

Nitinol - Material with Unusual Properties

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Abstract:

Nitinol (Nickel-Titanium) alloys exhibit a combination of properties which make these alloys particularly suited for self-expanding stents. Some of these properties cannot be found in engineering materials used for stents today. The paper describes the fundamental mechanism of shape memory and superelasticity. Material properties and device characteristics like elastic deployment, thermal deployment, kink resistance, constancy of stress, dynamic interference, biased stiffness, MRI compatibility, radiopacity and biocompatibility are discussed.

Introduction

Nitinol (Nickel-Titanium) alloys are rapidly becoming the material of choice for self-expanding stents, graft support systems, filters, baskets, and various other devices for interventional procedures. Companies like Bard-Angiomed (Memotherm), Boston Scientific (Symphony a.o.), Medtronic-AneuRx, Nitinol Medical Technologies, World Medical Technologies, and, last but not least, Cordis, a Johnson & Johnson Company, offer products, the performance of which is based on the highly unusual properties of these materials.

Nitinol alloys are most commonly known for their superelasticity and thermal shape memory. While the term shape memory is used to describe the phenomenon of restoring a predetermined shape through heating, after having "plastically" deformed that shape, the term superelasticity refers to the enormous elasticity of the alloys, which can be ten times more than the elasticity of the best stainless steels used in medicine today. Although both effects are clearly spectacular, they are by no means the only important properties of the material. In this paper, features like biomechanical compatibility, constancy of stress, dynamic interference, "biased stiffness" will be described. In combination with strength, fatigue resistance, biocompatibility, and MRI compatibility, these Nitinol-specific properties allow interesting solutions for the design of superior medical devices [1].

Superelasticity and Shape Memory in Nitinol

Conventional metallic materials, like Stainless Steel, Titanium, Elgilloy a.o., used in stents, filters and other interventional devices exhibit a distinctly different elastic deformation behavior from structural materials of the living body. The elastic deformation of these metals and alloys is limited to approx. 1% strain, and elongation typically increases and decreases linearly (proportionally) with the applied force. Natural materials, like hair, tendon, bone, on the other hand, can be elastically deformed, in some cases, up to 10% strain in a nonlinear way [2]. When the deforming stress is released, the strain is recovered at lower stresses. As shown in Fig. 1, the loading/unloading cycle is characterized by a pronounced hysteresis.

A similar behavior is found in Nitinol alloys, equiatomic or near-equiatomic intermetallic compounds of Titanium and Nickel. Fig. 2 shows a characteristic load/deflection (stress/strain) curve for a Nitinol alloy wire at body temperature (T in Fig. 2; *as will be shown later, the properties of Nitinol alloys are strongly temperature dependent*). As with natural materials, the loading and unloading curves show plateaus, along which large deflection (strains) can be accumulated on loading, or recovered on unloading, without significant increase, or decrease, respectively, in load (stress). Because deformation of more than 10%

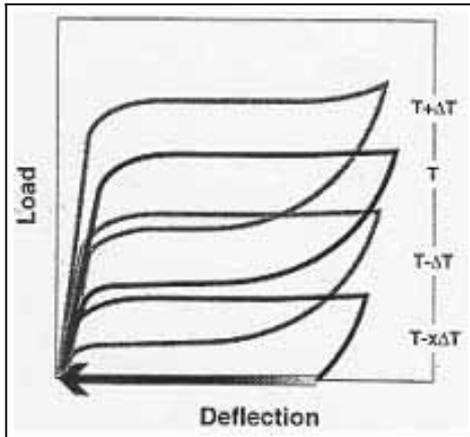


Fig. 1: Deformation characteristics of natural materials and Nitinol [2]

strain can be elastically recovered, this behavior is called "superelasticity", or sometimes more scientifically "pseudo-elasticity". It is the basis for most applications of Nitinol in medical devices.

If the temperature is raised 10°C, for instance, in the test in Fig. 2 ($T+\Delta T$), the complete hysteresis loop, i.e. loading and unloading curves, shifts to higher levels. The qualitative appearance is maintained, however. Lowering the temperature by 10°C, on the other hand, will shift the hysteresis loop to lower levels ($T-\Delta T$). Lowering the temperature even further will cause the load to reach zero before the deflection is recovered, i.e. the sample will stay deformed at this temperature ($T-x\Delta T$). If the temperature is raised back to 25°C or higher after unloading, the deformation will be recovered thermally. This effect is called thermal shape memory, or simply shape memory.

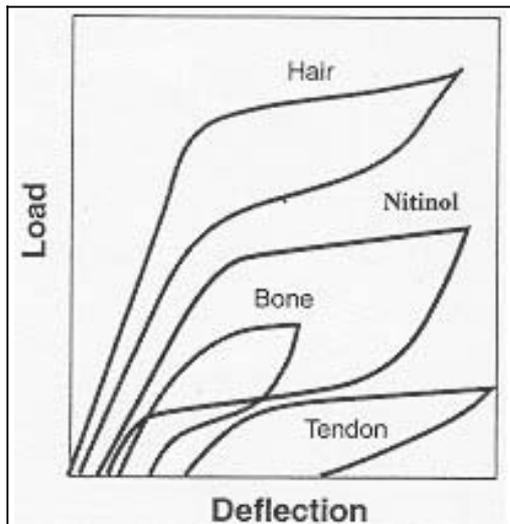


Fig. 1: Influence of temperature on the deformation characteristics of Nitinol

The temperature at which the material can no longer recover the elastic strain, is dependent on the alloy composition and processing, and can be adjusted to between approximately -20°C and approximately +100°C. This transition temperature is an important characteristic of Nitinol components for medical applications. Nitinol alloys are superelastic in a temperature range of approx. 50 degrees above the transition temperature. At higher temperatures, they gradually lose their ability to recover the deforming strain, until, at a certain maximum temperature they behave like a "normal" material (typically >100°C). An alloy with a transition temperature of 25°C, after being deformed 8%, will recover all but approx. 0,5% in the temperature range between 25 and 75°C. The same alloy can be deformed "plastically" up to 8% (under

ideal circumstances) below 25°C and the shape restored by heating to above 25°C (*note: this description is simplistic. The transition temperature in reality is not a distinct temperature, but a temperature range. See side bar for further explanation*).

The mechanism responsible for both superelasticity and shape memory is a solid state phase transformation, scientifically called "thermoelastic martensitic transformation". A metallurgical explanation can be found in the side bar. In the following, some important device characteristics will be discussed, all of which can be attributed to the specific Nitinol properties and used advantageously in self-expanding stents and other medical devices.

Elastic Deployment

The enormous elasticity of Nitinol allows devices brought into the body through catheters or other delivery systems with a small profile. Once inside the body, the devices can be released from their constraining means and unfold or expand to a much larger size. Fig. 3a shows the elastic deployment of a stent from a 3 mm I.D. cartridge to a 20 mm diameter. In order to fully expand at body temperature (37°C), the transition temperature of the alloy should be 30°C or less. If full deployment is wanted at room temperature (20°C), the transition temperature of the alloy should be 15°C or less. Typical expansion ratios for self-expanding Nitinol stents are between 1:2 and 1:5.

Like stents, filters and occlusion devices (ASD occlusion, PDA occlusion) can be deployed superelastically through small sized catheters. Nitinol is also used in retrieval baskets and snares.

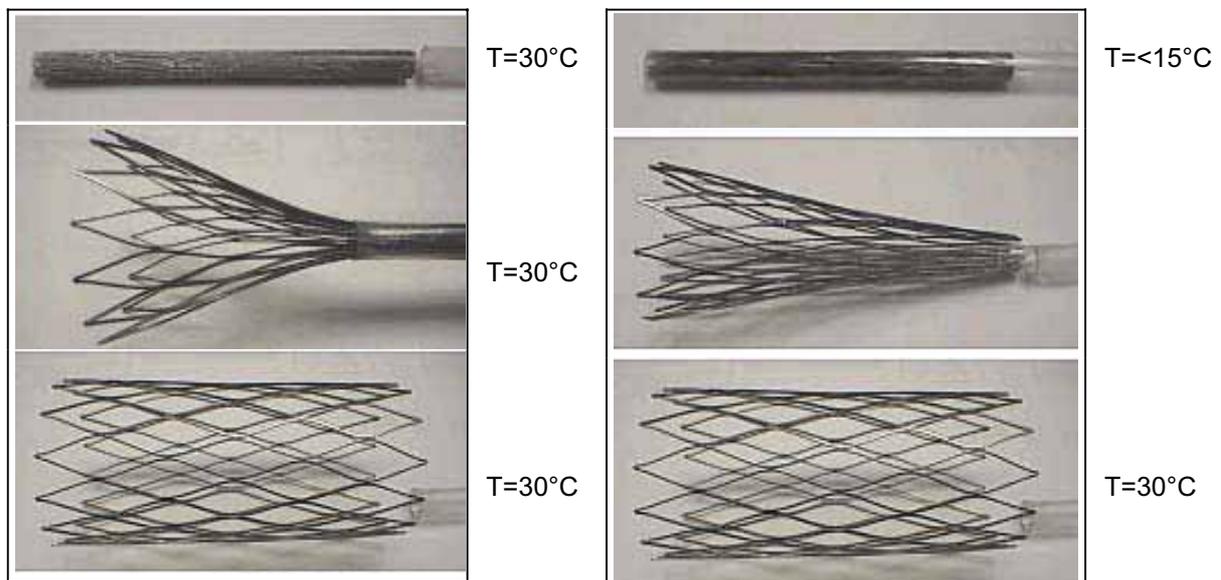


Fig. 3: Elastic deployment of a “slotted tube” type Nitinol stent (3a left), cold deployment and thermal recovery of the stent (3b right) (*demonstration device*)

Thermal Deployment

A stent with a transition temperature of 30°C can be compressed at room or lower temperature. It will stay compressed until the temperature is raised to above 30°C. It will then expand to its preset shape. If this stent could be kept cold during introduction into the body, it would not expand. At the desired location it would warm up through body heat and expand. This, of course, is rather difficult to accomplish. All self-expanding stents, therefore, are constrained in the delivery systems to prevent premature deployment. Stents could theoretically be built with transition temperatures of 40°C. These stents would have to be heated after delivery to the site to make them expand. Fig. 3b shows the stent shown in Fig. 3a released from a cooled delivery cartridge. The stent stays compressed until its temperature exceeds the transition temperature of 30°C.

The Simon Vena Cava filter was the first shape memory vascular implant using thermal deployment. The device is preloaded in a catheter in its low-temperature state. Flushing with chilled saline solution through the catheter keeps the device in this state while positioning it to the deployment site. When released from the catheter, the device is warmed by body heat and recovers its “preprogrammed” shape.

Constant Force (Stress)

As shown in Fig. 2, an important feature of superelastic Nitinol alloys is that their unloading curves are flat over large deflections (strains). This allows the design of devices which apply a constant force or load (stress) over a wide range of shapes. Stents deployed in vessels, therefore, exert an almost constant force independent of the amount of unresolved recovery (*note: it is typically recommended to use stents with diameters 1 to 2 mm larger than the vessel diameter*).

The orthodontic archwire was the first product to use this property. Stainless steel and other conventional wires are tightened by the orthodontist regularly. As treatment continues, the teeth move and the force applied by stainless steel wires quickly relax according to Hook's law. This causes treatment to slow, retarding tooth movement. Nitinol wires, on the other hand, are able to "move with the teeth", applying a constant force over a very broad treatment time and tooth position.

Dynamic Interference

Self-expanding Nitinol stents will always expand to their preset diameters with no recoil, while balloon expandable stents have to be overexpanded to achieve a certain diameter (due to the elastic spring-back after deflation). The Nitinol stent will continue to gently push outward against the vessel wall after deployment. Typically, the preset diameter of a Nitinol stent is about 1 to 2 mm larger than the target vessel diameter. It will, therefore, try to reach this diameter. Should the vessel grow in diameter, the Nitinol stent will follow until it reaches its final diameter.

Biased Stiffness (Force Hysteresis)

The most unusual feature of Nitinol alloys is the force or load hysteresis. While in most engineering materials load increases with deflection upon loading in a linear way and decreases along the same path upon unloading, Nitinol exhibits a distinctly different behavior. Force and deflection are normalized in Fig. 4 to illustrate this behavior schematically in a stress/strain curve. Upon loading, stress first increases linearly with strain up to approx. 1% strain. After a first "yield point", several percent strain can be accumulated with only a small stress increase. The end of this plateau ("loading plateau") is reached at about 8% strain. After that, there is another linear increase of stress with strain. Unloading

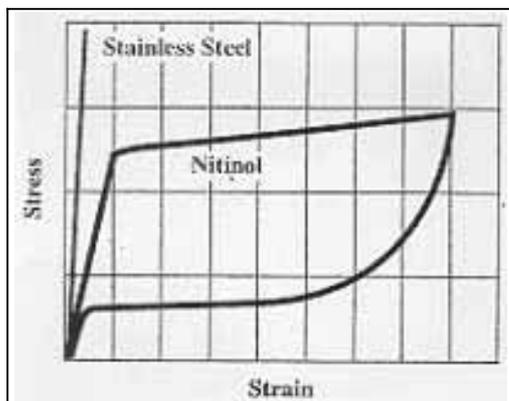


Fig. 4: Linear elasticity of steel and non-linear elasticity with stress hysteresis of Nitinol

from the end of the plateau region, causes the stress to decrease rapidly until a lower plateau ("unloading plateau") is reached. Strain is recovered in this region with only small decrease of stress. The last portion of the deforming strain is finally recovered in a linear fashion again. The unloading stress can be as low as 25% of the loading stress. For comparison, the straight line representing the linear elastic behavior according to Hook's law for stainless steel is shown in Fig. 4, too.

The "biased stiffness" of a stent made from superelastic Nitinol is illustrated in Fig. 5. A stent is compressed into the delivery system following the loading curve to point A. Upon release from the delivery system inside the vessel, it expands following the

unloading path of the stress/strain curve. At point B it reaches the diameter of the vessel lumen, appositioning itself against the vessel wall with a low outward force (COF, chronic outward force). As can be seen from the figure, this force remains nearly constant, even if the vessel would increase in diameter (dynamic interference). If the vessel contracts, through spasms for instance, or is compressed from the outside, the stent resists deformation with a higher force (RRF, radial resistive force). As such, the stress hysteresis of Nitinol allows the design of self-expanding stents with biased stiffness, meaning that the stents exert only low outward force, but resist deformation with a much higher force.

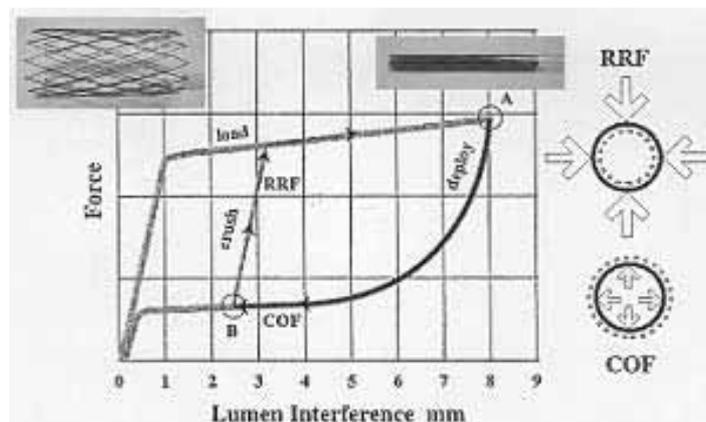


Fig. 5: "Biased stiffness" of a stent as a result of the stress hysteresis of Nitinol

Kink Resistance

Nitinol wires have been used in guidewires for their kink resistance and torquability since the early 1980s. These wires can be bent 10 times more than stainless steel wire without permanent deformation. For example, a 0.035" Nitinol wire can be wrapped around a ½ inch diameter mandrel without taking a set, while a stainless steel wire of the same diameter can only be bent around a 5 inch diameter mandrel without being plastically deformed.

Kink resistance is an important feature of Nitinol for stents in superficial vessels that could be deformed through outside forces. The carotid artery is a prime example. There is a perceived risk for balloon-expandable stents in carotid arteries to be permanently deformed through outside pressure resulting in a partially or completely blocked vessel, once the buckling strength of the stent is exceeded. Although Nitinol stents typically don't have the buckling strength of stainless steel stents, they cannot be permanently deformed through outside forces. Nitinol stents can be completely compressed (crushed) flat and will return to their original diameter when the deforming force is removed.

MRI Compatibility

Nitinol is non-ferromagnetic with a lower magnetic susceptibility than stainless steel. MRI compatibility is directly related to the susceptibility properties of a material, relative to human tissue. Therefore, Nitinol produces less artifacts than stainless steel, similar to pure titanium. Fig. 6 shows an MRI image of a partially deployed Nitinol stent (spin echo sequence, 0.2 tesla scanner) [3]. Most features of the stent are clearly visible. It has to be noted, however, that processing of the material can influence the quality of the MR image substantially.

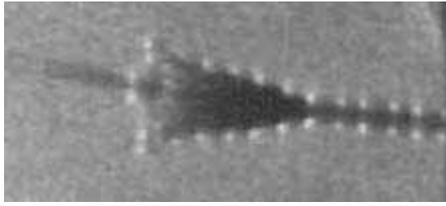


Fig. 6: MRI image of a partially deployed Nitinol stent [3]

Biocompatibility

Nitinol alloys contain more Nickel than stainless steels. This causes understandable concern, because Nickel is considered toxic. However, as Nitinol is an intermetallic compound and not an alloy in the metallurgical sense, the bonding force of Nickel to Titanium is much stronger than to the alloy components in stainless steel. Moreover, as Nitinol oxidizes after proper surface treatment, it forms a TiO_2 layer with no Nickel present at the surface [4]. Polarization testing in Hank's solution has repeatedly shown that Nitinol is chemically more stable and less corrosive than stainless steel [5]. In Europe and Asia, Nitinol components have been implanted in humans since the early 1980s, with vascular and non-vascular stents since the early 1990s. A few years ago, the Simon Vena Cava Filter (manufactured by Nitinol Medical Technologies) was approved by the FDA in the USA, as well as the Mitek Suture Anchor System, both permanent Nitinol implants. Recently, the FDA has approved the Nitinol Radius Coronary Stent, manufactured by Scimed.

Radiopacity

Nitinol produces a fluoroscopic image which is comparable to that of stainless steel, if the mass and dimensions of the parts examined are similar. Although sufficient in many cases, an improvement would be beneficial. While stainless steel can be gold-coated, for instance, with sufficient thickness to enhance radiopacity, layers of gold and other radiopaque materials might negatively influence the superelastic performance of Nitinol.

Conclusions

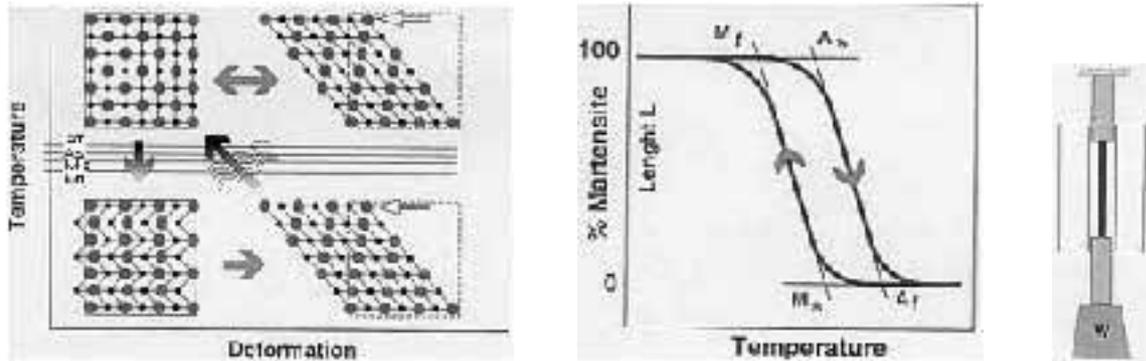
Nitinol offers an intriguing array of properties, not found in other engineering materials, that are useful for self-expanding stents. The medical device industry has recognized the potential of this material and uses it in a wide range of vascular and non-vascular stents, as well as for other devices and accessories.

References

- [1] Duerig TW, Pelton AR, Stöckel D. The utility of superelasticity in medicine. *Biomedical Materials and Engineering* 1996, 6:255-66
- [2] Shabalovskaya SA. On the nature of the biocompatibility and on medical applications of NiTi shape memory and superelastic alloys. *Biomedical Materials and Engineering* 1996, 6:267-89
- [3] picture provided by A. Melzer, Mühlheimer Radiologie Institut
- [4] Chan CM, Trigwell S, Duerig TW. Oxidation of an NiTi Alloy. *Surf. and Interf. Analysis* 1990, 15:349-54
- [5] Speck KM, Fraker AC. Anodic Polarization Behavior of Ti-Ni and Ti-6Al-4V in Simulated Physiological Solutions. *J. Dent. Res.* 1980, 59:1590-5

Shape Memory Basics

“Shape Memory” describes the effect of restoring the original shape of a plastically deformed sample by heating it. This phenomenon results from a crystalline phase change known as “thermoelastic martensitic transformation”. At temperatures below the transformation temperature, shape memory alloys are martensitic. In this condition, their microstructure is characterized by “self-accommodating twins”, a zig-zag-like arrangement. The martensite is soft and can be deformed quite easily by de-twinning. Heating above the transformation temperature recovers the original shape and converts the material to its high strength, austenitic, condition (see atomistic model, below left)



The transformation from austenite to martensite and the reverse transformation from martensite to austenite do not take place at the same temperature. A plot of the volume fraction of martensite, or more practically, the length of a wire loaded with a constant weight, as a function of temperature provides a curve of the type shown schematically in the Figure above (right). The complete transformation cycle is characterized by the following temperatures: martensite start temperature (Ms), martensite finish temperature (Mf), austenite start temperature (As) and austenite finish temperature (Af).

If stress is applied to a shape memory alloy in the temperature range above Af, martensite can be stress-induced. Less energy is needed to stress-induce and deform martensite than to deform the austenite by conventional mechanisms. Up to 10% strain can be accommodated by this process. As austenite is the stable phase at this temperature under no-load conditions, the material springs back into its original shape when the stress is no longer applied. This extraordinary elasticity is also called pseudoelasticity or transformational superelasticity.

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