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# Shape-Memory Alloys: Forming a Tight Fit

Alloys that alter their shape in response to temperature changes are being made into fasteners, clamps, and seals that offer low-temperature installation, accurate and predictable stress response, immunity to vibration, shock and thermal cycling, wide operating temperature range, and low installed cost.

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hape-memory alloys (SMA) are a unique family of metals with the ability to change shape — and return to their original shape--depending on their temperature. This property, which is unrelated to, and far more dramatic than, thermal expansion makes SMAs ideally suited for use as fasteners, seals, connectors, and clamps.

SMAs include copper aluminum nickel, copper zinc aluminum, iron manganese silicon, and nickel titanium. The most useful SMAs are based on a nominal composition of 50/50 atomic percent nickel titanium. The information in this article is based on the properties of Raychem Corp.'s Tinel family of nickel titanium alloys. Depending on the alloy and its processing, Tinel can be deformed five to seven percent in tension, compression, or shear. Heated beyond a critical temperature, the metal returns to its original memory shape and, if resisted, can generate stresses as high as 700 MPa (100 kpsi).

This unique effect is produced by a crystalline phase change known as a martensitic transformation. The transformation occurs over a range of temperature, above which the material is in the austenitic phase and below which it is in the martensitic phase. The geometric shape of the material when austenitic is its memory shape. Martensite forms on cooling from austenite by a shear process. If stress is not applied to the material during cooling, its macroscopic shape does not change. The martensite forms in several different orientations called twins, each with alternating senses of shear. It is the alternating nature of these twins that allows the martensitic transformation to occur without an external shape change.

By causing a "flipping over" type of shear, a low applied stress can easily deform these twins into a single orientation, as illustrated in Figure 1. This deformation is reversible, that is, it involves no permanent plastic deformation. The strain available from the deformation is the same five to seven percent that can be realized on a macroscopic level. This deformed martensite will hold its shape indefinitely, as long as the temperature of the material is held below the transformation temperature of the alloy.

If the deformed martensite is now heated through its transformation temperature range, it reverts to austenite. However, the austenitic crystalline structure cannot accommodate the deformation that was applied to the martensite. The material must return to its original memory shape as it reverts to austenite. This cycle of cooling, deformation, and shape recovery is the fundamental shape-memory process.

The more familiar martensitic materials cannot be deformed in this manner. In most steels, for example, the formation of martensite is associated with a substantial increase in hardness. This martensite is "locked in" so that reorientation by simple shear cannot easily occur.

### **Macroscopic Deformation**

The deformation mechanism of the martensite is manifested macroscopically by the stress-strain curve of a shape-memory alloy, as shown in Figure 2. The martensitic curve shows an initial low yield, on the order of 70 MPa (10 kpsi), which is the stress required to reorient the structure. Beyond this, several percent strain is accumulated with little stress increase. The reorientation process is essentially complete at the end of this plateau. Subsequent deformation is conventional elastic loading followed by permanent plastic deformation at higher stresses. In the austenitic phase, this twin reorientation mechanism is not available, so the yield strength is much higher from 410 to 700 MPa (60 to 100 kpsi). Typical elongation to failure is 25 percent.

Figure 3 illustrates the stretching, unloading, and subsequent recovery to austenite by heating. Two possible recovery curves are shown. In one (dashed "recover" line), the material is allowed to return freely to its memory shape at zero stress. In the other (solid "recover" line), which is what would happen when an SMA clamp is heated, the material is allowed to recover partially, then is constrained. The material consequently builds up stress in attempting to return to its memory shape.

The stress generated is a function of the final strain, or unresolved recovery. Figure 4 plots this function. At unresolved recoveries less than 1.5 percent, the stress rises rapidly with strain. Above this point, a plateau is reached where stress increases only slightly with increasing strain. This plateau stress is on the order of 410 MPa for most alloys.

It is no coincidence that the stress-versus-unresolved recovery curve looks much like the austenitic stress-strain curve. During constrained recovery, the nickel-titanium alloy yields itself in trying to recover to its memory shape. The stress produced is about 85 percent of the corresponding stress from the austenitic stress-strain curve. Because the material has yielded during constrained recovery, it will now



Figure 1. Schematic of crystal structures.



have a new memory shape. This new shape will be smaller than the constraint size by the amount of stored elastic strain in the nickel titanium alloy part.

For example, given a recovery stress of 410 MPa and an austenitic elastic modulus of 83 GPa  $(12 \times 10^6$ psi). this elastic interference will be 0.5 percent. If a part were recovered at 3 percent unresolved recovery and the constraint subsequently removed, it would spring down to a size that is 2.5 percent larger than its original memory shape.

Transformation to martensite, deformation of martensite, and recovery to austenite are all essentially constant-volume processes. So, as a previously stretched part is recovered, its cross-sectional area will increase one percent for every one percent that the part decreases in length.

### Transformation Temperatures

The temperature at which the material transforms from martensite to austenite is controlled by alloy composition and processing. There is a hysteresis between the heating curve (martensite to austenite) and the cooling curve (austenite) and the cooling curve (austenite to martensite). The temperature at which martensite begins to form is called the martensite start temperature,  $M_s$ . Similarly, the temperature at which austenite begins to form is called  $A_s$ .

A ring made of a material with an A, of 50°C and an M, of 30°C would be martensitic at room temperature. It could be expanded to a larger diameter and held indefinitely at temperatures up to 50°C. If the ring were placed over a substrate with a diameter larger than the memory diameter of the ring and heated to above 75°C (167°F). the ring would recover and be locked in place. However, when the ring cooled back down to room temperature it would transform back to martensite and its gripping force would be reduced to an unusable level.

To make a practical fastener, a low-transition-temperature alloy is required. The reversion to martensite must take place at a temperature lower than the minimum required operating temperature of the installed ring. A ring made of this "cryogenic" alloy, which consists of nickel, titanium, and iron, would be expanded at a temperature less than  $-125^{\circ}C$  ( $-193^{\circ}F$ ). Such a ring would typically be kept in a dewar of liquid nitrogen until ready for installation. Put in place and warmed to room temperature, it would recover,

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shrinking onto the substrate. As long as the temperature of the ring stayed above  $-125^{\circ}$ C it would maintain its grip. Since  $-65^{\circ}$ C ( $-85^{\circ}$ F) is the likely minimum ambient temperature, except for some very specialized applications, this material could be made into useful fasteners.

For some applications, cryogenic installation is an advantage. However, in many instances, assembly procedures do not allow use of a part that will recover shortly after it is removed from a dewar. Because of this limitation, Raychem developed a new heat-to-recover (HTR) alloy consisting of nickel, titanium, and niobium, which has an extremely wide one-time hysteresis. The deformed martensitic ring can be stored or handled at temperatures up to 50°C (122°F). The ring is heated for installation. At just above 50°C the ring begins to transform to austenite. To generate full recovery stress, the ring is heated to 165°C  $(330^{\circ}\text{F})$  or  $220^{\circ}\text{C}$  ( $430^{\circ}\text{F}$ ), depending on the alloy. Products composed of this HTR alloy are typically marked with thermochromic paint, which changes color when the part has been heated sufficiently. Once installed, the part maintains its grip down to  $-100^{\circ}$ C ( $-148^{\circ}$ F).

The cryogenic alloy and the HTR alloy can be made into fasteners with equivalent installed performance. The choice between the two is based primarily on the logistics of installation.

## Stress-Temperature Relationship

The transformation temperature of a given alloy is actually a function of the stress applied to it. An applied stress increases the transformation temperature, just as applying pressure to water raises its boiling temperature. The typical rate of increase for M, and A, is  $0.14^{\circ}$ C/MPa  $(1.8^{\circ}$ F/kpsi). For example, the cryogenic alloy with a  $-125^{\circ}$ C M, at zero stress would have an  $M_s$  of  $-86^{\circ}$ C  $(-121^{\circ}$ F) when under a 275-MPa (40-kpsi) stress.

Consider a stress-strain test of this same material at  $-86^{\circ}$ C. At the start of the test, the material is fully austenitic. As the stress is gradually increased. the material will remain austenitic until the stress reaches 275 MPa, at which point martensite will begin to form and the material will begin to deform in response to the stress. Martensite produced this way is called stress-induced martensite.

This stress-temperature dependence has implications for shapememory fasteners. A ring of the



Figure 3. Deformation of rnartensite, unloading, and recovery to austenite.



Figure 4. Recovery stress versus unresolved recovery

cryogenic alloy installed on a rigid substrate with a recovery stress of 410 MPa will have an  $M_s$  of  $-67^{\circ}$ C ( $-88^{\circ}$ F), as calculated using the stress-temperature dependence described earlier. As the assembly is cooled from room temperature, the stress will be constant until  $-67^{\circ}$ C is reached. At this point, the stress in the ring will begin to decay at a rate of 7 MPa/°C (0.55 kpsi/°F), until  $-125^{\circ}$ C is reached and the stress has gone essentially to zero.

This effect can be used to produce dematable fasteners that grip down to the design minimum ambient temperature but release on further cooling from a cryogenic medium such as liquid nitrogen.

This stress-temperature relationship also manifests itself during the initial recovery of a ring onto a substrate. An expanded ring of the cryogenic alloy would begin to shrink in diameter at  $-100^{\circ}$ C. At a temperature several degrees above this, the ring would come into contact with the substrate. As the temperature continued to rise. the stress in the ring would increase at the rate of 7 MPal°C until the full recovery was achieved.

### Elastic Modulus

Stress-induced martensite is not the only factor that controls stress in a fastener design. There is also a significant variation in elastic modulus with temperature. At temperatures more than 250°C (450°F) above the zero-stress transformation temperature, the elastic modulus of nickel titanium alloy is 83 GPa. As the fastener cools toward  $M_s$ , the modulus decreases. At  $M_s$ , the modulus is on the order of 21 GPa (3×10<sup>6</sup> psi).

Consider the cryogenic ring recovered on a constraint that is rigid

and has the same coefficient of thermal expansion as nickel titanium alloy. As the assembly cools, the elastic interference remains the same and the alloy modulus decreases. Since the stress is equal to the strain multiplied by the modulus. the stress in the nickel titanium part will decrease in direct proportion to the modulus. The modulus of this alloy would be about 38 GPa  $(5.5 \times 10^6 \text{ psi})$  at  $-55^{\circ}\text{C}$  ( $-67^{\circ}\text{F}$ ). Thus, a part with an initial installed stress of 410 MPa would decline to 190 MPa (27 kpsi) at  $-55^{\circ}$ C. This stress is below the 410 MPa that would be required to stress-induce martensite. In this example, it is only when approaching zero-stress  $M_s$ that stress-induced martensite overtakes the stress decay due to the modulus change.

During cooling, the stress change in a nickel titanium ring is also affected by the difference in thermal expansion coefficients between the alloy and its substrate and by the compliance of the substrate. If the coefficient of thermal expansion of the substrate is less than that of the nickel titanium alloy, the stress will decline more slowly during cooling. If the substrate is elastically deformed by the **SMA** ring, this stored elastic energy will cause the stress to fall off more slowly.

There is no significant hysteresis in the variation of modulus with temperature. Therefore, the stress decay during cooling will be recovered on heating. This is just as true for multiple cool-heat cycles as it is for a single cycle.

### Shape-Memory Alloy Advantages

A unique combination of properties gives shape-memory alloys a variety of advantages over conventional fastening techniques: larger tolerances on mating parts; operatorinsensitive assembly; low-temperature installation; accurate and predictable stresses; immunity to vibration, shock, and thermal cycling; wide operating temperature range; and lower installed cost.

The large recovery strains available in shape-memory alloys make it possible to accommodate large tolerances and clearances on mating parts. The five to seven percent shape-memory strain is an order of magnitude larger than the 0.5 percent strain typically available in thermal shrink-fit installations. The looser tolerances and more generous clearances allowed with shape-memory materials lead to cheaper moreproducible parts that are easier to as-



semble than thermal shrink-fits. While the motion available from an SMA ring is large relative to thermal expansion or elastic strains, it is often the limiting factor in SMA fastener design. Some applications require more motion than a ring can deliver due to large tolerances, clearances, or compressibility relative to

the substrate diameter. Fastener rings are typically designed with a minimum of 1.5 percent unresolved recovery so that they operate on the stress plateau illustrated in Figure 4. The stress generated is thus relatively independent of the tolerances of the parts onto which the rings are recovered. This, coupled with the fact that recovery stress is a fundamental property of the material. means the fastener ring clamping force is extremely predictable and consistent.

As installed, fasteners based on crimping, elastic deformation, and differential thermal expansion usually operate on the elastic portion of their stress-strain curves. Because of the steepness of the curve, a small change in strain produces a large variation in stress. Consider a 0.1 percent variation in installed strain due to tolerances of the mating parts. In an elastically stressed steel part, the stress could vary by 207 MPa (30,000 psi). In a shape-memory part, such a variation in strain would cause a variation in stress of less than 13.8 MPa (2000 psi).

Because shape memory is present throughout the material in a ring, the stress generated by constrained recovery is uniform around its circumference. Press-fit and thermal shrinkfit rings offer the same benefit. However, installation logistics or the need for significant radial motion often precludes the use of these techniques. When compared with multipoint crimping, split clamps, or hose clamps, the stress applied by a nickel titanium ring is much more uniform. For this reason, sealing of cylindrical parts has been a highly successful application of this technology.

The monolithic nature of SMA ring fasteners also eliminates vibration loosening, one of the biggest drawbacks of threaded fasteners. A ring simply cannot come apart in the way that a nut unscrews from a bolt.

Because of the low modulus and high recovery stress of nickel titanium. installed shape-memory rings have a large residual elastic interference with their substrates. This means that the rings will be highly resistant to the effects of thermal cycling and vibration. As the substrate changes dimensions under these conditions, the ring's excess of stored elastic energy allows it to follow the excursions while maintaining a relatively consistent level of stress.

A nickel titanium ring typically has an elastic interference with its substrate of 0.5 percent. This compares with 0.13 percent strain for 316 stainless steel at its yield stress. A 0.05 percent decrease in the effective diameter of the substrate would decrease the stress in a steel ring, initially at yield. by 40 percent and in a nickel titanium ring by 10 percent. In a typical crimped, elastic, threaded, or shrink-fit application. the conventional fastener probably will be operating at a stress well be-



Figure 6. Assembly of piezoelectric accelerometer.

low yield, once installed. The initial elastic interference will likewise be suboptimal.

Nickel titanium can be installed at low or cryogenic temperatures. Possible alloys for fasteners are installed either by warming from cryogenic temperatures or by heating to 165°C. This can be a considerable advantage over welding, brazing, or soldering. Soldering requires heating the mating parts to temperatures above 200°C (392°F). Brazing requires temperatures above 760°C (1400°F). As a result, many applications of SMA fastener rings involve heat-sensitive materials such as electronic circuitry, polymeric materials, and pyrotechnics.

The installation of shape-memory rings is extremely operator-insensitive. Installation requires that the ring be positioned properly, then be warmed to installation temperature. Typically, a thermochromic paint indicator is used on HTR parts to signal when heating is complete. The performance of a shape-memory fastener is determined when it and its mating parts are manufactured, not when they are assembled. This is markedly different from craft-sensitive techniques such as soldering and welding and from tooling-sensitive techniques such as crimping and threaded fastening.

Shape-memory alloys have an operating temperature range from  $-65^{\circ}$ C to more than 300°C (570°F). The low end is limited by stress decay due to the elastic modulus decline or martensite formation. The top end is limited by thermally activated stress relaxation of the alloy. This range is much wider than that provided by soldering, adhesives, or many mechanical systems.

Shape-memory alloy rings are attractive for fastening applications because when compared with conventional fastening techniques, they offer high diametral motion, provide consistent stress generation, apply uniform radial pressure, produce large residual elastic interference, have low installation temperatures, provide operator-insensitive installation, and exhibit wide operating temperature ranges.

### **Fastener Applications**

A wide variety of fastener applications for nickel titanium have been introduced. Examples include braid termination, shaft-mounted components, radial assembly, hermetic sealing, electrical connectors, and hose clamps.

### **Braid Termination**

In braid termination, HTR rings are used to attach electromagnetic interference cable-shielding braids permanently to the backshells of connectors. A ring can be recovered in several seconds using a resistance heater, which drives a large current at low voltage through the ring. This provides a joint with a dc resistance of well under 1 milliohm and a tensile strength of 890 newtons (200 pounds). High-frequency shielding is optimal due to the 360-degree peripheral contact between the braid and adapter. The joint is insensitive to ambient temperatures from -65" to 150°C (-85" to 300°F) and to mechanical shock and vibration.

The primary advantages of this

system are:

Operator- and tooling-insensitive installation as compared to soldering, hose clamps, and other mechanical fastener methods.

- Quick installation.
- Small size and low weight.

• Long-term reliability and resistance to severe environments.

### Shaft-Mounted Components

When assemblies are made up on shafts, an axially adjustable locating collar is often needed to take up the accumulated tolerances of the components on the shaft. In addition, it is often necessary to apply a controlled axial preload to the stack of components, so that the bearings will function properly.

This problem has traditionally been addressed with threaded fasteners, thermal shrink-fit rings, and snap rings (spring-retaining rings). All three of these methods, however, have limitations. Threaded fasteners are bulky. They often have an eccentric mass that makes them unsuitable for use on high-speed rotating equipment. And they must be torqued precisely when installed to function properly. Even then they are susceptible to loosening.

Thermal shrink-fit collars, on the other hand, require close tolerances on the shaft and collar to insure a consistent grip on the shaft. The assembly sequence is restricted by the short time available to install the collar before it cools down. This makes the technique especially difficult to use in very small assemblies such as gyroscopes.

Snap rings, the third traditional fastener type, present several difficulties. When used with a groove, they cannot take up axial tolerances. Oversize snap rings have been designed for use on smooth shafts, but they have very limited holding capacities. At high rpm, snap rings loosen due to centrifugal force.

In contrast, shape-memory collars provide the best solution to the problems posed by shaft-mount components. The installation procedure is to slip the collar onto the shaft, preload the collar and components, and heat the collar to lock it in place. Figure 5 shows a nickel titanium ring locking in the angular and axial location of a gear blank on a shaft. Next to it is a mechanical clamp, which has about 30 percent less torque and tensile strength.

### **Radial Assembly**

Another area where shape-memory alloy rings offer an advantage is the radial clamping of angularly seg-



Figure 7. Hermetic seal of thin-walled canister to header.

mented assemblies. One example is the accelerometer pictured in Figure 6, where the ring clamps mass elements and piezoelectric elements against a center post. Other examples include magnet assemblies for motors and solenoids and various types of sensors.

Angularly segmented assemblies typically use thermal shrink-fit rings, press-fit rings, or adhesive bonding. However, the tolerance stack-up of the components makes it difficult to get a consistent clamping force with a thermal shrink-fit. It is difficult to maintain the proper positioning of all of the components during a press-fit ring installation. Adhesive bonding often produces results, and inconsistent the operating temperature range is limited.

The use of an **HTR** shape-memory ring, however, leads to consistent product performance with reduced rework rates. This, combined with the looser tolerances permissible, results in significantly reduced manufacturing costs.

### **Hermetic Sealing**

It is often difficult to seal thinwalled metal cylinders to metal, ceramic, and plastic substrates. This type of construction is widely used in the packaging of gyroscopes, fuses, detonators, infrared detectors, batteries, and electronics packages. Organic sealing methods such as Orings, gaskets, adhesives, and sealants do not produce true hermetic seals. Soldering, brazing, electron beam welding, and other sophisticated welding techniques are currently used for metal-to-metal seals. However, these techniques are often difficult in terms of capital expense, sealing yield, contamination, and overheating of the package contents.

Shape-memory alloys offer an alternative sealing technique. One possible sealing geometry is illustrated in Figure 7. Here a shape-memory ring swages a cylinder into a groove cut in a header. Two seals, one of which is redundant, are achieved at the corners of the groove where the material of the cylinder and the bulkhead are plastically deformed into each other.

The advantages of this method include:

- Simple installation tooling.
- Low-temperature installation.
- Loose tolerances on mating parts.

• No contamination of the package internals.

Low leakage rate.

• Allows sealing of dissimilar materials, such as an aluminum canister to a Kovar leader. Kovar is a nickelbased alloy made by Carpenter Technology Corp. (Reading, Pa.).

### **Electrical Connector**

High-amperage electrical connections in harsh thermal and vibration environments often suffer reliability problems. Screw terminals are typically used but are prone to loosening. Nickel titanium rings can be used to make semipermanent connections for this application. When recovered, the **HTR** ring compresses a copper alloy collet onto a mating pin. The ring exerts a very high normal force, producing a gas-tight seal between the contact surfaces and a connection with a very stable low resistance. The high normal force also results in a high pin-retention force and high vibration resistance.

The connector is designed to be semipermanent. If it must be demated, the ring can be pushed or cut off. This type of connector can also be demated by chilling the ring with liquid nitrogen, which relaxes the ring and opens the collet. In this way the connector can be mated and demated repeatedly. While liquid nitrogen is considered impractical for some applications, it is used for many high-reliability connectors in military applications.

### Hose Clamp

Nickel titanium bands offer an attractive alternative to conventional hose clamps when performance is the chief concern. The foremost advantage is that nickel titanium bands are a continuous 360-degree structure. The closure mechanism on conventional hose clamps produces a discontinuity in the radial pressure exerted by the clamp. This can lead to a leakage path, especially when the hose is thin or made of a lesscompliant material. With its high force and 360-degree pressure, an SMA band can terminate a thinwalled composite duct to an aluminum fitting.

The closure mechanism of traditional clamps also represents a discontinuity on the outside diameter of the assembly. If the clamp is rotating, as in the case of boot closures in automotive applications, the closure has the potential to catch on loose objects such as road debris. Because the hoop tension of conventional clamps is limited by the closure, the stress level in the strap portion of these clamps is very low. This means the strap material is not being used efficiently, so for the same clamping pressure, a nickel titanium band will be much smaller than a conventional clamp. Also, there is very little stored elastic energy in some types of hose clamps. This makes them susceptible to loosening due to differential thermal expansion and to cold flow of the hose material.