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Chemistry and History

The Story of Nitinol: The Serendipitous Discovery of the Memory Metal and Its Applications

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Science and technology abound with examples of serendipity….

The shape-retaining alloy Nitinol (Nickel Titanium Naval Ordance Laboratory), the "metal with a memory," is revolutionizing manufacturing, engineering, and medicine as countless products that "think" for themselves enter the marketplace. This article recounts its discovery in 1959 by William J. Buehler of the U.S. Naval Ordnance Laboratory, its subsequent development by Buehler and Frederick E. Wang, and its applications in orthopedic and cardiovascular surger, orthodontics, solid-state heat engines, "shrink-to-fit" pipe couplers for aircraft, safety products, eyeglass frames, and toys. The serendipitous nature of the discovery, the solid-to-solid (austenite to martensite)

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phase transition that produces the alloy's unusual properties, its numerous practical applications, and the ready availability of samples make the alloy an ideal, exciting, and thought-provoking topic for chemistry courses at all levels in both lecture and laboratory.

What do these technological advances have in common—fire, cooking, agriculture, the wheel, and weapons? All were probably encountered by chance rather than as the result of a planned search and discovery. In Mark Twain's words, "Name the greatest of inventors. Accident."

These cases are examples of serendipity—the accidental happening became a discovery only when the inventor realized its significance. The best historical example of serendipity is probably Christopher Columbus' discovery of America while seeking a sea route to the East Indies. The word itself was coined and first used in 1754 by Horace Walpole, 4th Earl of Orford. Walpole insisted that the serendipitous discovery be not only accidental but also be arrived at in the course of seeking something else [1].

Science and technology abound with examples of serendipity: Pasteur's discovery of optical asymmetry, Fleming's discovery of penicillin, and the discovery of a unique property of the nickel–titanium alloy Nitinol, which can "memorize" a predetermined shape and return to this shape under certain temperature conditions.

Nitinol's Beginnings

In January 1958 William J. Buehler (Figure 1), a metallurgist at the Naval Ordnance Laboratory (NOL) had completed research on a series of iron–aluminum alloys [2]. Buehler, born in Detroit, Michigan on October 25, 1923, had received his Bachelor of Science degree in chemical engineering (1944) and his Master of Science degree in metallurgical engineering (1948) from Michigan State University at East Lansing. In 1948 he was hired as an Instructor in Metallurgy at North Carolina State University in Raleigh. In June 1951 NOL in White Oak, Maryland was looking for a mechanical engineer for their staff, and Buehler was hired. He was promoted to Metallurgist in January 1952 and by July 1956 was a Supervisory Physical Metallurgist [3].

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FIGURE 1. WILLIAM J. BUEHLER IN 1968, PICTURED WITH A DEMONSTRATION OF NITINOL WIRE. ELECTRICITY WAS PASSED THROUGH A STRAIGHT PIECE OF WIRE, AND THE WIRE WOULD CHANGE INTO THE WORD "INNOVATIONS." THE OAK LEAF, U.S. NAVAL ORDNANCE LABORATORY, WHITE OAK, MARYLAND, JUNE 1968.

The "between-projects boredom" began to set in for Buehler after completing the iron–aluminum alloy project [2]:

> It was at this point… that lady luck played a key role. I found within the U.S. Naval Ordnance Laboratory an ongoing materials project which had the goal of developing metallic materials for the nose cone of the U.S. Navy Polaris reentry vehicle…. The in-house project was under the direction of Mr. Jerry Persh, an aerodynamicist. I was able to attach myself to this project, and my initial task was to provide physical and mechanical property data on existing metals and alloys for computer-assisted boundary layer calculations. These calculations were to simulate the heating, etc. of a reentry body through the earth's atmosphere. My informational role in this project very quickly became somewhat boring, and I almost immediately began to think in terms of possibly tailoring newly developed alloys that might better satisfy the drastic thermal requirements of the reentry body. My initial thought was to look more closely at intermetallic compound alloys, where the two component metals form a metallic phase that has simple stoichiometric proportions and generally possesses a high melting temperature—major limitation, DUCTILITY.

Events in Buehler's personal life at this same time exacerbated his ennui [4]:

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> My first wife and I separated, and I spent a tremendous amount of time working in the laboratory… you might say it's a good feature that came out of a disastrous situation. I had lots of time at that point… in the state of Maryland the law required a three-year waiting period of separation before formal divorce could be handled. During that three-year period I literally worked day and night. Many days I would get up at 4 o'clock in the morning, go to the lab, and not go home until 11 o'clock at night. Between working at the laboratory and playing golf, I really didn't do anything other than eat or sleep.

To initiate the reentry material project Buehler consulted Max Hansen's recently published *Constitution of Binary Alloys* [5]. This book contained what was then the most complete collection of binary constitution diagrams, showing the solid-state phase relationships of two–component metallic alloys as a function of composition and temperature. Buehler selected approximately sixty intermetallic compound alloys for further study [6]. This number was then reduced, for various logical reasons, to twelve alloy systems. One of the systems, an equiatomic nickel–titanium alloy, immediately exhibited considerably more impact resistance and ductility than the other eleven alloys [7]. In 1953 Dr. Harold Margolin of New York University and his associates had carried out some studies on phase changes of nickel–titanium alloys but had sensed no uniqueness among them [8].

In 1959 Buehler decided to concentrate on the equiatomic nickel–titanium composition alloys and relegated the intermetallic compound systems to secondary status. He named his discovery NITINOL (**Ni**ckel **Ti**tanium **N**aval **O**rdnance **L**aboratory) [7]. That same year he made an observation about his discovery that hinted at the extraordinary, but still undiscovered, property of Nitinol [2].

> I distinctly remember my very exciting discovery of the acoustic damping change with temperature change near room temperature. This unusual event unfolded when my…assistant… and I were melting a number of [Nitinol] bars in the arc-melting furnace. On the day in question (circa 1959), six arc-cast bars were made. While cooling on the transite-topped table, the first bars arc-cast into bar form had cooled to near room temperature, while the last bars to be cast were still too hot… to be handled with bare hands. Between the cool (first bar) and the very warm bar (last bar) were four arc-cast bars possessing a broad spectrum of temperatures…. My "hands-on" approach caused me to take the cooler bar(s) to the shop grinder to manually grind away any surface irregularities that might produce a subsequent scaly or bad… surface. In going from the table to the bench grinder, I *purposely* dropped the cool (near room temperature) bar on the concrete laboratory floor [a quick test to determine roughly the damping capacity of an alloy]. It produced a very dull "thud," very

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much like what one would expect from a similar size and shape lead bar. My immediate concern was that the arc-casting process may have in some way produced a multitude of micro cracks within the bar—thus producing the unexpected damping phenomena. With this possibly discouraging development in mind, I decided to drop the others on the concrete floor. To my amazement, the warmer bars rang with bell-like quality. Following this I literally ran with one of the warmer bars (that rang) to the closest source of cold water—the drinking fountain—and chilled the warm bar. After thorough cooling the bar was again dropped on the floor. To my continued amazement it now exhibited the leaden-like acoustic response. To confirm this unique change, the cooled bars were heated through in boiling water—they now rang brilliantly when dropped upon the concrete floor. Subsequent discussions with my melter assistant revealed that he had in no way mixed or altered the alloy compositions during repeated melting. This immediately alerted me to the fact that the marked acoustic damping change was related to a major atomic structural change, related only to minor temperature variation.

Following the startling acoustic damping discovery, other seemingly related unique changes were observed. More interestingly, these changes also occurred in about the same temperature range as the acoustic damping change. Examples of some of these correlatable phenomena were:

- Polished plane metallographic alloy surface when heated slightly (100 °C to 200 °C; 212 °F to 392 °F) exhibited an obvious eruption or recontouring of the surface. Plate-like surface shearing occurred and appeared to form along certain crystallographic planes.

- Microhardness indentations made at room temperature remained stable in size at room temperature. However, when heated slightly (100 °C to 200 °C; 212 °F to 392 °F), they tended to significantly reduce in size.

- Metallography specimens polished using standard Al_2O_3 abrasive followed by etching always revealed a typical acicular martensitic structure that one would typically find in quench-hardened steel. It was only after very careful diamond polishing (with minimal surface strain) that the true NITINOL base structure was revealed.

- Acoustic damping, strain, and microstructure combined with minor temperature variation were all, in their way, trying to tell me that this was an overtly dimensionally mobile alloy capable of major atomic movement in a rather low temperature regime—near room temperature. With all of the signals above what major act did NITINOL finally have to perform to reveal its incredibly unique shape-memory property?

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Strain and Heat-actuated Recovery—A Serendipitous Discovery

In the early 1960s Buehler prepared a long, thin (0.010-inch thick) strip of Nitinol to use in demonstrations of the material's unique fatigue-resistant properties. He bent the strip into short folds longitudinally, forming a sort of metallic accordion. The strip was then compressed and stretched (as an accordion) repeatedly and rapidly at room temperature without breaking. In 1961 a laboratory management meeting was scheduled to review ongoing projects. Unable to attend, Buehler sent the late Raymond C. Wiley, his newly acquired professional metallurgical assistant, to the meeting to present Buehler's work. As one of their "props" for the review, Wiley took the accordion folded fatigue-resistant strip. During the presentation, it was passed around the conference table and flexed repeatedly by all present. One of the Associate Technical Directors, Dr. David S. Muzzey, who was a pipe smoker, applied heat from his pipe lighter to the compressed strip. To everyone's amazement, the Nitinol stretched out longitudinally [7]. The mechanical memory discovery, while not made in Buehler's metallurgical laboratory, was the missing piece of the puzzle of the earlier-mentioned acoustic damping and other unique changes during temperature variation. This serendipitous discovery became the ultimate payoff for Nitinol [7].

In 1962 Dr. Frederick E. Wang (Figure 2) joined Buehler's group at the Naval Ordnance Laboratory, his expertise in crystal physics being vitally needed. Wang, born on August 1, 1932 in Su-Tou, Formosa (now Taiwan), emigrated to the United States and did his undergraduate work in chemistry and physics at the University of Tennessee at Knoxville. After receiving his doctorate in physical chemistry from Syracuse University in 1960 [9, 10], he worked as a postdoctoral associate for future (1976) Nobel chemistry laureate William Nunn Lipscomb, Jr. at Harvard University, until he left to join Buehler at NOL. The commercial applications of Nitinol that were to come would not have been possible without Wang's discovery of how the shape-memory property of Nitinol works [11].

An alloy such as Nitinol with a mechanical memory requires certain basic atomic structural characteristics. The first requisite is an atomically ordered solid-state parent phase, classically called austenite (named for the English metallurgist Sir William Chandler Roberts-Austen, 1843–1902) that exists in the higher temperature regime. Secondly, at a lower temperature, the atoms of the ordered austenite phase must be capable of solid-to-solid "shearing" into a very complex, new atomic arrangement or phase, which has been given the name martensite (named for the German

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FIGURE 2. DR. FREDERICK E. WANG.

metallographer, Adolf Martens, 1850–1914). The austenite ⇌ martensite transformation (transition) proceeds through a critical temperature range or in special situations with applied stress and strain (stress-induced martensite). Thus Nitinol is said to undergo a martensite transformation. The complex relative movement of atoms within the martensite phase is far too complicated to be described in detail here. For the sake of simplicity, one can think of the solid Nitinol alloy in terms of a decreasing temperature profile. Starting below the alloy melting point and down to 600–700 °C (1112–1292 °F) the crystal structure is disordered body-centered cubic. From 600 °C (1112 °F) to the austenite ⇌ martensite transformation temperature range (TTR), the crystal structure becomes that of an "ordered" cubic, frequently called a CsCl, structure. As the alloy cools through the transformation temperature range (TTR), its atoms "shear," forming the new, rather complex martensite phase. The critical features to be emphasized here are the austenite ⇌ martensite transformation (transition) and the temperature or temperature range (TTR) where this solid-state shear mechanism occurs [12] (Figure 3). In the Nitinol–type alloys this TTR can be varied over a realistic temperature range from 100 °C to well below liquid nitrogen temperature (bp –195.8 °C or –320 °F) by varying the nickel–titanium ratio or ternary alloying with small amounts of other metallic elements, e.g., Co, Fe, V, etc.

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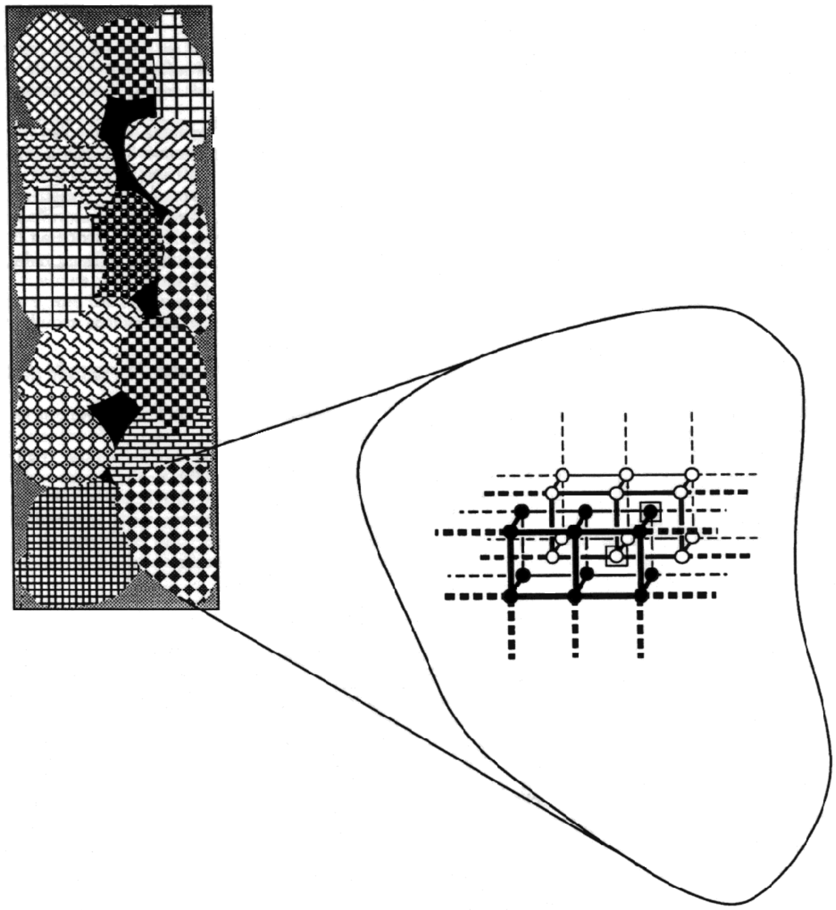

FIGURE 3. A MULTICRYSTALLINE METAL SAMPLE. EACH PATTERN REPRESENTS A DIFFERENT GRAIN OF RANDOM SHAPE, SIZE, AND ORIENTATION OF THE ATOM LATTICE. BLACK INDICATES GAPS BETWEEN GRAINS. THE BLOW-UP ON THE RIGHT SHOWS THE STRUCTURE OF THE AUSTENITE PHASE OF THE NITINOL ATOMIC LATTICE CALLED "BODY-CENTERED CUBIC:" THE CUBES ARE INTERTWINED SUCH THAT EACH CORNER IS IN THE CENTER OF ANOTHER CUBE. THE DISTANCE TO THE CENTER OF A CUBE FROM A CORNER IS SHORTER THAN THE DISTANCE TO A NEIGHBORING CORNER. THUS THE "NEAREST NEIGHBORS" OF EACH NICKEL ATOM (SHOWN BY THE WHITE BALLS) ARE TITANIUM ATOMS (BLACK BALLS), NOT OTHER NICKEL ATOMS; AND VICE-VERSA [13].

Nitinol is a conglomeration of tiny regions of single crystals, called grains, all of random size, shape, and orientation. To fix a desired shape in Nitinol, it must be heated to approximately 500 °C (932 °F) while being constrained in its desired fixed position. The effect of the heating is the restructuring of the atomic lattice within the individual grains, and the atoms of the grains adopt the austenite (atomically ordered) phase, which has an atomic structure in which each nickel atom is surrounded by eight titanium atoms at the corners of the cube. Each titanium atom is likewise surrounded by a cube of nickel atoms. Figure 3 shows a sketch of this arrangement [13].

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For example, when a Nitinol wire cools below its transition temperature range (TTR), the austenite phase inside the grains changes to the martensite phase, which means that the nickel and titanium atoms within the wire assume a different and more complex three-dimensional arrangement. The austenite structure is slightly distorted, but these accommodating distortions are on the atomic scale and thus are not visible. There are 24 three-dimensional variants of this slight, atomic-scale distortion [13]. Thus the Nitinol wire can be cooled from the austenite temperature range, through the TTR, to room temperature without changing its shape, even though austenite-to-martensite phase transformations occur. If the cooled wire (at a temperature lower than its TTR) is put under strain by stretching, some of the martensite undergoes atomic shear that is caused by the strain. Greater strain leads to more transformation [14]. In Nitinol an overall strain approaching 8% can be attributed to martensite shear. Strains in excess of about 8% are not the result of martensite shear and are therefore not recoverable.

When distorted Nitinol alloy is warmed, the motion of the atoms is again increased. To accommodate the increased thermal motion the atoms slip back into the austenite phase configuration, which also restores the original shape of the alloy. In nonmemory metals, the strain of a deformation must be absorbed by the rearrangement of entire grains because the atoms within the grains are locked rigidly into their lattice positions. It is impossible to get the grains back into exactly the same positions after such a deformation. In Nitinol, however, the grains stay in place—instead, the atoms move [13]. If the recovery of shape is restrained when heating above the TTR (austenite phase), a force will be available for doing work or gripping another object [15].

No discussion of Nitinol, the preeminent shape–memory alloy, would be complete without a brief mention of other alloy systems that have exhibited the shape-memory property in at least some limited form. The most significant examples are copper–zinc (brass), copper–zinc–aluminum, and gold–cadmium alloys [15]. Also, to a lesser and varying degree, shape memory is found in such diverse alloy systems as iron–platinum, indium–cadmium, iron–nickel, nickel–aluminum, and stainless steel [15]. What limits the shape-memory applications potential of these other alloy systems? Basically, none possess the combined property advantages of Nitinol. The list of a few key Nitinol advantages would include overall physical and mechanical properties, magnitude of strain-heat recovery, energy conversion, general corrosion resistance, human tissue and body fluid compatibility for medical applications, ease in reliably altering the

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memory-recovery temperature through alloying variations, and a reasonable fabricated alloy cost.

Early Research and Uses of Nitinol

Progress in getting Nitinol into consumer applications came slowly because of early problems with its manufacture and because of its expense [16]. A major problem was inconsistency among batches of Nitinol. Supposedly identical batches did not possess the same transition temperature. These inconsistencies were not a problem for laboratory demonstrations, but they hindered the manufacture of viable engineering materials [17]. Buehler and Wang's research group at NOL continued to work on and refine the Nitinol manufacturing process until the bugs and glitches were eliminated [18, 19]. In April 1967 Wang organized and chaired a symposium on Nitinol and associated compounds. Thirteen papers were presented at the meeting [20].

The first successful Nitinol product was the Raychem Corporation's Cryofit™ "shrink-to-fit" pipe coupler, introduced in 1969 [21, 22]. Nitinol solved the problem of coupling hydraulic-fluid lines in the F-14 jet fighter built by the Grumman Aerospace Corporation. Grumman engineers were seeking an alternative to the difficult task of joining lines that lie close to the aircraft's aluminum skin. Raychem, which had wide experience in heat-shrinkable plastics, proposed a coupling in which a low-TTR (below –120 °C; –184 °F) Nitinol alloy was fabricated at room temperature (austenite phase) to the final *deployed* coupling dimensions. To produce the desired coupling effect the coupler was placed in a liquid nitrogen bath (martensite phase) and while there, the coupler was radially expanded. This was accomplished by forcing an oversize tapered mandrel longitudinally through the coupler bore. When continually cooled in liquid nitrogen, the coupler remained stably expanded. Coupling two sections of hydraulic pipe was then accomplished by simply inserting the pipe ends into the expanded Nitinol coupler and allowing the coupler to warm to its near original, or memory, diameter. The radial contraction of the coupler, combined with the very high associated force, provided a continuously clamping and totally sealed joint at well below the required –120 °C (–184 °F) temperature [23]. In this Nitinol application the TTR was designed to be less than –120 °C (–184 °F) [15], which was the required minimum operating temperature specification. These proven couplers are currently being used to join hydraulic tubes in the F-14 fighter aircraft as well as in many other similar industrial applications [21].

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FIGURE 4. DR. GEORGE ANDREASEN DISPLAYING NITINOL WIRE THAT HE ADAPTED FOR ORTHODONTIC USE. NITINOL ORTHODONTIC DEVICES REQUIRE FEWER READJUSTMENTS THAN THEIR STAINLESS STEEL COUNTERPARTS [24].

Another early use of Nitinol was in orthodontic bridge wires [24]. The late George B. Andreasen, D.D.S. of the University of Iowa developed Nitinol for use in orthodontics (Figure 4). In standard binding tests Andreasen found that Nitinol wires had a recoverable strain that was ten or more times that of stainless steel. The large recoverable strain, combined with a low elastic modulus (stress divided by strain) means that only one Nitinol wire is needed for most of the teeth-straightening procedure, even for badly maloccluded teeth, as opposed to the continuous changing to thicker and thicker stainless steel braces as the teeth are gradually brought into line. Andreasen wrote to Buehler after Buehler's present wife had undergone some orthodontic work [26]:

> The dignity you are still receiving has spread around the world in your development of the alloy Nitinol. If it hadn't been for you, your wife would be treated with stainless steel wire. If you had not sent me the 3–foot piece of Nitinol wire, I could not have applied it to orthodontics. In fact, I'll be in your debt forever.

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With improved manufacturing techniques the commercial use of Nitinol increased during the 1970s and 1980s. Nitinol was incorporated into medical products, safety products, military products, and even ladies' undergarments.

Medical Applications

One revolutionary use of Nitinol in medicine has been in orthopedic surgery. In September 1989 the U.S. Food and Drug Administration (FDA) approved the use of Mitek Surgical Products' Mitek Anchor, constructed of Nitinol. Presently, the most common way of treating torn ligaments and tendons is immobilizing the limb of the patient in the hope that tissue will grow back onto the bone. Another option is surgery involving screws, staples, and other devices which reattach torn muscles to bone. Most of the surgeries involving this type of hardware are expensive as well as quite invasive to the body, making them somewhat dangerous. Mitek's anchor is a fraction of the size of the older devices and is implanted through tiny incisions. It is shaped like a tiny anchor with two arms that hook into the bones. What makes the design work is the fact that compressed Nitinol returns to its original anchor shape after it is squeezed through a tiny hole in the body and subsequently warms to body temperature (37 °C or 98.6 °F). Until now, use of the anchor has been FDA-approved only for shoulder surgery, but Mitek is hoping for expanded approval for other orthopedic surgeries [27].

Physicians in the former Soviet Union are using Nitinol splints, with which simple fractures can be mended several times faster than with conventional splints. The Nitinol splints not only hold the fractured bones in place more securely, but they also push the bones together so that the break heals more rapidly [28].

Perhaps no field of medicine has been changed by Nitinol as much as cardiovascular surgery. In 1989 radiologist Morris Simon, M.D. of Boston's Beth Israel Medical Center patented a design for a blood filter that can be set in a vein to trap blood clots *without surgery* [15]. These blood colts (pulmonary embolisms) kill about 200,000 victims each year, and the process of surgically implanting blood filters is both dangerous and expensive. With the Simon–Nitinol filter, below-body-temperature–TTR Nitinol wires are preformed in the desired mushroom shape. They are then cooled and straightened well below body temperature. When inserted into a large vein through a catheter and warmed to body temperature, the Nitinol wires spring back into their original mushroom shape while the filter's splay feet attach to the wall of the vein.

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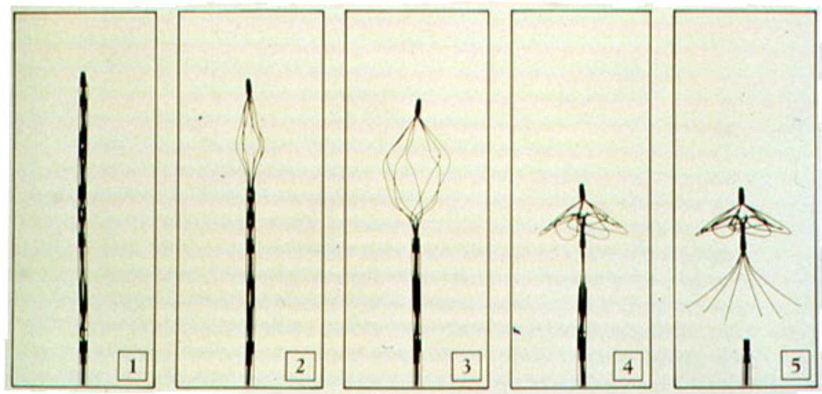

FIGURE 5. DIAGRAM 1 SHOWS THE SIMON–NITINOL PULMONARY EMBOLISM FILTER PRIOR TO ITS INSERTION IN A CATHETER. THE FILTER'S STRAIGHT, PLIABLE FORM IS MAINTAINED BY A COLD SALINE SOLUTION. DIAGRAMS 2–5 SHOW THE FILTER CHANGING TO ITS CLOT-TRAPPING SHAPE AS IT IS WARMED TO BODY TEMPERATURE [31].

Once deployed in position, the filter is capable of catching clots en route to the heart, holding them until they dissolve naturally. Figure 5 shows the filter as it changes from the straight wire shape to its parent shape [29–31].

Cardiovascular surgeons in Moscow have devised a procedure using a Nitinol prosthesis to reinforce sections of blood vessels. A small Nitinol wire, introduced into a vessel, transforms to its spiral parent shape when it warms to body temperature [32].

Many other areas of medicine are feeling the impact of Nitinol. Catheter Research Corporation of Indianapolis, Indiana is currently marketing a "steerable" catheter for the placement of medical microinstruments, drugs, and electrodes in blood vessels [33]. The electronically controlled tip of the catheter is made of Nitinol supplied by Innovative Technology International (ITI), the company that Frederick Wang founded after he left the government in 1980 [34].

In his doctoral project at the University of Twente in Enschede, the Netherlands, mechanical engineer Marc Sanders has experimented with the use of Nitinol as a gentler method of correcting scoliosis, a lateral bending and twisting of the spine that in most cases develops in infancy or childhood. In severe cases surgeons try to force the spine to straighten by implanting a rigid rod that is screwed to the vertebrae. According to Sanders, "we can apply a corrective force over several weeks, instead of

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the transient force obtained by traditional methods…. We can achieve a better correction," changing the twist as well as the bend in the spine [35].

Extracting foreign objects from human organs such as the ear canal often requires a physician to force a large and rigid instrument past the object to grasp it, which often poses grave risks to the organ. Earl Angulo, a researcher with the Goddard Space Flight Center, has designed an instrument that eliminates such risks by incorporating Nitinol in its tip. The device is constructed from a small, flat loop for easy insertion past the object lodged in the organ canal. Electrical current is passed through the wire, heating it until it resumes the previously programmed hook shape and allowing the physician to grasp and remove the object [36].

Energy, Engineering, and the Military

Wang now researches, among other applications, the possibility of using Nitinol as a source of energy. Because solid-state heat engines require nothing more than a heat source to generate power, they could become a very clean power source. ITI has studied the feasibility of power plants based on Nitinol. To date, energy yields from Nitinol engines have been low. Wang has found no easy way to increase their output, but he hopes to overcome these problems [17].

Wang has built a number of prototypes of Nitinol engines, based on the conversion of thermal energy to mechanical energy (Figure 6). The changes in Nitinol as it passes through two water baths—one hot and one cold—causes the motion in the prototype engines. The hot water heats the Nitinol to its transition temperature, and it contracts, while the cold water cools it below its transition temperature, and it expands. The resulting force and torque can drive an engine which could theoretically generate electricity, turn flywheels, propel an airplane, or power a car [17]. ITI markets the Thermobile™, an educational toy that demonstrates the conversion of heat energy to mechanical energy [37]. One end of the toy is inserted into warm water, and several loops of Nitinol wire, each encircling two pulleys, contract. The resulting torque forces the pulleys to rotate [38]. Prior to the development at ITI of new technologies for treating Nitinol, the memory effect of the Nitinol wires would fade after approximately 10^4–10^5 cycles; also, the welded joint made in forming the continuous wire loop would fail after only around 10^3 cycles [39]. After Wang's company began its new manufacturing techniques, it built a Thermobile™-type engine that operated

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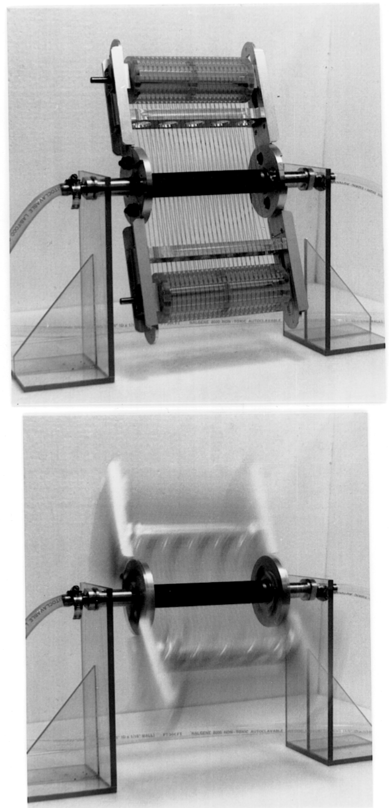

FIGURE 6. A PROTOTYPE OF A NITINOL-BASED ENGINE, BUILT BY INNOVATIVE TECHNOLOGY INTERNATIONAL. IN THE TOP PHOTOGRAPH, THE ENGINE IS AT REST. IN THE BOTTOM PHOTOGRAPH, ALTERNATING HOT AND COLD WATER IS APPLIED TO THE DEVICE, LEADING TO A TORQUE WHICH CAUSES THE ENGINE TO ROTATE [40].

continuously (under controlled temperature conditions) for a year and a half. During this time interval the Nitinol wires underwent 2.1×10^8 cycles (nearly 10^4-fold longer than the original Nitinol wire lifetime) without breakage and showed no ill effects of fatigue [40].

The resistance of Nitinol to sea water as well as its unusual mechanical properties make it especially suitable for applications in ocean engineering [12]. Under a grant from the U.S. Department of Energy, Memory Metals, Inc. of Stamford, Connecticut is studying high-pressure, corrosion-resistant seals made of Nitinol. Seals are prepared by stretching the alloy into the desired shape, then compressing them into another, smaller shape. The company will be looking at applications in geothermal brine wells, where pressures of 4,000–6,000 pounds per square inch and extreme corrosivity exist.

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Exposure to the elevated temperature in the geothermal well causes the seal to expand to its original shape [41].

Beta Phase, Inc. of Menlo Park, California has received two patents for its Nitinol electrical connector products. The Beta Phase connectors, when heated, "remember" their factory-trained shapes and return to them, supplying the force to open or close electrical connections between components [15].

Researchers Craig Rogers and Harry Robertshaw at the Virginia Polytechnic Institute at Blacksburg are working with an electrical engineer, Richard Claus, to add fiber-optic sensors and microprocessors to increase Nitinol's "intelligence." An important application is seen in aerospace vehicles if control surfaces without hinges can be designed. In robotics, a goal is machinery closer to human models, in which embedded Nitinol fibers act as muscles and embedded optical fibers act as nerves [43].

The Boeing Corporation of Seattle, Washington is now researching ways to use Nitinol. The Boeing Defense and Space Group, led by researcher Jerry Julien, has patented a system to align laser beams precisely by using a simple Nitinol device called the Shape Memory Metal Precision Actuator. The actuator replaces complex mechanical alignment devices. The alloy also is being used to position the antenna in a Boeing advanced millimeter-wave radar and is being investigated as a replacement for motors, pulleys, and gears in airplanes and weaponry [44].

Safety Products

Nitinol's sensitivity to changes in temperature makes it particularly suitable for use in two home and office products—automatic water-tap turn-offs and fire sprinkler systems [21]. Memry Corporation of Brookfield, Connecticut has developed a Nitinol anti-scald valve that shuts off the tap in sinks, tubs, or showers when the temperature of the water rises dangerously high. A spring made of Nitinol expands at 120 °F (49 °C) and pushes a plunger to stop the flow of hot water. A return spring pushes the plunger back to its original position once the temperature of the water is readjusted. With some 37,000 children a year in the United States alone being scalded by hot water, this device will save injury, pain, and medical costs [45].

A fire sprinkler system was developed by Battelle Columbus Laboratories in Ohio in which contraction of a piece of Nitinol, used as a heat-sensor component, releases the

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water. The response time from fire to water release was significantly decreased. The system had an on–off sprinkler (based on Nitinol's two-way memory characteristic) to stop the water flow automatically after the fire is out so as to reduce water damage to property [46–49].

Eyeglasses

An application of Nitinol with perhaps the greatest potential consumer appeal is in the fabrication of eyeglass frames [21] (Figure 7). Researchers in California's Silicon Valley began experimenting with Nitinol's use in such frames in the mid-1980s. It was then difficult to fabricate frames of Nitinol since it could not be readily welded or plated. Several years of design and research and development in the United States and Japan were necessary before Marchon & Marcolin Eyewear of Melville, New York launched the first large-scale application of Nitinol eyewear in 1988 [23]. The alloy is used in the frame's bridge, top bar, and temples, where flexibility is most needed, allowing the frame to retain its original shape. Nitinol frames are also more durable and corrosion-resistant than conventional frames [50].

Other Uses

Hinges made from a Nitinol spring are now used to open greenhouse windows whenever the temperature inside the building becomes too high [21]. A coffeemaker is being marketed with a Nitinol valve that will not open to release the water onto the coffee grounds until the water reaches a predetermined temperature [23]. A Japanese research project investigating the use of Nitinol in automobile fenders is under way. If successful, these fenders will make many trips to the body shop unnecessary [51]. A toy called Space Wings consists of a pair of wings, a piece of Nitinol wire, and a printed-circuit-board/battery module that electrically heats the wire. When heated briefly, the wire contracts and flaps the wings. As it cools, the wire expands, moving the wings in the opposite direction. The cycle repeats over and over again, and the toy flaps away [52].

The Past and the Future

Hard work in the laboratory and some serendipity—these two ingredients were the recipe for Nitinol's success in the thirty-eight years since Buehler and Wang started

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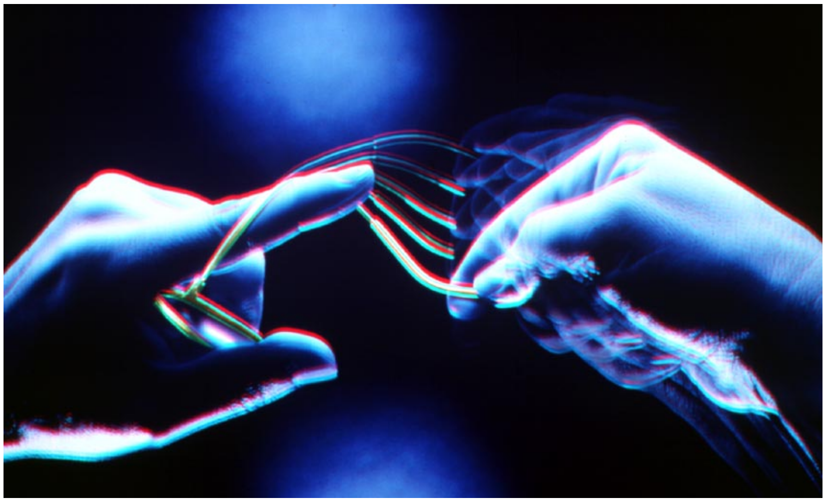

FIGURE 7. EYEGLASS FRAMES BEING RADICALLY DEFORMED. FRAMES CAN BE PLACED IN WARM WATER AND ALLOWED TO RETURN TO THEIR ORIGINAL SHAPE [50].

working with the alloy [53]. If the late David Muzzey had not held his pipe lighter to the Nitinol sample at that 1961 management meeting, it could have been years before Nitinol's memory characteristics came to light. Equally important, of course, were the years of scientific research that Buehler and Wang devoted to their remarkable alloy. Buehler wrote of their relationship [2]:

> I was able to provide Dr. Wang with a new uncharacterized unique material and he, in turn, devised the basic understanding of the useful overt properties. In retrospect, an unbeatable combination.

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