Shape Memory Alloys

Darel E. Hodgson, Shape Memory Applications, Inc., Ming H. Wu, Memry Corporation, and Robert J. Biermann, Harrison Alloys, Inc.

THE TERM SHAPE MEMORY ALLOYS (SMA) is applied to that group of metallic materials that demonstrate the ability to return to some previously defined shape or size when subjected to the appropriate thermal procedure. Generally, these materials can be plastically deformed at some relatively low temperature, and upon exposure to some higher temperature will return to their shape prior to the deformation. Materials that exhibit shape memory only upon heating are referred to as having a one-way shape memory. Some materials also undergo a change in shape upon recrystallization. These materials have a two-way shape memory.

Although a relatively wide variety of alloys are known to exhibit the shape memory effect, only those that can recover substantial amounts of strain or that generate significant force upon changing shape are of commercial interest. To date, this has been the nickel-titanium alloys and copper-base alloys such as Cu-Zn-Al and Cu-Al-Ni.

A shape memory alloy may be further defined as one that yields a thermoelastic martensite transformation, which allows the alloy to be deformed by a twinning mechanism below the transformation temperature. The deformation is then reversed when the twinned structure reverts upon heating to the parent phase.

History

The first recorded observation of the shape memory transformation was by Chang and Read in 1932 (Ref 1). They noted the reversibility of the transformation in AuCd by metallographic observation of resistivity changes, and in 1951 the shape memory effect (SME) was observed in a bent bar of AuCd. In 1938, the transformation was seen in brass (copper-zinc). However, it was not until 1962, when Buehler and co-workers (Ref 2) discovered the effect in equiatomic nickel-titanium (Ni-Ti), that research into both the metallurgy and potential practical uses began in earnest. Within 10 years, a number of commercial products were on the market, and understanding of the effect was much advanced. Study of shape memory alloys has continued at an increasing pace since then, and more products using these materials are coming to the market each year (Ref 3, 4).

As the shape memory effect became better understood, a number of other alloy systems that exhibited shape memory were investigated. Table 1 lists a number of these systems (Ref 5) with some details of each system. Of all these systems, the Ni-Ti alloys and a few of the copper-base alloys have received the most development effort and commercial exploitation. These will be the focus of the balance of this article.

General Characteristics

The martensitic transformation that occurs in the shape memory alloys yields a thermoelastic martensite and develops from a high-temperature austenite phase with long-range order. The martensite typically occurs as alternately sheared platelets, which are seen as a herringbone structure when viewed metallographically. The transformation, although a first-order phase change, does not occur at a single temperature but over a range of temperatures that varies with each alloy system. The usual way of characterizing the transformation and naming each point in the cycle is shown in Fig. 1. Most of the transformation occurs over a relatively narrow temperature range, although the beginning and end of the transformation during heating or cooling actually extends over a much larger temperature range. The transformation also exhibits hysteresis in that the transformation on heating and on cooling does not overlap (Fig. 1). This transformation hysteresis (shown as T in Fig. 1) varies with the alloy system (Table 1).

### Table 1 Alloys having a shape memory effect

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>Transformation-temperature range °C</th>
<th>Transformation hysteresis Δ°C</th>
<th>Δ°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-Cd</td>
<td>44/49 at. % Cd</td>
<td>-190 to -50 °C to -310 to -60 °C</td>
<td>≈15 °C</td>
<td>≈25 °F</td>
</tr>
<tr>
<td>Au-Cd</td>
<td>46.5/50 at. % Cd</td>
<td>30 to 100 °C to 85 to 212 °C</td>
<td>≈15 °C</td>
<td>≈25 °F</td>
</tr>
<tr>
<td>Cu-Al-Ni</td>
<td>14/14.5 wt % Al</td>
<td>-140 to 100 °C to -220 to 212 °C</td>
<td>≈35 °C</td>
<td>≈65 °F</td>
</tr>
<tr>
<td>Cu-Sn</td>
<td>3/4.5 wt % Ni</td>
<td>-120 to 30 °C to -185 to 85 °C</td>
<td>≈10 °C</td>
<td>≈20 °F</td>
</tr>
<tr>
<td>Cu-Zn</td>
<td>38.9/4.5 wt % Sn</td>
<td>-180 to -10 °C to -290 to 15 °C</td>
<td>≈10 °C</td>
<td>≈20 °F</td>
</tr>
<tr>
<td>Cu-Zn-X (X = Si, Sn, Al)</td>
<td>a few wt % of X</td>
<td>-180 to 200 °C to -290 to 390 °C</td>
<td>≈10 °C</td>
<td>≈20 °F</td>
</tr>
<tr>
<td>In-Ti</td>
<td>18/23 at. % Ti</td>
<td>60 to 100 °C to 140 to 212 °C</td>
<td>≈4 °C</td>
<td>≈7 °F</td>
</tr>
<tr>
<td>Ni-Al</td>
<td>36/38 at. % Al</td>
<td>-160 to 100 °C to -290 to 212 °C</td>
<td>≈10 °C</td>
<td>≈20 °F</td>
</tr>
<tr>
<td>Ni-Ti</td>
<td>49/51 at. % Ni</td>
<td>-50 to 110 °C to -60 to 230 °C</td>
<td>≈30 °C</td>
<td>≈55 °F</td>
</tr>
<tr>
<td>Fe-Pt</td>
<td>25 at. % Pt</td>
<td>≈-130 °C to ≈-200 °C</td>
<td>≈4 °C</td>
<td>≈7 °F</td>
</tr>
<tr>
<td>Mn-Cu</td>
<td>5/35 at. % Cu</td>
<td>-250 to 180 °C to -420 to 355 °C</td>
<td>≈25 °C</td>
<td>≈45 °F</td>
</tr>
<tr>
<td>Fe-Mn-St</td>
<td>32 wt % Mn, 6 wt % Si</td>
<td>-200 to 150 °C to -330 to 300 °C</td>
<td>≈100 °C</td>
<td>≈180 °F</td>
</tr>
</tbody>
</table>

Source: Ref 5

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### Footnotes

1. Chang and Read, in 1932, observed the effect in equiatomic nickel-titanium.
2. Buehler and co-workers, in 1962, discovered the effect in equiatomic nickel-titanium.
3. Materials have been on the market since the 1960s.
4. Research into shape memory alloys has continued at an increasing pace.
5. Table 1 lists a number of these systems with some details of each system.
Thermoelastic martensites are characterized by their low energy and glissile interfaces, which can be driven by small temperature or stress changes. As a consequence of this, and of the constraint due to the loss of symmetry during transformation, thermoelastic martensites are crystallographically reversible. The herringbone structure of athermal martensites essentially consists of twin-related, self-accommodating variants (Fig. 2b). The shape change among the variants tends to cause them to eliminate each other. As a result, little macroscopic strain is generated. In the case of stress-induced martensites, or when stressing a self-accommodating structure, the variant that can transform and yield the greatest shape change in the direction of the applied stress is stabilized and becomes dominant in the configuration (Fig. 2c). This process creates a macroscopic strain, which is recoverable as the crystal structure reverts to austenite during reverse transformation.

**Thermomechanical Behavior**

The mechanical properties of shape memory alloys vary greatly over the temperature range spanning their transformation. This is seen in Fig. 3, where simple stress-strain curves are shown for a nickel-titanium alloy that was tested in tension below, in the middle of, and above its transformation range. The martensite is easily deformed to several percent strain at quite a low stress, whereas the austenite (high-temperature phase) has much higher yield and flow stresses. The dashed line on the martensite curve indicates that upon heating after removing the stress, the sample ‘‘remembered’’ its unstrained shape and reverted to it as the material transformed to austenite. No such shape recovery is found in the austenite phase upon straining and heating, because no phase change occurs.

An interesting feature of the stress-strain behavior is seen in Fig. 3(c), where the material is tested slightly above its transformation temperature. At this temperature, martensite can be stress induced. It then immediately strains and exhibits the increasing strain at constant stress behavior, seen in AB. Upon unloading, though, the material reverts to austenite at a lower stress, as seen in line CD, and shape recovery occurs, not upon the application of heat but upon a reduction of stress. This effect, which causes the material to be extremely elastic, is known as pseudoelasticity. Pseudoelasticity is nonlinear. The Young’s modulus is therefore difficult to define in this temperature range as it exhibits both temperature and strain dependence.

In most cases, the memory effect is one way. That is, upon cooling, a shape memory alloy does not undergo any shape change, even though the structure changes to martensite. When the martensite is strained up to several percent, however, that strain is retained until the material is heated, at which time shape recovery occurs. Upon recoiling, the material does not spontaneously change shape, but must be deliberately strained if shape recovery is again desired.

It is possible in some of the shape memory alloys to cause two-way shape memory. That is, shape change occurs upon both heating and cooling. The amount of this shape change is always significantly less than obtained with one-way memory, and very little stress can be exerted by the alloy as it tries to assume its low-temperature shape. The heating shape change can still exert very high forces, as with the one-way memory.

A number of heat-treatment and mechanical training methods have been proposed to create the two-way shape memory effect (Ref 6, 7). All rely on the introduction of microstructural stress concentrations, which cause the martensite plates to initiate in particular directions when they form upon cooling, resulting in an overall net-shape change in the desired direction.

**Characterization Methods**

There are four major methods of characterizing the transformation in SMAs and a large number of minor methods that are only rarely used and will not be discussed.

The most direct method is by differential scanning calorimeter (DSC). This technique measures the heat absorbed or given off by a small sample of the material as it is heated and cooled through the transformation-temperature range. The sample can be very small, such as a few milligrams, and because the sample is unstrained this is not a factor in the measurement. The endotherm and exotherm peaks, as the sample absorbs or gives off energy due to the transformation, are easily measured for the beginning, peak, and end of the phase change in each direction.
The second method often used is to measure the resistivity of the sample as it is heated and cooled. The alloys exhibit interesting changes and peaks in the resistivity (by up to 20%) over the transformation-temperature range; however, correlating these changes with measured phase changes or mechanical properties has not always been very successful. Also, there are often large changes in the resistivity curves after cycling samples through the transformation a number of times. Thus, resistivity is often measured as a phenomenon in its own right, but is rarely used to definitely characterize one alloy versus another.

The most direct method of characterizing an alloy mechanically is to prepare an appropriate sample, then apply a constant stress to the sample and cycle it through the transformation while measuring the strain that occurs during the transformation in both directions. The curve shown in Fig. 1 is the direct information one obtains from this test. The values obtained for the transformation points, such as $M_s$ and $A_t$, from this method are offset to slightly higher temperatures from the values obtained from DSC testing. This happens because the DSC test occurs at no applied stress, and the transformation is not stress induced; therefore, increasing test stress will lead to increasing transformation-temperature results. This test is directly indicative of the property one can expect in a mechanical device used to perform some function using shape memory. Its disadvantages are that specimens are often difficult to make, and results are quite susceptible to the way the test is conducted.

Finally, the stress-strain properties can be measured in a standard tensile test at a number of temperatures across the transformation-temperature range, and from the change in properties the approximate transformation-temperature values can be interpolated. This is very imprecise, though, and is much better applied as a measure of the change in properties of each phase, due to such things as work hardening or different heat treatments.

**Commercial SME Alloys**

The only two alloy systems that have achieved any level of commercial exploitation are the Ni-Ti alloys and the copper-base alloys. Properties of the two systems are quite different. The Ni-Ti alloys have greater shape memory strain (up to 8% versus 4 to 5% for the copper-base alloys), tend to be much more thermally stable, have excellent corrosion resistance compared to the copper-base alloys' medium corrosion resistance and susceptibility to stress-corrosion cracking, and have much higher ductility. On the other hand, the copper-base alloys are much less expensive, can be melted and extruded in air with ease, and have a wider range of potential transformation temperatures. The two alloy systems thus have advantages and disadvantages that must be considered in a particular application.

**Nickel-Titanium Alloys.** The basis of the nickel-titanium system of alloys is the binary, equiatomic intermetallic compound of Ni-Ti. This intermetallic compound is extraordinary because it has a moderate solubility range for excess nickel or titanium, as well as most other metallic elements, and it also exhibits a ductility comparable to most ordinary alloys. This solubility allows alloying with many of the elements to modify both the mechanical properties and the transformation properties of the system. Excess nickel, in amounts up to about 1%, is the most common alloying addition. Excess nickel strongly depresses the transformation temperature and increases the yield strength of the austenite. Other frequently used elements are iron and chromium (to lower the transformation temperature), and copper (to decrease the hysteresis and lower the deformation stress of the martensite). Because common contaminants such as oxygen and carbon can also shift the transformation temperature and degrade the mechanical properties, it is also desirable to minimize the amount of these elements.

The major physical properties of the basic binary Ni-Ti system and some of the mechanical properties of the alloy in the annealed condition are shown in Table 2. Note that this is for the equiatomic alloy with an $A_t$ value of about 110 °C (230 °F). Selective work hardening, which can exceed 50% reduction in some cases, and proper heat treatment can greatly improve the ease with which the martensite is deformed, give an austenite with much greater strength, and create material that spontaneously moves itself both on heating and on cooling (two-way shape memory). One of the biggest challenges in using this family of alloys is in developing the proper processing procedures to yield the properties desired.

Because of the reactivity of the titanium in these alloys, all melting of them must be done in a vacuum or an inert atmosphere. Methods such as plasma-arc melting, electron-beam melting, and vacuum-induction melting are all used commercially. After ingots are melted, standard hot-forming processes such as forging, bar rolling, and extrusion can be used for initial breakdown. The alloys react slowly with air, so hot working in air is quite successful. Most cold-working processes can also be applied to these alloys, but they work harden extremely rapidly, and frequent annealing is required. Wire drawing is probably the most widely used of the techniques, and excellent surface properties and sizes as small as 0.05 mm (0.002 in.) are made routinely.

Fabrication of articles from the Ni-Ti alloys can usually be done with care, but some of the normal processes are difficult. Machining by turning or milling is very difficult except with special tools and practices. Welding, brazing, or soldering the alloys is generally difficult. The materials do respond well to abrasive removal, such as grinding, and shearing or punching can be done if thicknesses are kept small. Heat treating to impart the desired memory shape is often done at 500 to 800 °C (950 to 1450 °F), but it can be done as low as 300 to 350 °C (600 to 650 °F) if sufficient time is allowed. The SMA component may need to be restrained in the desired memory shape during the heat treatment; otherwise, it may not remain there.

**Commercial copper-base shape memory alloys** are available in ternary Cu-Zn-Al and Cu-Al-Ni alloys, or in their quaternary modifications containing manganese. Elements such as boron, cerium, cobalt, iron, titanium, vanadium, and zirconium are also added for grain refinement.

The major alloy properties are listed in Table 3. The martensite-start ($M_s$) transformation temperatures of the compositions of Cu-Zn-Al alloys are plotted in Fig. 4. Compositions of Cu-Al-Ni alloys usually fall in the range of 11 to 14.5 wt% Al and 3 to 5 wt% Ni. The martensitic transformation temperatures can be adjusted by varying chemical composition. Figure 4 and the following empirical relationships are useful in obtaining a first estimate:

- **Cu-Zn-Al: $M_s (°C) = 2212 - 66.9 (at.% Zn) - 90.65 (at.% Al) (Ref 8)***
- **Cu-Al-Ni: $M_s (°C) = 2020 - 134 (wt% Al) - 45 (wt% Ni) (Ref 9)**
Table 3 Properties of copper-base shape memory alloys

<table>
<thead>
<tr>
<th>Property</th>
<th>Cu-Zn-Al</th>
<th>Cu-Al-Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Young’s modulus, GPa (10^6 psi/ι)</td>
<td>72 (10.4a)</td>
<td>85 (12.3a)</td>
</tr>
<tr>
<td>Yield strength, MPa (ksi)</td>
<td>350 (51)</td>
<td>400 (58)</td>
</tr>
<tr>
<td>Martensite strength, %</td>
<td>80 (11.5)</td>
<td>130 (19)</td>
</tr>
<tr>
<td>Ultimate tensile strength, MPa (ksi)</td>
<td>600 (87)</td>
<td>500-800 (73-116)</td>
</tr>
<tr>
<td>Shape memory properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transformation temperatures, °C (°F)</td>
<td>&lt;120 (250)</td>
<td>&lt;200 (390)</td>
</tr>
<tr>
<td>Recoverable strain, %</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Hysteresis, °C/°F</td>
<td>15-25 (30-45)</td>
<td>15-20 (30-35)</td>
</tr>
</tbody>
</table>

(a) The Young’s modulus of shape memory alloys becomes difficult to define between the Ms and the A1 transformation temperatures. At these temperatures, the alloys exhibit nonlinear elasticity, and the modulus is both temperature- and strain-dependent.

The melting of Cu-base shape memory alloys is similar to that of aluminum bronzes. Most commercial alloys are induction melted. Protective flux on the melt and the use of nitrogen or inert-gas shielding during pouring are necessary to prevent zinc evaporation and aluminum oxidation. Powder metallurgy and rapid solidification processing are also used to produce fine-grain alloys without grain-refining additives.

Copper-base alloys can be readily hot worked in air. With low aluminum content (<6 wt%), Cu-Zn-Al alloys can be cold finished with interpass annealing. Alloys with higher aluminum content are not as easily cold workable. Cu-Al-Ni alloys, on the other hand, are quite brittle at low temperatures and can only be hot finished.

Manganese depresses transformation temperatures of both Cu-Zn-Al and Cu-Al-Ni alloys and shifts the eutectoid to higher aluminum content (Ref 10). It often replaces aluminum for better ductility.

Because copper-base shape memory alloys are metastable in nature, solution heat treatment in the parent β-phase region and subsequent controlled cooling are necessary to retain β phase for shape memory effects. Prolonged solution heat treatment causes zinc evaporation and grain growth and should be avoided. Water quench is widely used as a quenching process, but air cooling may be sufficient for some high-aluminum content Cu-Zn-Al alloys and Cu-Al-Ni alloys. The as-quenched transformation temperature is usually unstable. Postquench aging at temperatures above the nominal A1 temperature is generally needed to establish stable transformation temperatures.

Cu-Zn-Al alloys, when quenched rapidly and directly into the martensitic phase, are susceptible to the martensite stabilization effect (Ref 11). This effect causes the reverse transformation to shift toward higher temperatures. It therefore delays and may completely inhibit the shape recovery. For alloys with Ms temperatures above the ambient, slow cooling or step quenching with intermediate aging in the parent β-phase state should be adopted.

The thermal stability of copper-base alloys is ultimately limited by the decomposition kinetics. For this reason, prolonged exposure of Cu-Zn-Al and Cu-Al-Ni alloys at temperatures above 150 °C (300 °F) and 200 °C (390 °F) respectively, should be avoided. Aging at lower temperatures may also shift the transformation temperatures. In case of aging in the β phase, this results from the change in long-range order (Ref 12). When aged in the martensitic state, the alloys exhibit an aging-induced martensite stabilization effect (Ref 11). For high-temperature stability, Cu-Al-Ni is generally a better alloy system than Cu-Zn-Al. However, even for moderate temperature applications, which demand tight control of transformation temperatures, these effects need to be evaluated.

Applications

There is a wide variety of uses for the shape memory alloys. The following will illustrate one or two products in several categories of application.

Free recovery is illustrated when an SMA component is deformed while martensitic, and the only function required of the shape memory is that the component return to its previous shape (while doing minimal work) upon heating. A prime application of this is the blood-clot filter developed by M. Simon (Ref 13). The Ni-Ti wire is shaped to anchor itself in a vein and catch passing clots. The part is chilled so it can be collapsed and inserted into the vein, then body heat is sufficient to turn the part to its functional shape.

Constrained Recovery. The most successful example of this type of product is undoubtedly the Cryofit hydraulic couplings made by Raychem Corporation (Ref 14). These fittings are manufactured as cylindrical sleeves slightly smaller than the metal tubing they are to join. Their diameters are then expanded while martensitic, and, upon warming to austenite, they shrink in diameter and strongly hold the tube ends. The tubes prevent the coupling from fully recovering its manufactured shape, and the stresses created as the coupling attempts to do so are great enough to create a joint that, in many ways, is superior to a weld.

Similar to the Cryofit coupling, the Betalloy coupling (Ref 15) is a Cu-Zn-Al coupling also designed and marketed by Raychem Corporation for copper and aluminum tubing. In this application, the Cu-Zn-Al shape memory cylinder shrinks on heating and acts as a driver to squeeze a tubular liner onto the tubes being joined. The joint strength is enhanced by a sealant coating on the liner.

Force Actuators. In some applications, the shape memory component is designed to exert force over a considerable range of motion, often for many cycles. Such an application is the circuit-board edge connector made by Beta Phase Inc. (Ref 16). In this electrical connector system, the SMA component is used to force open a spring when the connector is heated. This allows force-free insertion or withdrawal of a circuit board in the connector. Upon cooling, the Ni-Ti actuator becomes weaker and the spring easily deforms the actuator while it closes tightly on the circuit board and forms the connections.

Based on the same principle, Cu-Zn-Al shape memory alloys have found several applications in this area. One such example is a fire safety valve, which incorporates a Cu-Zn-Al actuator designed to shut off toxic or flammable gas flow when fire occurs (Ref 17).

Proportional Control. It is possible to use only a part of the shape recovery to accurately position a mechanism by using only a selected portion of the recovery because the transformation occurs over a range of temperatures rather than at a single temperature. A device has been developed by Beta Phase Inc. (Ref 18) in which a valve controls the rate of fluid flow by carefully heating a shape-memory-alloy component just enough to close the valve the desired amount. Repeatable positioning within 0.25 μm (10^-5 in.) is possible with this technique.

Superelastic Applications. A number of products have been brought to market that use the pseudoelastic (or superelastic) property of these alloys. Eyeglass frames that use superelastic Ni-Ti to absorb large deformations without damaging the frames are
Fig. 4 $M_s$ temperatures and compositions of Cu-Zn-Al shape memory alloys

now marketed, and guide wires for steering catheters into vessels in the body have been developed using Ni-Ti wire, which resists permanent deformation if bent severely. Arch wires for orthodontic correction using Ni-Ti have been used for many years to give large rapid movement of teeth.

The properties of the Ni-Ti alloys, particularly, indicate their probable greater use in biomedical applications. The material is extremely corrosion resistant, demonstrates excellent biocompatibility, can be fabricated into the very small sizes often required, and has properties of elasticity and force delivery that allow uses not possible any other way.

Future Prospects

Although specific products that might use the Ni-Ti alloys in the future cannot be foretold, some directions are obvious. The cost of these alloys has slowly decreased as use has increased, so uses that require lower-cost alloys to be viable are being explored. Alloy development has yielded several ternary compositions with properties improved over those obtained with binary material, and alloys tailored to specific product needs are likely to multiply. The medical industry has developed a number of products using Ni-Ti alloys because of their excellent biocompatibility and large pseudoelasticity, and many more of these applications are likely. Finally, the availability of small wire that is stable, is easily heated by a small electrical current, and gives a large repeatable stroke should lead to a new family of actuator devices (Ref 19). These devices can be inexpensive, are reliable for thousands of cycles, and are expected to move Ni-Ti into the high-volume consumer marketplace.

Recent interest in the development of iron-base shape memory alloys has challenged the concept that long-range order and thermoelastic martensitic transformation are necessary conditions for shape memory effect. Among the alloys, Fe-Pt (Ref 20), Fe-Pd (Ref 21), and Fe-Ni-Co-Ti (Ref 22) can be heat treated to exhibit thermoelastic martensitic transformation, and, therefore, shape memory effect. However, alloys such as Fe-Ni-C (Ref 23), Fe-Mn-Si (Ref 24), and Fe-Mn-Cr-Ni (Ref 25) are not ordered and undergo nonthermoelastic transformation, and yet exhibit good shape memory effect. These alloys are characteristically different from conventional shape memory alloys in that they rely on stress-induced martensite for shape memory effect, exhibit fairly large transformation hysteresis, and, in general, have less than 4% recoverable strain. The commercial potential of these alloys has yet to be determined, but the effort has opened up new classes of alloys for exploration as shape memory alloys. These new classes include β-Ti alloys and iron-base alloys.

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