Metallurgy: Extraordinary Alloys That Remember Their Past

Metals are captives of their past. The mechanical properties of metals are intimately related to their thermal history and to previous states of mechanical strain. Yet most metals do not explicitly remember this past; by returning them to a former temperature and condition of strain, the metallurgist cannot restore metals to their earlier shape or bring back their old mechanical properties.

There is a class of metal alloys, however, that, like patients emerging from psychoanalysis, do remember their past. Known as shape memory alloys, these extraordinary materials are already finding use in certain industrial applications. But still more exciting is the possibility that shape memory alloys may be specially suited for a number of surgical and dental devices. And heat engines constructed from such metals may turn out to provide a practical way to use low-grade heat, such as waste heat from electric power plants, heat from geothermal sources, or solar heat.

Members of the family of shape memory alloys are drawn from the transition metals and the precious metals. The most studied of these materials and the ones that so far show the most promise for exploitation by commercial interests are alloys of nickel and titanium containing about 50 atomic percent of each component. The special properties of these alloys, usually referred to as Nitinol, were discovered by William Buehler at the Naval Ordnance Laboratory, White Oak, Maryland (now named the Naval Surface Weapons Center), in 1962, although metallurgists knew of similar effects in other metals as far back as the 1930's. Other metal alloy systems showing the shape memory effect include alloys of copper and zinc, aluminum, or tin; indium and thallium; gold and cadmium; iron and platinum; and some ternary alloys, such as copper-aluminum-nickel.

How the shape memory alloys work is diagrammed in Fig. 1. All of these metals exist in two phases, one at high temperatures and another at low temperatures. The highly symmetric cesium chloride structure, with one atom of a binary alloy at each corner of the simple cubic unit cell and the second atom in the center, is by far the most common structure of the high-temperature phase. The low-temperature phase exhibits a lower symmetry.

The researcher forms the shape memory alloy into the desired configuration, such as the spiral in the figure, and may also anneal the specimen at some elevated temperature to "fix" the shape. The crystal structure changes as the alloy cools through the temperature range appropriate for the phase change. At the low temperature, the researcher reshapes the specimen, for example, by straightening the spiral. Upon heating to a temperature above the phase change but well below the annealing temperature, the alloy returns to its first shape (the spiral in the figure).

Considerable force can be generated during the shape change. A parlor or board room magician who coils a normally straight piece of small gauge Nitinol wire and then drops the deformed wire into a hot cup of coffee can leave his audience highly impressed when the rapidly uncoiling wire leaps out of the cup and across the room. In more controlled tests, Nitinol has generated stresses of 80,000 pounds per square inch (5×10^7 newtons per square meter) or more when heated.

Uses for a material with such properties would seem to be limited only by one's imagination, but, as is often the case with metals having somewhat unorthodox behavior, the shape memory effect is least spectacular when the alloy is in a bulky configuration. Thus, wires, ribbons, rods, and foils are the shapes best exploited.

The Raychem Corporation, Menlo Park, California, has been an early commercial exploiter of Nitinol. Researchers at Raychem used Nitinol to make weldless connectors for the tubing in the high-pressure air and hydraulic system of the Navy's F-14 fighter. In principle, the connectors are simplicity itself. A Nitinol cylindrical sleeve with an inside diameter slightly smaller than the outside diameter of the tubing to be joined is cooled to liquid nitrogen temperature (77°K) and mechanically deformed so that its diameter is increased by about 8.5 percent. The cooled, expanded sleeve is placed over the ends of the two pieces of tubing and allowed to warm to room temperature. The warm Nitinol returns to its original dimensions and holds the tubing as securely as a weld, but without some of the metallurgical problems caused by trying to weld the thin-walled tubing used in the aircraft.

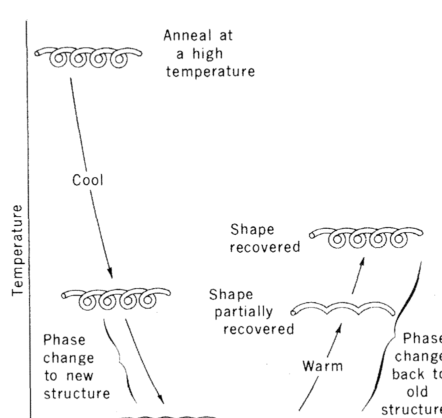

Fig. 1. Schematic diagram of the shape memory effect. Annealing at a high temperature "fixes" the permanent shape. After being deformed into any other shape at a low temperature, the alloy returns to its permanent shape upon being warmed up.

The Foxboro Company, Foxboro, Massachusetts, manufactures strip chart recorders and indicator meters for use in industrial process controller panels. The drive motors for the pens in the recorders and the pointers in the meters have traditionally been the least reliable components of these instruments. Replacement of the motors with Nitinol wires that change their length under the influence of the heat generated when an electric current passes through the wire has solved this problem by eliminating many moving parts. The current and hence the length of the Nitinol varies with the magnitude of the signal being recorded. The changing length of the Nitinol wire moves a lever which in turn pushes the pen or needle of the instrument.

Navy researchers were initially enthusiastic about Nitinol in part because they visualized making expandable structures for space satellites from this material. While this concept has since been abandoned, the Navy is also looking for ways to apply Nitinol to civilian problems.

Hot boxes on railroad freight cars are just such a problem. Overheated journal bearings on freight cars can cause axles to fail and, hence, cars to derail. Each journal box has to be monitored individually if such accidents are to be prevented because there is no way to predict when hot boxes will occur. Researchers from the Surface Weapons Center have constructed a device in which the Nitinol acts both as a temperature sensor and an actuator of the emergency brake system. They are now testing it on ore hopper cars in trains in Minnesota where the extremes in temperature and weather help create a rugged testing environment. In one such design, a short piece of Nitinol in the device, which is located near the journal box, automatically shortens when the temperature rises beyond a predetermined point.

The sudden shortening of the Nitinol releases a spring-loaded firing pin. The firing pin action initiates a series of processes culminating in the activation of the braking system.

The temperature range over which the transition from the high- to low-temperature phase of Nitinol occurs is determined by the relative proportions of nickel and titanium in the alloy. A wrought stoichiometric alloy of commercial purity with 50 atomic percent nickel and 50 percent titanium transforms in the temperature range 385° to 400°K. Increasing the nickel content lowers the transition temperature range, which is in the neighborhood of 190°K in the case of the Raychem connectors. Substituting small amounts (a few percent) of cobalt or iron for nickel can lower the transition temperature range to liquid nitrogen temperature or lower and is the method of choice, at least at Raychem, because the transition temperature range is easier to control and the alloy has better mechanical properties.

Shape memory alloys are especially suited for certain medical devices, and these applications seem to represent a more exciting and revolutionary development than the relatively straightforward use of these materials in the industrial world so far. Potentially one of the most exciting of these developments is the blood clot filter recently reported by Morris Simon of Boston's Beth Israel Hospital and Harvard Medical School.

The filter shape, of which there are several possible, is the normal configuration of a 40-centimeter-long Nitinol wire in the high-temperature phase (stable at body temperature in this case). The surgeon injects a wire, straightened below room temperature, into the patient's venous system via a plastic catheter of the type used to inject contrast media for angiographic x-ray studies. A cooled solution keeps the wire below its transformation temperature and hence straight during this procedure. When the wire reaches the vena cava, a large vein in the abdomen which returns blood to the heart, the body-temperature blood warms the wire, whereupon it resumes the filter configuration.

In this way blood clots formed in the legs, thighs, or pelvis (sources of 95 percent of all emboli) and subsequently dislodged are prevented from reaching the lungs and causing a pulmonary embolism. A mesh-shaped filter that is being tested catches all clots with diameters of 2 millimeters or more, for example. Smaller emboli than this are not considered dangerous. Anticoagulants, the usual preventive measure for embolism, are not appropriate when internal bleeding is a danger, and the heretofore available alternative surgical procedures have all involved some risk.

Research so far, done collaboratively by Simon, Edwin Salzman and David Freiman of Harvard, and Roy Kaplow of the Massachusetts Institute of Technology, has been confined to in vitro tests and experiments with dogs. While the dog experiments have been encouraging, Simon reports that optimizing the mechanical efficiency of the devices, determining the biological effects of the Nitinol, and characterizing the corrosive effects of the body on the Nitinol all remain to be done before experiments with human patients.

Several groups have conducted tissue compatibility studies with Nitinol. For example, Alan Johnson now at the University of Louisville and Frank Alicandri of the Polytechnic Institute of New York want to use Nitinol to make bone plates. Such plates are several centimeters long, 1 centimeter wide, and 0.2 centimeter thick and are attached to the ends of a fractured long bone, such as the tibia or femur, with screws. As a plate made of Nitinol warms up, it would contract and pull the ends of the bone together. Existing methods of compression fixation, as the technique is called, require a longer surgical procedure than would be the case if Nitinol bone plates could be perfected.

Johnson, Louis Castleman of the Polytechnic Institute of New York, and their colleagues have collaborated on a tissue compatibility study of Nitinol in beagles. The researchers attached bone plates to the dogs' femurs for periods of up to 17 months. As compared to the cobalt-chromium alloy (vitallium) that is normally used or with a sham operation in which no plate was implanted, histological studies and neutron activation analysis of surrounding tissue and internal organs indicated no adverse effects. In particular, loss of nickel, which is carcinogenic, or titanium ions from the Nitinol into surrounding tissue was not observed.

James Hughes of the Mississippi Methodist Rehabilitation Center, Jackson, is also enthusiastic over the prospect of using Nitinol for orthopedic devices. For example, in a total hip prosthesis, the different elastic moduli of the present alloys used and of the normal bone are such that loosening is a problem that can only be solved by using cement to hold the stem of the prosthesis in place. If Nitinol were used to make the stem of the prosthesis, its shape memory properties could be exploited to lock the stem in place.

Hughes and his colleagues (including Gerald Finerman of the University of California, Los Angeles) have carried out several short-term tissue compatibility experiments that compared the relative effects of Nitinol and stainless steel or titanium controls in human fibroblast tissue culture, fetal rat calvaria tissue, and laboratory mice. The investigators found no differences between Nitinol alloys of five different compositions and the controls. Long-term studies involving sheep are currently under way at the rehabilitation center.

Researchers at the University of Texas, Austin, are investigating Nitinol's suitability for still another orthopedic device. Scoliosis is an abnormality of the growing spine such that one or more sideways curves are formed. Besides being disfiguring and painful, the buckled spine can interfere with internal organs. One method of treating scoliosis has been the use of a metal rod called (after its inventor) the Harrington rod. The surgeon temporarily straightens the patient's spine and connects the straight rod to it. Unfortunately, as the stretched body tissue relaxes, some of the correcting force is lost, and sometimes a second operation is required.

Nitinol rods could alleviate this problem if a curved rod were attached to the spine. Subsequently, after the relaxation process ends, the Nitinol rod could be heated and straightened out, thus counteracting the relaxation phenomenon. M. A. Schmerling and M. A. Wilkov at Texas and their colleagues have demonstrated that this concept works on cadavers and have carried out studies with rats that show the Nitinol can be heated by radio-frequency induction heating inside the body without damaging nearby tissue.

Nitinol may also have a profound effect on the practice of orthodontics, although in this case it is the unique mechanical properties of the low-temperature phase of this alloy, rather than the shape memory effect itself, that are crucial. Orthodontists commonly use stainless steel wires that are attached to bands on the patient's teeth in order to bring about the corrective force needed to straighten crooked teeth. The force arises from the elasticity of the wire; if the wire is bent too far and permanent or plastic deformation occurs, the restoring force of a slightly bent wire as it tries to contract is lost.

George Andreasen of the University of Iowa has been developing Nitinol wires for use in orthodontics. In his studies, Andreasen has found that, in certain standard bending tests, Nitinol wires had a recoverable strain that was ten or more times that of stainless steel, depending on the wire thickness. In addition, the stress needed to cause plastic deformation (the yield strength) of Nitinol is comparable to that of stainless steel, thus the elastic modulus (stress divided by strain) is low. The large recoverable strain combined with a moderate, continuous restoring force (product of the elastic modulus and the displacement)

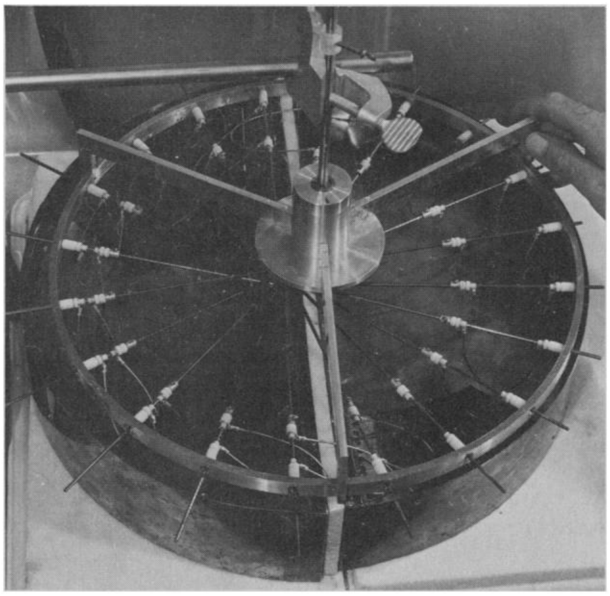

Fig. 2. The original prototype of the Nitinol heat engine. Hot water is in the left semicircular trough under the wheel, and cold water is in the right trough. A Styrofoam heat insulator separates the two troughs, and the two ramps in the troughs deflect the Nitinol loops over the insulator. The Nitinol loops expand and push against the rim of the wheel, turning it in a clockwise direction as they pass through the hot water, but they contract again on passing through the cold water. [Source: Ridgway Banks, Lawrence Berkeley Laboratory]

means that only one Nitinol wire is needed for most of the straightening procedure, even for badly maloccluded teeth, as opposed to the continuous changing to thicker and thicker stainless steel wires as the teeth are gradually brought into line, and means less pain to the patient.

The idea of using the shape memory effect in an engine to convert small temperature differences to mechanical motion has been around for some time. As early as 1957 the late T. A. Read and his associates at the University of Illinois had used a gold-cadmium alloy to build a device to lift weights. A more practical engine, however, has been constructed by Ridgway Banks and his colleagues at the University of California's Lawrence Berkeley Laboratory. The Banks engine uses Nitinol. Since the transformation from the low- to high-temperature phases in Nitinol can occur over a range of temperatures as small as 10°C, an obvious heat source to drive such an engine is the waste heat from electric power plants or low-grade heat from solar energy collectors. Because of the corrosion resistance of Nitinol, engines made from this material might also be used in geothermal power applications where the hot salt brines easily damage other materials.

The principle of the Banks engine is illustrated in Fig. 2. Loops of Nitinol wire mounted on the spokes of a wheel attempt to expand from their hairpin shape when they feel the hot water in a trough below one half of the wheel-shaped engine. The expanding loops of wire push against the rim of the wheel, causing it to turn. A turning force exists because the spokes on which the loops are mounted are on an axis that is eccentric to the axis of the wheel. When the Nitinol wires enter the cold water in a trough under the other half of the wheel, they are cooled to below the transformation temperature, and little work is expended in pushing them back into the hairpin shape as the wheel turns. In fact, an additional memory effect called the two-way memory effect aids in the bending.

Banks and his associates have had a small version of their engine running since August 1973, and have encountered no problems with fatigue, an obvious potential problem with metals that have to bend and unbend several million times. The Berkeley researchers are now working on a larger, ½ horsepower model of their engine, powerful enough to run an air conditioner. Besides the problems associated with scale-up, the researchers must optimize the actual efficiency of the engine (which theoretically could approach that of an ideal heat engine) and the cost of a power plant (which Banks estimates could be considerably less than that of a conventional power plant in dollars per installed kilowatt, even given the high cost of titanium). Recently, Luc Delaey of the Catholic University of Louvain in Belgium and his associates have built a similar engine using a copper-zinc-aluminum alloy.

It is probably fair to say that the crystallography and a phenomenological understanding of the shape memory effect are fairly well in hand, but that there is considerable controversy over the more detailed aspects of the phenomenon. (Much of this research has been concerned with alloys other than Nitinol, which behaves somewhat differently from the other alloys.) Researchers seem to agree that the transformation from the high- to the low-temperature phase is what is known as a diffusionless or martensitic transition, as opposed to a more conventional nucleation and growth process in which small particles of the new phase nucleate and subsequently grow at the expense of the old phase by a diffusion process. In this martensitic transition, individual atoms do not move very far, effectively keep the same neighbor atoms as before the transition, and all strains brought about by the change in structure are accommodated elastically.

The martensitic phase exists in the form of platelets or lamellae that have various crystallographic orientations. When the martensitic phase is initially deformed, platelets with preferred orientations relative to the applied stress grow at the expense of others, at least up to a point, but exactly how is hotly disputed. The key to recovering the high-temperature shape apparently is the higher symmetry of the high-temperature structure as compared to that of the low-temperature structure. On the transition to the low-temperature phase, there are many crystallographically equivalent martensite variants, as they are called, to which the transition can go. But in the reverse transition, there is only one possible place to go and that is to the original orientation and shape.

A detailed understanding of the physics of a process is not always necessary for successful exploitation of the phenomenon, if one can figure out how to make the material needed. Unfortunately, in the case of Nitinol, even this has yet to be done to everyone's satisfaction. Nitinol is usually made by melting nickel and titanium sponge in a vacuum induction furnace in a graphite crucible. Vacuum is required because the titanium is so reactive. But the titanium invariably contains oxygen to start with, carbon is picked up from the crucible, and exactly how much of the nickel and titanium will react is hard to control. Since the transition temperature range is extremely sensitive to the composition (down to the level of a few tenths of a percent), the result is that many commercial suppliers cannot tell in advance what the properties of the Nitinol they make will be. According to Edward Keible, Jr., at Raychem, extreme care in keeping the preparation process free of all contaminants has enabled researchers there to solve this problem to their satisfaction.

Other alloys do not have these difficulties. For this reason, and because of lower materials costs and easier machinability, alloys such as those based on copper may eventually supplant Nitinol as the shape memory alloy of choice, according to some metallurgists. A good deal of metallurgy, however, is yet to be done on all the shape memory alloys.—ARTHUR L. ROBINSON

Additional Reading

1. *Shape Memory Effects in Alloys*, J. Perkins, Ed. (Plenum, New York, 1975).