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# Shape-Memory Alloys

*If one of these new alloys has been formed into a shape at a certain temperature and is then deformed at another temperature, it can "remember" the original shape. The effect has many applications*

by L. McDonald Schetky

**M**etals are characterized by such physical qualities as tensile strength, ductility, malleability and conductivity. To these, in the case of a new family of alloys, one can now add the anthropomorphic qualities of memory and trainability. The new alloys exhibit what is called the shape-memory effect. If such alloys are plastically deformed at one temperature, they will completely recover their original shape on being raised to a higher temperature. In recovering their shape the alloys can produce a displacement or a force, or a combination of the two, as a function of temperature. Because of these novel and remarkable properties shape-memory alloys are helping to solve a wide variety of problems. In one well-developed application shape-memory alloys provide simple and virtually leakproof couplings for pneumatic and hydraulic lines. They are also serving as tight seals and couplings in electronic assemblies. Most recently the alloys have been exploited in mechanical and electromechanical control systems to provide, for example, a precise mechanical response to small and repeated temperature changes. Several promising applications

are being tested in medicine. More remote, but nonetheless tantalizing, is the possibility of harnessing shape-memory alloys to convert low-grade heat (such as the heat of water at the surface of the ocean) into mechanical energy.

In order for an alloy to exhibit the shape-memory effect it must have a crystal structure that can shift into the configuration known as martensite when it is subjected to a certain temperature or stress and then shift out of it. In a simple example a wire of shape-memory alloy might be bent at room temperature into the form of a four-leaf clover. Then the wire is heated until its crystal structure assumes a high-temperature configuration called the beta or parent phase. Next the wire is rapidly cooled so that the atoms in the metal rearrange themselves into the crystal form of martensite. One can now bend or twist the wire into any other form. If the wire is later heated to a temperature above that at which the martensite reverts to the parent phase, there is an orderly shift of large groups of atoms that restores the original cloverleaf form. Since the martensite transformation is essential for the shape-memory effect, alloys that ex-

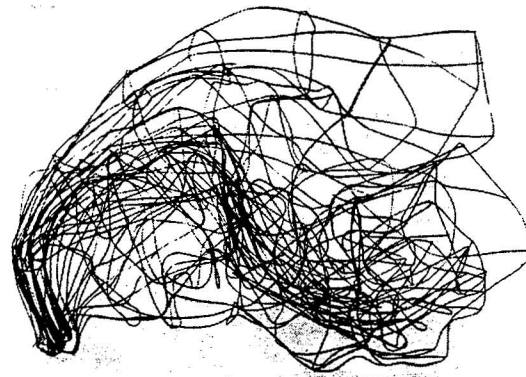
hibit memory are also known as mar-mem alloys.

The shape-memory effect had been noted as early as 1938, when Alden B. Greninger of Harvard University and V. G. Mooradian of the Massachusetts Institute of Technology showed that the martensite phase in brass (an alloy of copper and zinc) could be made to form and disappear with a change in temperature. At about the same time G. V. Kurdymov, a Russian metallurgist noted for his early work on the crystallography of martensites, particularly in steel, studied the phase relations in brass between the high-temperature beta phase and the martensite formed by rapid cooling. Later Thomas A. Read and his associates at the University of Illinois investigated the shape-memory effect in gold-cadmium alloys and demonstrated the forces that could be developed by the phase transitions. Alloys as diverse as iron-platinum, indium-cadmium, iron-nickel, nickel-aluminum and stainless steel have been observed to exhibit shape memory in varying degrees.

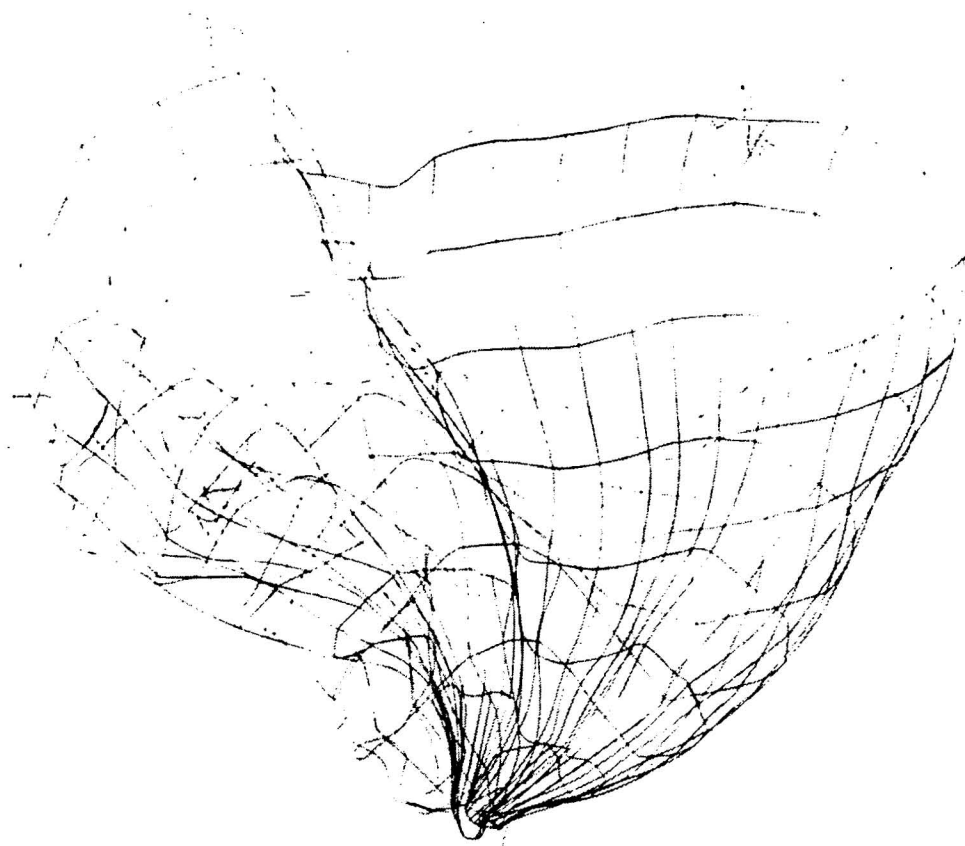
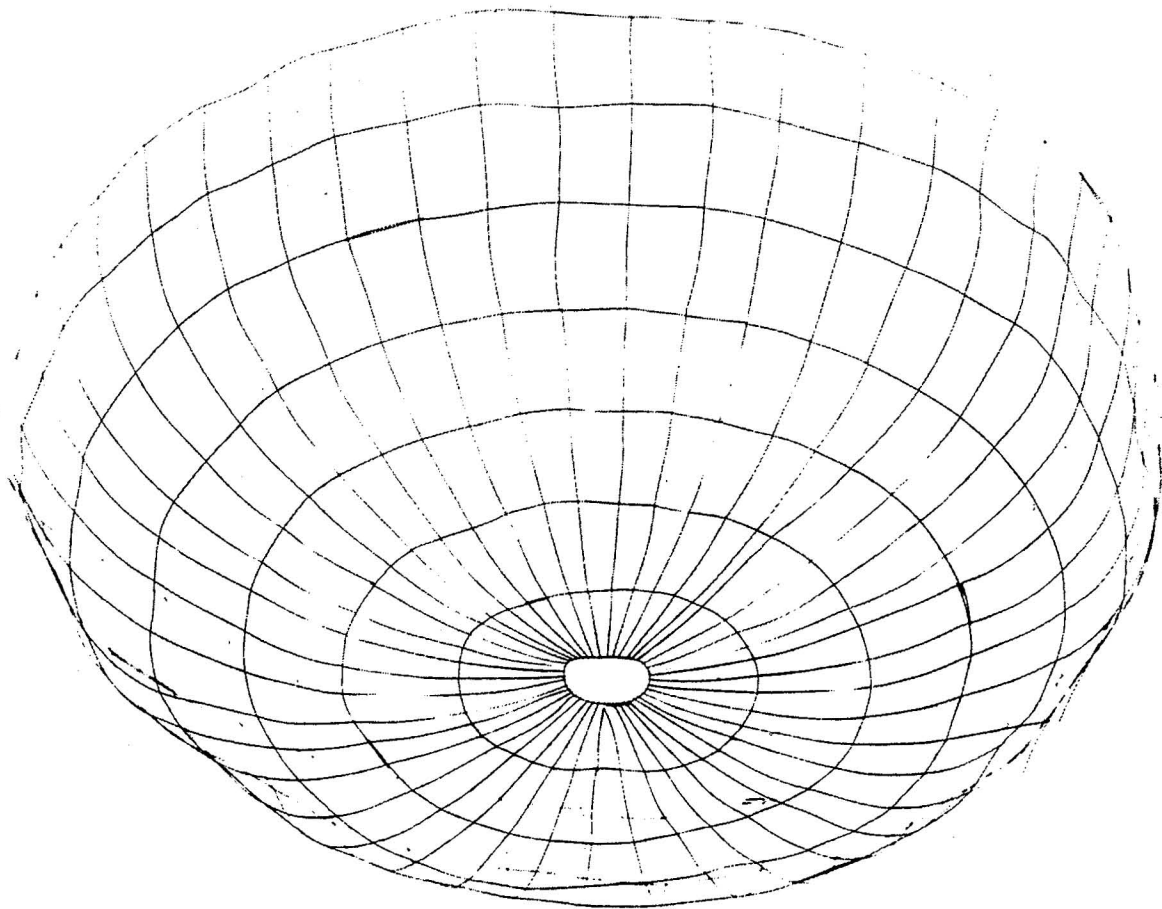
It was not until 1962, however, that the phenomenon came to worldwide attention with the announcement of shape



**SPONTANEOUS UNFOLDING** of a wire hemisphere that could serve as a small antenna for a spacecraft is shown in this sequence of four photographs. The antenna is made of an alloy of nickel and titanium.



**graph at the left the fully formed antenna has been crushed at room temperature into a tight ball less than five centimeters across. As the temperature of the mass of wire is increased the antenna gradually**



ture assumes its original configuration (*top right*). The diameter of the unfolded antenna is about 25 centimeters. The restoration of the antenna's shape coincides with the disappearance of crystals of martensite in the material and their replacement by crystals of austenite

which has a simpler crystal structure. The crystallographic history of the sequence is illustrated on the next page. The antenna was designed by the Goodyear Aerospace Corporation. Although it has never seen actual service, it vividly demonstrates the importance of material

memory in an alloy of nickel and titanium. The alloy was discovered by William J. Buehler of the U.S. Naval Ordnance Laboratory (since renamed the Naval Surface Weapons Center) in Silver Spring, Md. Buehler's alloy was dubbed Nitinol (for nickel-titanium Naval Ordnance Laboratory).

Before going into the various ways the shape-memory effect can be exploited

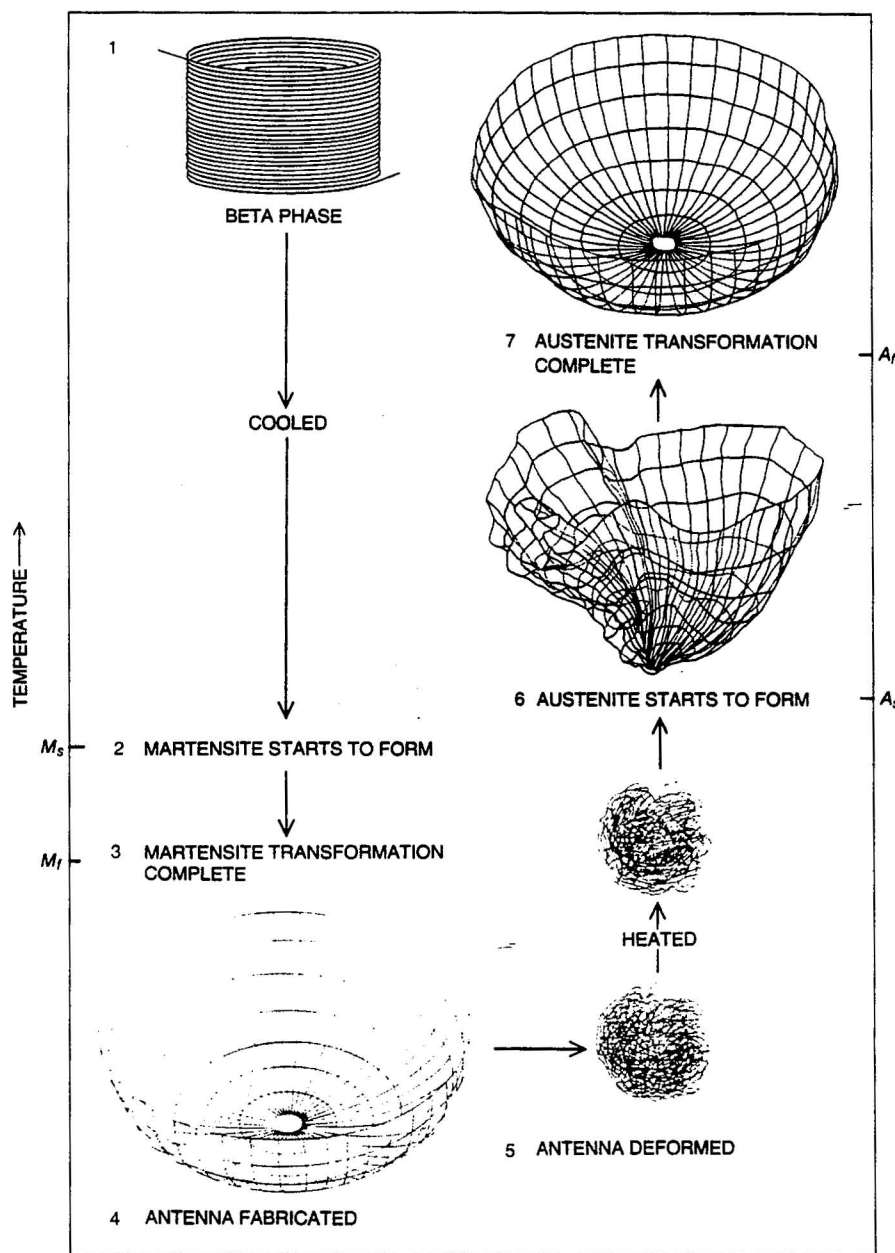
I shall describe in somewhat more detail the phenomenon itself, the conditions of temperature and stress needed to give rise to it and the crystallography that underlies it. The martensite crystal structure that is essential for the effect can be produced in two general ways: by subjecting an alloy to a stress whose magnitude is related to temperature or by rapidly quenching a suitable alloy to

some critical temperature. In the second method, which is the one most commonly applied, the martensite structure appears spontaneously through a shearing motion of the atoms in the alloy or through a process of nucleation and crystal growth. In each case the shift is classed as a "diffusionless transformation" resulting from the coordinated movement of large blocks of atoms.


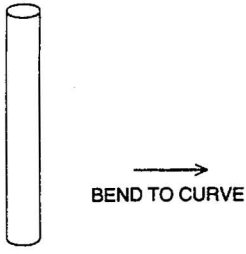
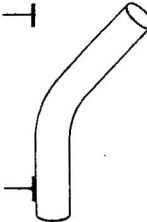
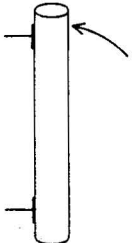

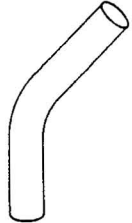
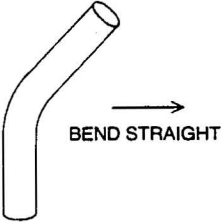

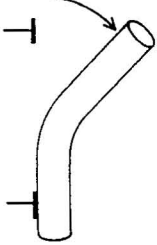
The establishment of a thermodynamic equilibrium between the parent phase and the martensite phase depends on the composition of the alloy, the temperature and the internal stress. The nucleation and growth of martensite are controlled by shear strains that develop between adjacent martensite regions as the alloy is cooled or stressed. The balancing of such internal strains and any external stress causes the martensite regions to grow as an array of self-accommodating plates. The orientation of a plate with respect to the orientation of its neighbor is the one that is energetically stablest in that particular strain field. Whether the field results from an applied stress or from a change in temperature, in the material as a whole the plates assume a variety of orientations and a range of sizes.

Although the structure of the parent phase and of the martensite varies in detail with each alloy, the typical elevated-temperature phase is a disordered body-centered-cubic one (where the atoms form a cubic lattice with one atom in the center of each cube of eight other atoms). As the temperature is lowered that phase shifts into a structure that is either an ordered body-centered-cubic one or a superlattice. In the ordered structure atoms of one species in the alloy take up preferred sites in the cubic lattice with respect to the atoms of the other species. The superlattice can be visualized as interpenetrating cells in which the unit cell of the crystal, the smallest unit that when repeated and extended in all directions defines the crystal structure, consists of several dozen atoms or more. This complexity of crystal structure makes it difficult to describe the relative movements of atoms that result in the martensite transformation. Often invoked to describe the movements are terms such as shuffling and shear. In the marmem alloy of copper, zinc and aluminum four variants of martensite form out of the parent beta phase, each with a crystal orientation displaced by 60 degrees from the others.

The strain associated with one variant compensates the strain in the other variants, so that the growth of multiple self-accommodating fields of martensite plates is energetically favored over the growth of a single plate. The boundaries between the adjacent plates are, however, quite mobile and move readily under the influence of an applied stress. As a result a specimen can be deformed not



**CRYSTALLOGRAPHIC HISTORY** of the spacecraft antenna shows the role of temperature in the shape-memory effect. The construction material, Nitinol wire in a large coil, is raised to a temperature of 650 degrees C. and is stabilized so that the crystal structure of the material is entirely in the beta, or "parent," phase (1). This phase is often the crystal structure austenite. The wire is now cooled. At the temperature  $M_s$  (60 degrees C.) the new crystal phase martensite starts to form, replacing the beta phase (2). At  $M_f$  (52 degrees) the transformation to martensite is finished (3). While the Nitinol wire is held at a temperature below  $M_f$  it is cut into short lengths, which are gently bent to form the segments of the intended hemisphere (4). Where the segments cross one another they are fastened by tack welding. One can now crush the antenna into a small volume (5). In order to restore the original shape the crushed structure is heated. At temperature  $A_s$  (71 degrees) austenite begins to replace martensite (6). On reaching  $A_f$  (77 degrees) the antenna has unfolded completely (7). In this particular case what the shape-memory alloy "remembers" is not the actual configuration of the antenna but the gentle curves of the coiled wire from which the antenna was constructed. As the wire tries to straighten itself it is constrained to the shape of a bowl by the multiple welds of the previous joints

| INITIAL SHAPE   | ADDITIONAL COLD OR HOT SHAPING  | SHAPE AFTER BETATIZING AND QUENCHING  | POSITION AT ROOM TEMPERATURE  | "REMEMBERED" POSITION (ABOVE $A_f$ )  |
|---|---|---|---|---|
|   | NO MARTENSITE   | NOW CONTAINS MARTENSITE   | MARTENSITE UNDER STRESS   | NO MARTENSITE   |
|  | NONE  |  |   |  |
|  |  |  |  |  |

**TEMPERATURE-ACTUATED SWITCH** can be designed so that it opens or closes above a particular temperature. The temperature depends on the alloy selected and coincides with the temperature ( $A_f$ ) at which martensite is replaced by austenite. If the switch is designed to close above the temperature  $A_f$  (top), a straight rod of alloy is heated to the "betatizing" temperature and then quenched. The rod

now contains martensite (color). For the rod to serve as a switching element it is bent, which puts the martensite under stress. When the rod is heated above  $A_f$ , the martensite then disappears and the rod straightens, closing the switch. If the switch is designed to open above  $A_f$ , the rod must be bent before betatizing and quenching (bottom). The rod is then straightened out before it is placed in the switch.

through the slippage of adjacent plates, the usual mechanism of plastic deformation, but through the growth and compensating contraction of adjacent plates.

In an alloy that has a beta phase capable of producing martensite under stress one can observe an unusual elastic property called pseudoelasticity or superelasticity. In a typical alloy with this property the metal exhibits normal elastic behavior under stress (that is, it gets longer in some dimension) until the critical stress is reached at which martensite plates begin to form. With further stress the specimen continues to elongate, as if it were being plastically deformed, but when the stress is removed, the martensite plates that have formed revert to the parent phase and the specimen contracts to its original dimension, showing no permanent deformation.

When the temperature of a marmem alloy is reduced to the critical temperature at which martensite starts to form, the transformation proceeds spontaneously. As the temperature is increased above the critical one martensite can still form, but only if an increasing amount of stress is applied. In the temperature range where martensite can form under the influence of stress the elasticity of the material can exceed the elasticity of ordinary alloys by a factor of 10 or more: the material is superelastic. Although superelasticity is not the

amount of configurational memory (or equivalent force) for special purposes. Hence an alloy that has already been transformed into martensite will exhibit superelastic strain resulting from the reversible motion of the boundaries between martensite plates. The reorientation of the plates will cause one variant of martensite to grow at the expense of another, depending on the direction of stress with respect to the internal strain energy associated with each boundary.

Trainability, a feature of marmem alloys mentioned at the outset, yields a specimen with memory for two different configurations, a "two-way" memory effect. Training is accomplished by limiting the number of variants of martensite formed when an alloy is repeatedly heated and cooled below the critical temperature. Such limitation inhibits the self-accommodation of the martensite plates and increases the amount of internal strain. The number of variants can be limited by stressing the specimen while it is cooling from the elevated temperature of the beta phase down to the critical temperature. The stress favors the initial formation of particular variants of martensite in the same way that stress at constant temperature favors the growth of one variant at the expense of another. Hence a structure can be trained by repeating many times the sequence of "betatizing" (heating the alloy until it goes into the beta

shape occurs spontaneously; the change is in one direction at a temperature corresponding to the beta phase and in another direction at a temperature below the martensite-transformation one.

Let me now summarize the conditions involved in the attainment of shape memory and therefore the variables that must be controlled if a useful device is to be fabricated. In order to exhibit memory an alloy must undergo a martensite phase transformation. The temperature at which the memory is accomplished is a function of the temperature at which martensite formation begins or the higher temperature at which the alloy reverts to the parent phase (usually the beta phase). The martensite-transformation temperature depends on the composition of the alloy but can be shifted by an applied stress. If the recovery of shape is restrained, a proportional force will be available for doing work or gripping another object. In order to achieve 100 percent recovery of shape the deformation of a part must be limited to an internal strain of between 3 and 9 percent, depending on the particular alloy. Finally, memory can be one-way or, with training, two-way.

The number of uses for marmem alloys has been growing steadily. The original Nitinol alloys were in spite of their high cost soon exploited for a variety of tasks in spacecraft. One of the first

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