Kirk-Othmer Encyclopedia of Chemical Technology.

SHAPE-MEMORY ALLOYS

1. Phenomenology

As the name suggests, the shape-memory effect (SME) refers to a phenomenon wherein a material on being mechanically deformed and then heated, "remembers" and returns to a preset shape. Associated with this behavior is the superelastic or pseudoelastic effect (SE) wherein large and completely recoverable strains are generated mechanically rather than thermally. Both these effects are associated with the martensite transformation, a first-order displacive transformation usually related to the hardening of steel. In steel, an alloy heated to the temperature where the elevated temperature face-centered cubic (fcc) austenite phase is stable, is rapidly cooled to produce the hard martensite phase. In SME alloys, however, the martensite transformation is thermoelastic and the martensite forms and disappears on heating and cooling over a relatively small temperature range. The intermetallic phase in these alloys undergoes a displacive, shear-like transformation when cooled below a critical temperature designated as M_{S} (martensite start). Upon further cooling, to a temperature designated as M_{F}(martensite finish), the transformation is complete and the alloy is said to be in its martensitic state. When this martensite is deformed, it undergoes a strain that is completely recovered when the alloy is heated. This recovery is due to a reverse transformation to the corresponding austenite phase. The recovery process starts at the temperature A_{S}(austenite start) and is completed at a higher temperature, A_{F}(austenite finish). This is a first-order phase transformation and there is hysteresis associated with the formation of martensite and its reverse transformation to the elevated temperature parent austenite phase. The temperatures M_{S}, M_{F}, A_{S}, and A_{F} depend on the particular alloy, alloy composition, and processing. The hysteresis loop associated with the transformation in a typical SME alloy is illustrated in Figure 1.

The martensite in shape-memory alloys (SMAs) may also be isothermally generated by applying stress at a temperature above M_{S}. Large strains are usually associated with this stress-induced transformation. Upon unloading (or removal of the stress), the stress-induced martensite (SIM) is no longer stable and reverts to the parent austenite phase with concomitant recovery of all the strain. The strains involved are typically large (up to 8%) when compared to similar material systems and are different in that they do not involve elasticity associated with conventional stretching of interatomic bonds. Hence, the superleastic or pseudoelastic nomenclature. Above a temperature designated as M_{D}, martensite cannot be generated, no matter how high the stress.

Another property associated with SMAs is the linear superelastic effect (LSE), which is distinguished from the SE. Many of the martensitic alloys, when deformed well beyond the point where the initial single coalesced martensite has formed, exhibit a stress-induced martensite-to-martensite transformation. In this mode of deformation, strain recovery occurs through the release of stress, not by a phase change. This behavior has been exploited for medical devices and typical stress–strain responses are linear with reduced hysteresis.

SME and SE are unique in the operative mode of mechanical deformation. Conventional metallic materials deform elastically (by stretching the interatomic bonds) or plastically (by rearranging the atomic lattice through

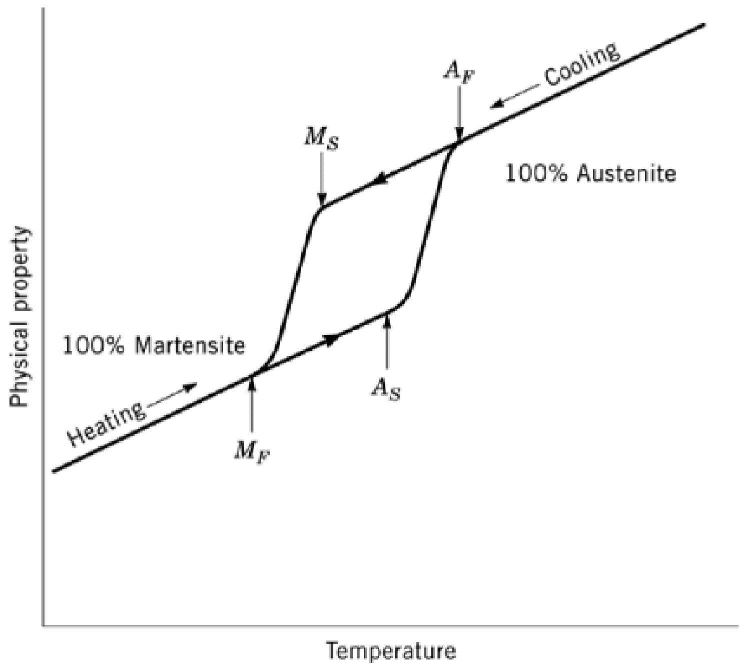

Fig. 1. Schematic of the hysteresis loop associated with a SME transformation, where M_S and M_F correspond to the martensite start and finish temperatures, respectively, and A_S and A_F correspond to the start and finish of the reverse transformation of martensite, respectively. The physical property can be volume, length, electrical resistance, and so on. On cooling, the austenite (parent) phase transforms to one of the various martensite structures.

dislocation, slip or grain boundary motion). Mechanical deformation in SMAs involves phase transformation and/or twinning and results in the SME and/or the SE. Twinning is an imperfection in polycrystals involving the intergrowth of two or more polycrystal grains so that each grain in a twinned system is a reflected image of its neighbor. In essence, twinning is a special type of grain boundary defect where a polycrystal grain is joined to its mirror image. Additionally, these alloys exhibit excellent damping properties. Damping is the property that causes a vibration, once induced in a material, to decay. Bell bronzes have a specific damping capacity of $<1\%$, a gray cast iron formulated for use as a machine-tool bed for resistance to vibration might have a specific damping capacity of 10%. By contrast, SMAs can have a damping capacity of $>40\%$. This characteristic can be exploited in smart or adaptive materials (see Smart materials (Supplement)). Damping is the result of the high mobility of the interfaces between martensite variants or plates (crystallographic orientations). When martensite is stressed, the deformation is accompanied by the growth and shrinkage of martensite variants or the motion of twin boundaries. When subjected to an oscillating stress these mobile boundaries move back and forth, giving rise to a frictional loss that accounts for the damping.

Simple shape-memory behavior, ie, one-way memory, may be extended to two-way memory. When a deformed martensite is heated to austenite to recover its original shape, it is a one-time event; to repeat the sequence the SMA must be cooled and the martensite must again be deformed. In two-way memory, the part spontaneously changes from one shape to another upon cooling or heating. This behavior, requiring a special conditioning or biasing of the martensite, is effected by limiting the number of martensite variants that form upon cooling through the application of an external stress during the transformation. The stress favors the initial formation of selected variants, similar to the stressing of a martensite group causing the selective growth and shrinkage of suitably oriented plates. Limiting the number of variants formed reduces the

Table 1. Nonferrous SMAs[a]

Alloy	Composition,[b] atomic %	Crystallographic structure change[c]	Hysteresis, ΔT, °C
Ag—Cd	44–49 Cd	B2–2H	15
Au—Cd	46.5–50 Cd	B2–2H	15
Cu—Zn	38.5–41.5 Zn	B2–9R	10
Cu—Zn—X[d]		B2(DO_3)–9R, M9R, 18R, M18R	10
Cu—Al—Ni	28–29 Al, 3–4 Ni	DO_3–2H	35
Cu—Sn	15 Sn	DO_3–2H, 18R	
Cu—Au—Sn	23–28 Au, 45–47 Zn	Hesuler–18R	6
Ni—Al	36–38 Al	B2–3R	10
Ni—Ti	49–51 Ni	B2–rhombohedral; B2–monoclinic	1–2; 10–100
In—Tl[e]	18–23 Tl	fcc–fct	4
In—Cd[e]	4–5 Cd	fcc–fct	3
Mn—Cu[e]	5–35 Cu	fcc–fct	

[a] Alloys are ordered except where noted.
[b] To determine the percentage of the remaining constituents, subtract from 100%.
[c] Fct = face – centered tetragonal.
[d] A few atomic % of $_{X = Si}$, Sn, Al, or Ga, plus 38.5–41.5 atomic % Zn.
[e] Alloy is disordered.

self-accommodating feature of the transformation and increases the residual internal stress. By repeating the cycle a number of times, referred to as the training process, the restricted variant group and its associated internal stress spontaneously revert to the parent phase on heating and then to a singular martensite on cooling.

2. Crystallography and SMA Systems

The SME was first reported in 1951 involving a Au—Cd alloy (1). Many other alloys exhibiting this behavior have since been discovered; some of these are listed in Table 1. It was, however, the discovery of the SME in the near-equiatomic Ni—Ti alloy that led to large-scale commercial applications. This alloy is usually called Nitinol, after Ni—Ti Naval Ordinance Laboratory where it was first investigated (2). Nitinol and its variations are the most frequently employed shape-memory alloys, although two other SMA systems based on Cu— Zn—Al and Cu— Al—Ni, also find use in special applications. Nitinol is relatively expensive, owing to the extremely tight composition control required to prepare an alloy having specific transformation temperatures. A difference of 1 at.% in the relative Ni and Ti compositions can shift transformation temperatures by up to ~150°C. Copper-based SMAs were developed as less expensive alternatives. Although these alloys were employed for a period as actuators of various designs, shortcomings related to fatigue strength and thermodynamic stability restrict use. Certain ferrous alloys, listed in Table 2, have also been discovered. These are potentially less expensive SMA candidates, but as of 2002 have not achieved broad commercial use.

SME involves a martensitic transformation from an ordered parent phase to an ordered martensite that is crystallographically reversible and thermoelastic, although there are a few exceptions to the requirement of ordering for nonferrous alloys (Table 1), and more exceptions for the ferrous SMAs (Table 2). In some alloy systems, the various martensites are internally faulted or internally twinned and can possess different crystal structures, the most common being 2H, 3R, 9R, 18R, monoclinic, and rhombohedral. An initial parent phase transforms to self-accommodating martensite plates, which can be characterized eg, by six plate groups, each plate group consisting of four variants. Owing to the self-accommodating nature of the transformation, the average shape deformation in a particular plate group is near zero. A body-centered cubic (bcc) parent phase that initially transforms to an ordered B2 or DO_3 phase is the dominant precursor or parent for SMAs. This

Table 2. Ferrous SMAs Having Perfect or Near-Perfect SME

Alloy	Composition,[a] at %	Crystallographic structure change[b]	Ordering
		Small hysteresis	
Fe—Pt	25Pt	LI_2–ordered bct	ordered
Fe—Pd	30Pd	fcc–fct	disordered
Fe—Ni—Co—Ti	33Ni—10Co–4Ti[c]	fcc—fct	disordered
		Large hysteresis	
Fe—Ni—C	31Ni—0.4C[c]	fcc–bct	disordered
Fe—Mn—Si	30Mn—5Si[c]	fcc–hcp	disordered
Fe—Mn—Si + (Ni—Cr—Co)	15Mn—7Si—10Cr—10Ni—15Co[c]	fcc–hcp	disordered

[a] To determine the percentage of the remaining constituents, subtract from 100%.
[b] Bct = Body-centered tetragonal.
[c] Value is in wt %.

is a result of the comparatively large thermodynamic difference that exists between the transformation from bcc to 2H, 3R, 9R, 18R, and monoclinic martensites and the typical ferrous martensites that transform from an fcc austenite to a bcc or bct martensite.

The SME can be illustrated by the Cu—Zn system, one of the first SMAs to be studied. A single orientation of the bcc β-phase on cooling goes through an ordering process to a B2 phase. In a disordered alloy, the lattice sites are randomly occupied by both types of atoms, but on ordering, the atoms locate at particular atomic sites, yielding what is called a superlattice. When the B2 phase is cooled below the M_F, it transforms to self-accommodating variants of ordered martensite. The habit planes for the transformation are symmetrically disposed around the {110} family of planes, of which there are six in the cubic system. Thus, for the (011) plane the four variants are (2 11 12), (2 12 11), (2 12 11), and (2 11 12). These are termed the plate group. The six {110} planes of the bcc parent then yield a total of 24 martensite variants. When the martensite group is deformed, the deformation proceeds by the gradual conversion of four variants to a single martensite plate. The surviving orientation depends on the strain direction, and the growth or shrinkage of the variants is such as to minimize the strain energy accumulation. In other words, the surviving variant is the one that allows the greatest extension in the applied stress direction. This varies with the nature of the strain, tension, compression, bending, or torsion. Once a group becomes a single variant, it can change its orientation to that of an adjacent group by the process of twinning. Upon heating, the reverse transformation from martensite to the β-phase occurs between A_S and A_F, and the single crystal (plate) of martensite transforms to the single β-crystal having the original orientation of the parent phase.

In the case of Cu—Zn and other systems that have relatively complex ordered martensite structures (9R or 18R), the reverse transformation is crystallographically restricted. This means that although there are many variants that can form on transformation from parent to martensite, only a single parent orientation is possible in the reverse, or shape-recovery, transformation. This process is illustrated in Figure 2**a**; the shape recovery effect is shown in Figure 2**b**. A detailed discussion of the crystallography of martensitic transformations and lattice-invariant shear is available (3,4). When a martensite group is deformed to coalesce into a single orientation, the dominant mechanism is twinning, where each twin is actually an alternate variant of the martensite crystal. Thus, for the four variants that cluster about the (110) habit plane, each orientation is a twin of another, and by the degenerate variant-twin relationship, a group of martensite plates from a single parent crystal can, on deformation, coalesce to a single crystal (single variant) of martensite. The parent phase, usually ordered B2 or DO_3, transforms to one of the martensite crystal forms that exhibit shape memory. Examples are 2H, Cu—Al— Ni, Cu—Sn, and Ag—Cd; 3R, Ni— Al; 9R, Cu—Zn; 18R, Cu—Zn— Al; and the monoclinic, NiTi.

A distinction exists in the habit and deformation characteristics of the 2H and 3R types and the 9R and 18R martensites. The former are internally twinned and deformation occurs by detwinning of a variant

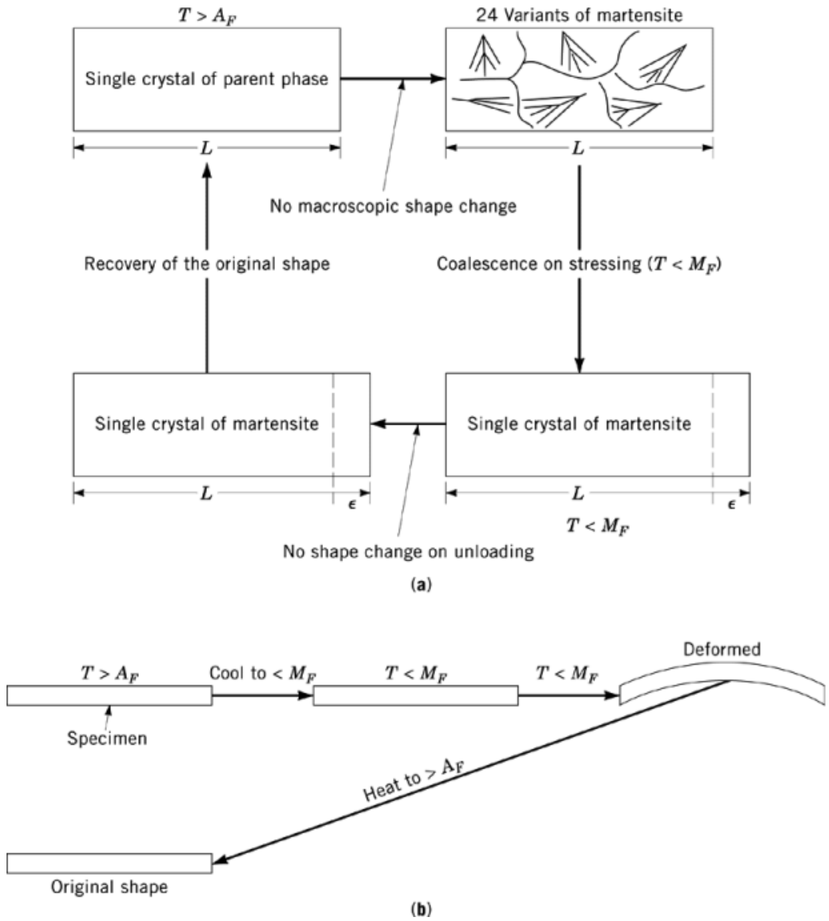

Fig. 2. The shape-memory process, where T is temperature. (**a**) The cycle where the parent phase undergoes a self-accommodating martensite transformation on cooling to the 24 variants of martensite. No macroscopic shape change occurs. The variants coalesce under stress to a single martensite variant, resulting in deformation. Then, upon heating, they revert back to the original austenite crystallographic orientation, and reverse transformation, undergoing complete recovery to complete the cycle. (**b**) Shape deformation. Strain recovery is typically ~7–8%.

plate. The latter are internally faulted and deformation proceeds by variant-to-variant coalescence, followed by group-to-group coalescence. Although these structural differences exist, the self-accommodating habit-plane grouping with respect to a {011} plane is common to all systems exhibiting the SME. The 9R martensite is derived from a B2 parent; the 18R transforms from a DO_3 superlattice. The difference in stacking of {110} planes in these two structures results from the requirement for an invariant plane strain that involves a restricted stacking of close-packed planes. In order to obtain the required plane strain condition, both the 9R and 18R contain stacking faults to provide the necessary accommodation. The atomic displacements required to yield these structures combine the processes of shuffling and shear. The 3R martensite twin plane is identical to the 9R and 18R fault plane. For the case of 2H martensites, no such twin-fault correspondence exists, and the twin is derived from a different parent {110} plane. A more exhaustive review of the martensitic phase transformation in shape-memory alloys is available (5).

3. Applications of the SME

Applications for nonferrous shape-memory alloys can be categorized into the following: one-way SMA devices, virtual two-way devices using one-way SMAs, two-way SMA applications, and SIM/superelastic devices. Ferrous alloy devices are considered separately. Over 20,000 patents have been issued on applications for SMAs; the actual number of these that have resulted in commercially successful products, however, is probably only ~100. Some of the limitations that impact the chances for broad commercial acceptance of these alloys are (*1*) recoverable strain, depending on the alloy, varying from 1 to 8%; (*2*) cyclic strain limit, ie., the required fatigue life determines the permissible shape recovery from 4 to <0.5%; (*3*) cyclic stability, ie, some alloys exhibit a change in transformation temperature after many cycles of shape recovery; (*4*) temperature limitations, ie, the maximum shape-recovery temperature known for an alloy requiring long-term exposure is ~130°C; (*5*) hysteresis, ie, alloys having a set hysteresis are required for various applications and the alloys available do not always meet the requirement; (*6*) processibility, ie, compositional control is exacting and the hot and cold working of these alloys is quite difficult compared to conventional alloys; and (7) fabricability, where the ease of forming a device or the available room temperature ductility of the alloy is not always satisfactory.

3.1. One-Way SMA Applications

The first successful application for nitinol (alloyed with Fe) was as a tube coupling for titanium hydraulic tubing in Grumman F-14 aircraft. In this application, a coupling is fabricated having an inner diameter smaller than the tube to be joined. The coupling is then cooled to its martensitic state and expanded by ~8% so that it fits over the tube. On warming to the shape-recovery temperature, the coupling transforms to austenite, shrinks and produces a joint having a very high reliability. The original couplings required cooling to cryogenic temperature and after expansion were maintained at this temperature until installation. A newer alloy, NiTi alloyed with Nb, has a very wide hysteresis that allows the alloy, after cryogenic expansion, to be stored at room temperature. Upon installation, the coupling is heated to ~100°C for recovery, creating the joint. A primary consideration in the use of SMA couplings is the range of temperatures to which it is to be exposed. High temperature use is limited by stress relaxation and thermodynamic stability; the low temperature limit is dictated by the M_S temperature of the alloy, the temperature where loosening occurs. SMA couplings of this type have been installed in chemical and petroleum plants, power plants, and in piping systems aboard ships.

By using the wide hysteresis alloy, seals of various types have been developed based on the closing force of a wire ring of suitable diameter. Such seals are used for a wide variety of electronic device closures, eg, the attachment of shielding on electrical cables, and as closures on thin-wall cylindrical packages used in the semiconductor industry (see PACKAGING, ELECTRONIC MATERIALS). These seals avoid the heat of soldering, brazing, or welding; thus, there is less chance of damage to the temperature-sensitive electronic components. Using couplings similar to the tube coupling, SMA fiber optic connectors have been produced that provide the necessary accuracy of axial alignment and a good hermetic seal, and do not require excessive heat for installation.

SMA actuators are particularly advantageous in that: (*1*) They integrate sensory and actuation functions. The SMA element inherently senses a change in temperature and actuates by undergoing a shape change as a result of a phase transformation. Consequently, the need for external electronic sensors and control is eliminated. (*2*) They function in a clean, debris-less, spark-free manner. The shape change that is responsible for the actuator displacement is again an inherent material property. It is not associated with moving parts that require lubrication or electrical signals with a potential to spark. (*3*) They have high power/weight and stroke length/weight ratios. The operating range includes strain and stress limits of 8% and 700 MPa, respectively, depending on the number of required cycles. (*4*) They posses the ability to function in zero-gravity environments with small, controlled accelerations. The displacement strains are a result of a thermally- induced phase transformation that can be controlled by controlling the heat transfer rate (eg, through appropriate insulation).

In many of the operations of spacecraft, it is necessary to separate the craft from its mooring before launch, and then to separate the booster and subsequent stages from the payload. The most frequently employed device for these procedures is an explosive bolt. These are also used in a variety of safety-release and closure systems in industrial plants. As these devices are considered hazardous, the installation involves many precautions. In addition, a severe electrical storm can induce voltages in the system sufficient to activate the explosive charge accidentally. An SMA device has been developed that consists of a prestrained cylinder surrounding a bolt that has a machined notch in its surface (6). When the SMA device is electrically heated above A_F it expands, causing the bolt to fracture at the notch, releasing the load. The electrical energy required is well above that which can be generated by an accidental static electric charge pickup.

3.2. Virtual Two-Way Devices Using One-Way SMAs

Although alloys such as NiTi are considered to be one-way SMAs, by using a bias elastic spring to provide the reverse motion (a recocking), a two-way device can be designed. A typical linear actuator consists of a shape-memory spring that produces motion and force in one direction and a steel spring that opposes this motion. When heated, the SMA spring has sufficient force to overcome the bias, but when the system cools, the bias spring has greater force and causes a reverse motion. A salient feature of SMA devices is that the modulus of elasticity increases with increasing temperature. This is quite unlike conventional materials. The modulus difference between the martensitic structure and the parent-phase austenitic structure is typically 300%. Virtual two-way devices have found many applications, eg, as electrical connectors in computer systems. At the high operating frequencies ($>$100 MHz) of modern computers there are problems of cross-talk between adjacent channels, noise, switching delays, and signal velocity, requiring very close pin spacing, shielding, and high contact force. The high forces needed in these multipin connectors make it difficult to make the male–female connection without damage to the contact surfaces. A device that opens and closes the jaws of the female component, thus providing what is termed a zero-insertion-force (ZIF) connector, is readily produced using SMA actuators. The closing force is provided by a SMA spring-like member when at ambient temperature. If the device is cooled by a cold jet of inert gas to below M_S, its modulus decreases as it transforms to martensite and a second spring then opens the connector, allowing easy insertion of the male connector. When the connector warms back to the normal operating temperature, it closes with the required high force, providing a low contact resistance connection. Other versions of this device have been employed for military electronics requiring resistance to loosening under severe vibration conditions, (fig. 3).

Circuit breakers have severe demands on performance and reliability, and the bimetals usually employed in the tripping mechanism have several disadvantages. As their motion on heating is very small, the circuit breaker, depending on its size and capacity, must be calibrated to ensure that at the prescribed trip current the circuit breaker opens. In addition, because the force output of a bimetal is modest, a large circuit breaker may require the use of a cascading series of spring-actuated levers to provide the required interruption force and speed. One of the salient features of shape-memory actuators is that they produce larger motions and forces in a lighter and smaller device than wax motors, solenoids, bimetals, or electric motors. Shape-memory actuators do, however, have one disadvantage, ie, a relatively low cyclic speed. Although a shape-memory device can be heated in milliseconds or less to provide the shape recovery, the reverse cycle of cooling is limited by convective, conductive, or radiation heat transfer, thus placing a practical limit on all but very small actuators typically having a cyclic rate of $\sim$4 Hz. By using very thin wires and optimizing the cooling rates, frequencies of up to 30 Hz have been demonstrated in a laboratory setting.

Some notable examples exist of SMA actuators that perform a function far more efficiently than alternatives, in some cases, a function that cannot be performed by other actuator devices. An automatic transmission fluid temperature controller for Mercedes Benz cars is one example. Smooth gear shifting at low temperatures is assured by the control of the transmission fluid pressure, allowing full fluid flow only when the proper operating temperature is reached. Other automotive applications have been designed that take advantage of

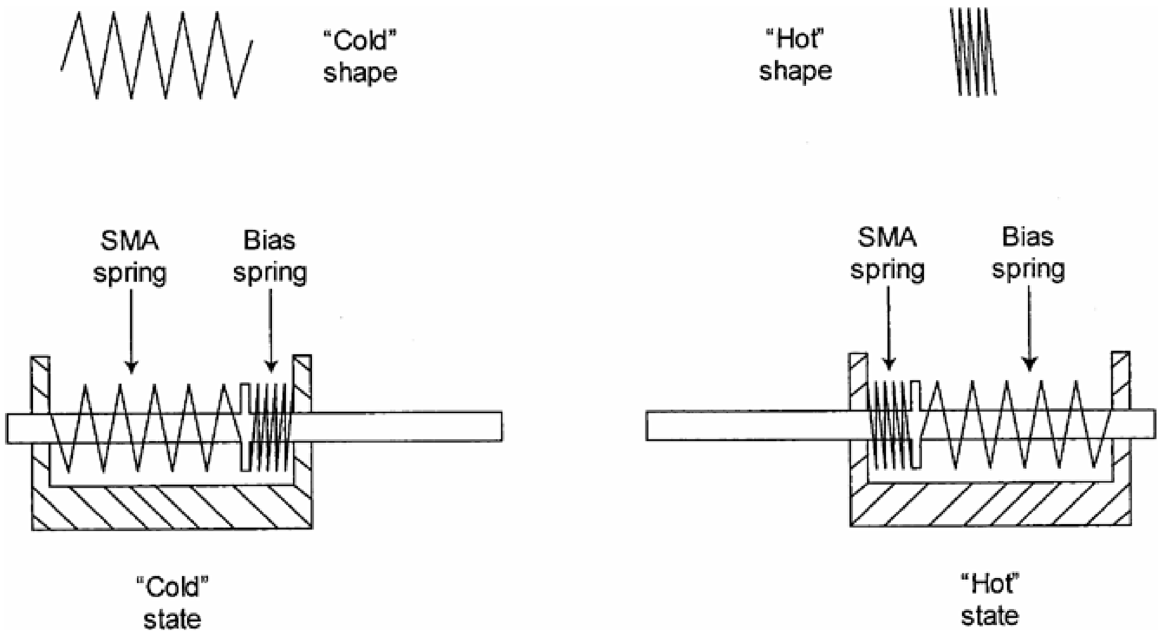

Fig. 3. Schematic of a SMA spring together with a bias spring. When heated, the SMA spring has sufficient force to overcome the bias spring, but when the system cools, the bias spring has greater force and causes a reverse motion. A simple switch, sensitive to temperature changes, can thus be designed.

the compact, simple actuators that are possible using the high force and large strain capability of SMAs. Many devices have been demonstrated, eg, engine controls, climate controls, mirror motions, windshield wipers, cooling fan control, and retractable headlights. The best available NiTi SMAs have an upper actuation limit of ~80–120°C, and summer under-the-hood temperatures of cars operating in North America and in many other countries can reach >125°C. Although the Cu— Al—Ni family of SMAs can be alloyed to give an A_S temperature in excess of 150(C, the long-term thermodynamic stability of these alloys is considerably lower. There is a considerable amount of research ongoing as of 2002 to develop high temperature shape-memory alloys, and many applications await their successful implementation. The NiTi alloys having additions of Hf, Zr, or Pt have shown promise, and A_S temperatures in excess of 200(C showing good stability have been noted. Either cost or fabricability limitations have inhibited commercialization as of the early-2000s.

Other successful actuators have been developed for various domestic safety devices. One such device is a shape-memory-actuated valve that fits in line with a bathroom sink, tub, or shower, and in the event that through some system imbalance or malfunction the water discharge approaches the temperature that would cause scalding, the valve automatically shuts off the flow and does not allow water flow to resume until the temperature is safe. A similar thermally triggered valve has been developed for shutting off the flow in industrial gas or fluid lines in the event of an excessive temperature or a fire. Shape-memory actuators are also candidate actuators to replace the glass bulb or fusible link in overhead fire extinguisher systems. Regulations stress the protection of human life, requiring that the sprinkler actuation speed be decreased to 14 s, well within the capability of an inexpensive SMA device but more difficult to achieve in the conventional trip devices.

In addition to the circuit breaker, there have been a number of other SMA applications for various functions in electric power generation, distribution, and transmission systems. One such device is a thermal indicator that provides a signal visible from the ground of a hot junction or connector in a distribution yard.

Such hot spots occur as a result of the loosening of bus bar connectors owing to cyclic temperature as the electric load varies. In addition to the use of SMA flags as a hot-spot indicators, actuators that automatically maintain the contact force in a bus bar connection have been demonstrated. Based on a Belleville washer fabricated from a Cu—Al— Ni SMA trained to exhibit two-way memory, these washers, when heated by a hot joint, increase their force output and correct the condition. A 30-mm diameter washer 3 mm thick can produce a force of > 4000 N. Similar in purpose to circuit breakers, fuses are also candidates for shape-memory actuation, particularly on the large fuses used in power station distribution yards. The difficulty in detecting which phase in a system has overloaded has led to the design of resettable fuses as well as fuses that have shape-memory indicator flags that signal which phase has overloaded. The performance of overhead transmission lines is degraded when, as a result of overheating, usually from a combination of ambient conditions and power overload, the lines sag to a point where ground capacitance becomes excessive. In addition, safety regulations require that the distance from the conductors to the ground be some minimum height. To correct the sag, shape-memory actuators in parallel with the conductors retension the lines when the lines reach a specified temperature. Sag-control models using SMA devices have been demonstrated by the electrical utilities in the Ukraine and Japan. Another problem, prevalent in areas where severe icing conditions exist, is referred to as galloping of power lines. When ice forms on a power line, there is frequently a prevailing wind that causes the ice to take a teardrop or airfoil shape. This foil provides an aerodynamic lift to the conductors and under certain conditions the conductors can go into a resonant vibration such that large standing waves are created that exert enormous forces on the system. Miles of power lines and the towers along them have been destroyed by this phenomenon. A system for exploiting shape-memory damping to reduce the severity of these resonance conditions has been designed. Various schemes are being investigated for damping transmission line vibration using passive damping devices. In a related problem, the use of SMAs for seismic vibration control has been studied in national earthquake engineering centers in the United States and Japan. Two modes of operation have been explored: ground isolation and cross-brace stiffening. Ground isolation is effected by using large SIM devices in the foundations that exhibit a large change in modulus as a result of the stress developed by the seismic event. Copper-based SMAs have been studied for this application owing to availability in large cross-section and at moderate cost. In cross-brace stiffening of a building, a shape-memory element is placed in a diagonal position in the structure. In the event of a seismic disturbance the shape-memory element is electrically heated, producing an increase in its modulus and thus creating a stiffening effect to resist building deflection. In the first case, the damping is passive and in the second a signal from an accelerometer is sent to a controller, which powers the SMA actuator. Seismic control is a problem worldwide for general civilian structures but is a particular concern in cases of power plants that are sited near a known geological fault. More details on the use of shape-memory alloys for structural vibration control are available (7,8). Another problem in power generation is the cavitation erosion that occurs on the faces of hydroelectric turbines. This severe form of erosion must be periodically repaired to avoid a serious degradation in turbine efficiency. SMAs have a unique resistance to cavitation erosion and exhibit orders of magnitude lower levels of metal loss than any other alloys. Early studies showed the exceptional cavitation resistance of NiTi. The reactive nature of NiTi has, however, impeded extending laboratory trials to the cladding of giant turbine runners. The CuAlNi SMA shows equivalent cavitation resistance and offers the advantage of being amenable to weld overlay techniques.

Space exploration presents a unique array of problems, involving in-space construction of structures, deployment of large antennas, control of antenna geometry, actuators for robotic devices, and control elements for a broad variety of scientific experimental apparatus. SMA joining techniques have been designed for the robotic assembly of large space structures. Usually, these structures are truss-like members having many struts that must be joined using a minimum of energy and extravehicular work by the astronauts. SMA couplings that can be attached and then detached to move to a new location are possible. These could be a useful tool for this area of space engineering. One problem inherent in space structures (9) is vibration, which can impact on the function of space experiments and the accuracy of instruments. Large flexible structures, once put in motion by some external or internal force or shift of mass, have by themselves no substantial damping, operating in the vacuum of space. In essence, a smart material is one that can change its characteristics in such a way as to correct a condition that degrades its performance. These systems have incorporated into their structures sensors, controllers, and actuators. The detector, sensing a vibration, sends a signal to a microprocessor–controller that in turn energizes some form of actuator to change the local structural dynamics, causing the vibration to decrease or be canceled. Shape-memory wires and ribbons embedded in the composite materials of construction have proved to be very effective. The wire or ribbon is prestrained before being embedded and then held under constraint while the composite, typically a graphite epoxy, is cured. When these SMA actuators are electrically heated, they attempt to recover their original dimensions. Owing to the constraint offered by the composite to which the SMAs are bonded, however, they can only produce an in-plane stress that alters the modal response of the structure, reducing its vibrational amplitude. In addition to acoustic and vibration control, SMA actuators are also used in smart materials for shape control, for eg, changing the contour of an airfoil or hydrofoil, fine-tuning the contour of an antenna, and changing the focal point of microwave reflectors. The design of smart materials and adaptive structures has required the development of constitutive equations that describe the temperature, stress, strain, and percentage of martensite volume transformation of a shape-memory alloy. These equations can be integrated with similar constitutive equations for composite materials to make possible the quantitative design of structures having embedded sensors and actuators for vibration control. The constitutive equations for one-dimensional (1D) systems as well as a (3D) representation have been developed to a certain extent(7).

3.3. Superelastic and Pseudoelastic Devices

Medical instruments and devices have become an important application for shape-memory alloys (see Prosthetics and biomedical devices). Both shape recovery and superelastic behavior are exploited in biocompatible nitinol. The first application that has achieved broad acceptance is the use of pseudoelastic SMA wire for orthodontic arch wires (see Dental materials). These wires, attached to the teeth by small adhesively bonded clips, provide the correcting force for adjusting the position of teeth. The wires have a resistance to permanent deformation, which translates into much faster correction of the misalignment and far fewer periodic adjustments by the orthodontist. The use of traditional bridges and plates for teeth replacement is giving way to tooth implant procedures. This involves the attachment of a metal peg in the jaw bone and when the two are stabilized, the new tooth is attached to the peg. By using conventional implant techniques it can take > 6 months for the metal implant to stabilize before the replacement tooth is attached. By using shape-memory implant posts that lock into the bone immediately, reduces the time for the procedure to days. In maxillofacial surgery, which often involves reshaping the mandible and other cranial bones, shape-memory bone fasteners are proving superior to the usual screwed metal plates. If the SMA plate is prestrained and then attached to the two bone elements, as it warms to body temperature it pulls the mating surfaces into intimate contact, accelerating the healing process. Fractures in other bones such as in the arms and legs have benefitted from this procedure. Often fractures are associated with detachment of tendons that are normally difficult to reattach to the bone. Shape-memory anchors can make this a simple procedure. A small anchor with shape-memory wings is forced into a small hole drilled in the bone, and the wings provide secure locking in the hole. The tendon is then sutured to the anchor and in time attaches itself to the bone (10). If it is not dissolved or trapped, an embolism moving from the lower extremities can be life-threatening. A shape-memory trap has been devised that, when deployed in the vena cava, is like a multileaved mesh that traps a traveling embolism, retaining it until medication can dissolve it. Introduced in a folded form by a catheter, the mesh is prevented from deploying by subjecting it to a flow of cold saline water. Once in place, it is released from the catheter and, warmed by body heat, opens into its final shape (11). A variety of procedures have been developed to improve spinal fusion. Shape-memory rings are used to separate adjacent vertebrae and allow bone implants or bone chips to be inserted to develop the solid fusion section. Abnormal curvature of the spine, ie, scoliosis, has seen dramatic improvement in treatment in a procedure developed in China involving NiTi rods. The rods, cooled to their martensitic condition, are bent to match the curvature of the spine and, while maintained at a low temperature, are attached to vertebrae in a number of places along the spine. When the incision is closed, the SMA rods warm to their shape-recovery temperature and in attempting to revert to their original straight shape exert a continuous moderate corrective force on the spine. Badly curved spines have been brought to an essentially straight condition in $\sim$2 years' time, and even after the rods are removed, there is little tendency to revert to the previous condition. Fracture of bones, common in other treatments, is avoided in this procedure (12).

NiTi superelastic wires have a remarkable resistance to kinking or developing permanent deformation after bending. This feature is exploited in the long thin wires used to guide a catheter to its required position in the body. The wires allow safe introduction of a catheter through the sometimes tortuous passages of veins and arteries in cardiology procedures such as angioplasty. This flexibility and resistance to kinking of superelastic SMAs also makes possible superior needles and probes for arthroscopic procedures. Breast lesions, once located by radiology, are difficult to identify when the surgeon operates to remove them. A superelastic probe having a curved hook end can be introduced by a hypodermic needle during radiography and when the needle is retracted the curved end keeps the probe (13), in place, thus identifying the location of the lesion.

Currently, shape-memory stents are beginning to find widespread application in the human body. Stents, spiral tubular spring-like devices used to restore the patency of a vessel such as an artery, various ducts, and even the esophagus, have been made using conventional polymers and metals, but with only partial success. The ability to make such a device of SMA ribbon or wire in coiled form, then stretch it almost straight to allow its placement in a catheter for introduction to the desired location, and then on deployment have the ribbon reform into a rigid coil that supports the vessel walls, is a great advance. This type of stent has also been demonstrated to be a fast and effective repair device for an abdominal aortic aneurysm.

In addition to these medical applications, superelastic wires in very large quantities have been used for eyeglass frames, where their resistance to accidental damage and light weight are attractive features. Another large market is in the cellular telephone. The short antenna of superelastic shape-memory wire is very resistant to kinking and bending damage. A substantial tonnage market for superelastic memory alloy wire also exists for stiffening wire in brassieres. Resistance to permanent bending during machine washing and drying is provided by the SMA.

Devices required to produce exceptionally high forces have also been developed. Industrial force generators, using the recovery of a prestrained SMA shape having the capability of producing forces from 10 to 100 t, have been introduced. In one form, developed in Japan, a number of small cylinders of NiTi are compressed and then placed in a cylindrical holder, which in turn is placed into a hole, usually in a cement or stone structure that is to be fractured. When the set of NiTi cylinders is electrically heated they go through shape recovery, expand, and fracture the structure, but without the hazard, noise, and dust created by conventional explosives (14) (see EXPLOSIVES AND PROPELLANTS). A Russian force generator has been developed that is capable of exerting the 100 t of force necessary to remove gas turbine wheels from their shafts.

3.4. Ferrous SMAs

Ferrous shape-memory alloys have potential as low cost, readily fabricated one-way devices. These alloys, with one exception, do not form thermoelastic martensite. The alloy family of greatest interest, Fe—Mn—Si, forms martensite on cooling. However, if this martensite is deformed, it does not exhibit shape memory on heating to the A_F temperature. On the other hand, if the alloy is subjected to sufficient stress, an epsilon martensite forms by the SIM reaction. This deformation is recovered on heating, yielding a one-way shape-memory behavior. The basic alloy does not have the corrosion resistance required for many industrial applications, and to improve this feature, the alloy has been further alloyed with Ni, Cr, and Co (see Table 2). The recoverable strain is modest when the alloy is subjected to its first deformation and recovery cycle, but on subsequent cycling, more or less similar to the training cycles used to impart two-way memory, the recoverable strain increases and up to 4% shape recovery has been achieved. This is sufficient for many applications, although the stress generated on shape recovery is only a modest 250 MPa (36,250 psi). If this can be increased to ~700 MPa (101,500 psi), a very interesting application is possible: The use of prestrained ferrous SMA rods as prestressing tendons to produce prestressed concrete structures.

4. Processing

The transformation temperatures in SMAs are sensitive to composition. Consequently, the alloy melting method and starting materials must be selected so as to ensure high purity. The two most common melting methods are vacuum induction melting (VIM) and vacuum arc remelting (VAR). VIM consists of placing all of the constituents in an electrically conductive crucible in a vacuum chamber, followed by inductive heating. In VAR, an electrical arc is struck between a consumable electrode (made from compacted elemental powders or previously fabricated ingots) and a crucible. Adequate electric power is provided to melt the electrode. The melted alloy is usually hot-worked using metallurgical techniques such as forging, rolling, swaging or extrusion in order to obtain a microstructure with favorable properties. Hot-working is followed by cold-working and techniques such as wire-drawing, sheet-rolling and tube- drawing are used. Prior to use in any application a final heat treatment is applied in order to obtain the desired shape-memory or superelastic properties (15).

5. Latest Trends

Recently, emphasis has been placed on fabricating thin films of NiTi and NiTi with Cu, Pd and Hf through sputtering. The motivation is to create microactuators. Both the SME and the SE have been demonstrated at these reduced size-scales. Potential applications include microvalves, microswitches, micropumps, and comparable microelectromechanical systems (MEMS) (16). Large strains (~5%) have been produced in Ni—Mn—Ga SMAs by applying magnetic fields. The strains are a result of martensite variant redistribution (17). In order to be comprehensive, mention has to be made here of shape-memory polymers and ceramics (18). While polymers exhibit the SME as a result of entirely different mechanisms, some ceramics may demonstrate a ferroelastic phase transformation (19).

In conclusion, with the advent of better processing, SMAs have found widespread application as actuators, flexible devices (eg, cellular phone antennae), and medical devices in the human body (eg, stents). However, their potential has still to be fully exploited as research continues on increasing transformation temperatures, thin film, and magnetic SMAs. A comprehensive thermomechanical theory, while still elusive, continues to be pursued through novel characterization techniques (20). Informative references on all aspects of SMAs are available (21–25).

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