Advanced Materials '93, VI / Frontiers in
Materials Science and Engineering, edited by S. Sōmiya et al.
Trans. Mat. Res. Soc. Jpn., Volume 19B
1994 Elsevier Science B.V.

About Shape Memory Alloys

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Abstract

Numerous metallic alloys are now known to exhibit a shape memory effect through which an article deformed at a lower temperature will regain its original undeformed shape when heated to a higher temperature. This behavior is basically a consequence of a martensitic phase transformation. When compared, the various shape memory materials are found to have common characteristics such as atomic ordering, a thermoelastic martensitic transformation which is crystallographically reversible, and a martensite phase which forms in a self-accommodating manner. The explanation of the shape memory phenomenon is now universal and well in hand. In addition to the familiar "one-way" memory, shape memory alloys also exhibit a "two-way" memory as well and a "mechanical" shape memory resulting from the formation and reversal of stress-induced martensite.

Introduction

Fundamental to the shape memory effect (SME) is the occurrence of a martensitic phase transformation and its subsequent reversal.* Basically, a shape memory alloy (SMA) is deformed in the martensitic condition (martensite), and the shape recovery occurs during heating when the specimen undergoes a reverse transformation of the martensite to its parent phase. This is the essence of the shape memory effect. Materials which exhibit the shape memory behavior also show a two-way shape memory as well as a phenomenon called superelasticity. These are also discussed.

The shape memory response after deformation and thermal stimulation constitutes "smart" behavior, i.e., stimulated martensite-austenite reverse transformation

Principal applications of shape memory effect alloys in high performance products include aircraft hydraulic couplings and electrical connectors. Because of their dramatic strength in response to temperature, SME alloys (SMAs) have continuously been proposed as alternatives to solenoids, motors, and bimetallic or wax-type actuators. Alternatively, a SME approach to actuation offers advantages which conventional approaches would find difficult or impossible to achieve.

- Large amounts of recoverable strain offer work densities up to ten times higher than conventional approaches. Applications

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* This same type of phase transformation occurs when steels are hardened by quenching, but ordinarily no shape memory is found in steels because the martensite does not reverse, but undergoes tempering instead.

concerned with maximizing the work/volume or work/weight of a device find the SME approach attractive.

- Direct actuation without extra parts and with efficient use of available energy is possible.
- Large available material strains permit relatively long strokes, constant force during the stroke, and high starting force.
- SME actuators can be linear, rotary or a combination of each.

Additionally, typical applications of SMAs are in a variety of sensor actuators such as thermal protection, replacing motors, solenoids, etc. where small space and quiet operation are required, fasteners and connectors, flexible robot structures, and many medical products. In most cases the actuation is available "on demand" from a simple signal.

Most frequently shape memory is viewed as a one time operation: for example, shrinking a fitting around hydraulic tubing. However, it should be noted that if the material is returned to its martensitic state, it can be redeformed, reheated, re-recovered, etc. repeatedly. The object must be deformed each time before shape recovery.

The Formation of Martensite in Shape Memory Alloys

A typical plot of property changes vs. temperature for a shape memory alloy is shown in Fig. 1, where symbolically the parent phase (usually called austenite) is represented as a two dimensional square lattice, and the martensite is a rhombus, derived by a spontaneous distortion of the parent. Note that the formation of martensite is really a deformation process. Various temperatures, M_s, M_f, A_s and A_f are indicated in the graph and are explained in the legend to the figure. It is to be noted that, comparing the formation of martensite between M_s and M_f and the reversal of martensite (formation of parent) between A_s and A_f, there is a certain hysteresis, which is usually on the order of 20°C for shape memory alloys. As indicated at the y-axis, plots such as that shown in Fig. 1 are obtained when a variety of physical properties are measured during the course of a martensitic transformation upon cooling and its subsequent reversal during heating.

Figure 2 is a series of optical micrographs showing the formation of martensite between M_s (Fig. 2a) and M_f (Fig. 2h) in a polycrystalline Ni-Al shape memory alloy. The individual plates of martensite show a characteristic crystallographic habit plane. The plates having different variants of the habit plane exhibit different senses of transformation distortion (shape deformation) as evidenced by the different surface tilts (light and dark shading) and combine to form a chevron or spear morphology. This morphology is self-accommodating as will be seen later.

The Nature of the Shape Memory Effect

The shape memory effect can be described with reference to the cooling and heating curves such as shown in Fig. 1 and this is done in Fig. 3. There is no change in shape of a specimen cooled from above A_f to below M_f. When the specimen is deformed below M_f it remains so deformed until it is heated. The shape recovery begins at A_s and is completed at A_f. At the inflection point between A_s and A_f, about 50% of the original shape is recovered. Once the shape has recovered at A_f there is no change in shape when the specimen is cooled to below M_f and the shape memory can only be reactivated by deforming the martensitic specimen once again. In other words, the shape memory effect is a one time only occurrence and because of this is frequently referred to as the one-way shape memory, in contrast to the two-way shape memory which will be described later. As Fig. 3 indicates, recoverable strains on the order of 7% are typical of shape memory alloys, but some show recoveries as high as 10%.

Table 1 shows that many alloys exhibit the shape memory effect. The listing given is only partial. Of those alloy systems shown, the Cu-Zn-Al, Cu-Al-Ni and Ti-Ni alloys are presently of commercial importance. Comparing the shape memory alloys listed in Table 1, one finds that in all cases the parent phase is ordered. The meaning of ordering is shown in Fig. 4. Since a martensitic transformation is diffusionless, the product martensite is also ordered. The formation of martensite is also a thermoelastic process whereby an incremental decrease in temperature between M_s and M_f results in a slight growth of existing martensite plates and the nucleation of some new ones, but when the temperature is incrementally raised, those newly nucleated plates disappear and those which grew slightly on incremental cooling correspondingly shrink back a little. The martensite is also crystallographically reversible, which means that the reversal of given plate upon heating is just the inverse of the formation process. In other words, the plate undergoes a "backwards shear" as it disappears.

That martensite plates self-accommodate each other is clearly seen in Fig. 5 by noting the scratch running from the upper left of the figure to the lower right. Although the scratch is locally deviated or displaced by a given plate of martensite, the adjoining plate with opposite displacement (tilt) displaces the scratch back. Thus, the martensite system of plates as a whole produces no net macroscopic displacement of the scratch. The nature of self-accommodation in three dimensions is shown schematically in Fig. 6, where the "ins", "outs", "ups" and "downs" form a mutually self-accommodating unit of martensite.

Referring again to Fig. 1, in two dimensions we envision the formation of martensite as the distortion of a square lattice into a rhombus. In two dimensions, there are four ways to distort a square into a rhombus as shown by the arrow sequences at the left of Fig 7. The distortions can be viewed as right-, left-, up- or down-arrow, respectively. However, once a particular rhombic orientation is formed, it can only return to its cubic parent by means of the inverse arrow. This is fundamentally the nature of the shape memory effect on a micro-scale.

Because of self-accommodation the four rhombic variants tend to group together in more or less equal portions as shown in Fig. 8, and on a larger scale a section of a martensitic specimen would appear as shown enclosed by A, B, C and D in Fig. 9. If such a specimen is stressed in the up-arrow sense, as indicated, three variants of the rhombs will be unstable with respect to the direction of the stress. These variants will actually be consumed by the up-arrow variant which is favorably aligned with respect to the applied stress. This variant will advance into the other three by the movement of its boundaries (actually observed in SME martensites) and eventually, given enough strain, a single crystal of martensite of the up-arrow orientation is formed, Fig. 10. Figure 10 is nothing but a large rhombus which, as before, has only one return path to its parent square. The behavior just described is fundamentally the macroscopic basis of the shape memory. The important thing is that the initially formed martensite must be deformed in order to obtain a select variant, which then executes the shape memory when heated to form the parent phase.

Figure 11 is a stress-strain curve for a Cu-39.8%Zn SMA deformed in the martensitic condition 25°C below the M_f temperature. Two features are worthy of note. First, the martensite was strained to over 5%, yet all of this strain was recovered when the specimen was heated to above the A_f temperature. Secondly, the yield stress of the martensite is fairly low, about 35 MPa(5Ksi). Above A_f the yield stress of the parent was found to be about 350 MPa(50 Ksi). In fact, a good working rule of thumb for SMA's is that the martensite yield stress is about 10% of that of the parent phase. Usually the design stress (i.e., recovery stress) of SMA's is taken to be the yield strength of the parent phase. This would be the stress generated for making a coupling, powering an engine, etc.

Superelasticity and Stress-Induced Martensite

The discussion up to now shows that the shape memory effect is both a thermal and mechanical one. The martensite is initially formed by cooling and is then deformed below the M_f temperature. The deformed martensite is then heated to above the A_f temperature to cause the shape recovery, i.e., the shape memory is caused by heating.

We now consider another type of shape memory which is temperature independent--superelasticity. Normally, on cooling, the martensite forms at M_s under no stress. But in the same material, martensite can form above M_s if a stress is applied, and the martensite so-formed is termed stress-induced martensite (SIM). The driving force for the transformation is now mechanical, as opposed to thermal, as in the case of "cooling martensite." The SIM reverts when the applied stress is released, giving rise to a mechanical shape memory.

Figure 12 shows a "superelastic" stress strain curve (actually a superelastic loop) for a Cu-39.8%Zn SMA. The upper plateau corresponds to the formation of SIM under stress while the lower plateau represents the reversion of the SIM when the stress is released. Note that 9% strain is fully recovered, and this corresponds to the mechanical shape memory. When the SIM is formed, usually only variant of martensite plates forms, as shown in Fig. 13 for a single crystal of the same Cu-Zn alloy. In Fig. 13a, only a few plates of SIM are formed, with a habit plane that is sympathetic with respect to the applied stress axis. That is, the shape deformation of that particular habit plane variant produces maximum elongation of the specimen along the tensile axis. Figure 13b shows the same specimen at a higher strain level with many more SIM plates of the same habit variant. Since only one martensite variant is formed under stress, there is a shape change (elongation) due to the formation of only one variant which is fully recovered upon release of the stress. This situation is unlike that shown in Fig 2, where because of self-accommodation there is no shape change attendant to the formation of many variants of martensite.

As mentioned earlier, when a specimen is cooled, martensite forms at M_s under no stress. Thus, it is not surprising that the stress required to produce SIM increases with increasing temperature above M_s as shown in Fig 14. These stress-strain curves correspond to the upper plateau shown in Fig. 12. In fact, the variation in the stress to produce SIM increases linearly with temperature above M_s as shown in Fig. 15. Note that the extrapolated stress drops to zero at M_s. The linear variation in stress to induce martensite as a function of temperature obeys the Clausius-Clapeyron equation, usually written as

$$dP/dT = \Delta H/T\Delta V$$

where P is the pressure, T is the temperature, ΔH is the transformation latent heat and ΔV is the transformation volume change. This equation has been traditionally used by chemists, but metallurgists, on the other hand, use the Clausius-Clapeyron equation in the form

$$d\sigma_a/dM_s = -\Delta H/T\varepsilon_o$$

where ΔH and T have the same meanings as before, and σ_a, M_s and ε_o are, respectively, the applied stress, the M_s temperature and the transformation strain resolved along the direction of the applied stress. For a number of SMA systems the agreement of the temperature dependence of the stress to form SIM according to the Clausius-Clapeyron equation is quite striking.

For purposes of comparison, Fig. 16 shows a superelastic stress-strain curve for a Ti-Ni SMA spring compared to that for a typical spring material, piano wire. For the shape memory alloy the strain is completely recovered, but when the piano wire spring is extended the same amount, it undergoes permanent deformation and only a part of the strain is recovered.

The mechanical behavior of shape memory alloys is summarized graphically in Fig. 17, adapted from the behavior of a Ti-Ni alloy. At the extreme rear the stress-strain curve shown in the x-y plane corresponds to the deformation of martensite below M_f. The induced strain, about 4%, recovers between A_s and A_f after the applied stress has been removed and the specimen heated, as seen in the x-T plane. At a temperature above M_s (and A_f) SIM is formed, leading to the usual superelastic loop with an upper and lower plateau, in which case the SIM disappears completely when the applied stress is released. At a still higher temperature, the front x-y plane, no SIM is formed. Instead, the parent phase undergoes ordinary plastic deformation. This temperature is above the M_d temperature, which by definition is the lowest temperature above which martensite cannot be induced by deformation (stress). Note that the stress to deform the parent phase above the M_d temperature is about ten times that needed to deform the martensite below M_f.

<u>The Two-Way Shape Memory</u>

Finally, we consider the two-way shape memory effect (TWSM). This is illustrated for spring-type specimens in Fig. 18. In the upper part of the figure a collapsed SMA spring is deformed by extension below M_f. The original spring shape (contracted) is recovered following heating to above A_f. The contracted shape remains when the specimen is again cooled to below M_f. This is the one-way shape memory behavior, where, as noted before, is a one time only deployment. In contrast, the TWSM is depicted in the lower half of the figure, in which case a contracted spring below M_f extends when heated to above A_f. But now, the extended spring spontaneously contracts when again cooled below M_f. The spring extends again when heated above A_f and contracts again when cooled below M_f. This behavior repeats indefinitely. Figure 19 is a similar sketch showing the two-way behavior of a bar-shaped specimen.

To produce the two-way behavior, thermomechanical treatment is required, usually involving several transformation cycles. Figure 20 is an optical micrograph of a Cu-39.8%Zn alloy. Figure 20a shows a specimen region featuring principally four habit variants of martensite, A, B, C and D. These variants are present in equal proportions. The same specimen region is shown in Fig. 20b, only in this case the structure shown in Fig. 20a was deformed below M_f, heated to above A_f while under constraint, and then cooled again to below M_f. The predominance of variant D in Fig. 20b is seen clearly. After six or so thermomechanical cycles, the deformation scheme (and amount) below M_f being identical each time, the entire microstructure would consist of only variant D.

Figure 21 is a schematic indicating the "training" procedure used to obtain the TWSM. After the indicated thermomechanical cycling, microstresses become inbuilt in the parent phase. These stresses bias the normal martensitic transformation to the extent that a preferred variant of martensite is formed on cooling. In essence, a crystal of the parent phase transforms into a single crystal of martensite. Accordingly, the transformation shape change of this single variant of martensite gives rise to a spontaneous deformation of the specimen upon cooling (the first part of the TWSM). When such a specimen is heated, this spontaneous deformation recovers via the usual one-way shape memory mechanism (the second part of the TWSM).

Again, reference is made to Fig. 17, which summarizes the deformation behavior of shape memory alloys over a range of stresses, strains and temperatures, and to Fig. 19, which compares the one-way and two-way shape memories.

Summary

The shape memory effect is a consequence of a crystallographically reversible martensitic phase transformation occurring in the solid state. Although there are many ways (orientations) to produce the martensite phase from its parent during cooling, once the lower symmetry martensite is formed it has only one unique reversion path during the reverse transformation because of crystallographic restrictions. The transformation of the parent phase into martensite is basically a deformation process, but because the individual units of martensite self-accommodate, the overall macroscopic deformation upon transformation is zero. When the shape memory martensite is deformed, a particular orientation of the various self-accommodating units--that most favorably oriented with respect to the applied stress--grows at the expense of others, eventually leading to a single orientation of martensite. As before, this orientation has only one reversion path, which is the essence of the shape memory--a deformed and reoriented martensitic phase which is thermally responsive. Strains on the order of seven percent are typically recoverable in this manner.

Shape memory alloys also display superelasticity, a mechanical type of shape memory as opposed to the thermally induced (by heating) shape memory described above. In this case, when the parent phase is deformed above the martensite start temperature, the martensitic transformation occurs "prematurely" because the applied stress substitutes for the thermodynamic driving force usually obtained by cooling. But since the applied stress is basically uniaxial, only one orientation (out of many) of martensite is selectively formed, and this imparts an overall deformation to the specimen. This deformation disappears when the stress is released and the original specimen shape is restored, leading to a mechanical shape memory.

Finally, a two-way shape memory can be realized in shape memory materials, whereby a specimen is programmed by means of thermomechanical treatment. Typically, a specimen deformed in the martensitic condition is intentionally constrained during heating in order to suppress the normal one-way shape memory. This process generates in-built microstresses in the parent phase which in turn program the specimen to behave as in a stress-induced martensitic transformation. That is, the microstresses favor only a single orientation of martensite upon subsequent cooling, which produces a spontaneous deformation. When the specimen is heated the normal one-way shape memory process occurs and its original shape is reproduced. The two-way process can be repeated indefinitely (as with a thermostat) as opposed to the one-way memory, which is a one time only operation (as in making a mechanical connection).

Further Reading

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Table 1. Some Alloy Systems Exhibiting the Shape Memory Effect

CuZn	
CuZnAl	
CuZnGa	
CuZnSn	Their characteristics:
CuZnSi	
CuAlNi	1. Ordered parent → ordered martensite
CuAuZn	
CuSn	2. Martensite is thermoelastic
AuCd	
AgCd	3. Martensite is crystallographically reversible
TiNi	
NiAl	
FePt	
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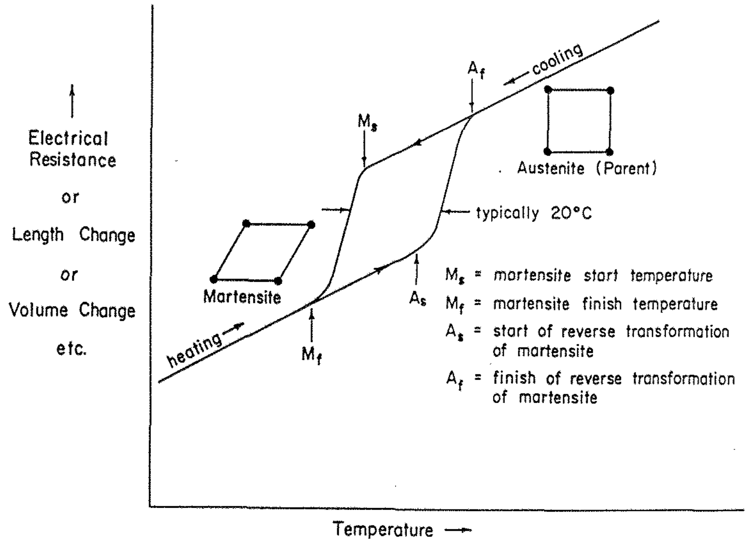
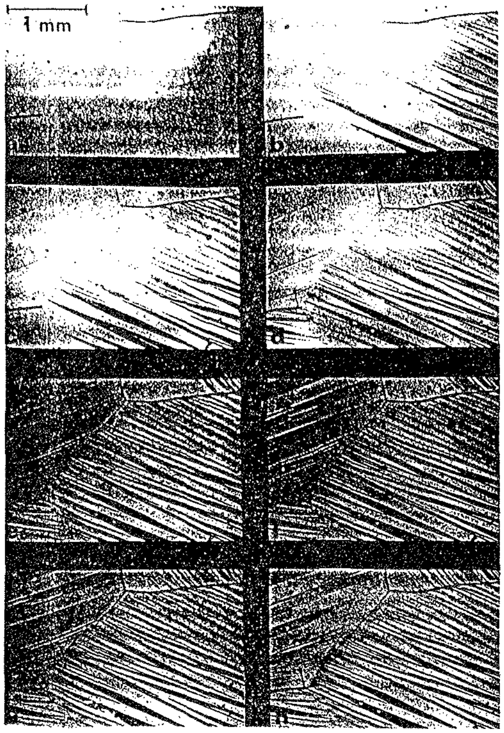
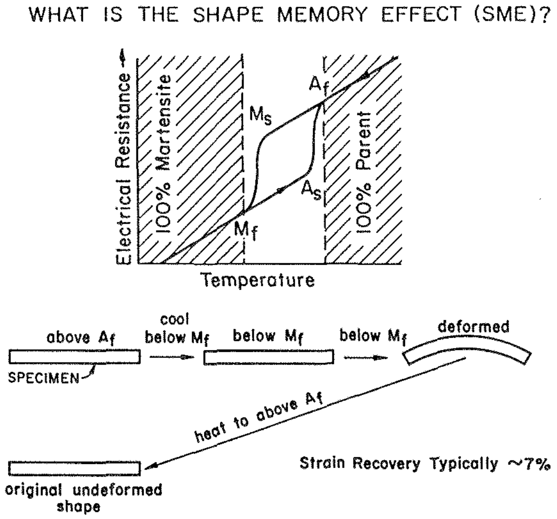


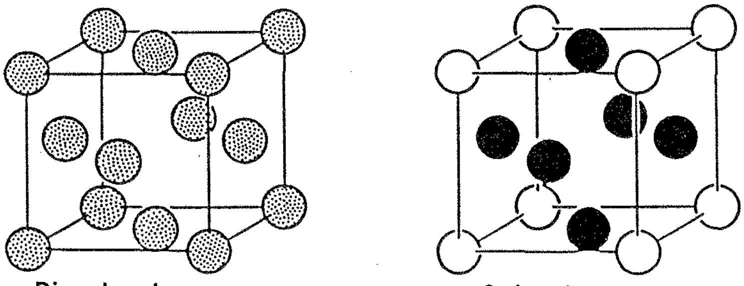
1. Hypothetical plot of property change vs. temperature for a martensitic transformation occurring in a shape memory alloy. The parent phase (austenite) is represented by the square lattice, which upon martensitic transformation is distorted into the rhombic product phase (martensite). Characteristic temperatures are defined in the inset.



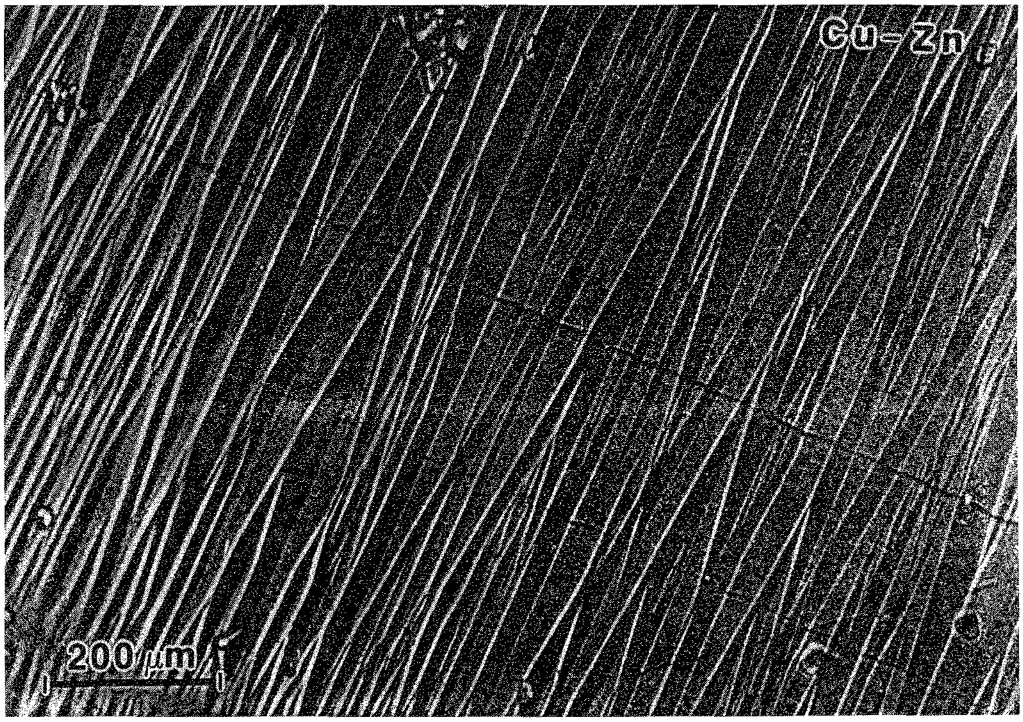
2. Sequence of optical micrographs showing the formation of martensite between M_s (a) and M_f(h) in a Ni-Al shape memory alloy. See text for discussion.



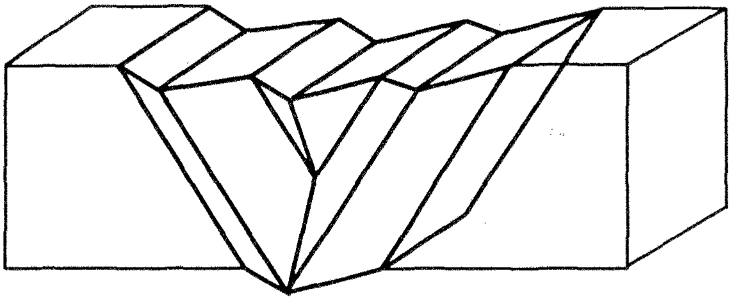
3. The shape memory effect is described with reference to a plot of electrical resistance vs. temperature from which the characteristic transformation temperatures M_s, M_f, A_s and A_f are determined.



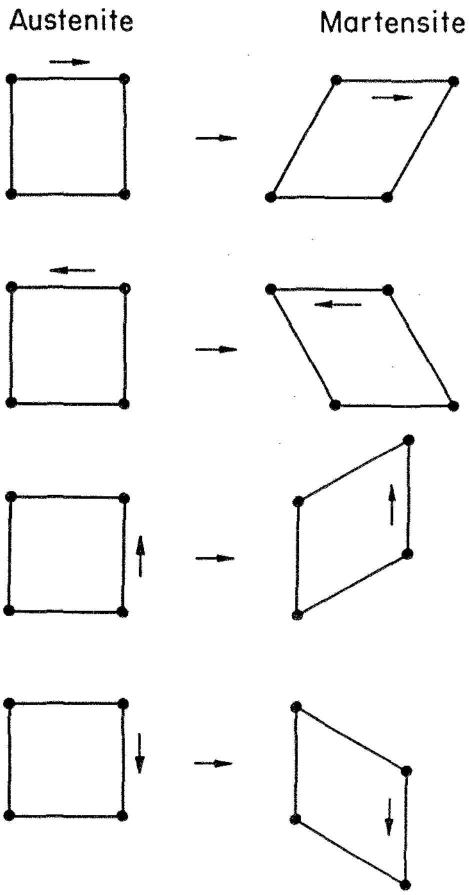
4. An example of atomic ordering. In a disordered alloy, the lattice sites are randomly occupied by both species of atoms, but in an ordered alloy the species locate at particular atomic sites.



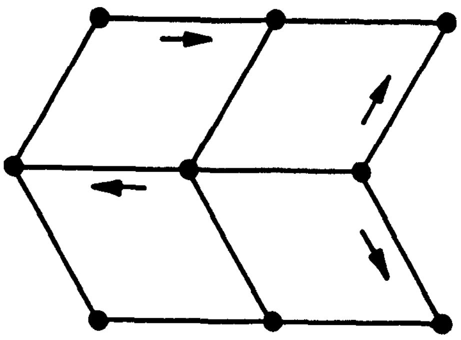
5. Optical micrograph showing surface relief due to the formation of martensite in a Cu-Zn shape memory alloy. The overall macroscopic displacement of the scratch running from upper left to lower right is nil, although on a local scale the individual plates of martensite displace the scratch differently.



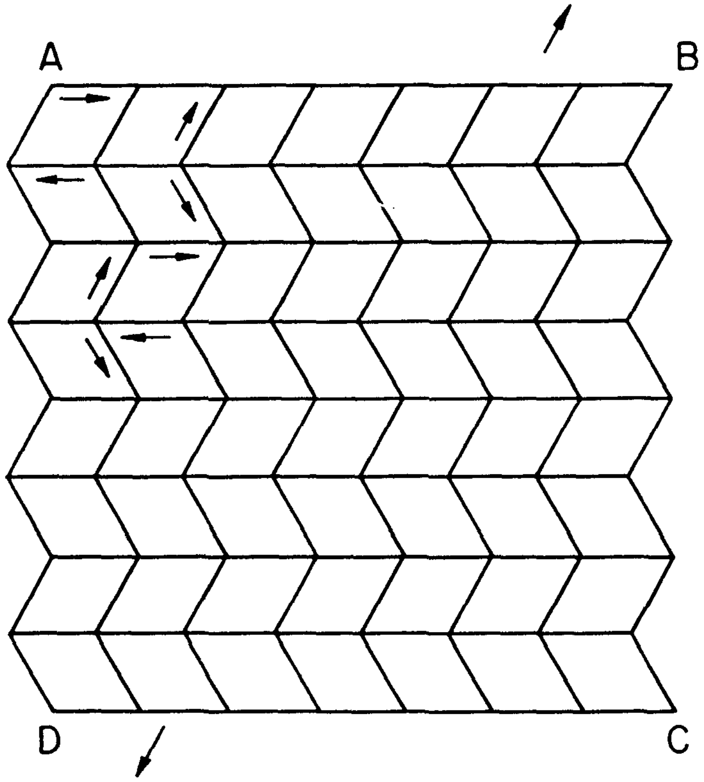
6. Schematic drawing showing self-accommodating martensite plates as seen in three dimensions. Habit plane variants sympathetically group together so that the net transformation distortion averages out to zero.



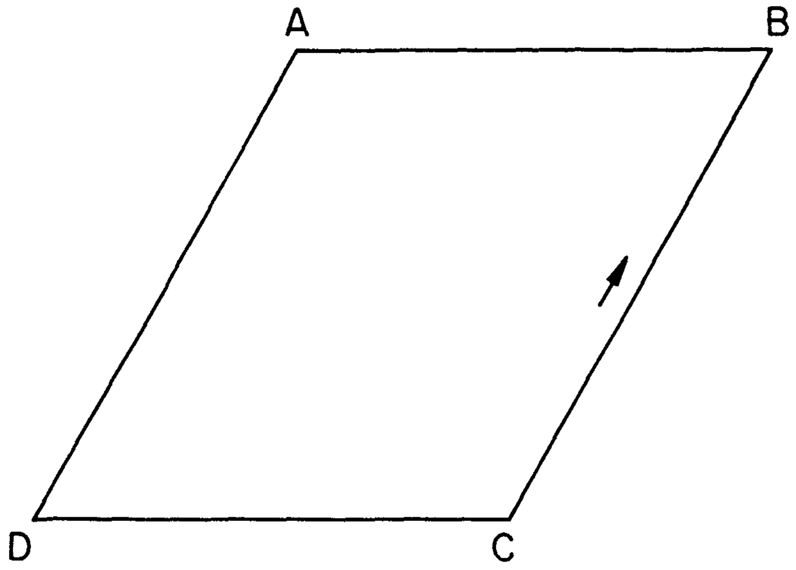
7. Schematic drawing showing in two dimensions four possible ways to generate the rhombic martensite from the cubic austenite. Each rhombic orientation can return to its parent condition in only one way, by undergoing the inverse transformation distortion.



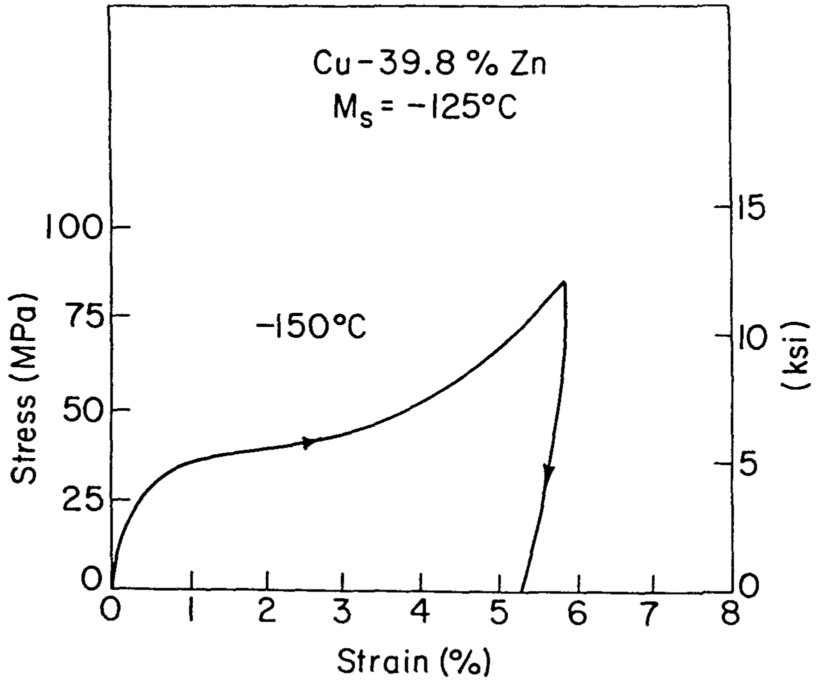
8. The four rhombic orientations of martensite described in Figure 7 fit together in a self-accommodating manner.



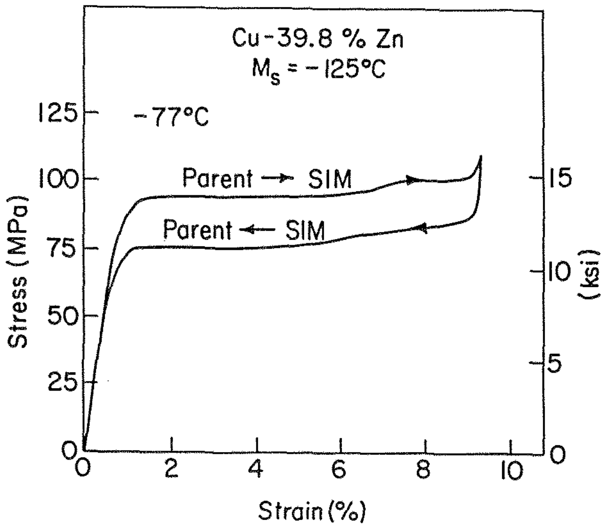
9. Portion of a martensitic specimen comprised of self-accommodating units of martensite as shown in Figure 8. Region ABCD is deformed in tension in the direction indicated by the upper-right and lower-left arrows.



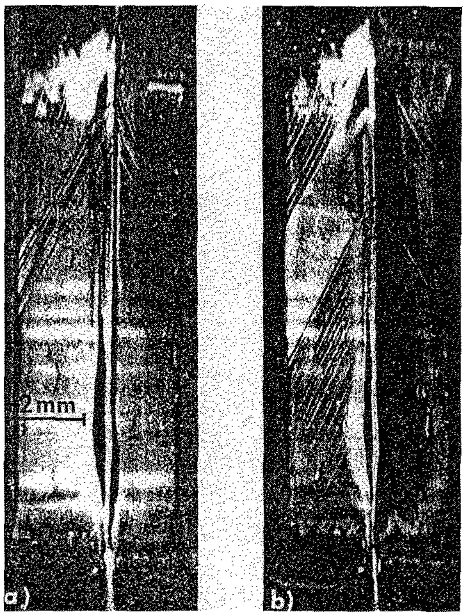
10. End result of deforming the structure shown in Figure 9. A single crystal of martensite is obtained, which has only one return path to its parent phase condition.



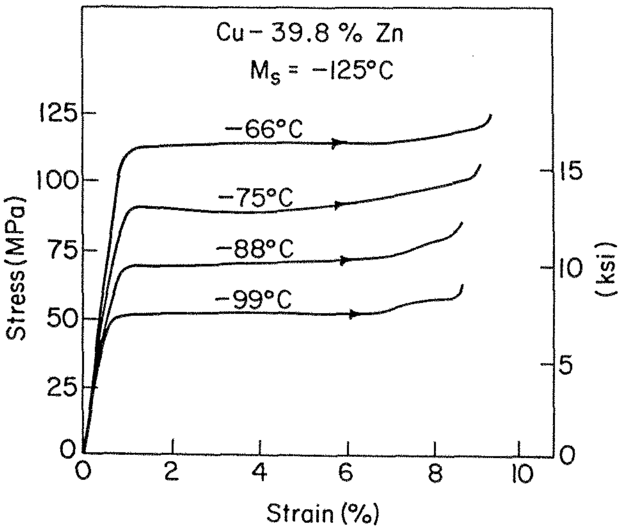
11. Stress-strain curve for a martensitic Cu-Zn shape memory alloy. The strain of over five percent is completely recovered when the unloaded specimen is heated to above the A_f temperature.



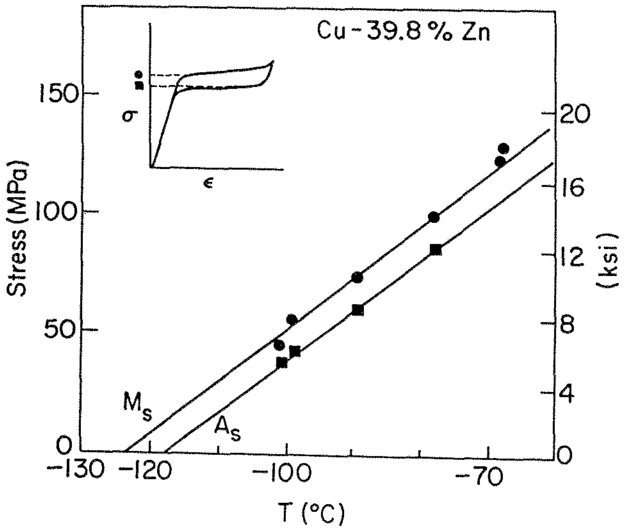
12. Stress-strain curve for a Cu-Zn shape memory alloy loaded above the M_s temperature and then unloaded. Stress-induced martensite is formed during loading, which disappears upon unloading.



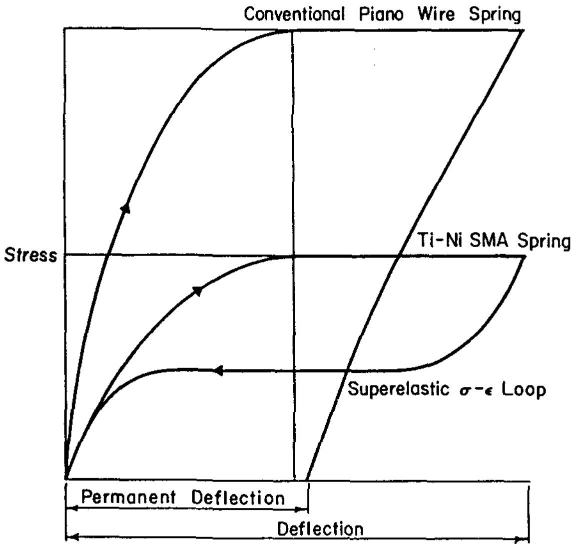
13 Gage length portion of a Cu-Zn single crystal showing the formation of only one variant (orientation) of stress-induced martensite during tensile loading above the M_s temperature.



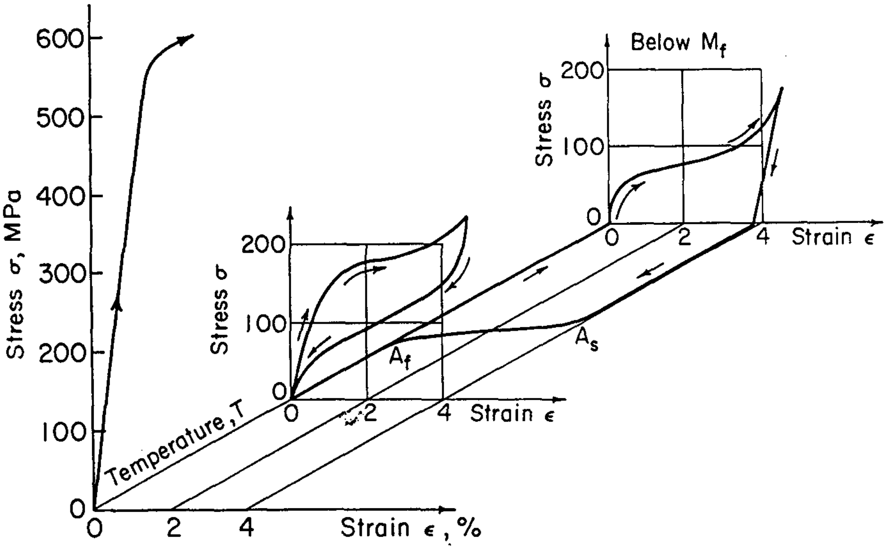
14. Stress-strain curves for a Cu-Zn single crystal loaded in tension above the M_s temperature. As the M_s temperature is approached, the stress required to induce martensite is lowered.



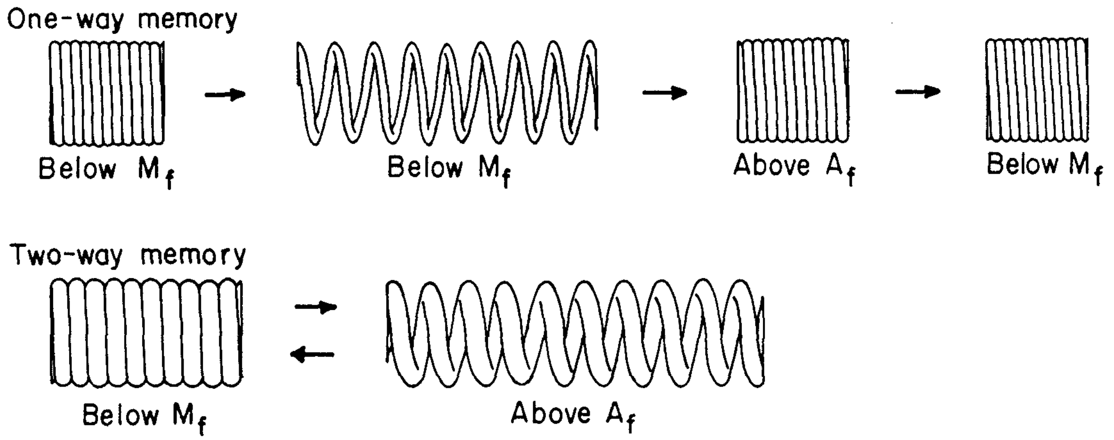
15. Plotting the plateau stresses such as shown in Figure 12 as a function of temperature gives a linear plot which obeys the Clausius-Clapeyron relationship.



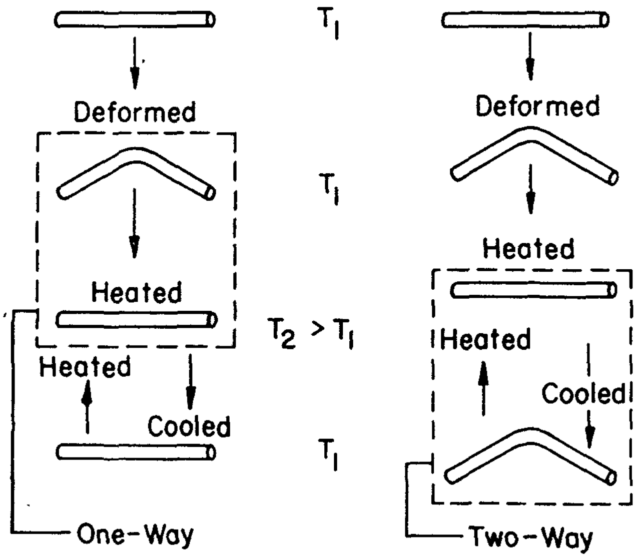
16. Comparison of springs made of superelastic shape memory alloy and conventional piano wire.



17. Three-dimensional stress-strain-temperature diagram showing the deformation and shape memory behavior of a Ti-Ni alloy deformed below M_f, above M_s and above A_f (and M_d). See text for discussion.

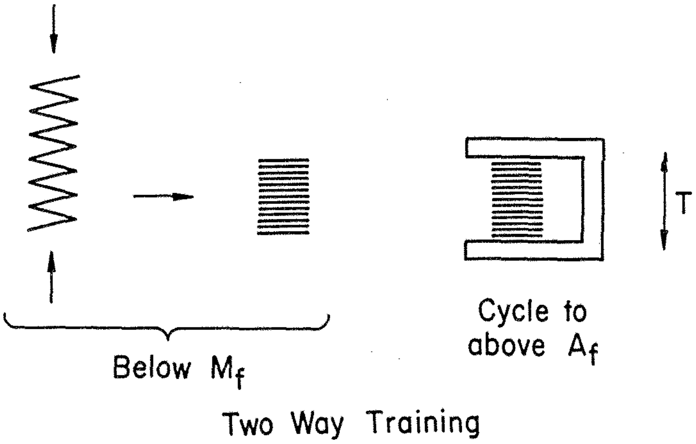


18 Comparison of the one-way (upper) and two-way (lower) shape memories using a coil spring as an example.



19. Comparison of the one-way (left) and two-way (right) shape memories using a bar-shaped specimen.

20. Optical micrograph showing martensite in a Cu-Zn shape memory alloy. (a) was taken after the initial cooling to below M_f. (b) shows the result of constraining the structure shown in (a) during heating to above A_f removing the constraint, and cooling to below M_f again. This treatment results in a dominance of variant D.



21. Diagram indicating a method for training a shape memory specimen to exhibit the shape memory effect. After compressing the spring in the martensitic condition below M_f, the spring is constrained and cycled from below M_f to above A_f several times. When the constraint is removed the spring will spontaneous close when cooled below M_f and spontaneously open when heated to above A_f.

Brief Biographical Sketch

Professor C. M. Wayman has researched the field of martensitic transformations for the past 30 years during which he has published over 400 papers, more than 100 of which deal with shape memory materials. He has edited numerous books. His textbook on the Crystallography of Martensitic Transformations has also been translated into Japanese and Chinese. His work on martensitic transformations has been recognized by the AIME Mathewson Gold Medal, The Buehler Award from the International Metallographic Society, the Eminent Faculty Award of the College of Engineering at the University of Illinois, Honorary Professorships at Harbin and Dalian Universities in China, and Fellowships in ASM International, the Metallurgical Society of AIME, the Institution of Metallurgists, the Japan Society for the Promotion of Science, the Guggenheim Foundation, and Churchill College at the University of Cambridge.