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Memory Metal

by George B. Kauffman and Issac Mayo

Three years ago, Los Angeles Dodgers pitcher Orel Hershiser suddenly found his brilliant career threatened by severe shoulder problems. After seven years of major league pitching, Hershiser had torn the tissue and tendons in his shoulder so badly that his arm was no longer fixed firmly in the socket. Every time he hurled the ball, he felt more pain and lost more control. The problem and put many a pitcher before him out of business.

But thanks to Nitinol, a strong and flexible nickel-titanium alloy, Hershiser was out only one season and steadily regained most of his original power. Orthopedic surgeons drilled a hole in his shoulder bone and inserted a tiny metal anchor that wedged itself into the hole by the action of a Nitinol hook. Sutures tied to the metal anchor allowed the surgeons to firmly reattach the tendons to bone.

Nitinol can straighten teeth and intercept blood clots. Eyeglass frames constructed of Nitinol can weather severe abuse (you can twist them, sit on them, and otherwise torture them) and they will spring back to their original shape.

Recently, a NASA engineer devised a pair of automatic Nitinol tweezers that are expected to be useful to doctors who must extract minute objects through small incisions.

A lot of work and a little luck

Just where did Nitinol come from and, more importantly, how was its ability to remember and return to a predetermined shape discovered? In the late 1950s and early 1960s, William J. Buehler, a researcher at the Naval Ordnance Laboratory in White Oak, Maryland, was looking for a fatigue-, impact-, and heat-resistant alloy (a substance composed of two or more metals) to use in the nose cone of a Navy missile. One of the alloys he investigated was an equiatomic (50%-50%) mixture of nickel and titanium, which exhibited the qualities Buehler desired. He named his discovery Nitinol (Nickel Titanium Naval Ordnance Laboratory). Buehler made up long, thin strips of Nitinol to use as "props" in demonstrations for his superiors at the laboratory. He would bend the strip into short folds longitudinally, forming a sort of metal accordion. The strip was then bent and stretched (as an accordion) to show that it wouldn't break. At a routine demonstration at a laboratory management meeting in 1961 an accordion-folded, fatigue-resistant strip of Nitinol was passed around a conference table and flexed repeatedly by all present. One of the Associate Technical Directors, the late Dr. David S. Muzzey, heated the compressed Nitinol strip with his pipe lighter. To the startled amazement of all, it stretched out to its original shape!

The secret of a good memory

What made Nitinol remember its shape? To help get the answer to that Buehler asked Dr. Frederick E. Wang, an expert in crystal physics, to join his research team. It was Wang who discovered the atomic structural changes that endowed the alloy with its unique characteristic.

Phase changes between solids and liquids (melting or solidifying) or liquids and gases (vaporization or condensation) are well known. Less well known, however, is the fact that such changes can occur when both phases are solids. Such phase changes involve the rearrangement of the position of particles (atoms, molecules, or ions) within the crystal structure of the solid. To fix the parent shape (the shape to which you will want Nitinol to return) the Nitinol must be held in the parent position and heated to about 500 °C (932 °F). There is no visible change in the shape of the metal; all the changes occur at the atomic level. Nitinol metal is a conglomeration of crystals of random size, shape, and orientation. When Nitinol is heated to the high temperature, the thermal energy causes the atoms to arrange themselves into the most compact and regular pattern possible. The Nitinol crystals take on a cubic arrangement called the austenite phase (see Figure 1).

When Nitinol wire cools below a certain temperature (the transition temperature), the atoms in the crystals rearrange into the martensite phase. (Remember, there is no change at the visible level. The phase change occurs only at the atomic level.)

As the solid changes from the austenite phase to the martensite phase, the atoms within a crystal rearrange into a slightly different three-dimensional shape, though the crystal retains its original neighbors (see side bar, Crystals with good neighbors).

To see how this happens, let's examine NASA's Nitinol tweezers, shown in Figure 3. During its manufacture, the alloy's composition (Ni-Ti ratio) was selected so that the transition temperature is 43 °C (110 °F). Before insertion, the Nitinol is in the martensite phase and the tweezers' tip is closed. At room temperature, the doctor bends the tips open, then inserts the tweezers into the ear canal and guides the tip to the foreign object. At the push of a button, electricity flows and the wire quickly warms up to slightly above body temperature. The thermal motion of the atoms increases and the atoms bump and push away from one another. At 43 °C the crystals are strained and, to relieve this strain, they revert to their austenite configuration, which restores the parent shape of the metal. As the tweezers tips change from the open (deformed) state to the closed (parent) state, they grab the object firmly, making it easy to remove.

What's Nitinol good for?

Once some early manufacturing problems had been solved in the late 1960s, the military began to use Nitinol couplers to join hydraulic lines in F-14 fighter planes. When cooled in liquid nitrogen the couplers expand to a large inner diameter, making them easy to slip over the hydraulic lines to be joined. On warming to room temperature, the coupler shrinks with great force to form a totally sealed joint. These couplers are still being used in the F-14 today.

The health profession is using Nitinol to simplify and remove risk from previously dangerous procedures, as illustrated by the Hershiser surgery. Cardiovascular surgeons often implant wire filters (which resemble birds' nests) in the bodies of patients who are prone to develop potentially fatal pulmonary embolisms (blood clots). At one time this was a major surgical procedure, involving large incisions. Now, by using Nitinol, a surgeon can deform the birdnest-shaped filter into a bundle of wires that can be inserted to the proper position through a catheter in the patient's vein. When released from the catheter, the bundle of wires springs back into its original birds' nest shape, ready to trap any blood clots. The patient, who required only local anesthesia, can go home the same day.

Do you wear braces? If the orthodontic wire in your mouth is Nitinol, you probably need to go to the orthodontist for readjustments far less often than a friend who wears the old-fashioned stainless steel braces. Your braces tend to remember their parent shape and, as your growing teeth deform them, they are always trying to revert to that shape.

An application of Nitinol with perhaps the greatest consumer appeal is in the manufacture of eyeglass frames. Conventional frames are always loosening, falling down your nose, or getting sat upon. Using Nitinol in the frame's bridge, top bar, and temples allows the frames to return to their parent shape upon warming.

Nitinol is also used in safety devices because of its unique sensitivity to heat. A Nitinol anti-scalding valve on the market can be inserted into water faucets and shower heads. The springlike apparatus is designed so that if the temperature of the water approaches 120 °F (49 °C) the water flow is automatically shut off. With more than 30,000 people (mostly children) receiving scald burns in the bath and shower every year in the U.S. alone, this device will certainly save a lot of pain and suffering.

Nitinol-based fire sprinkler systems are also available. The response time from fire to water release is significantly reduced from that of the older solder systems.

A toy now, an engine later?

In 1980 Dr. Wang left the military and started his own company, Innovative Technology International (ITI), to manufacture Nitinol and do research into possible applications. In 1985 ITI began marketing a toy called the Thermobile™, constructed of two pulleys and a single piece of Nitinol wire wrapped around the pulleys. One end of the Thermobile is inserted in 75 °C (167 °F) water. The single strand of Nitinol wire, passing through the hot water, contracts and tries to straighten out to its parent shape — a straight wire. The resultant torque forces the two pulleys to rotate. Thus the Thermobile converts heat energy to mechanical energy.

Can this type of system be adapted and used as a clean power source? After all, the resulting torque and force could theoretically generate electricity, turn flywheels, propel an airplane, or power a car. Research and experimentation on Nitinol-based engines is under way. ITI and Wang have designed several prototypes of Nitinol-based engines. Wang has demonstrated 40-watt Nitinol engines with internal hot water reservoirs.

Perhaps one day there will no longer be controversy about supposedly "clean" nuclear power plants; maybe our electricity will be generated by Buehler and Wang's incredible alloy. Hey, maybe the fenders of Dad's car will be made of Nitinol. This isn't so far-fetched — research and development on Nitinol car frames is also under way. So you get a little dent in the car? Just apply warm water, and no one, including Dad, will be the wiser.

SIDE BARS

Crystals with good neighbors

A metal object begins as a hot, molten liquid. As the liquid cools, a few atoms attach to each other in a geometric pattern, and this minute solid grows as other atoms cool and join. Because these solid crystals start at many locations, they grow until they eventually bump into other crystals. The boundary, where neighboring crystals meet, is not as strong as the crystal itself. When a metal bends or breaks, it is because the crystal boundaries slide or rupture. Metallurgists are constantly seeking to strengthen these boundaries.

When you bend ordinary metal—such as the iron in a coat hanger—neighboring crystals slide past each other and then stay in their new positions.

Nitinol's unusual behavior is due to the fact that, when it is bent, each martensite crystal can deform to relieve the strain instead of sliding at the crystal boundaries.

In steps A, B, and C, the Nitinol wire is treated at high temperature to set the parent shape. When it is cooled, D, the phase changes from austenite to martensite. Because martensite crystals are slightly flexible, they can deform to accommodate bending of the wire, E, while remaining attached to neighboring crystals. When warmed, F, the martensite crystals revert to their undeformed shape, and the wire magically unbends.

Nitinol sources

Memory Metal is the latest kit produced by the Institute for Chemical Education. It consists of a booklet containing a brief discussion and description of the chemistry of Nitinol's shape-memory retention and about two feet of Nitinol wire in the form of the letters "ICE." You can experiment by deforming the wire and then heating it to above 80 °C (176 °F) to observe the recovery. Memory Metal (order number 91-011A2) is available for $12 from: Institute for Chemical Education, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1396 (Phone: 608/262-3033; Fax: 608/262-0381).

If you would like a Thermobile, send a check for $22.00 to Innovative Technology International, 10747-3 Tucker Street, Beltsville, MD 20705.

CAPTIONS

These expensive glasses were twisted like a pretzel. Who would deliberately do this? Someone who had Nitinol wire frames, which snap back to a proper fit even without being heated. The frames spring back instantly because they are made of a Nitinol alloy whose critical temperature is well below room temperature. This means that the alloy is always in the return-to-memorized-shape mode and, therefore, behaves like a super-elastic spring. Similar alloys are used for the wires in dental braces and surgical anchors, which cannot be heated after insertion.

Figure 1. The austenite phase of Nitinol. Nickel atoms (white) are positioned at the corner of a cube that has a titanium atom at its center. The titanium atoms (black) form their own cubes that interlock with the nickel cubes. Each Ni atom is in the center of a Ti cube and vice versa.

Figure 2 Wire Crystals

Figure 2. In Orel Hershiser's injury, one of the three ligaments that comprise the capsule, illustration A, was pulled from the bone. To heal properly, the ligament must be held tightly in place. A hole was drilled in the bone and an anchor composed of a titanium body and a Nitinol hook was inserted. When the surgeon pulled on the sutures attached to the anchor, the springy hook was set in the porous bone, B. The sutures were threaded through the capsule, then tied together to hold the ligament firmly against the bone. The sutures eventually dissolved, but the anchor remained embedded in the bone. Prior to the invention of the Nitinol anchor, sutures were held by screws or staples (about 50 times larger than the Nitinol anchor), or by being threaded through a hole drilled completely through the bone.

Figure 3: Automatic tweezers recently invented by NASA engineer Earl Angulo. The tips of the tweezers are made of Nitinol wire that is connected to an electrical circuit powered either by a power supply or by a battery in the handle of the instrument. When current flows, the tips are heated slightly and close on the foreign object.

The Thermobile is a simple loop of Nitinol wire mounted on two pulleys. If one pulley is dipped in hot water, one side of the loop tries to straighten, which makes the tension in the two sides of the loop unequal and spins the pulleys. In addition to being a charming toy, the Thermobile may be the world's simplest heat engine. Researcher Frederick Wang has constructed multiloop engines that produce useful power.

BIOGRAPHY

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