Nickel-titanium alloys: properties and applications

Background

Nitinol, an approximately equiatomic alloy of nickel and titanium, is known for its unique deformation properties, namely shape memory and superelasticity. The name nitinol arose from its place of discovery (Nickel Titanium Naval Ordnance Laboratory), but as with many breakthrough materials, it came about through an act of serendipity. Its unusual shape memory properties were first discovered and described by William J. Buehler and Frederick E. Wang of the U.S. Naval Ordnance Laboratory between 1959 and 1965 [1], [2], while attempting to design a heat and impact resistant metal for missile nose cones. The NiTi alloy developed to meet these requirements was presented at a laboratory management meeting, at which one participant held his pipe lighter to a folded sample and found that it sprung back to its original shape [3]. This chance discovery sparked intense interest in nitinol over the following decades.

Today, nitinol is commercially available and is widely used in the biomedical, robotics, aerospace, and automotive industries, among others. Based on a 2017 report, the nitinol market for medical devices alone is projected to be around $24 billion by 2025 [4], positioning it as one of the most important and fastest-growing modern materials. Its unique properties relative to other metals also give it enormous potential to expand into novel fields and applications. This paper will begin by describing the fundamental theory behind the shape memory effect and superelasticity, the property whereby the metal acts as a “super spring” in a
certain temperature range, explain the methods used to process nitinol, and finally provide an overview of its applications in industry and the current frontiers in the research of nitinol alloys.

The shape memory effect and superplasticity in nitinol

There are two interconnected phenomena involved in the unique deformation properties of nitinol—the shape memory effect and superelasticity. This section will describe the fundamental mechanisms of each in the nickel-titanium system, and the properties that make nitinol the most important shape memory alloy for practical applications.

The shape memory effect was first observed by Arne Ölander in 1932 during a study of the electrochemical properties of gold-cadmium alloys [5]. However, the underlying mechanism was not well understood and the effect was not extensively studied until Buehler’s discovery of the phenomenon in nitinol, an alloy with much better mechanical properties and thus a greater potential for industry application. It took decades of intensive research before the phase transition behavior of the Ni-Ti system could be understood due to its extraordinary complexity. The Ni-Ti phase diagram is shown in Fig. 1 [6]. Nitinol is made in roughly equal atomic percent, typically between 50 and 51 at% Ni, placing it in the phase equilibrium region between NiTi and Ni₃Ti₄ very close to the NiTi intermetallic; the relevant region of the phase diagram for the shape memory effect and superelasticity is shown in the inset of Fig. 1.

One key requirement for both phenomena is that the alloy must undergo reversible and instantaneous martensitic phase transitions. The transitions occur between two key phases, an austenitic “parent” phase and a martensitic “daughter” phase. The parent phase is typically a simple cubic interpenetrated lattice and is energetically favorable at high temperatures, while
the daughter phase is of a lower symmetry and is present at lower temperatures. The process can be described by the thermomechanical hysteresis loops shown in Fig. 2 [7]. $M_s$ and $M_f$ represent the start and finish temperatures of the transformation to martensite during cooling, and $A_s$ and $A_f$ likewise for the austenite transformation during heating. The magnitude of the hysteresis is typically about 20–40°C, depending on the alloying composition, processing conditions, and other factors. The martensitic transformation is a shear-like deformation, as shown schematically in Fig. 3. This martensitic reorientation can result in a noticeable change in the material, as demonstrated by the fact that straight-line scratch on a specimen was observed to change direction after the martensitic transition (Fig. 4) [8]. In nitinol, the relevant transition occurs between the cubic B2 phase and the B19’ martensitic phase, which has a highly complex monoclinic structure [6].

The second key requirement for the shape memory effect to be possible is that the primary deformation mode of the low-temperature martensitic phase is twinning rather than slip. This is because slip deformation, which is driven by the movement of dislocations through the crystal, is irreversible. On the other hand, twinning refers to the highly-coordinated shearing of a section of the crystal lattice relative to a twin boundary (Fig. 5) [9],[10]. The transition from austenite to martensite results in a twinned lattice correspondence variant structure to mitigate the strain induced by the phase transformation, a process known as self-accommodation. This twinned martensite can then be de-twinned under stress, resulting in a new thermodynamically stable martensite structure and deformation of the material, as shown in Fig. 6 [11]. Crucially, this twinning mechanism promotes the full recovery of strain upon the reverse transformation from martensite to austenite. This property makes the shape memory
effect possible because in the low-temperature martensite phase nitinol can be deformed under an applied load, but as soon as the temperature increases above $A_s$, it undergoes the austenite transition and recovers to its original shape.

Superelasticity, also known as pseudoelasticity, is intrinsically tied to the shape memory effect and thus occurs in the same materials, including nitinol. At temperatures above $M_s$, the temperature-induced martensitic transformation is not possible. However, at these temperatures, stress can induce the transformation due to the fact that it occurs by a shear-like deformation mechanism as described above. Under external stress sufficient to overcome the free energy difference between the two phases, the material will assume a martensitic phase and allow significant twinning deformation. When the stress is released, the austenitic phase once again becomes favorable and the material recovers its original shape [6]. This superelastic phenomenon can allow for strains of over 20% in certain alloys, far greater than that of typical elastic materials [11].

Nitinol can exhibit both the shape memory effect and superelasticity, making it suitable for a wide range of applications. Whether a specific alloy is considered a shape memory alloy or a superelastic alloy depends on its transformation temperature, i.e., whether $A_f$ is higher or lower than the reference temperature for the application in question (typically either room temperature or body temperature). If $A_f$ is higher than the reference temperature, the nitinol acts like a shape memory alloy; otherwise, it is considered superelastic. The transformation temperature of nitinol varies widely depending on the alloy composition and processing conditions. Due to the fact that the martensitic transition is driven by both temperature and
stress, the transformation temperature is also impacted by any applied stresses on the material. This relationship is governed by the Clausius-Clapeyron equation:

$$\frac{d\sigma}{dT} = \frac{-\Delta H}{\epsilon T}$$

where $\sigma$ is the applied stress, $\epsilon$ is the strain of the material, and $\Delta H$ is the enthalpy of transformation per unit volume [6]. This results in a linear relationship between stress and transformation temperature, as shown in Fig. 7 [11].

Shape memory and superelasticity properties exist in many other alloy systems that exhibit martensitic phase transformations, such as Au-Cd, In-Tl, Cu-Zn, and Cu-Al-Ni. However, the Ni-Ti system is considered the most useful due to its unique thermal and mechanical properties. One of these properties is the unusually high ductility of TiNi relative to other intermetallics and shape memory alloys, with cold working of over 60% possible. This is due to a low elastic anisotropy of ~2 (compared to 10-20 for other shape memory alloys) and lattice softening near $M_s$, as well as the abundance of twinning modes that allow for high ductility in the martensitic phase [6]. Nitinol also exhibits superior corrosion and abrasion resistance along with its obvious thermomechanical advantages, making it an attractive material for a wide variety of applications.

**Nitinol processing**

The properties of nitinol are significantly affected by its process history. This includes not only control of the specific alloying composition, but also the conditions for processing the alloy in order to ensure that it retains its valuable properties. As mentioned above, alloy composition is critical, and it must be extremely tightly controlled during processing because
even a 1 at% change in nickel content can result in a 100°C change in transformation temperature (Fig. 8) [12]. Such a large change would likely render the alloy useless for its intended application. However, chemical analysis methods are not sufficiently precise to measure such small compositional changes, so the transformation temperature is measured by differential scanning calorimetry (DSC) and used to confirm the alloy composition.

It is very difficult to control the composition to such a degree of precision, particularly given titanium’s high reactivity with oxygen, carbon, and many other elements. Any impurities present during processing will likely result in titanium precipitating out of the melt and changing the alloy composition. The two most commonly used melting methods to maximize purity and homogeneity are vacuum induction melting (VIM) and vacuum arc remelting (VAR). VIM involves heating and stirring the melt in a crucible using induction coils (Fig. 9). While a small amount of carbon contamination occurs from the crucible surface, control of transformation temperature is possible to within 1–2°C. VAR melting involves continuous melting of a sacrificial electrode in a copper crucible (Fig. 10), resulting in a melt with very high purity but requiring multiple melting steps for homogenization.

Nitinol is then generally subjected to hot and cold working processes. Hot working serves to reduce size and increase ductility, shape memory, and superelasticity, while cold working provides the final shape and mechanical properties. However, in order to preserve the desired shape memory and superelasticity properties, an additional step of partial heat treating is required. To set the final shape of the “remembered” state, the material must be heat treated in a constrained position in a process called “shape setting” so that it can solidify in its
austenitic parent structure. This final heat treatment has the greatest effect on the final material’s properties, and is thus crucial in engineering the nitinol for its intended application.

**Nitinol applications in industry**

One of the biggest applications of nitinol is in the biomedical industry. Nitinol is a particularly appropriate material for medical devices and other in vivo applications due to its anti-corrosion properties and inherent biocompatibility. A concern with nickel-containing alloys is the diffusion of nickel into the body, as it has been shown to be toxic and allergenic in many cases. However, although some initial passive release of nickel from the surface has been measured, it rapidly becomes indetectable and the biological responses to nitinol have been generally positive. It is believed that this is due to the formation of a TiO$_2$-based surface oxide layer that helps prevent corrosion and nickel release [13]. This and many similar results have made nitinol a promising material for medical implants, and have led to several nitinol-based implants being approved by the FDA for clinical use [14].

Once its biocompatibility was established, nitinol’s unique mechanical properties made it an area of significant interest in a wide range of biomedical applications. Implanting devices into the body or performing endoscopic surgery in a minimally invasive way requires materials that are flexible enough to pass through very small openings, but strong and elastic enough to regain their shape when they reach their target locations [14]. Nitinol is the perfect material for such purposes, being more elastic than stainless steel due to the superelastic effect, but more able to hold its shape than flexible polymeric materials. Devices such as stents, which must expand to hold blood vessels to a certain diameter, can also take advantage of the shape
memory effect (Fig. 11). Nitinol stents with a transformation temperature just above room temperature (typically 30°C) can be manufactured in the austenitic phase to a diameter just larger than that of the blood vessel, then deployed in the martensitic phase (through a catheter for example). They then expand when they reach body temperature inside the blood vessel, becoming superelastic to match the body’s movements [15]. Eyeglasses and orthodontic wires exploit the fact that stress and temperature are directly related in nitinol (see Eq. (1)) to apply a constant stress over long time periods despite variations in strain and deformation [14].

One of the largest industrial applications of nitinol outside of medicine is in thermomechanical actuators, couplings, and fasteners. Such devices take advantage of the shape memory effect by deforming the material at low temperatures and then harnessing the work done during recovery under constrained conditions. Shape memory alloys such as nitinol are capable of generating significant pressure (over 500 MPa) if the martensitic transformation is physically constrained. This is due to the highly ordered lattice positions of the atoms in the NiTi intermetallic compound, and makes nitinol highly suited for use as thermal actuators [6]. Thin film nitinol-based microactuators were found to outperform other traditional microactuation methods in terms of work output per volume and cycling frequency [16]. In general, they have the highest power/weight ratio of all current actuator technologies. They also have the benefits of simplicity and silence of operation, cleanliness, remotability, temperature-sensing ability, and low driving voltage. However, they do have a low energy efficiency of less than 10%, a low response speed, and the possibility of fatigue in certain strain regimes (although nitinol exhibits longer fatigue life under intermediate-high strains than most conventional materials) [7]. Couplings and fasteners that shrink or expand to fit are also a large
area of application for nitinol, as such devices have many advantages, including ease of installation, light weight, and high strain resistance [17]. Couplings of this type have been widely used for tubing connections and sealing mechanisms in aerospace and other advanced industries.

Recent innovations in smart structural materials have incorporated NiTi-based shape memory alloys into civil engineering projects to provide damping and absorb seismic energy. The superelastic properties of nitinol allow it to have low strain and high stiffness under typical loads, a reduced modulus under intermediate strain to absorb stresses at moderate deformation levels, and control of deformation through the stress-induced martensitic transformation under high loads. Then, when the structure is unloaded, the alloy dissipates energy hysteresitically through the reverse transformation, helping to control seismic stresses [18]. These properties can be similarly leveraged in any structural engineering application that requires damping, energy dissipation, or deformation control. One example of an innovative use of nitinol wires in civil engineering is that of Intelligent Reinforced Concrete (IRC). Introduced by Song and Mo, IRC measures the strain distribution in the concrete using the electrical resistance of the shape memory alloy wires. If the system detects cracking or damage to the concrete structure, the wires are electrically heated to induce the martensitic phase transformation and close the cracks (Fig. 12). The IRC system was shown to be effective on macro-scale cracks, illustrating the potential of nitinol for use in smart materials [19].

**Conclusion**
Nitinol is a unique material in that it exhibits the phenomena of shape memory and superelasticity, as well as excellent mechanical and thermal properties, corrosion resistance, and biocompatibility. This special combination of properties, arising from the complex process of martensitic phase transformations, make it able to recover fully from large deformations, generate significant work in constrained configurations, and exhibit superelastic ability. These abilities have led to it becoming one of the fastest-growing materials in industry today. With increasing amounts of resources and funding dedicated to cutting-edge shape memory alloy research, it can be expected that nitinol will continue to have a sustained impact on medicine, robotics, and materials science as we move increasingly into the era of “smart” structural materials.

References


Figures

Figure 1. Phase diagram of Ni-Ti alloy system; inset shows the relevant region for nitinol [6].

Figure 2. Thermal hysteresis loop of austenite-martensite transformations, including the temperature response of both martensite composition and strain [7].
Figure 3. Schematic of the martensitic transformation, showing the coordinated motion of atomic planes. Note that the two martensite phases are mirrored structures [8].

Figure 4. Illustration of martensite phase transition causing surface relief and linear transformation of scratch in sample surface [8].
Figure 5. Illustration of twinning deformation, showing the shear movement of atomic lattice positions such that the twin lattices are mirrored across the boundary [10].

Figure 6. Mechanism of the shape memory effect; the twinned martensite initially self-accommodates and does not change shape until a stress is applied [11].

Figure 7. Stress–transformation temperature relationship for martensitic transformation [11].
Figure 8. Plot of Ni content vs. transformation temperature of NiTi; the shaded region represents typical compositions for medical applications [12].

Figure 9. Schematic of vacuum induction melting (VIM) process [12].
**Figure 10.** Schematic of vacuum arc remelting (VAR) process [12].

**Figure 11.** (a) Cutaway view of a deployed arterial stent, (b) example of the recoverable deformation possible in nitinol stents [15].

**Figure 12.** Intelligent Reinforced Concrete: (a) schematic of design, (b) the cracking that appears under loading of an IRC beam, and (c) the crack closing when load is released [19].