

Kirk-Othmer
**Encyclopedia
of Chemical
Technology**

Third Edition

Volume 20 Refractories to Silk

KIRK-OTHMER
ENCYCLOPEDIA
OF CHEMICAL
TECHNOLOGY

Third Edition

VOLUME 20

Refractories
to
Silk

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THIRD EDITION

VOLUME 20

REFRACTORIES
TO
SILK



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SHALE OIL. See Oil shale.

SHAPE-MEMORY ALLOYS

The shape-memory effect is based on the continuous appearance and disappearance of martensite with falling and rising temperatures. This thermoelastic behavior is the result of transformation from a phase stable at elevated temperature to the martensite phase. A specimen in the martensite condition may be deformed in what appears to be a plastic manner but is actually deforming as a result of the growth and shrinkage of self-accommodating martensite plates. When the specimen is heated to the temperature of the parent phase, a complete recovery of the deformation takes place. Complete recovery in this process is limited by the fact that strain must not exceed a critical value which ranges from 3–4% for copper memory-effect alloys to 6–8% for the Ni–Ti system. A number of other characteristics associated with shape memory are referred to as pseudoelasticity or superelasticity, two-way shape-memory effect, martensite-to-martensite transformations, and rubberlike behavior.

Martensite is a metastable phase that forms when a phase stable at elevated temperature, such as austenite in steel, is cooled at a certain rate, thereby suppressing the formation of phases that are diffusion-controlled (see Steel). A characteristic of martensite is the relationship between the parent-phase crystal and the martensite. For steel, the austenitic phase is fcc. When it transforms to martensite, the orderly shift to a bct (body-centered tetragonal) structure takes place (see Fig. 1). The structure stable at elevated temperature varies with the alloy system, and the martensite varies from a simple bcc to a more complex structure which may have as many as 18 atom layers to define the unit cell.

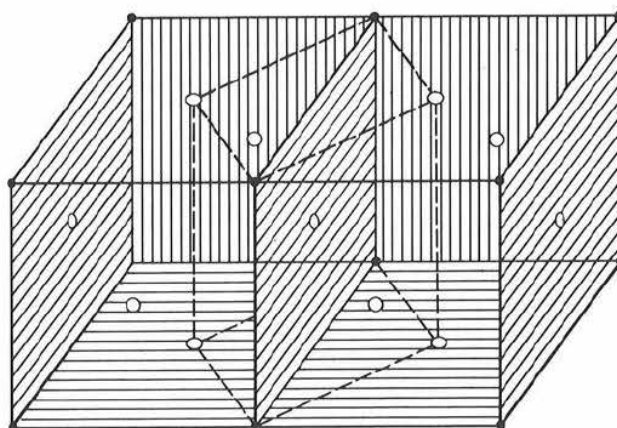


Figure 1. The original fcc structure (0) changes to the bct with (111) γ $\parallel$ (110) α and the [110] γ $\parallel$ [111] α .

The temperature at which martensite starts to form on cooling is referred to as the M_s and the temperature at which the elevated temperature phase has been completely transformed is the M_f . On heating a martensitic specimen, the temperature at which the reaction reverses to the elevated temperature phase is designated A_s ; the reaction is completed at a higher temperature designated A_f (see Fig. 2).

Thermoelastic behavior was first discussed in 1938 in a study of a Cu-Zn alloy which showed that martensite could be made to appear and disappear with a change in temperature (1). In a later study in the USSR, the phase relationships in brass between the high temperature β phase and martensite were examined (2). The length changes that occur on martensite transformations under load in the Fe-Ni system were determined (3). A later investigation of the shape-memory effect in Au-Cd alloys demonstrated that useful force could be generated in this type of transformation. These findings led to research on the practical applications for the shape-memory effect, and investigation of the martensite transformation kinetics in the Ni-Ti system (4). This system is commonly referred to as Nitinol (Nickel-Titanium Naval Ordnance Laboratory). The essential features of the martensite transformation are common to all alloy systems exhibiting the memory effect, whether they be 2H, 3R, 9R, or 18R structures (5-6). In some alloy systems, the various martensites are both internally faulted or internally twinned and may possess different crystal structures. However, in all cases studied to date, an initial parent phase transforms to self-accommodating martensite plates that are characterized by six plate groups, each consisting of four variants. Because of the self-accommodating character of the transformation, the average shape deformation in a particular plate group is effectively zero.

Table 1 lists the martensite alloy systems that have been investigated with respect to thermoelasticity, pseudoelasticity, shape-memory effect, and two-way shape-memory effect. The bcc (β) phase is the dominant parent because of the comparatively large thermodynamic difference between the martensite transformation from a bcc parent to 3R, 2H, 18R, or 9R, and from an fcc parent to bcc or bct. The former is typical for nonferrous alloys, whereas the latter accounts for the hardening of steel.

For an excellent general review of martensite kinetics, microstructure, and thermodynamics as they relate to shape memory, see ref. 7 and the First International Conference on Shape Memory (8).

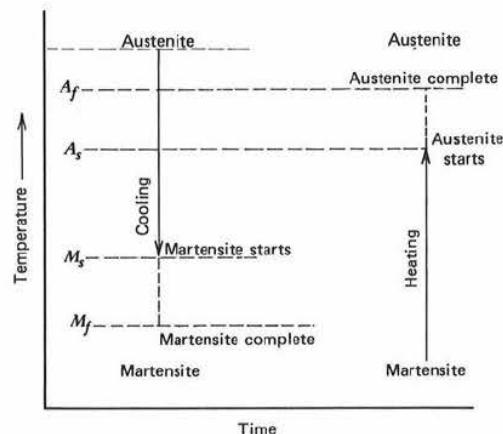


Figure 2. Martensite phases as a function of temperature. A_f = reverse reaction is finished; A_s = reverse reaction starts; M_s = martensite starts to form; and M_f = martensite is completely transformed.

Table 1. Alloys Exhibiting Martensitic Effects

Thermoelastic	Pseudoelastic	Shape memory	Two-way shape memory
Ag-Cd	Ag-Cd	Ag-Cd	Cu-Al
Au-Cu-Zn	Au-Cd	Au-Cd	Cu-Zn-Al
Cu-Al-Ni	Au-Cu-Zn	Au-Cu-Zn	In-Tl
Cu-Zn	Cu-Al-Mn	Cu-Al	Ti-Ni
Cu-Zn ^a	Cu-Al-Ni	Cu-Al-Ni	
Fe-Pt	Cu-Au-Zn	Cu-Zn	
Ti-Ni	Cu-Zn	Cu-Zn-Al	
	Cu-Zn-Al	Cu-Zn-Ga	
	Cu-Zn-Sn	Cu-Zn-Si	
	Cu-Zn-X	Cu-Zn-Sn	
	Fe ₃ Be	Fe-Pt	
	Fe ₃ Pt	Fe-Ni	
	In-Tl	In-Cd	
	Ni-Ti	In-Tl	
	Ti-Ni	Ni-Al	
		Ni-Ti	
		304 stainless steel	
		Ti-Nb	
		Ti-Ni	

^a With ternary additions of Ni, Ag, Au, Cd, In, Ga, Si, Ge, Sn, and Sb.

The behavior of shape-memory-effect (SME) alloys is exactly opposite to that of normal metals in the following essential feature: as the temperature rises above A_s and martensite is increasingly converted to the β phase, the modulus of elasticity increases. This change is spectacular for Cu-Al-Zn SME alloys where the Young's modulus changes by a factor of 50 from 0.4 GPa (58,000 psi) at the A_s to 20.7 GPa (3×10^6 psi) near the A_f . Obviously, a spring tension or torsion device develops a greater force with increasing temperature and this force can be either static or it can be used to produce a controlled motion. The force that can be developed by an SME device is as much as 200 times the force that could be developed by a bimetallic element of the same size or volume.

The Crystallographic Nature of Shape Memory

The martensitic memory or marmem effect occurs in alloys where both the parent and the martensite are ordered and exhibit crystallographically reversible, thermoelastic martensite transformations (7,9-10).

It has been demonstrated in one of the simplest systems, Cu-Zn, that a single orientation of the bcc β phase transforms on cooling below the M_f to self-accommodating variants of 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. Habit planes are the planes in the parent phase from which transformation takes place. Thus, for the plane (011) the four variants are (2 11 12), (2 12 11), ($\bar{2}$ 12 11), and ($\bar{2}$ 11 12); this set is termed a plate group. The six (110) planes offer a total of 24 martensite variants. When the martensite group is deformed, deformation proceeds by a gradual conversion of four variants to a single martensite plate rather than by grain-boundary sliding or slip. The surviving orientation depends on whether the strain

is tensile or compressive and whether the growth or shrinkage is such as to minimize strain-energy accumulation. 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 a single β crystal with the original orientation of the parent phase. In the case of Cu-Zn and other systems with relatively complex ordered martensite structures (9R or 18R), the reverse transformation is crystallographically restricted. Thus, although there are many variants that can develop on transformation from parent to martensite, only a single-parent orientation is possible in the reverse, or shape-recovery, transformation.

When a martensite group is deformed to coalesce into a single orientation, the dominant mechanism is twinning. Each twin is actually an alternative variant of the martensite crystal. Thus, for the four variants that cluster about the (110) habit, each orientation is a twin of another, and by this degenerate variant-twin relationship, a group of martensite plates formed from a single parent crystal can, on deformation, coalesce to a single crystal (single variant) of martensite.

The parent phase is usually ordered B_2 or DO_3 symmetry, although initially a transformation can take place from disordered to an ordered or superlattice structure. This ordered structure transforms to one of the four martensite crystal forms 2H, 3R, 9R, or 18R that exhibit shape memory. These designations refer to the sequence of stacking of planes to form the ordered structure. A sequence could be *abab*, *abcabc* or *abcbacab* or similar variations. The repetition of these planes to define a unit cell is then 2, 3, and 9, respectively.

Typical alloys that transform to these various martensites are

2H, Cu-Al-Ni and Ag-Cd
3R, Ni-Al
9R, Cu-Zn
18R, Cu-Zn-Al.

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 a detwinning of a variant 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 an (011) plane is common to all systems exhibiting the marmem effect. The 9R martensite is derived from a B_2 parent, whereas the 18R transforms from a DO_3 superlattice. The difference in the stacking of (110) planes is because of the requirement for an invariant plane strain that involves a restricted stacking of close-packed planes. In order to obtain the required invariant plane-strain condition, both the 9R and 18R martensite contain stacking faults to provide the necessary accommodation. The sequence of β to β_2 to orthorhombic 9R for a Cu-Zn alloy is shown in Figure 1.

As noted previously, the atoms in each plane are displaced relative to those above and below and from a repetitive sequence of a nine-plane group. These complex atomic displacements take place by a combined process of shuffling and shear to arrive at the 9R structure. The 3R martensite twin plane is identical to the 9R and 18R fault plane. In the case of 2H martensites, no such twin-fault correspondence exists, and the twin is derived from a different parent (110) plane.

When sufficient strain takes place during deformation of a martensitic structure,

six plate groups coalesce to a single orientation where the surviving variant from the original 24 allows the greatest extension in strain direction. This process varies with the nature of the strain, tensile, compression, or bending properties (Fig. 2). Once a group becomes a single variant, it can change its orientation to that of an adjacent group by twinning.

Although some of the crystallographic details differ for different memory-alloy systems, the essential processes described above are common. Some systems such as Ni-Ti (Nitinol) and Cu-Zn-Al have premartensite transformations with ordering, but in the final analysis the sequence of β to martensite cluster to single-variant martensite to β parent is the same. Schematically, the memory effect is summarized in Figure 3. A stress-strain, temperature-strain diagram is shown in Figure 4. Assuming an initial martensite structure, as stress increases a point A is reached where the martensite starts to coalesce to form a single variant. When the stress is released at B, a residual strain ϵ is left. As the temperature is raised, transformation of the martensite starts at A_s and continues with increasing temperature to A_f at which point all the strain is recovered.

Simple shape-memory behavior can be extended to two-way memory. In order to exhibit two-way memory where the part spontaneously changes from one shape to another on cooling or heating, a conditioning of the martensite must take place. This

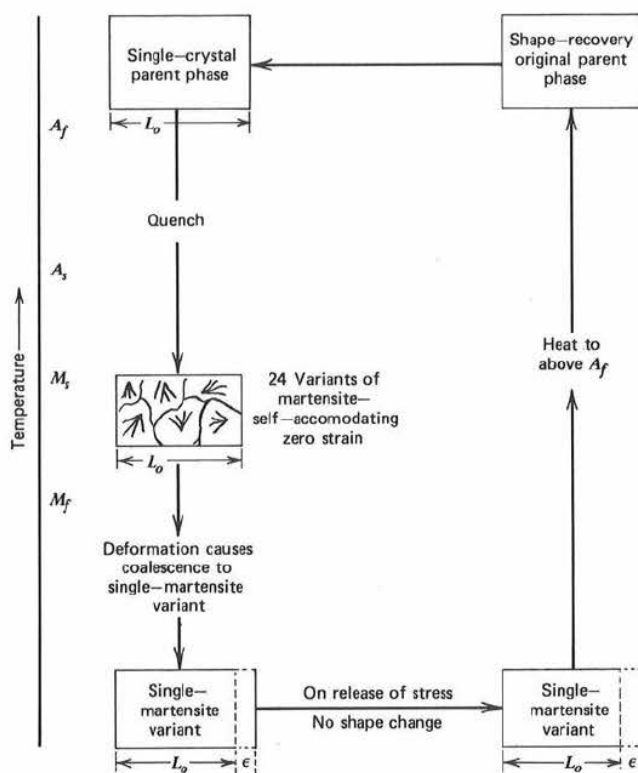


Figure 3. Illustration of the shape-memory effect. L_0 = original length. For other definitions, see Figure 2.

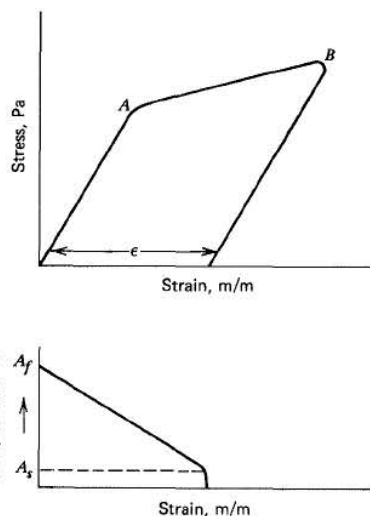


Figure 4. Stress-strain curve demonstrating the shape-memory effect. ϵ = residual strain.

conditioning is brought about by limiting the number of martensite variants that form upon cooling through the applications of an external stress during transformation. The stress favors the initial formation of selected variants, similar to the fact that stressing a martensite group causes the selective growth and shrinkage of suitably oriented plates. This limit imposed upon the number of variants formed reduces the self-accommodating feature of the usual transformation and increases the residual stress. By repeating the process a number of times, the restricted variant group and its associated internal stress spontaneously revert to β on heating and then to a singular martensite group on cooling.

Owing to the fact that the internal boundaries of martensite-martensite groups are relatively mobile, a cyclic stress causes a back-and-forth motion of these boundaries which produces a high internal friction. This behavior is the basis for using shape-memory alloys as vibration-damping materials.

The other property peculiar to marmem alloys is the ability under certain conditions to exhibit superelastic behavior. Although in one sense, the 3–8% apparently recoverable strain of the memory effect is truly an extended or pseudoelastic behavior, an even further elastic range is possible. When many of the martensitic alloys are deformed well beyond the point of the initial single-coalesced martensite stage, a stress-induced martensite-martensite transformation can occur. In this mode of deformation strain is reversible through stress release and not by a temperature-induced phase change, and recoverable strains as high as 17% have been observed.

In the shape-memory process, the temperature is controlled at which the effect takes place. The alloy composition determines the working temperature range of a device, whether one-way or two-way. In the case of Nitinol, the composition is usually ca 50:50. The M_s is extremely sensitive to variations in the Ni-Ti ratio. This sensitivity is reduced by the addition of copper to the Ni-Ti binary system. The other alloy system that has been exploited for a very broad range of applications is the Cu-Zn-Al ternary. The M_s of this alloy can be varied from 170° to -105°C, although a range of -100° to 60°C is more acceptable for long-term stability. This range of M_s temperature falls

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within the ternary field of Cu-(13-27%) Zn-(4.5-9%) Al. Additions of Sn, Mn, Si, and Ni to this ternary system have been investigated for special devices.

Economic Aspects

For a period, the United States Naval Surface Weapons Center was the sole supplier of Nitinol, usually as small-diameter wire; the supply was limited to a few compositions.

In 1981, Nitinol Devices (11) offered 0.457-mm wire with a zero-force transition temperature of 38°C for \$1.95/m or \$1760/kg.

The Raychem Corp. (12) produces Nitinol, but sells it only in the form of finished devices. This company also produces SME brass under the trade name of Betalloy, sold only as a finished actuator.

The price of SME brass, typically the Cu-Zn-Al family of alloys, is not published since it is sold only as a finished and heat-treated device. A typical small spring sells in the range of \$0.50-1.50.

At this time, only Delta Memorial Metal Ltd. (13), UK, and Proteus Metal (14), Brussels, Belgium, manufacture SME brass actuators. Both companies market finished, heat-treated components ready for installation.

Applications

The first shape-memory alloy to be placed in commercial use was Nitinol employed as a high reliability coupling. In this device, known as a Cryofit connector (12), a small tubular piece is machined to an initial inside diameter ca 4% smaller than the outside diameter of the tube to be joined. The tube is heated to the β phase at elevated temperature and quenched to yield martensite. It is then expanded to a diameter sufficient to allow it to fit over the tubes to be joined, usually ca 4%. Upon heating, the ca 8% strain is recovered, producing a very high compressive-force joint of superior reliability. An M_s of ca -120°C was chosen because these connectors were first used for aircraft hydraulic couplings which experience a service temperature range from -100°C to perhaps 45°C. This application was so successful that it was extended to the coupling of piping systems on ships where the pipe diameter ranged from 1.9-5 cm (see Piping systems). In spite of the high cost of Nitinol for both alloy shapes and components, the labor savings over other joining systems, particularly welding (qv), has made the process economically attractive. The fact that once expanded to the open position the coupling must be stored at cryogenic temperature has not prevented their use for undersea oil-line connections. Undersea pipes are usually joined by welding in a hyperbaric chamber, a difficult and costly operation. Using Cryofit units, pipes up to 15 cm dia have been joined at depths of >100 m.

Another use for the Ni-Ti memory alloys is in high reliability strip-chart pen-recorder drives (15). The usual D'Arsonval movement was replaced with a Nitinol wire which, when it expanded or contracted, moved the recording pen through a system of simple pivots. The wire is heated by a high frequency induction heater whose frequency, and therefore heat-coupling efficiency, is proportional to the input signal. Since this is a two-way memory effect, such wire must go through a training period to develop a repeatable shape recovery. These highly reliable and shock resistant recorders have been very successful.

Medical Applications. The alloy Nitinol resulted from a successful research program intended to create a high strength metal resistant to corrosion by seawater. With these properties, it is not surprising that it has interesting applications in memory devices for medical implants requiring passive chemical behavior (16) (see Prosthetic and biomedical devices).

An early medical device exploits the superelastic behavior of Nitinol rather than its memory effect. This device, the restraining wire arch in an orthodontic brace attached to teeth being straightened, provides a constant force which produces the desired effect more quickly than conventional braces. The wire is deformed in a martensitic condition to a point where martensite-martensite reaction occurs. Because of their wide elastic range, these wires are superior to the usual stainless-steel wires, which because of stress relaxation, require constant readjustment.

Exploiting the true memory effect has been the aim of a medical research team specializing in cardiovascular problems (see Blood, coagulants and anticoagulants; Cardiovascular agents). Addressing the prevention of blood clots, a group at Beth Israel Hospital in Boston has successfully demonstrated on animals a system for screening blood clots large enough to be hazardous (17). A Nitinol wire bundle in the martensitic state, with a composition selected to give an A_s slightly above body temperature, is deformed into an umbrella-like screen. The screen is collapsed into a straight strand of wires and inserted by means of a catheter into the vena cava where, upon warming, it opens to form a clot screen. This device may offer an effective method to guard against the aftereffects of operations on legs or lower trunk or in cases of phlebitis where clots are a common occurrence. This system avoids complicated and sometimes high risk surgery and the side-effect problems associated with anticoagulant drugs.

In the area of orthopedic surgery, Nitinol applications have been highly successful. Their range is as diverse as bone-fracture fixation, hip implants, and the reduction of bone deformities and structural abnormalities such as scoliosis.

A most common orthopedic problem is the accurate fixation of fractures, particularly multiple breaks common in sports. Screws and plates are generally employed but the alignment is not always exact and the fracture interfaces are not always in close contact. With a shape-memory plate that shrinks on heating, a fracture can be aligned by screwing the plate to bridge the fracture and, when it is warmed by body heat or artificially heated by diathermy, the contractions pull the surfaces into tight contact ensuring rapid calcification and healing. Devices of this type are under investigation in the FRG (18), as well as in the U.S. and the UK.

Although hip replacements are now a common procedure, they still present problems of fixing the new ball joint rigidly in the femur. A long spike is usually driven into the hollow of the bone and cemented with acrylic or similar organic adhesive. The occurrence of hairline fractures is common, and misalignment may require a second operation. A new device employs a beta-conditioned hollow tube which is split lengthwise and bent to the shape of a C. After quenching to martensite, it is closed. Upon insertion, the tube is warmed by the body heat and expands to the original C configuration, providing a tight fit, which, since the grip is along the entire length, minimizes the chance of fracture. The ball joint is then attached.

Scoliosis, a lateral curving of the spine, is a disfiguring and disabling ailment. The cure is long and difficult and requires the repeated and gradual straightening of a Harrington rod to force the spine into alignment. These rods have been replaced by a memory alloy which, when initially attached to the spine, has a matching curvature.

When heated externally, the rod attempts to straighten, applying a constant controlled force that gradually brings the spine into normal alignment (19).

Active exploration of memory-effect devices is underway for application in automatic drug dispensing, an artificial heart muscle, prosthetic devices for arthritic joints, and systems to generate artificial peristalsis action (see Pharmaceuticals, controlled release).

Mechanical Devices. As the Ni-Ti alloys have dominated the biomedical field, so have the Cu-Zn-Al family of alloys taken a commanding lead in the field of thermally actuated mechanical devices. These include circuit breakers and electric relays, thermostatic valves, window openers, climate-control devices for buildings and cars, safety devices, aerospace-antenna systems, and various fastener and connector devices.

Since the Cu-Zn-Al alloys are readily hot-worked, they have been generally used in the form of extruded wire. Springs in torsion, tension, or compression have been developed as well as tubes and rods in torsion. Flat strip or sheet can also be produced although not as readily because the cold workability of these alloys is limited.

The automobile industry was among the first to develop SME actuators. An automobile contains ca 25 devices which could exploit SME, including thermostatic fluid and air controls, air-conditioner valves, exhaust emission controls, carburetor valves, and automotive fans. Such devices are now in the development stage in many countries.

An interesting application now in road tests is an automotive-engine fan whose speed is proportional to the cooling demand. An SME spring controls the relative slip of a clutch that engages the belt drive and fan. A considerable amount of fuel is saved by this system. Exhaust-emission control is a worldwide concern and although various catalytic devices provide a reasonably effective reduction in toxic emission, climate changes, particularly temperature, reduce their efficiency because of a shift in the fuel-air mixture. A carburetor jet with an SME alloy orifice that changes diameter in response to fuel temperature maintains a constant mixture and, as a result, stabilizes the exhaust chemistry (see Exhaust control, automotive).

A concept to use the car-passenger heater as part of the engine cooling system allows a reduction in the size of the main engine radiator. When the heat generated by the interior heater is not needed, louvers controlled by SME devices conduct the heat to the outside.

In the area of home-climate installation, SME valves controlling water circulation in hydronic heating systems offer the advantage of simplicity and economy over the conventional combination of electric thermostat, relay, and electrically operated valves (see Air conditioning). An SME valve can be placed in each room to give individual temperature control. In solar heating, passive wall-heat absorbers, so-called Tromb walls, require the opening and closing of shutters to control the insolation. The SME actuators developed for the control of greenhouse windows offer reliable, automatic, and powerful operation (see Solar energy).

A broad variety of thermal-overload devices are candidates for SME actuation, ranging from small relay systems to large circuit breakers. Protection against thermal overload is required on industrial electrical machinery to improve their fail-safe operation. For example, SME spring elements, because of their high force and small size, are incorporated in these devices. In addition, copper-based SME alloys are used as

couplings for specialized tube connections, eg, the connection between copper and aluminum tube ends used in air-conditioning systems. The SME couple has a polymer inner liner that acts as a sealant as well as a barrier to possible galvanic corrosion (12).

As new forms of energy generation are needed, solar collectors, both passive and active, have been developed and the sun-induced temperature difference between the ocean surface waters and the ocean depths offers a particularly intriguing possibility. Shape-memory engines offer the potential of capturing this vast source of low temperature energy. No matter what the system, the scale would be enormous; however, active support is being given to such low temperature energy converters where the source is ocean thermal difference, thermoclines in high hydroelectric power-dam lakes, and effluents from conventional fossil and nuclear-fuel generator plants (20).

Theoretical studies of shape-memory engines (21) have compared the thermal efficiency of a shape-memory device operating as solid-state engine or solid-state heat-pumping device with more conventional Carnot fluid systems. The first SME engine demonstrating a useful power output with a modest temperature difference was a rotary engine in which Nitinol elements operated in a bending mode and provided the motive force as they dipped alternately in hot and cold water (22). Although relatively inefficient, it showed the possibilities inherent in solid-state engines.

In order to calculate the efficiency of a solid-state SME engine, a temperature-entropy diagram can be constructed similar to a Carnot cycle. The Gibbs free-energy change in the transformation of martensite to the parent phase is the driving force for such a system. Because of the hysteresis in the memory-effect transformation, the efficiency of a solid-state engine is always below that of a Carnot cycle. The sensible heat involved in the cycle, as compared with the latent heat of transformation must, for optimum efficiency, be kept low. This restriction is more difficult to achieve in a solid-state engine than in a fluid engine. Estimates of the efficiency of these engines range from 3–5%. These calculations are difficult because of the problem of accurately estimating entropy and free energy change for the martensite–parent and parent–martensite under stress.

Model engines built to date indicate that a solid-state engine can yield an efficiency at low temperature differences that is about equal to a gas- or fluid-phase engine and also offer a considerable advantage in size.

Another possible application for SME materials is the storage of large quantities of thermal energy by cycling between M_f and A_f . In effect, in heating from M_f to A_f the energy stored is the latent heat of transformation $T\Delta S$ plus the specific heat C_p . When the specimen is cooled from A_f to M_f , this energy is released. Since the temperature difference can, for a selected alloy, be on the order of 20°C, a large amount of energy can be stored in a relatively small volume.

A final area of interest in SME motors is in solar-driven irrigation pumps for use in underdeveloped countries. Efficiency is not as important as the ability to pump water at modest rates from modest depths with no fuel requirement and at a low capital cost. Several excellent designs have been demonstrated under a United Nations Development Program. Assuming 6 h of pumping per day and a peak pumping capacity twice the average, the required capacity is 5–10 L/s from a depth of 5 m. This corresponds to an average pumping power of 125–250 W/hm² of irrigated land (23).

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