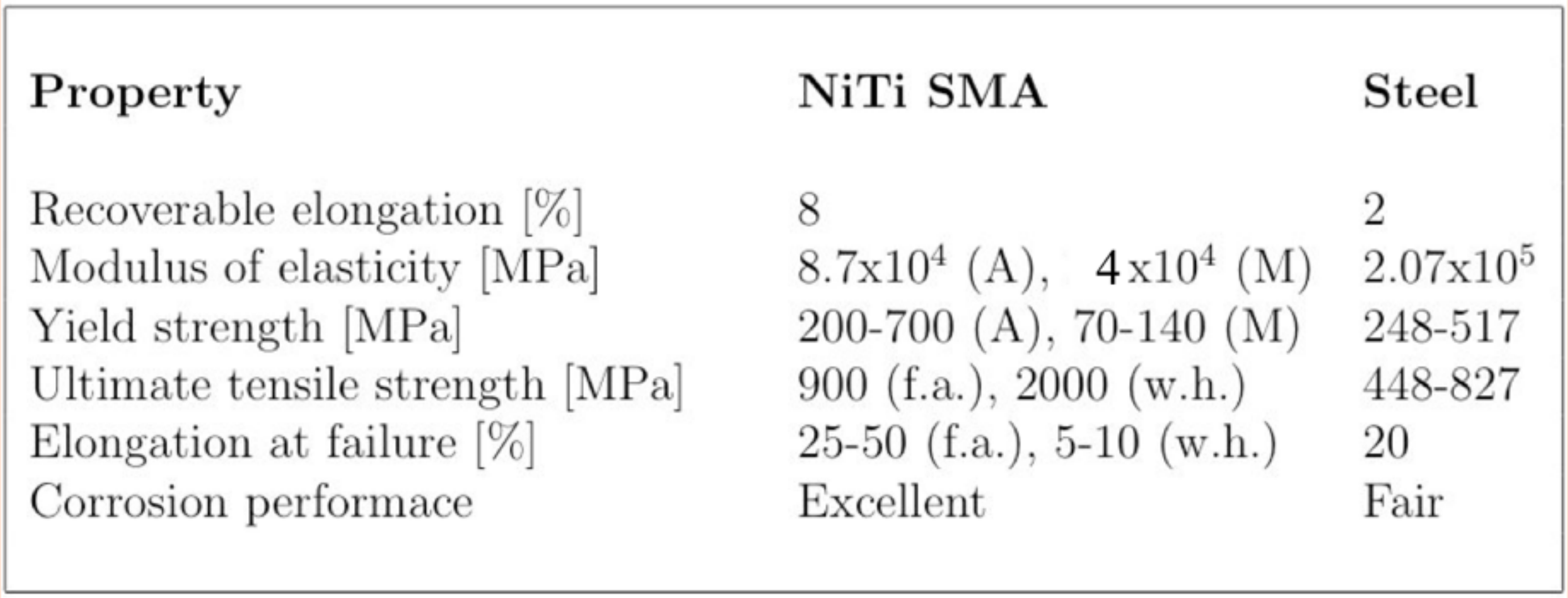
The Ms Temperature changes by approximately 80 degrees Kelvin for every atomic percent change in Ni content. For this reason, great control of the alloy content is required during the casting process



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.

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.**





Property	NiTi SMA	Steel
Recoverable elongation [%]	8	2
Modulus of elasticity [MPa]	8.7x10^4 (A), 4x10^4 (M)	2.07x10^5
Yield strength [MPa]	200-700 (A), 70-140 (M)	248-517
Ultimate tensile strength [MPa]	900 (f.a.), 2000 (w.h.)	448-827
Elongation at failure [%]	25-50 (f.a.), 5-10 (w.h.)	20
Corrosion performace	Excellent	Fair

Corrosion

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.

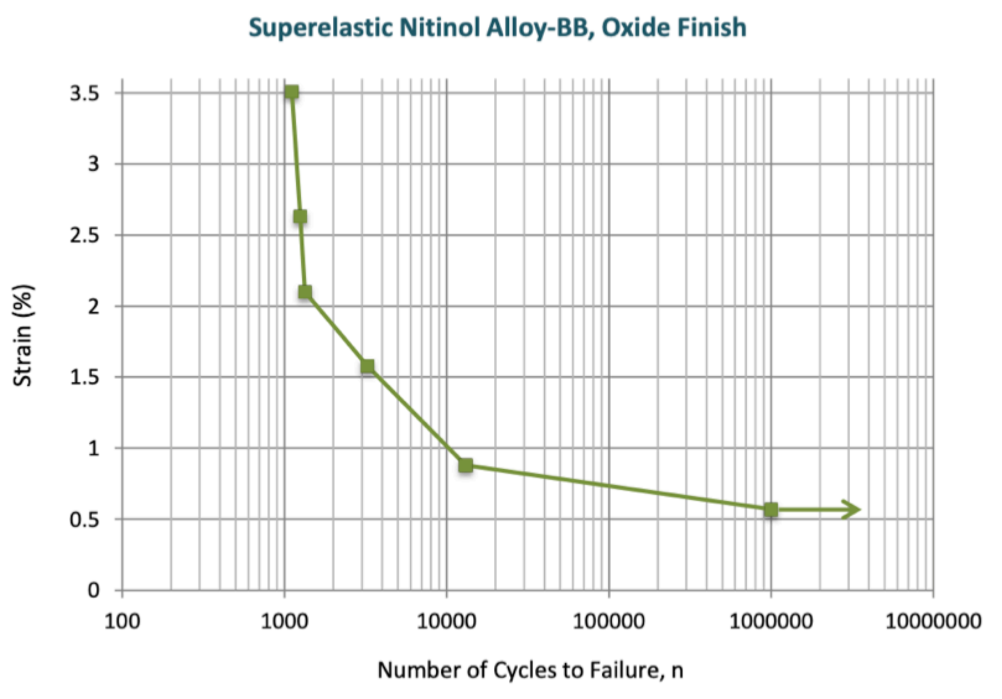
Sterilization of Nitinol

Medical devices made from Nitinol can be sterilized through most typical sterilization methods including **steam** (autoclave), **ethylene oxide** (EtO), or **radiation** (gamma). However, the temperature seen by the device must be considered and maintained below 300 C to ensure no effects on mechanical and functional properties.

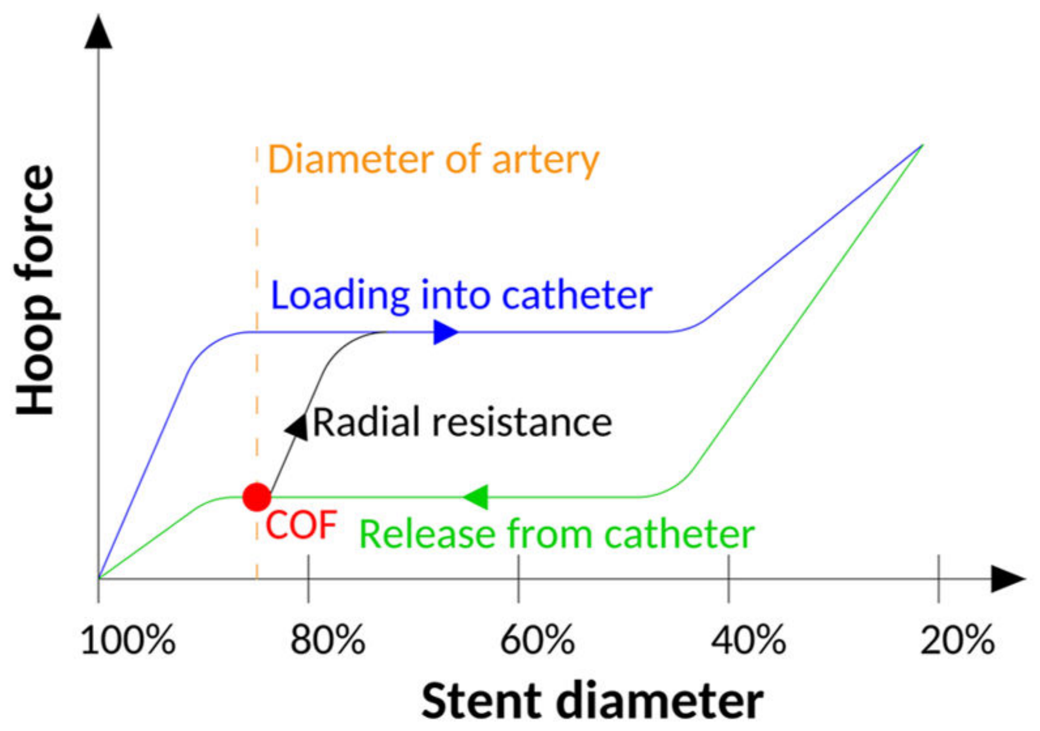
Fatigue

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 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.



Radial resistive force (RRF) and Chronic outward force (COF) are the two main characteristics that determine the force balance between the vessel wall and the stent. **RRF is a measure of the amount of force required to compress the stent radially, while COF correlates to a measure of the radial force the stent projects outward in its deployed configuration.** Both RRF and COF are determined by the unique force hysteresis of Nitinol. **Hoop strength is another important design parameter that defines the maximum hoop load that can be carried by the stent.**



$$\sigma = p \cdot d / 2\, t$$

Sometimes hoop force, Fd, or hoop force per unit length, fd, is used instead of hoop stress to characterize load acting on the stent

$$F_d = p \cdot d \;\; L / 2$$

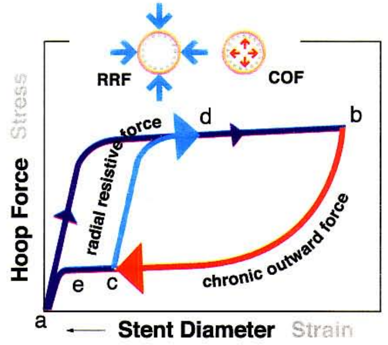


Fig. 7 Schematic stress hysteresis and concept of biased stiffness as demonstrated with the cycle insertion into delivery system/deployment/compression of a stent

Ti–Ni alloys consisting of equal atomic amounts of Ti and Ni (49–51 mol% Ni) show unique mechanical properties, such as **shape memory, superelasticity and efficient damping**. Because of the superelasticity, the Ti–Ni alloy is used for guide wires, stents, orthodontic arch wires, endodontic reamers and files.

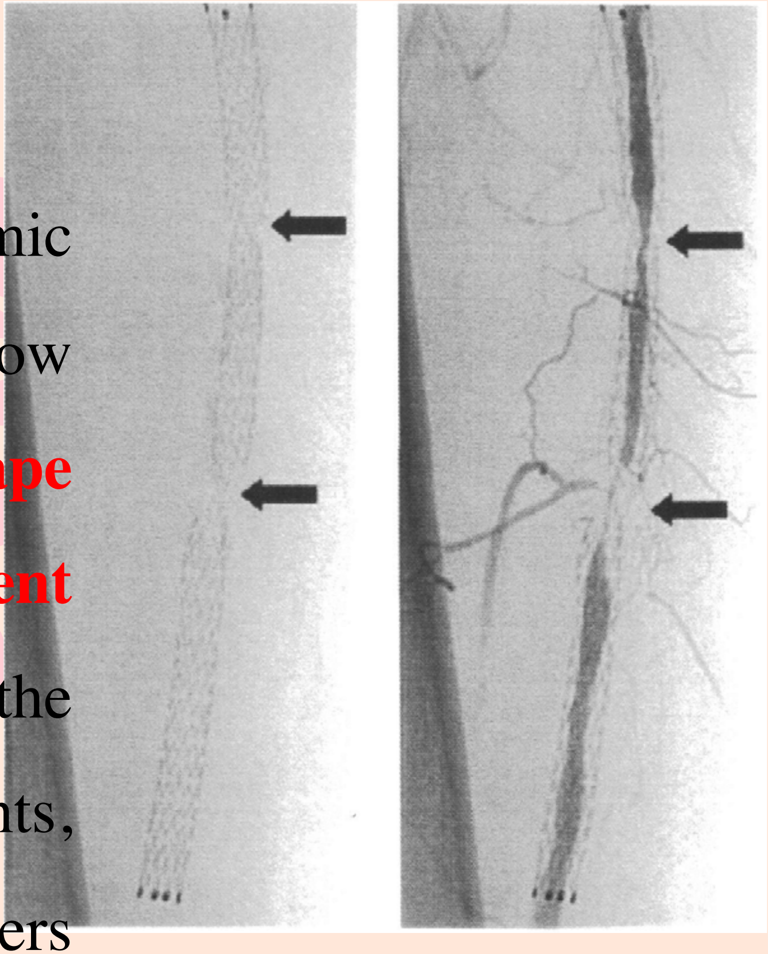


Figure 6. Early-stage fractures of self-expanding Ti–Ni femoral stents in service observed by x-ray examination [10].

Early-stage fractures of stents in service have been reported. Among self-expanding Ti–Ni femoral stents, 37.2% fractured within 10.7 months of implantation, The use of Ti–Ni alloy with about 50 mol% Ni in medicine is limited by safety. Therefore, there is a great demand for Ni-free shape-memory and superelastic alloys to solve such problems.

Ti–Sn–Nb

Ti–Nb–Al

Ti–Mo–Ga

Ti–Mo–Sn

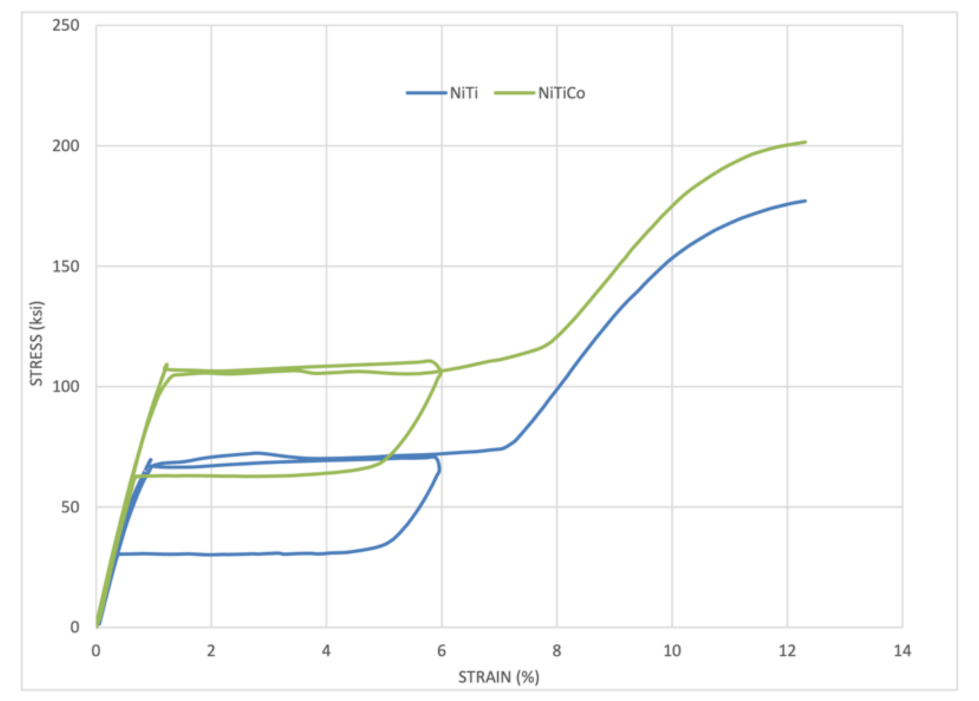
Ti–Nb–O

Ti–Nb–Zr exhibit shape-memory effect and superelasticity, while the recovery strain and superelastic deformation stress of these alloys are still lower than those of the Ti–Ni alloy.

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**.

NiTiCo alloys contains 1.2-1.5 wt. % Cobalt.



Low magnetic susceptibility alloys for MRI

Magnetic resonance imaging (MRI) is widely used as an important diagnostic tool, especially for orthopedic and brain surgery. This method has remarkable advantages for obtaining various cross-sectional views and for diagnosis of the human body with no invasion and no exposure of the human body to x-ray radiation**. However, MRI diagnosis is inhibited when metals are implanted in the body, since metallic implants, such as stainless steels, Co–Cr alloys and Ti alloys become magnetized in the intense magnetic field of the MRI instrument, and artifacts occur in the image.** Such artifacts can disturb the images of organs and tissues around the implant, preventing exact diagnosing. **The area affected by the artifacts is related to the magnetic susceptibility of the implants and decreases with decreasing magnetic susceptibility.** Therefore, metals with low magnetic susceptibility should be developed as MRI continues to increase in popularity.

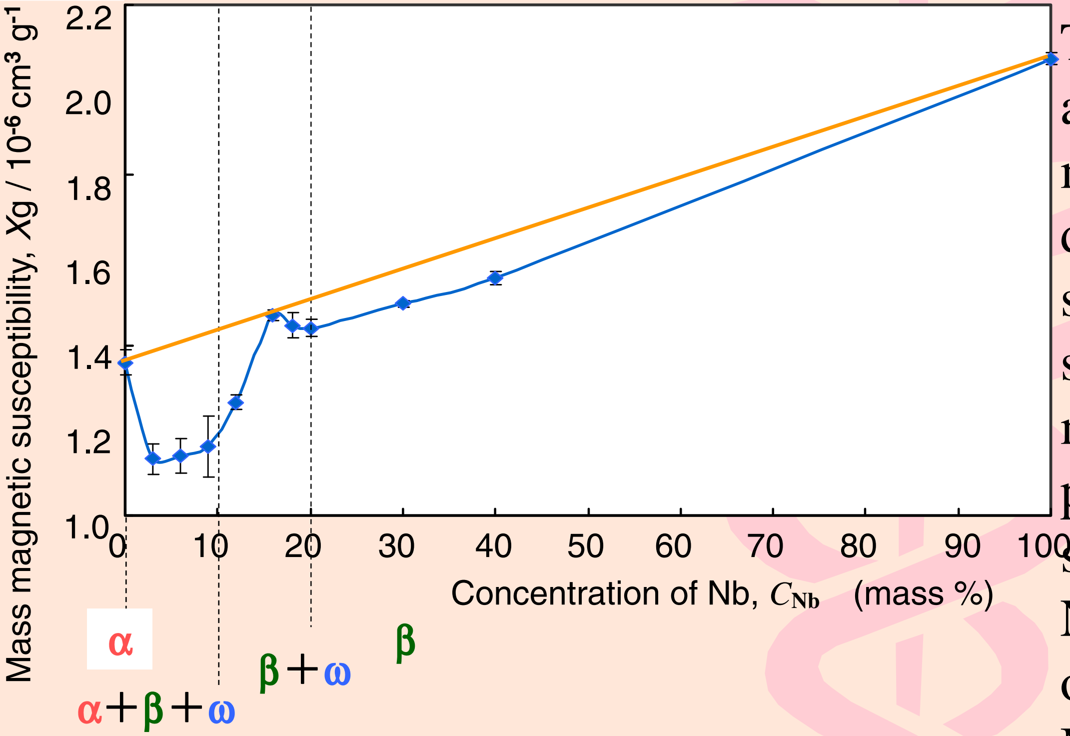


Figure 9. Effects of Nb content and constituent phases on the magnetic susceptibility of Zr–Nb alloy.

The magnetic susceptibility of a Au–Pt–Nb alloy is similar to that of water.

To reduce artifacts Ti–Zr, Zr–Nb, and Zr–Mo alloys with low magnetic susceptibility have been developed. The magnetic susceptibility of the Zr–Nb alloy is shown in figure; it exhibits minimum values where the ω phase is formed. The magnetic susceptibility was reduced in Zr–Nb and Zr–Mo alloys up to about one-seventh of that of the Co–Cr–Mo alloy and one-third of that of Ti and Ti alloys.

Among Zr-based alloys, Zr–9Nb and Zr–3Mo possess low magnetic susceptibility Although Zr–3Mo and Zr–9Nb alloys have low magnetic susceptibilities, it is difficult to apply plastic deformation to these alloys during processing for medical devices because their tensile strength and elongation are limited by the ω phase.