

## Fascinating Shape Memory Alloys

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**Summary:** This is a brief review of the Fascinating Shape Memory Alloys, commonly known as smart metal, memory metal, memory alloy, muscle wire, smart alloy. A shape memory alloy is a microtome alloy so as to remember (keeps memory) its initial or real shape and when heated or deformed turns in to its pre-deformed shape. Because of its unique properties, Shape Memory Alloys have found wide usage in hydraulic, pneumatic and motor-backed systems. These alloys contain applications to robots and automobile, aerospace as well as biomedical application. This article not only covers the discovery of the shape memory alloys but also the fundamental principles behind this phenomenon, the various metals and alloys exhibiting the characteristics. Physical phenomena and their applications are also discussed.

**Keywords:** Shape Memory Alloys, Superelasticity, Martensitic Transformations, One-way & Two-way Memory effects, Superplasticity, Manufacturing, Applications, etc.

### Introduction

As mentioned in the summary, shape memory alloys are alloys so as to remember the real shape and when heated turn in to their predetermined shapes. These materials are light weight, solid-state, and have applications in many industrial products, both mechanical and biomedical.

### 1. Historical Background

The shape memory alloys are known for almost eight decades, Otsuka and Wayman [1], Ölander [2] had discussed pseudoelastic performance of the Au-Cd alloy in the year of 1932, Greninger and Mooradian, 1938, observed the production and disappearance of a martensitic phase by the help temperature which is decreasing and increasing of a Cu-Zn alloy [3]. The Russian Academicians, Kurdjumov and Khandros [4], and Chang and Read [5], had widely reported the prime phenomenon of the memory effect govern by the thermoelastic behaviors of the martensite phase.

Superplasticity, martensitic transformation and twinning play an important role in the Shape Memory Effect.

Usually, the defence forces laboratories in the developed countries contribute valuable information, knowledge in various fields. This was the case with nickel titanium alloys which developed in 1962/1963 by the US Naval Ordnance Laboratory

and commercialized under the trade name Nitinol (stands for Nickel Titanium Naval Ordnance Laboratories). As is the case with many inventions, including some Nobel Prize winning inventions, the discovery of Nitinol was also made by accident. "A sample was bent out of shape a lot of times and presented at a laboratory management meeting. Dr. David S. Muzzey, an Associate Technical Director decided to see what would happen if he heated the sample, by a cigarette lighter underneath. To the amazement and surprise of all present, the sample stretched back to its original shape [6].

It is worth knowing that metallic alloys are not the only materials which respond to thermal response, shape memory polymers have also been developed and are commercially available for more than 25 years and are being used [7].

Before we further discuss the properties and applications of shape memory alloys, we would like to summarize the few definition of these alloys, e.g. (a) "A material first undergoes martensitic conversion. After deformation into martensitic form, the apparent permanent strain is formed when the specimen is heated to cause the reverse martensitic transformation. At cooling condition, it does not return to its previous shape [8].

Another definition of "Shape Memory" discusses the effect to restore the original shape of a

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plastically deformed sample by heating it. The phenomenon results from a crystalline phase change known as “thermoelastic martensitic transformation”. At temperatures below the transformation temperature, shape memory alloys are martensitic.

“This phenomenon is attributed to an elastic strain that might have been stored in the martensite during the initial transformation and thus might enhance the reverse transformation. In other words the growth and shrinkage of the martensite plates occur under a balance between thermal and elastic effects and thus the transformation can be reversible. Martensites that exhibit such reversibility on cooling and heating are generally called thermoelastic martensites. These martensites have ordered structures that cannot be destroyed by slip [4].

There are four characteristic temperatures which defining a thermoelastic martensitic conversion: the martensitic initial temperature,  $M_s$ , at which martensitic first appears in the austenite, the  $M_f$  temperature at which the martensitic formation ends, the  $A_s$  temperature at which the austenite starts forming and the  $A_f$  at which the austenite formation ends.

Shape memory alloys have also been described as new materials which are responsible to return a predetermined shape during heating. When a shape memory alloy is cold or below its transformation temperature, it has very low yield strength and it can be deformed very easily into any novel shape which it will retain.

Before we go further to discuss shape memory alloys, we would like to mention how this nomenclature came into being. C.M. Wayman and J.D. Harrison have mentioned it in their article the origins of the Shape Memory Effect [8]. This is what Wayman and Harrison said:

“A peculiarity was the discovery by the technician during heat treating a rod. Specifically, when the alloy was dropped during cold, it gave a dull thud, but when warm it produced a sharp ring. To demonstrate the room temperature ductility of the alloy for a 1961 project review, Buehler bent a strip of NiTi into a ridged shape. At the review, Muzzey, the director of engineering, heated the strip with a type of cigar lighter to test the sound change. The strip straightens out and demonstrated SME by special creation.

“The process was considered exceptional; complicated crystallographic processes were

hypothesized; articles for the general press were written; applications were envisioned; commercial suppliers were stimulated; lectures and trade show demonstrations spread the word. Energetic and constant promotion characterized the efforts of Buehler and his colleagues at the Naval Ordnance Laboratory (NOL) in making Nitinol (Ni + Ti + NOL) an engineering alloy. The term “shape memory” was coined by this group [8]. In every way, they pioneered shape memory. By the early 1970s, there was general acceptance that the SME in NiTi was due to the same crystallographic mechanism as in AuCd” [8].

Licce and Concilio [9] have defined the shape memory alloys as “peculiar materials within the fascinating characteristic of recovering apparent permanent deformations upto 10% and more. Moreover, they are metals and exhibit the typical peculiarities of metals like resistance, stiffness, workability etc. The combination of all their properties makes it easy to understand why these materials have experienced a growing interest in the field of engineering and gave rise to a definitely new way of thinking about the design of mechanical systems”.

In simple words, shape memory is a specific property some materials have to restore their original shape after a thermal load is applied [10]. In these substances, in fact, a rise of temperature may cause the full recovery of residual strains following a mechanical loading-unloading process and this is macroscopically perceived as a cancellation of the impressed deformation. In the following, metal alloys will be discussed.

This property emerges as a result of a phase shift, in which the crystal structure is reorganized. This atomic rearrangement can also occur when a stress field is imposed: thermal and mechanical fields show a reciprocal influence and the action of each of the two amends the characteristic values of the other. In the case of shape memory materials, two phases do exist, stable at low and high temperatures, respectively. The “cold” phase, martensite, is named after the German physicist Adolf Martens, and is characterized by an eccentric and highly crystalline phase, stable in two further different forms. Originally it indicated the metastable allotrope of steel, formed by rapid cooling. The “hot” phase, austenite, takes its name after the English physicist Charles Austen; it has a face-centered cubic structure, Fig.1A. The hot phase austenite is transferred to martensite and Fig. 1B shows the transformation of

austenite into a body-centered cubic (bcc) and then to body-centered tetragonal (bct) cell.

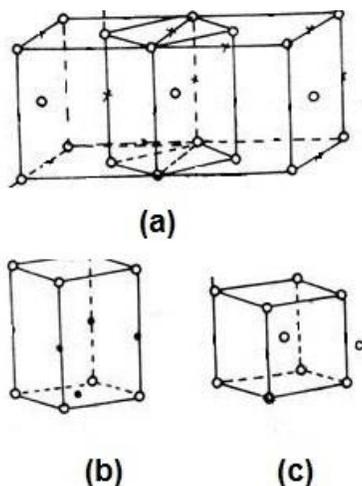


Fig. 1A: (a) Tetragonal cell outlined in austenite lattice, (b) – (c) Tetragonal cell before and after the pure deformation which produces martensite. X represents a carbon site.

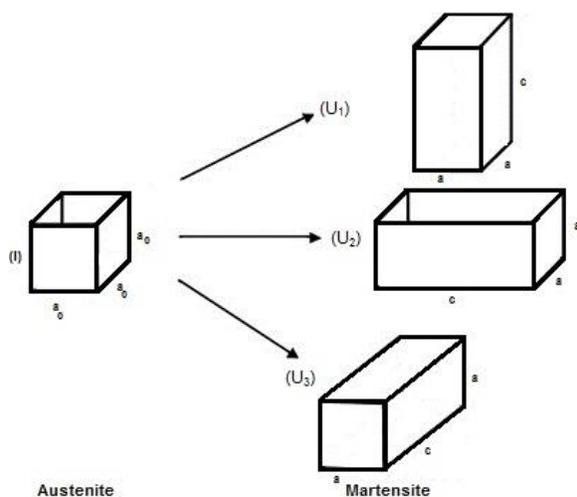


Fig. 1B: The three variants of martensite in a cubic to tetragonal transformation.

Ironically, none of these two scientists had a role in SMA research: both of them having lived at the turn of nineteenth and twentieth centuries, they are considered fathers of the materials science [9].

Two further characteristics are correlated to SME, namely pseudoelasticity and thermoelasticity. The former is the property of certain materials to completely recover their deformation (for some materials, they can attain very large values, like 10% and more) after having exhibited a sort of apparent yield. It is often referred as superelastic effect. The

latter indicates instead the functional dependence of the recoverable strain on thermal conditions [9].

“The phenomenon of phase change was first observed by Chang and Read in 1951, in a study on the Au-Cd alloy. They were the first to report the term “shape recovery” [5] although related behaviors as pseudoelasticity or superelasticity were previously seen by other scientists. In 1932, Ölander noticed pseudoelasticity in this same alloy and described this occurrence in his research on the “rubber like effect” [7]. In 1938, Greninger and Mooradian demonstrated thermoelasticity in Cu-Zn, during their investigation of brass alloys (copper-zinc and copper-tin) [3]. A detailed study of thermoelasticity in copper-zinc alloys was published in 1949, by Kurdyumov and Khandros [4]. A second alloy, indium-thallium, was then found to show SME, in 1954. These studies, however, did not lead to an outburst of scientific interest. Another alloy did, made of nickel and titanium.

In 1965, Buehler and Wiley of the U.S. Naval Ordnance Laboratory (NOL) received a United States patent [11] for a series of Ni-Ti alloys, whose generic name is 55-Nitinol, having therein detected shape memory behavior. These compounds have chemical compositions in the range of 53-57 weight percent, corresponding to a 48-52 atom percent nickel, which means they are equiatomic alloys. Because of their origin, these materials are usually called Nitinol, derived from the union of their chemical element symbols and the Naval Ordnance Laboratory acronym. Since then, SME has been observed in a remarkable number of other alloys systems. Apart from Ni-Ti, Cu-based alloys like Cu-Zn-Al and Cu-Al-Ni [12,13]. Also for further references and Fe-based alloys, which have been developed rather recently, like Fe-Pt and Fe-Pd, [14,15] have attracted considerable attention for specific applications.

To date, Nitinol is still the alloy showing the best shape memory characteristics together with three other remarkable properties, like an excellent corrosion resistance, a very stable configuration, and an almost perfect biocompatibility, which makes it the best choice for implementation in human bodies. On the other hand, it is much more expensive than Cu or Fe alloys, and difficult to melt and elaborate [16]. Wayman & Harrison [8] have widely defined some terminologies which are commonly used when discussing shape memory effects. They are reproduced in the Table-1, below:

Table 1: Glossary of Shape Memory Effect Technology.

Term	Definition
Shape Memory Effect	A material first undergoes a martensitic transformation. After de-formation in the martensitic condition the apparently permanent strain is recovered when the specimen is heated to cause the reverse martensitic transformation. Upon cooling, it does not return to its deformed shape.
Two-Way SME	A material normally exhibiting the SME is thermomechanically processed, after which, upon cooling through the martensite formation regime, it undergoes a spontaneous change in shape. Upon heating the inverse shape change occurs via the SME mechanism.
Superelasticity	When SME alloys are deformed in the temperature regime a little above that where martensite normally forms during cooling, a stress-induced martensite is formed. This martensite disappears (reverses) when the stress is released, giving rise to a superelastic stress-strain loop with some stress hysteresis. This property applies to the <i>parent phase</i> undergoing a stress-induced martensitic transformation.
Rubberlike Behavior	Some SME alloys show rubberlike flexibility. When bars are bent, they spontaneously unbend upon release of the stress. In order to obtain this behavior, the martensite after its initial formation usually must be aged for a period of time; unaged martensites show typical SME behavior. The rubberlike behavior, unlike superelasticity (also a rubberlike manifestation) is a characteristic of the <i>martensite phase</i> – not the parent phase.
Pseudoelasticity	This is a more generic term which encompasses both superelastic and rubberlike behavior. As such, it is less descriptive. Using the terms superelastic and rubberlike behavior is more specific and tends to avoid ambiguity by emphasizing parent phase and martensite properties, respectively.

Since martensitic phase transformation, twinning and superelasticity play a central role in shape memory alloys, we would like to discuss these two properties briefly.

## 2. Martensitic Transformation and Twinning

For the following definitions and explanations of martensite and terming we have used the following literature: Hodgson et.al. [17], Robert E. Reed-Hill [18], Morton C. Smith [19], J.W. Christian [20], Zenji Nishiyama [21], K. Otsuka and C.M. Wayman [22], Leonardo Lecce and Antonio Concilio [23], Dimitris C. Lagoudas [24], H.R. Chen [25], K. Bhattacharya [26] etc. First a brief summary of martensitic transformations:

“The hard product which is produced in many steels when rapidly quenched is called martensite. The martensitic transformations are found both in pure metals and in alloys. Many solid state transformations that start with nuclei depend on thermally activated atom movements for the growth of these nuclei. In some reactions of this type, a new phase grows at the expense of the old phase by the slow migration of the inter-phase boundary which depends markedly on temperature. This reaction proceeds isothermally to completion at fixed temperature, and the transformed materials generally do not undergo substantial changes in shape. These changes are known as nucleation and growth transformations and they are usually distinguished from martensitic transformations that are found only in solid state. This is rather an unfortunate

nomenclature as growth from nuclei also takes place during martensite reactions.

“Martensitic transformations depend on the regular arrangements of atoms in crystals and the possibility of changing from one arrangement to another by co-ordinated atom movements. Most atoms have the same neighbors (but differently arranged) after transformation and the growth process is formally equivalent to a deformation one crystal lattice into another and homogeneous in sufficiently small regions. The transforming regions, by changing their shape, are easily recognizable. In most cases, the amount of transformation is characteristics of martensitic transformations are quite different from those of nucleation and growth transformations: [20]

“Twinning and martensitic transformation have much in common. One, deformation or mechanical twinning is a mode of plastic deformation. Twinning, like slip, occurs as a result of plastic deformation while the other comprising martensitic reactions is a basic type of diffusionless solid to solid phase transformation. Twinning, similar to slip, occurs as the result of applied stresses. Occasionally, the applied stress may trigger partly a martensitic transformation, which is not of primary importance. Martensitic reactions take place in metals that undergo diffusionless phase transformations for which the driving force is the chemical energy difference between the parent phase and the transformed martensite phase.” [20]

The similarity between martensitic reactions and twinning lies in the analogous way twins and

martensite crystals form, because in both the cases the atoms inside finitic crystalline volumes of the present phase (usually referred to as austenite) are realigned as new crystal lattices. In twins this realignment produces the original crystal structure with a new orientation. In a martensite plate, not only is a new orientation produced but a basically different crystalline structure. It is because of this that when martensite is formed in steel quickly quenched to room temperature, the FCC (face centered cubic) stable phase at high temperature is converted into small crystalline units of a BCT (body centered tetragonal phase) (Fig.1). On the other hand, when twinning occurs in a metal such as zinc, both the parent crystal and the twinned volumes still keep the close-packed hexagonal zinc structure. In both twinning and martensite transformations, each realigned volume of material undergoes a change in shape which distorts the surrounding matrix. The changes in shape are quite similar, so that martensitic plates and deformation twins look alike, taking the form of small lenses or plates. Examples of deformation twins and martensite plates are shown in Fig. 2. As a matter of fact, it is quite possible to convert large volumes of the parent structure into elements of one of the new structures, but the plate like shapes as shown in Fig. 3 are much more common.” [20]

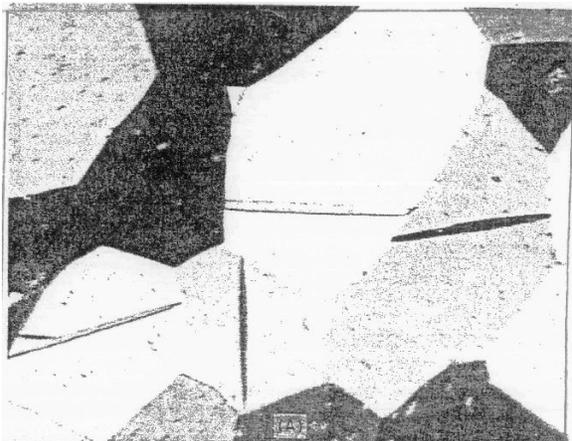


Fig. 2: Deformation twins in a polycrystalline zirconium specimen. Photographed with polarized light. (E.R. Buchanan) 1500 x

### 3. Deformation Twinning

We are first discussing the twinning phenomenon and then will discuss martensitic transformations.

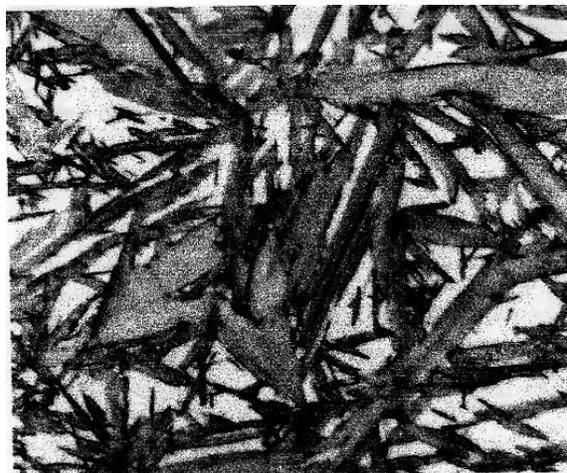


Fig. 3: Martensite plates in a 1.5% carbon-5, 10% nickel steel. (Courtesy of E.C. Bain Laboratory for Fundamental Research, United States Steel Corporation). 2500 x.

“The deformation accompanying mechanical Twinning is simpler than that associated with martensite transformations. It is because there is no change in crystal structure, whereby a reorientation of the lattice. The change of shape associated with deformation twinning is a simple shear, as shown in Fig. 4, where for simplicity it is assumed that the twin traverses the entire crystal. The difference between twinning and slip should be carefully recognized since in both cases, the lattice is sheared. In slip, the deformation occurs on individual lattice planes as indicated in Fig. 5. When measured on a single-slip plane, this shear may be many times larger than the lattice spacing and depends on the number of dislocations emitted by the dislocation source. The shear associated with deformation twinning, on the other hand, is uniformly distributed over a volume rather than localized on a discrete number of slip planes. Here, in contrast to slip, the atoms move only a fraction of an interatomic spacing relative to each other. The total shear deformation due to twinning is also small, so that slip is much more important primary mode of plastic deformation. It is also true that mechanical twinning is not readily obtained in metals of high symmetry (face-centered-cubic). Nevertheless, the importance of mechanical twinning is becoming increasingly more apparent in explaining certain elusive mechanical properties of many metals.” [20]

“For example, when a metal twins, the lattice inside the twin is frequently realigned into an orientation the slip planes of which can be more favorably aligned with respect to the applied stress for slip. Under certain conditions, a heavily twinned

metal can be more easily deformed than one free of twins. On the other hand, lattice realignment, if confined to a limited number of twins, can induce fracture by permitting very large deformations to occur inside the confined limits of twins. Twins are also of importance in recrystallization phenomena, for the intersections of twins are preferred positions for the nucleation of new grains during annealing.” [20]

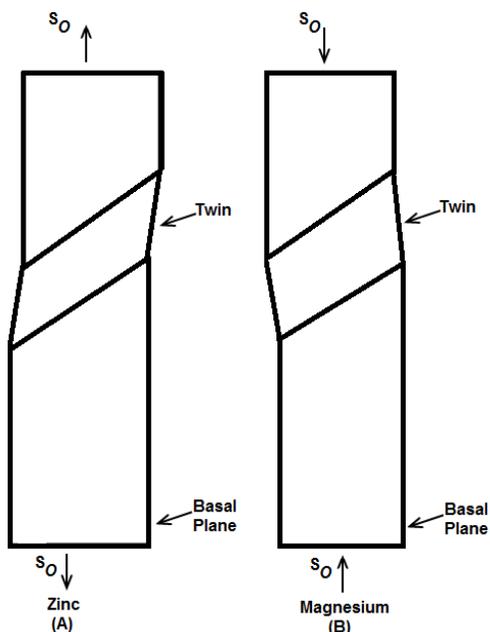
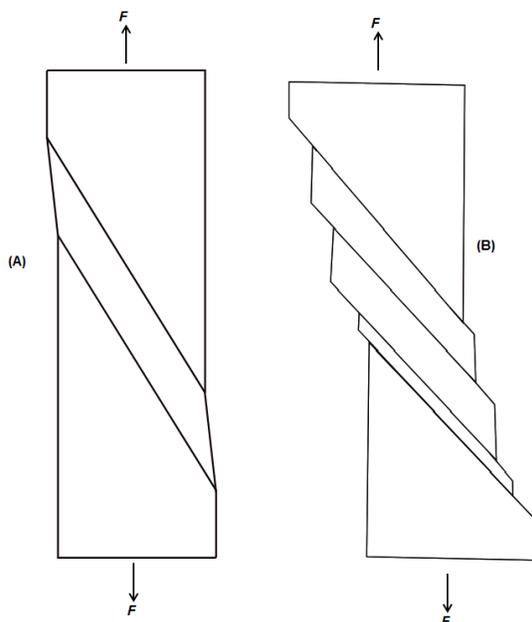
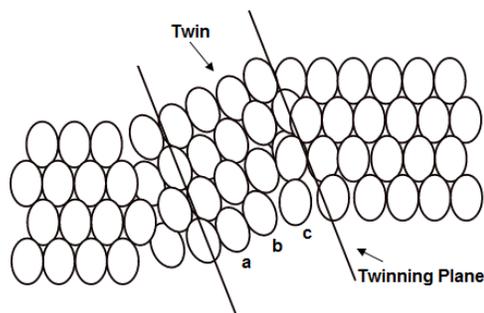
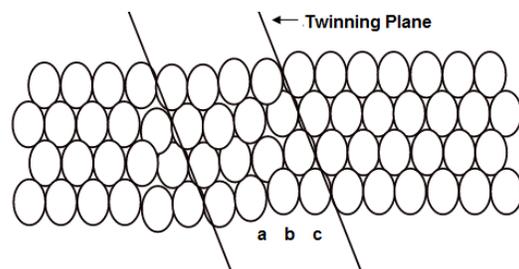


Fig. 4: The change of shape associated with deformation twinning is a simple shear. The twin traverses the entire crystal [20].

“A good insight into the mechanics of twinning can be gained by studying the simple diagrams of Fig. 7. The twinning represented in these sketches is only schematic and does not refer to twinning in any real crystal. The upper diagram represents a crystal structure composed of atoms assumed to have the shape of oblate spheroids. The lower diagram represents the same crystal after it has undergone a shearing action which produced a twin. The twin is formed by rotation of each atom in the deformed area about an axis through its center and perpendicular to the plane of the paper. Three atoms are marked with the symbols a, b, and c in both diagrams to show their relative positions before and after the shear. Notice that individual atoms are shifted very little with respect to their neighbors. While it is no way implied that the atom movements in a real crystal are the same as those shown in Fig. 8, it is true that in all cases the movement of an atom relative to its neighbors is very small.” [20]



Figs. 5 & 6: The difference between the shears associated with twinning (Fig. 5) and slip (Fig. 6).



Figs. 7: Schematic representation showing how a twin is produced by a simple movement of atoms.

The two parts of Fig 8 show another important characteristic of twinning: the lattice of the twin is a mirror image of the parent lattice. The lattices of twin and parent are symmetrically oriented across a symmetry plane called the *twinning plane*. The several ways that this symmetry can be attained will be discussed in the next section.

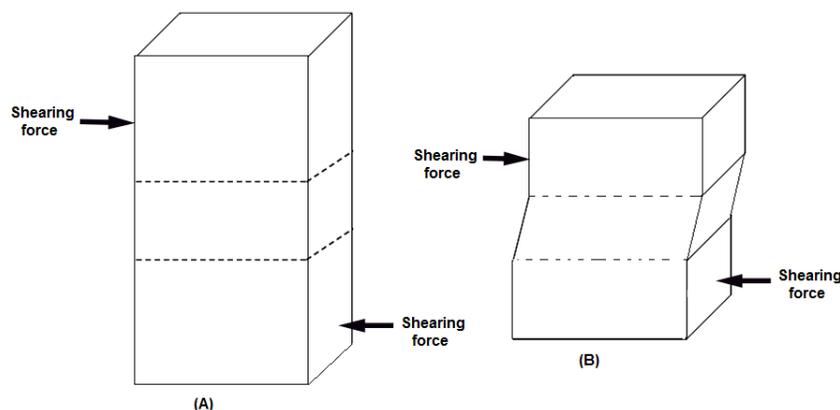


Fig. 8: (A) Shows a single crystal in a position where it is subject to shearing forces, (B) Shows a twinning shear that has occurred as a result of the force.

#### 4. Formal Crystallographic Theory of Twinning

“The formal crystallographic theory of twinning in metals has been summarized by Cahn [27] and the following treatment is largely based on his presentation.

Let us assume that shearing forces are applied to a single crystal specimen, as indicated on the left in Fig. 9, and that, as a result of this applied force, the crystal is sheared. The resulting shape of the crystal is shown in the second drawing. Furthermore, let us assume that after deformation, the sheared section still has the structure and symmetry of the original crystal. In other words, this region is to retain, after shearing, all the crystallographic properties of the metal of which it is composed, so that the size and shape of the unit cell must be unchanged. According to crystallographic theory, the size and shape of the unit cell will be unchanged only if it is possible to find three noncoplanar, rational lattice vectors in the original crystal that have the same lengths and mutual angles after shearing.” [20]

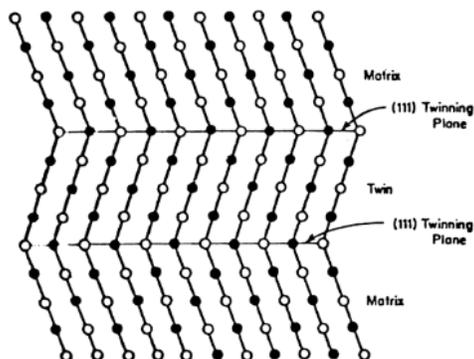


Fig. 9: Atomic arrangement of the twinning plane in a face-centered cubic metal. Black and white circles represent atoms on different levels (planes).

(After Barrett, C.S., ASM Seminar, Cold Working of Metals, Cleveland, Ohio, {1949}).

#### 5. Nucleation of Twins

“Twins form as the result of the shear-stress component of an applied stress which is parallel to the twinning plane and lies in the twinning direction  $\eta_1$ . The normal stress component (normal to the twinning plane) is unimportant in twin formation, a conclusion based on recent work [28] in which zinc crystals were deformed in tension while subjected to hydrostatic pressure. In these experiments, no measurable difference was found in the tensile stress required to form twins under hydrostatic pressures varying from 1 to 5000 atmospheres. Since the hydrostatic pressure has no shear component on the twinning form only as a result of shear stress.” [28]

It has been estimated [29] that the theoretical shear stress necessary to *homogeneously* nucleate deformation twins in zinc crystals lies between 40 and 120 kg per mm<sup>2</sup> (56,000 to 168,000 psi). Experimentally measured values of the shear stress to form twins lie much lower than the theoretical values, ranging from 0.5 to 3.5 kg per mm<sup>2</sup>. This is strong evidence for the belief that twins are nucleated heterogeneously.

“A great deal of evidence suggests that nucleation centers for twinning are positions of highly localized strain in the lattice. Confirmation for this assumption is given by the fact that twins appear to form only in metals that have suffered previous deformation by slip [29]. It would further appear that the slip process much become impeded so that barriers are formed which prevent the motion of dislocations in certain restricted areas. Suitable barriers can be formed in a number of ways. Thus, under the proper geometrical conditions, the

intersection of dislocations with each other can form barriers to the motion of other dislocations. Kink bands, grain boundaries, and deformation twins already present in the lattice can also act as impediments to the normal motion of dislocations. The significance of barriers lies in the fact that dislocations, as they move under an applied external stress, may pile up against them. Since a stress field exists around each dislocation, the concentration of large numbers of dislocations into relatively small volumes of a crystal should lead to intensification of the stress in the neighborhood of dislocation pile-ups. In order to explain the dependence of the twinning stress on prior plastic deformation, it has been proposed that stresses associated with local concentrations of dislocations can lower the magnitude of the external stress needed to nucleate deformation twins." [29]

"Because the localized stress fields (of twin nucleation centers) can be formed in a number of different ways, depending on the geometry and orientation of the specimen, as well as the nature of the applied stress, it is probable that there can be no universal critical resolved shear stress for twinning as there is for slip. This explains the experimentally observed wide range of shear stresses required for twinning (that is, 0.5 to 3.5 kg per mm<sup>2</sup> in zinc). If a specimen is so oriented as to make slip occur only at very high stress levels, then twins will also only form at high stress levels. If, on the other hand, complex slip patterns can occur at relatively low stress levels, twins will nucleate at moderate stress levels. Finally, if slip occurs only by easy glide, twinning should probably not occur." [29]

## 6. Twin Boundaries

We now discuss the interface between a twin and the parent crystal. The atomic arrangement at a twin boundary in a face-centered cubic metal is shown in Fig. 10. This diagram assumed that the twin interface is exactly parallel to the twinning plane  $K_1$ . In this structure, the two lattices (twin and parent) match perfectly at the interface. Atoms on either side of the boundary have the normal interatomic separation expected in a face-centered cubic lattice. The interfacial energy of the boundary is very small. In the case of copper, it has been determined [30] to be 24 erg per cm<sup>2</sup> which is very much smaller than the surface energy of a copper-copper grain boundary. Barrett [31] has drawn diagrams similar to that of Fig (10) for  $\{10\bar{1}2\}$  twins in hexagonal metals and  $\{112\}$  twins in body-centered cubic metals. He shows that in both cases a reasonable match between twin and parent lattices can be made across  $K_1$ .

However, atoms on both sides of the interface are displaced small distances from their normal lattice positions. Because atomic bonds are strained in these twin interfaces, they must possess higher interfacial energies than the  $\{111\}$  twin boundary of face-centered cubic metals. However, these energies are still much smaller than those of normal grain boundaries. The fact that deformation twins invariably form on planes of low indices may be explained in terms of the surface energy associated with the interface between twins and parent crystals. In general, the higher the indices, the poorer the fit at the inter-face, the higher the surface energy, and the lower the probability of twin formation.

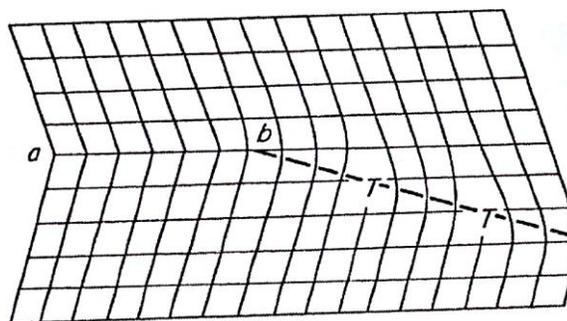


Fig. 10: The difference between a coherent twin boundary  $ab$  and an incoherent twin boundary  $bc$ . Notice the dislocations in the incoherent boundary. (After Siems, R., and Haasen, P., *Zeits. Für Metallkunde*, 49, {1958}).

A twin boundary that parallels the twinning plane is said to be a coherent boundary. Since most twins appear, at least in their beginnings, as small lens-shaped structures, it is clear that the average twin boundary cannot be strictly coherent. In a coherent boundary it is usually quite possible to match the two lattices without assuming the presence of dislocations in the boundaries. (See Fig.10). In an actual boundary where it is not coherent, it is generally accepted that a dislocation array is necessary in order to adjust the mismatch between lattices of parent and twin. This is demonstrated in Fig. 11, which shows schematically segments of both a coherent boundary and an incoherent boundary.

## 7. Twin Growth

"The dislocation array associated with lenticular (lens-shaped) twins represents a surface of considerably higher energy than a corresponding coherent boundary. The formation of a twin involves the creation of this surface, which explains the difficulty of twin nucleation. The movement of these

dislocation arrays is also believed to explain the growth of deformation twins. Unfortunately, the theories of twinning dislocations are not as advanced as those associated with slip, and we shall not discuss them in detail. Finally, the presence of dislocations in curved twin boundaries helps to explain an interesting experimental fact. Whenever possible, twins will try to grow in such a manner as to develop straight sides parallel to the twinning plane,  $K_1$ . The coherent twin boundaries thus formed possess interfacial energies that are much smaller than curved dislocation arrays.

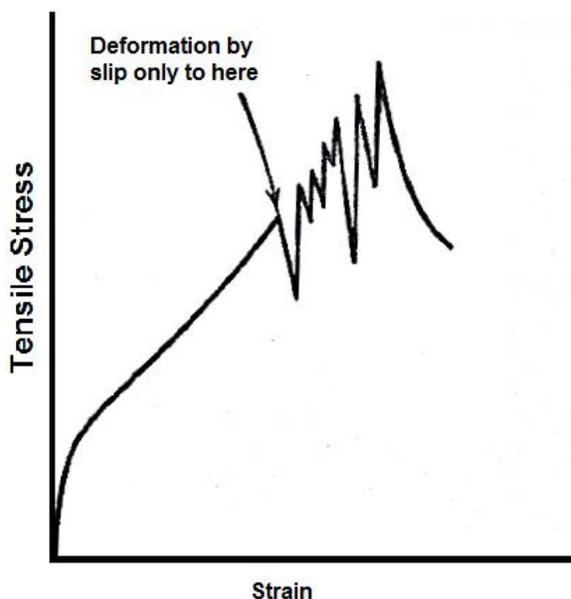


Fig. 11: Single-crystal tensile stress-strain curve showing discontinuous strain increments due to twinning. (After Schmid and Boas, *Kristallplastizität*, Julius Springer, Berlin, {1935}).

Twins grow in size by increasing both their length and thickness. Large volumes of twinned material often form by the coalescence of separately nucleated twinned areas. The speed of twin growth is primarily a function of two variables that are not entirely independent. The first is the speed of loading that directly influences the rate of growth. The other is the stress required to nucleate twins. If twins nucleate at very low stresses, the stress required for their growth will be of the same order of magnitude as the nucleating stress. In this case, a small submicroscopic twin may form and grow more or less uniformly with an increasing stress until its growth is impeded by some means or other. On the other hand, if twins form under conditions that result in very high stress levels before nucleation, the stress for growth may be much smaller than that for

nucleation. When this happens, twins grow at very rapid rates as soon as they are nucleated. Several interesting phenomena are associated with this rapid growth. First, the rapid deformations that ensue set up shock waves in the metal that can be heard as audible clicks. The crackling sound audible when a bar of tin is bent is due to deformation twinning. The other effect is visible in tensile tests of crystal specimens which undergo twinning during loading. The rapid formation of twins results in sudden increments in tensile strain. In a rigid machine, this causes the load to suddenly drop, giving the stress-strain curve a saw-tooth appearance in the region of twinning. A stress-strain curve of this nature is shown in Fig. 12.

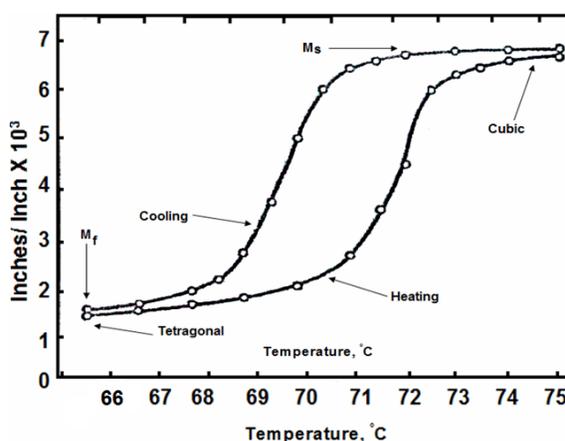


Fig. 12: The temperature dependence of the martensite transformation in an indium-thallium (18% TI) alloy. Transformation followed by measurement of change in length of specimen. (From data of Burkart, M.W., and Read, T.A., *Trans. AIME*, 197, {1953}).

## 8. Accommodation Kinks

The fact that newly formed twins are lens-shaped is probably a result of their growth characteristics. The sharp edges around the circumference of lenticular twins can be assumed to be a manifestation of the dislocation arrays, which permit the twin to grow laterally or lengthwise under an applied stress. In this regard, it is interesting to note that when a twinned structure is annealed, the twins can tend to disappear by shrinking inward from their sharp edges, with the result that the latter become blunted or squared off. The sharp leading edge of a twin is also lost when a growing twin intersects a free surface. If a twin meets a single free surface, it assumes the shape of a half-lens, and if it crosses a complete crystal, the twin acquires flat sides parallel to the twinning plane. In the last case, the

twin can be accommodated in the lattice without appreciable distortion of the latter. This is not true for lense or half-lense-shaped twins where the lattice around the twins is forced to accommodate the sheering strain. In this case of half-lense, one commonly finds accommodation kinks adjacent to the twins. [20]

### 9. The Martensite Transformation in an Indium-Thallium Alloy

“We have earlier, in section 2, discussed briefly the phenomenon known as Martensitic transformation. It is a transformation that occurs by cooperative atomic movements and the product is known as martensite. It is a diffusionless, solid-to-solid transformation, is a single phase to another single phase. Similarly, the chemical position of the untransformed part is not changed and it is the same as the transformed part. Martensite transformation entails a definite orientation relationship, a definite habit plane (the plane on which martensite plates form is also usually assumed to be an undistorted plane).

“In a martensite transformation in steel, a face-centered cubic lattice (fcc) can also be considered as a body-centered tetragonal lattice (Fig. 1). Similarly, a body-centered cubic structure (bcc) could be obtained from fcc structure by a impression parallel to the e-axis and an expansion along the two a axes. Any simple homogenous pure distortion of this nature, which converts one lattice to another by expansion or compression along the crystallographic axes, belongs to a class known as Bain distortions. However, there is no undistorted plane associated with this Bain distortion, so that the invariant plane strain associated with martensite transformation cannot be explained by a Bain distortion.” [18]

We shall now consider in some detail the martensite transformation in the indium-thallium alloy where the small size of the observed shear makes for easier understanding of the observed phenomena. Studies made of single crystals of this alloy are of special interest. Provided that the crystals are carefully annealed and not bent or damaged, they undergo martensitic transformations involving the motion of a single interface between the cubic (parent phase and the tetragonal (product phase), [28,29]. This transformation does not occur by the formation of lens-shaped plates, or even parallel-sided plates, but by the motion of a single planar boundary that crosses from one side of the crystal to the other. On cooling, an interface first appears at one end of a specimen and, with continued cooling, moves down

through the entire length of the crystal. Because of dimensional changes accompanying the reaction, its progress can be followed with the aid of a simple dilatometer that permits measurements of the specimen length to be made as a function of temperature. A typical set of data is shown in Fig. 13. Notice that, on cooling, the length of the specimen begins to change at approximately 72° C, signifying that the martensite transformation started at this temperature. It is customary in all martensite transformations to designate, by the symbol  $M_s$ , the temperature corresponding to the start of the transformation. The cure also shows that the specimen did not transform completely until the temperature was lowered to about 67° C. This latter temperature is designated as the  $M_f$ , or martensite finish temperature. In order to move the interface from one end of the specimen to the other, it was necessary to drop the temperature 5° below the  $M_s$  temperature. During this temperature interval between  $M_s$  and  $M_f$ , the interface, or habit plane does not move steadily and smoothly, but rather in a jerky fashion. It moves very rapidly for a short distance in a direction normal to itself and then stops until a further decrease in temperature gives it enough driving force to move forward again. The irregular motion of the interface is not apparent in the dilatometer measurements of Fig. 13, but may be readily observed by watching the movement of the interface under microscope. The necessity for an ever-increasing driving force to continue the reaction is an unusual phenomenon because it implies the existence of a volume relaxation [30] or an energy term opposing the transformation which is proportional to the volume of metal transformed. An explanation for the effect can be given in terms of the intersection of the interface with obstacles. It is now believed that martensitic and deformation twin interfaces can be composed of dislocation arrays. It is also recognized that a moving screw dislocation, which cuts through another screw dislocation, acquires a jog or discontinuity which produces a row of vacancies or interstitials as the moving dislocation continues its advance. While the geometry of the dislocation arrays in the crystals and in the interfaces is not known, the screw-dislocation-intersection picture gives us a tentative picture [31] of how a moving interface can develop a resistance to its motion proportional to the distance through which it moves. The screw components in an interface should cut other screw dislocations in a number proportional to the distance through which the interface moves: each intersection adding its own contribution to the total force holding back the boundary.

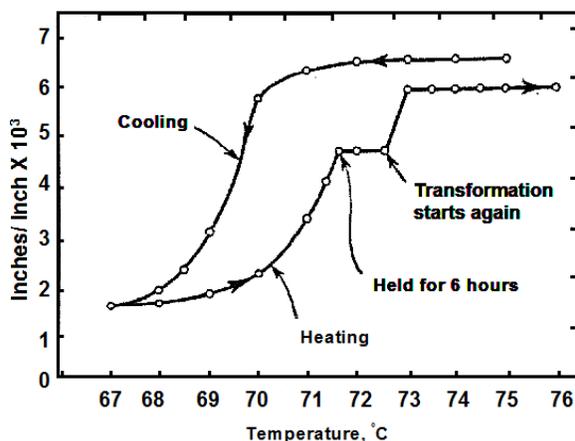


Fig. 13: Stabilization in the martensite transformation in an indium-thallium (18% TI) alloy. (From data of Burkart, M.W., and Read, T.A., Trans. AIME, {1953}).

### 10. Reversibility of the Martensite Transformation

The indium-thallium transformation is reversible for, on reheating, the specimen reverts not only to the cubic phase, but also to its original single-crystal orientation. If recorded, the original interface reappears and the cycle can be completely reproduced (provided the specimen is not heated to too high a temperature or held for too long a time between cycles).

The reverse transformation is shown in Fig. 13 by the return of the specimen to its original dimensions. It does not, however, retransform in the same temperature interval as that in which the forward transformation occurred, but in one averaging about  $2^\circ$  higher. A hysteresis in the temperature dependence of the transformation is characteristic of most martensite transformations.

### 11. Athermal Transformation

In the single-crystal experiments discussed in the above paragraph, we have seen that the martensite transformation in indium-thallium occurs as a result of temperature changes that increase the driving force for the reaction (free energy). The progress of transformation is, accordingly, not time dependent. In theory, the faster one cools the specimen, the faster the interface moves, with equal amounts of transformation resulting at equal temperatures. Time does, however, have a secondary, though negative, effect on this transformation, for isothermal holding of the specimen at any temperature between the start and end of the

transformation tends to stabilize the interface against further movement. This effect is demonstrated in Fig. 14 where the indicated transformation curve corresponds to a specimen whose heating cycle was interrupted at  $71.6^\circ\text{C}$  and held at this temperature 6 hr. Not only did the holding of the specimen at this temperature not induce additional transformation, but it stabilized the interface. In order to make the interface move again, it was necessary to increase the driving force by approximately  $1^\circ\text{C}$ . An equivalent phenomenon occurs on cooling, so that it can be concluded that the formation of martensite in the present alloy depends primarily on temperature. A transformation of this type is said to be athermal, in contrast to one that will occur at constant temperature (isothermal transformation). Although isothermal formation of martensite is observed in some alloys, martensitic transformations tend to be predominantly athermal.

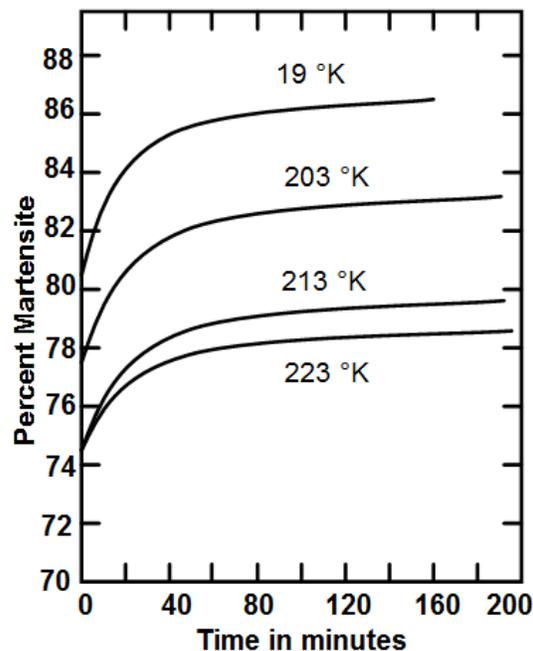


Fig. 14: Isothermal transformation subsequent to a direct quench to temperature shown. Notice that the amount of athermal martensite that forms prior to the isothermal transformation increases with decreasing holding temperature. (Fe-29 % Ni). (From data of Machlin, E.S. and Cohen, Morris, Trans. AIME, 194, {1952}).

### 12. Wechsler, Lieberman, and Read Theory

The nature of the atomic mechanisms that convert one crystal structure into the other in the narrow confines which we define as the interface are

not known. Wechsler, Lieberman, and Read [32] have shown, nevertheless, that the crystallographic features of martensite transformations can be completely explained in terms of three basic deformations which are enumerated below:

1. A *Bain distortion*, which forms the product lattice from the parent lattice, but which, in general, does not yield an undistorted plane that can be associated with the habit plane of the deformation.
2. A *shear deformation*, which maintains the lattice symmetry (does not change the crystal structure) and, in combination with the Bain distortion, produces an undistorted plane. In most cases, this undistorted plane possesses a different orientation in space in the parent and product lattices.
3. A *rotation of the transformed lattice*, so that the undistorted plane has the same orientation in space in both the parent and product crystals.

No attempt is made in this theory to give physical significance to the order of the steps listed above, and the entire theory is best viewed as an analytical explanation of how one lattice can be formed from the other.

### 13. Irrational Nature of the Habit Plane

One of the nice features of the Wechsler, Lieberman, and Read theory is that it shows quite clearly why the habit plane in martensitic transformations is usually irrational. This characteristic is in sharp contrast to the twinning plane in deformation twinning which is almost invariably a plane of low rational indices.

### 14. Multiplicity of Habit Planes

A word about the multiplicity of the orientations that can be obtained in a martensitic transformation. The number of possible habit planes can be quite large in most reactions. In the indium-thallium alloy there are 24 possible habit planes, all of which lie very close to  $\{110\}$  planes (within  $26'$ ), which signifies that there are four habit plane orientations closely clustered about each of the six  $\{110\}$  planes.

### 15. Isothermal Formation of Martensite

Martensite has been observed to form isothermally [33] as well as athermally, in 30 per cent

iron-nickel specimens. In either case, and not through the growth of existing plates. Curves showing the amount of isothermal martensite formed as a function of time are given in Fig. 15. These curves also serve another useful purpose because they demonstrate the interrelation between the athermal and isothermal transformations. The intersection of each isothermal curve with the ordinate axis gives the amount of martensite formed on the quench to the holding temperature.

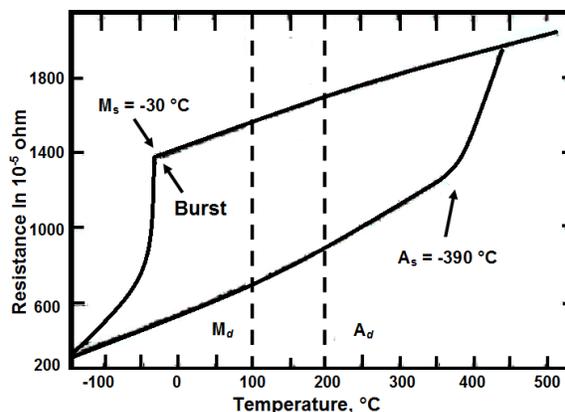


Fig. 15a: The martensitic transformation in an iron-nickel (29.5% Ni) alloy. (From Kaufman, Larry, and Cohen, Morris, Trans AIME, 206, {1956}).

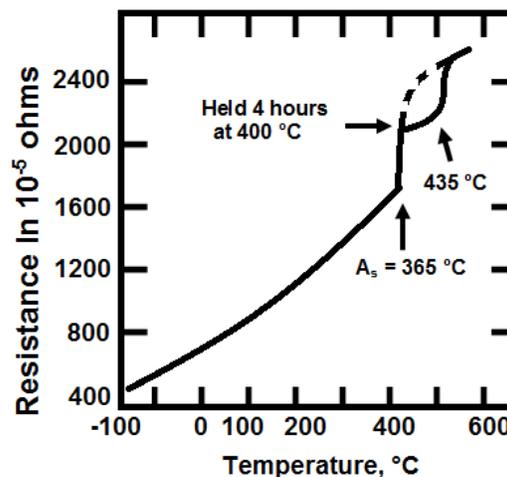


Fig.15b: Stabilization during reversed transformation (martensite to austenite) in Fe 29.7% Ni specimen held at 400°C for 4 hrs. Transformation following holding period did not start again until temperature reached 435°C (Kaufman, Larry, and Cohen, Morris, Trans. AIME, 206, {1956}).

## 16. Stabilization

The phenomenon of stabilization is also observed in iron-nickel alloys. The mechanism differs from that observed in the indium-thallium alloy, but the effect is the same; isothermal holding of the specimens at a temperature between  $M_s$  and  $M_f$  stabilizes the transformation so that additional supercooling is required in order to start the transformation again. In the indium-thallium specimens, stabilization occurs as a result of a retardation of the movement of the interface, whereas in the iron-nickel alloy, stabilization is manifested by an increased difficulty in the nucleation of additional plates. In order for the reaction to continue, an additional increment of driving force is needed to nucleate more plates. Stabilization is also observed during the reverse transformation when martensite is reached to form austenite. In this case, no observable isothermal reaction occurs, so that the stabilization effect appears clearly in a resistivity-temperature curve. Such a curve is shown in Fig. 16.

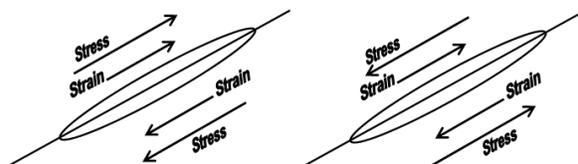


Fig. 16: The effect of external stress on martensite plate formation [20].

## 17. Nucleation of Martensite Plates

The nucleation of martensite plates is a subject of great interest and also of considerable controversy. The available experimental evidence favors the belief that martensite nuclei form heterogeneously, as is the case with nucleation in most other transformations, or changes of phases.

The evidence is also strong for the assumption that the locations at which nuclei form are internal positions of high strain (dislocation configurations), commonly called strain embryos.

No simple theory of martensite nucleation is yet available. This is probably due to the fact that martensite can form under two extremely different sets of conditions. First, it can form athermally, which means that it can form in a very small fraction of a second provided the temperature is lowered sufficiently to activate those nuclei which will respond in this manner. This type of nucleation apparently does not need thermal activation. The ability of martensite to form without the aid of thermal energy is also demonstrated by the fact that martensite plates can be nucleated in some alloys at

temperatures as low as 4° K, where the energy of thermal vibrations is vanishingly small. On the other hand, martensite is also capable of forming at constant temperature. The fact that, in this case, it has a nucleation rate which is time dependent shows that thermal energy can also be a factor in the nucleation of martensite.

## 18. Growth of Martensite Plates

The growth of martensite plates does not have the twofold nature of nucleation, for here it appears that thermal activation is not a factor. The evidence leading to this conclusion includes the fact that plates grow to their final sizes with great rapidity [33]. Recent measurements show that the growth velocity is of the order of one-third the velocity of sound in the matrix [34]. To this must be added the fact that the growth velocity is independent of temperature. If the growth of martensite plates occurred as the result of atoms jumping over an energy barrier from the parent phase to the product phase, then the jump rate should be a decreasing function of the temperature, and at some finite temperature a noticeable dropping off in the martensitic growth rate should become apparent. This does not occur. Martensite has been observed to form with great rapidity even at 4° K [35].

## 19. The Effect of Stress

Because of formation of martensite plates involves change of shape in a finite volume of matter, applied stress can influence the reaction. This is entirely analogous to the formation of deformation twins by stress. However, because the formation of a martensite plate involves both shear and normal components of strain, the dependence on stress is more complicated than in the case of twinning. Nevertheless, theoretical predictions of the effect of various stress patterns on the formation of martensite have been found to agree quite well with experiment [36, 37]. It is important to note that the  $M_s$  temperature can be either raised or lowered as a result of applied stresses. This may be understood in terms of the following, perhaps oversimplified picture. Suppose, as shown in Fig. 33 the macroscopic strain associated with the formation of a martensite plate is a pure shear (normal component zero). Then if the sense of an applied shear stress is the same as the strain, the stress should aid the formation of the plate. A lower driving force for the reaction is to be expected and  $M_s$  should be raised. Similarly, if the shear-stress vector is reversed, the formation of the plate becomes more difficult and the temperature at which the plate forms should be lowered. It is important to note that, in respect to this latter, a simple applied shear stress may not necessarily lower

$M_s$  because of the multiplicity of the habit planes on which martensite can form. While the indicated plate might not be favorably oriented to the stress, it is quite probable that there are other plate orientations in the crystal that are [37].

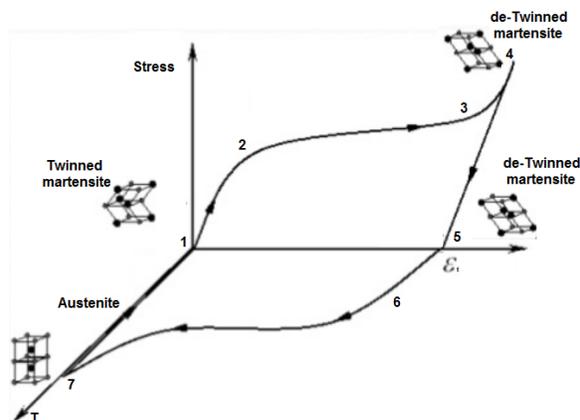


Fig. 17a: Shape memory effect.

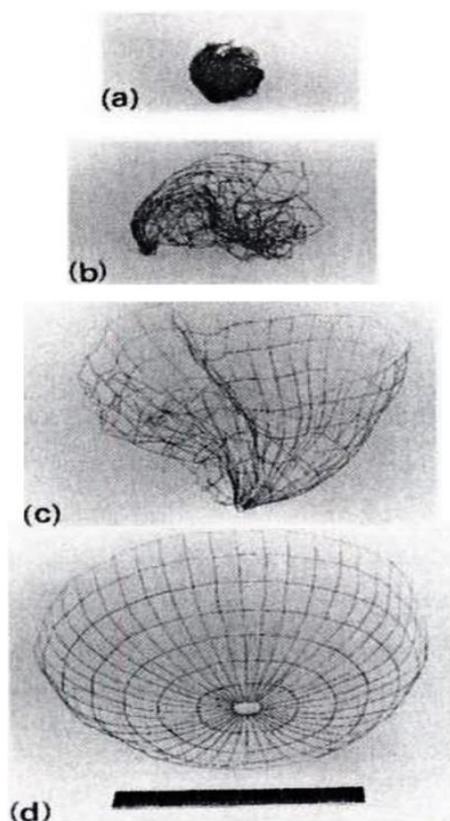


Fig.17b: Practical example of shape memory effect by a space antenna of Ti-Ni Wires. The antenna, deformed in the martensitic state in (a), reverts to the original shape (b-d) upon heating by solar heat. (Courtesy Goodyear Aerospace Corporation).

## 20. The Effect of Plastic Deformation

Plastic deformation of the matrix also has an effect on the formation of martensite which is primarily to increase the sizes of internal strains and make the nucleation of martensite easier [38]. As a result, martensite can form when the metal is plastically deformed at temperatures well above the  $M_s$  temperature. The amount of martensite thus formed decreases, however, as the temperature is raised, and it is common practice to designate the highest temperature at which martensite may be formed by deformation as the  $M_a$  temperature. In reversible martensitic transformations, plastic deformation usually has a similar effect on the reverse transformation. The temperature at which the reverse transformation starts is lowered by plastic deformation. The  $M_a$  and  $A_a$  (austenite start temperature for plastic deformation) are shown plotted as vertical dashed lines in Fig. (18). Notice that plastic deformation brings the start of the forward and reverse transformations much closer together – within approximately 100° C. The corresponding difference between  $M_s$  and  $A_s$  is 420° C.

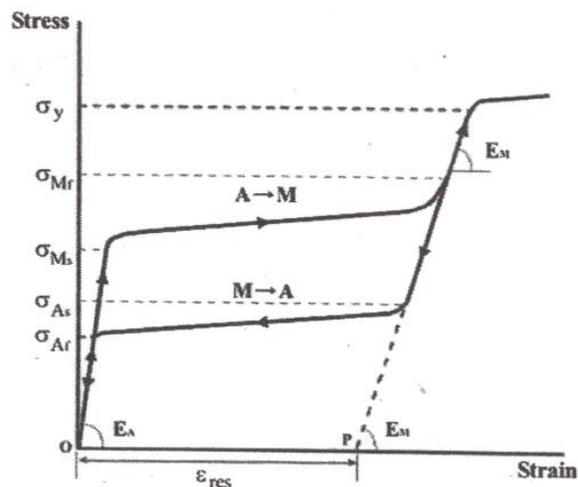


Fig. 18: The superelastic stress-strain curve.

## 21. Superplasticity or Pseudoelasticity

In section 1 we had mentioned that superelasticity, martensitic transformations and twinning play an important role in the Shape Memory Effect. Since we have already discussed Martensitic Transformations and Twinning, we would like to briefly discuss the Superplasticity or Pseudoplasticity phenomenon.

“Shape Memory Alloys are reported to show an interesting phenomenon known as Superplasticity

or Pseudoplasticity [26]. The superelastic property is very useful in industrial application. "It is characterized by the recovery of extraordinarily large strains. In place of transforming between the martensite and austenite phases in return to temperature, this change can be induced in return to mechanical stress. When shape memory alloys are laden in the austenite phase, the material will convert to the martensite phase above a critical stress, relative to the transformation temperatures. Continued loading, the twinned martensite will begin to detwin (Fig. 19), allowing the material to go through the large deformations. As the stress is released, the martensite converts back to austenite, and the material recovers to its original phase. As a result, these materials can reversibly deform to very high strains – up to 8 per cent. A more thorough discussion of the mechanisms of superelasticity and the shape memory effect can be found in the paper by Ma et al [46].

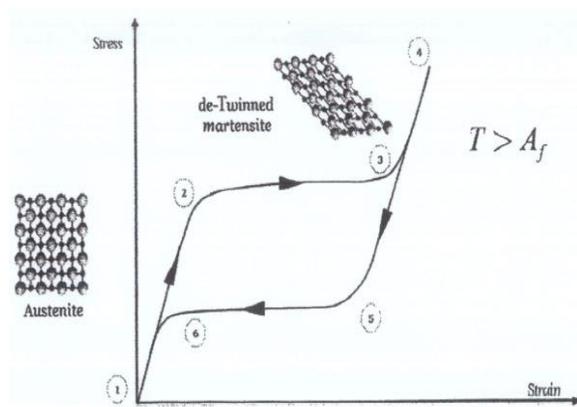


Fig. 19: Super elasticity. [47]

Most of the publications on martensitic transformations and shape memory alloys mention superplasticity/ pseudoplasticity. We have mentioned the work of Prof. K. Bhattacharya [26]. "He has given an example of a piece of wire of shape memory alloy above the transformation temperature where it is in austenite phase (Fig. 20). If a mechanical force is applied on it without changing its temperature, the wire behaves like an elastic material as indicated by the segment (OA) in (Fig. 20). At some critical load, the wire appears to yield and undergo large deformation (AB). After a certain amount of deformation, it begins to become once again and behaves elastically (CD) but then it regains much of the deformation at almost constant stress (DE), and finally unloads elastically (EO) thereby regaining all its deformation. A NiTi wire, suitably heat treated, will be able to regain stress as large as 5-8 percent. Thus this wire is able to regain/recover very large

deformations, and is termed as superelastic." Autonucci and Martone [47] have also discussed superelasticity or pseudoelasticity and more or less have said what Prof. Bhattacharya [26] has said. Their figure (Fig. 21) showing this phenomenon is reproduced here.

Fig. 22 [17] and Fig. 23 [48] show the same phenomenon.

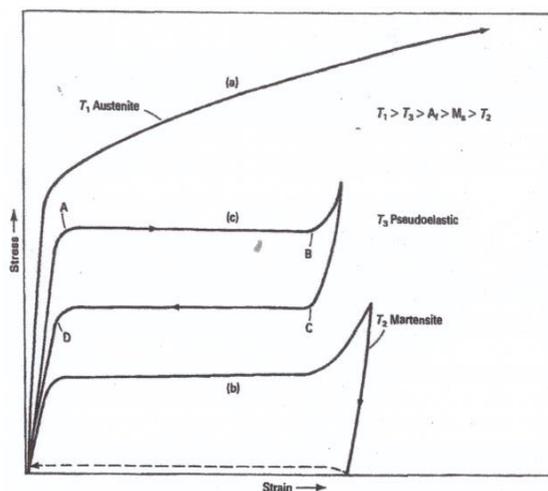


Fig. 20: Typical stress-strain curves at different temperatures relative to the transformation, showing (a) austenite, (b) martensite and (c) pseudoelastic behaviour [17].

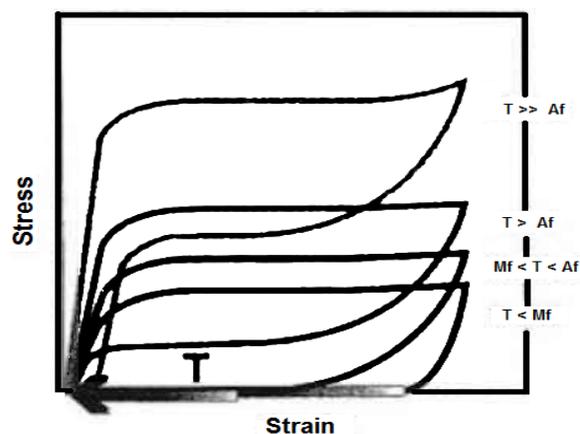


Fig. 21: Typical stress-strain curve for a superelastic SMA wire at various temperatures [58].

It must thus be realized that shape memory effect depends on martensitic, rather stress-induced, transformation and this leads to superelasticity/ pseudoelasticity in shape memory alloys. Rächinger [39] had discovered the superelasticity phenomenon in 1958 and even coined the term still in use today.

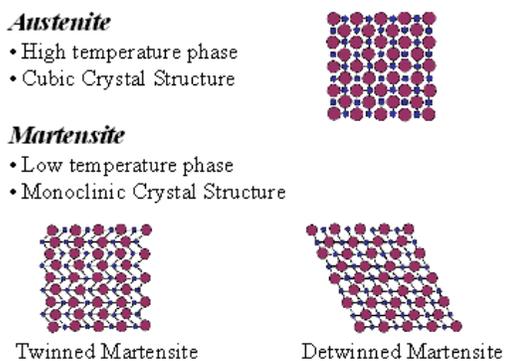


Fig. 22: Different phases of an SMA.

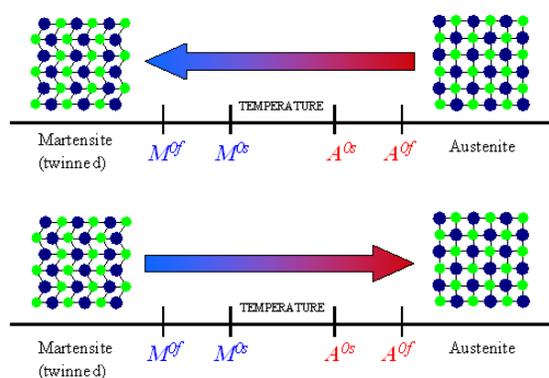


Fig. 23: Temperature-induced phase transformation of an SMA without mechanical loading.

A lot of work on Cu-based martensites (50), and Cu-Al-Zn martensites was carried out at the University of Leuven (now ranked no.1 in Europe) by a group under Prof. Dr. Luc Delaey, an intelligent and competent scientist who had his doctorate from Max Planck Institute, Stuttgart, under the famous Professor W. Koester and Prof. Hains Warlimont. The following book contain a large number of articles by Prof. Delaey with his friends, colleagues and students [51], and also references to their works published elsewhere [21]. He was a scientist par excellence, a thorough, kind gentleman but unfortunately died at an early age of 70 in 2009 after a prolonged illness.

Another excellent book, “Shape Memory Alloys Handbook” is written by the French Professor Christian Lexcellent [52]. It also contains somewhat similar topics and explanations as those by Lagoudas [24].

The Texas A&M University’s Smart Lab has launched a website on Shape Memory Alloys [53] with excellent explanation of the role of

martensite and twinning in Shape Memory Alloys. We are reproducing that website here as it is very clear and useful to understand the topic. We retrieved it on 24.07.2017. Texts and figures are:

## 22. Definition of a Shape Memory Alloy

Shape Memory Alloys (SMAs) are exclusive class of metal alloys which is recovering apparent lasting strains at a certain temperature. The SMAs provides two stable phases – the phase at high-temperature, known as *austenite* and at low-temperature phase, known as *martensite*. Moreover, the martensite can be in one of two forms: *twinned* and *detwinned*, mentioned in Fig. 24. A phase conversion occurs between two phases upon heating/cooling depends upon the unique properties of the SMAs. The key effects of SMAs associated with the phase transformation are *pseudoelasticity* and *shape memory effect*.

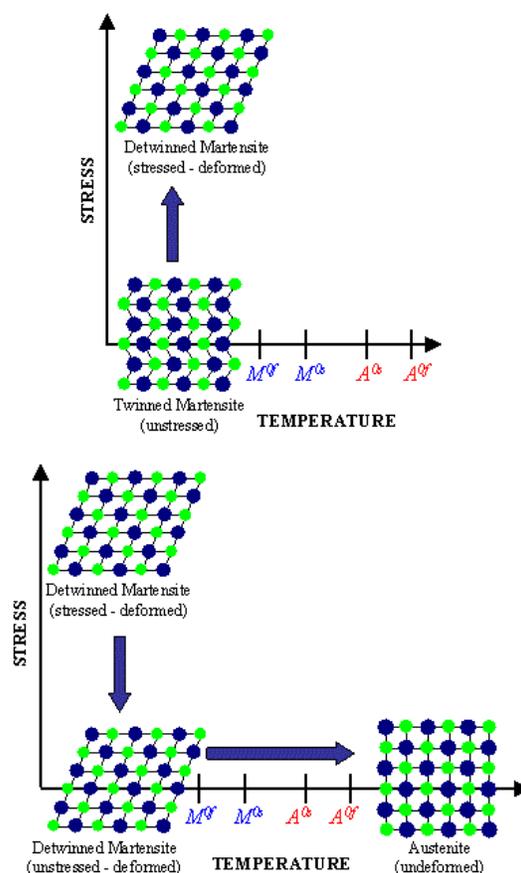


Fig. 24: Shape memory effect of an SMA.

At cooling in the absence of applied load the material conversion from austenite into twinned (self-accommodated) martensite. As a result of this phase

conversion no observable macroscopic shape change occurs. Upon heating the material in the martensitic phase, a reverse phase transformation takes place and as a result the material transforms to austenite. The above process is shown in Fig. 25. Four point temperatures are discussed in Figure (25) martensitic start temperature ( $M^{0s}$ ) mean the temperature at which the material starts converting from austenite to martensite; martensitic finish temperature ( $M^{0f}$ ), at which the conversion is complete and the material is fully in the martensitic phase; austenite start temperature ( $A^{0s}$ ) at which the reverse conversion (austenite to martensite) initiates; and austenite finish temperature ( $A^{0f}$ ) at which the reverse phase transformation is completed and the material is the austenitic change.

### 23. Thermally-Induced Transformation with Applied mechanical Load

In case of mechanical load is used for the material in the state of twinned martensite (at low temperature) probably to detwin the martensite. Upon

releasing of the load, the material remains deformed. A consequent heating of the material to a temperature above  $A^{0f}$  resulting in reverse phase transformation (martensite to austenite) and will go through to complete shape recovery, as shown in Fig. 26. The above described process results in manifestation of the Shape Memory Effect (SME). It is possible to make a martensitic transformation which would lead straight to detwinned martensite too. If load is used in the austenitic phase and the material is cooled, the phase transformation will result in detwinned martensite. Thus, very large strains (on the order of 5-8%) will be observed. Reheating the material resulting in complete shape recovery. The above-described loading path is shown in Fig. (27). The conversion of temperatures in this case strongly depend on the magnitude of the applied load. Higher values of the used load will go through to higher values of the transformation temperatures. Usually a linear relationship between the applied load and the transformation temperatures is implicit, as shown in Fig. (27).

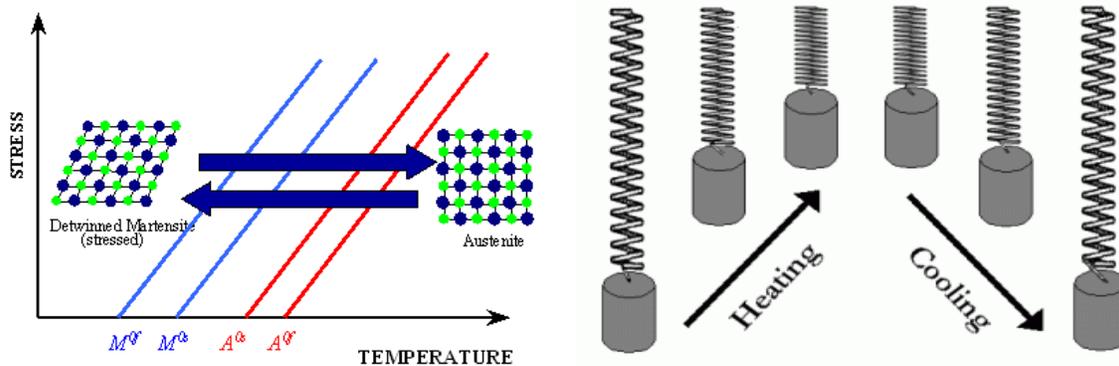


Fig. 25: Temperature-induced phase transformation with applied load.

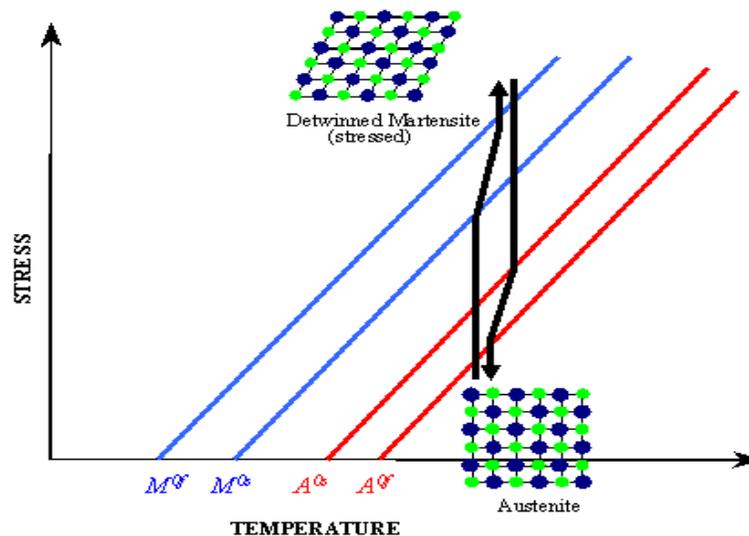


Fig. 26: Pseudoelastic loading path.

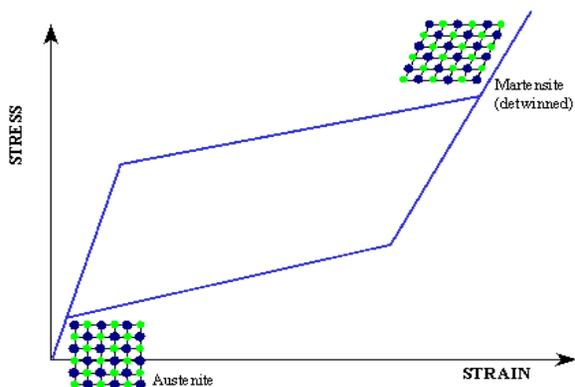


Fig. 27: Pseudoelastic stress-strain diagram.

**24. Pseudoelastic Behavior**

It is too possible to induce a phase transformation by applying a pure mechanical load. The result of this load application is fully detwinned martensite and extremely large strains observed. If the temperature of the material is above  $A_{0f}$ , an absolute shape recovery observed upon unloading, therefore, the behavior of material resembles elasticity. As a result the above-described effect is known under the name of *Pseudoelastic Effect*. A loading path representing the pseudoelastic effect is schematically shown in Fig. 28, while the resulting stress-strain figure is shown in Fig. 29.

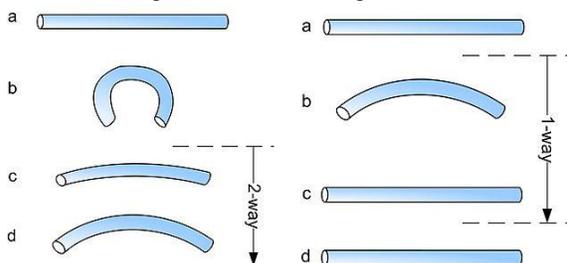


Fig. 28: The procedures are very similar: starting from martensite (a), adding a reversible deformation for the one-way effect or severe deformation with an irreversible amount for the two-way (b), heating the sample (c) and cooling it again (d). [54]..

**25. Shape Memory Alloys, their composition & mechanical properties**

Now we can go further. First, we give you a list of the alloys which show Shape Memory Effects and their composition, comparison between NiTi, CuZnAl & CuAlNi, alloys and physical and mechanical properties of their alloys.

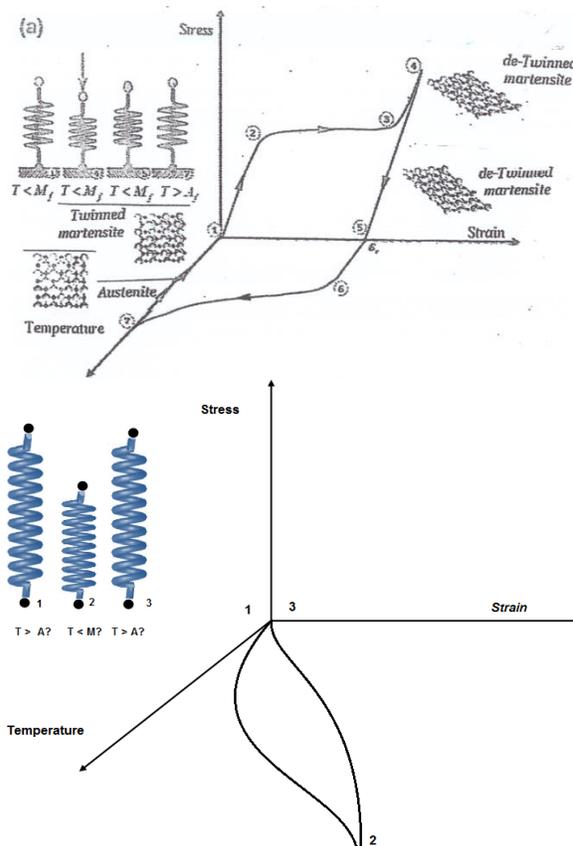


Fig. 29: One-way (a) and two-way (b) shape memory effect [23].

Table-2: Main SMAs.

Alloy	Composition	Transition Temperatures, °C	Hysteresis, °C
Ag-Cd	44/49 wt% Cd	[-190, -50]	15
Au-CD	46,5/50 wt% Cd	[30,100]	15
Cu-Al-Ni	14/14,5 wt% al, 34,5 wt% Ni	[-140,100]	35
Cu-Sn	15 wt% Sn	[-120,30]	10
Cu-Zn	38,5/41.5 wt% Zn	[-180,-10]	10
Cu-Zn-x (X = si, Sn, al)	Few wt% of X	[-180, 200]	10
In-ti	18/23 wt% Ti	[60,100]	4
Ni-Al	36/38 wt% al	[-180,100]	10
Ni-Ti	49/38 wt% Ni	[-50,110]	30
Fe-Pt	Approx. 25 wt% Pt	Around - 130	40

SMA, shape memory alloys.

Table-3: Comparison between NiTi, CuZnAl, and CuAlNi Alloys [ ].

Property	NiTi	CuZnAl	CuAlNi
Maximum temperature shape recovery	100 °C	°C	°C
Maximum recoverable strain	8%	6%	5%
Hysteresis	12-50 °C	10-25 °C	15-20 °C
Austenite yield stress (MPa)	415	350	400
Martensite yield stress (MPa)	70	80	130
Break stress (MPa)	700	600	500-800
Density (g/cm <sup>3</sup> )	6.05	7.6-8.0	7.02
Resistivity (μΩcm)	80-90	8.5-9.7	11-13
Thermal capacity (J/Kg K)	837	400	373-574

Table-4: Comparing the physical and mechanical properties.

Properties	Units	Ni-Ti	Cu-Zn-Al	Cu-Al-Ni	Cu-Al-Be
Melting point	°C	1260-1310	950-1020	1000-1050	970-990
Density	kg/m <sup>3</sup>	6400-6500	7800-8000	7100-7200	7300
Electrical resistance (aust-mart)	Ωm x 10 <sup>4</sup>	0.5-1.1	0.7-0.12	0.1-0.14	0.7-0.09
Thermal conductivity at room temp.	W/(m.K)	10-18	120	75	
Expansion coefficient (aust-mart)	10 <sup>-6</sup> K <sup>-1</sup>	6.6-10	17	17	
Specific heat	J/(kg.k)	490	390	440	
Transformation enthalpy	J/kg	2800	7000	9000	7200
Young's modulus	GPa	95	70-100	80-100	90
Tensile resistance	MPa	800-1000	800-900	1000	900-1000
Fracture elongation (in martensite)	%	30-50	15	8-10	15
Yield fatigue resistance	MPs	350	270	350	
Grain size	μm	20-100	50-300	30-300	100-500
Transformation domain	°C	-100 to 100	-100 to 100	-100 to 170	-200 to 150
Hysteresis (As-Mf)	°C	20-40	10-20	20-25	20-25
Spread (Af-As)	°C	30	10-20	20-30	15-20
Maximum strain:					
- one way shape memory effect		8	3-5	3-6	
- two way shape memory effect		5	2	3	3-5
Cycle (N) = 10 <sup>2</sup>		5	1	1.2	2
Cycle (N) = 10 <sup>5</sup>	%	2	0.8	0.8	
Cycle (N) = 10 <sup>7</sup>		2.5	0.5	0.5	
Maximum temperature use (1 hour)	°C	400	160	300	400
Superelastic maximum strain:					
- Polycrystal		4	2	2	3
- monocrystal	%	10	10	10	10
Damping	SDC-%	15	30	10	
Corrosion resistance		Excellent	Average	Good	Average
Biocompatibility		Good	Bad	Bad	Bad

Table-5: Mechanical Properties of SMA Alloys.

Alloy	Density (kg/m <sup>3</sup> )	Young Modulus (GPa)	Recoverable Strain (%)
Au-Cd	13.5	Austenite 100 Martensite 96	1.5
Cu-Zn-Al	7.7	Austenite 70 Martensite 70	5.0
Cu-Al-Ni	7.2	Austenite 85 Martensite 80	6.0
Ni-Ti	6.4	Austenite 83 Martensite 30	8.0
Fe-Mn-Si	7.5	Austenite 140 Martensite 190	3.0
Fe-Mn-Al-Ni	6.9	Austenite 100 Martensite 50	5.0

Table-6: Workability of SMA Alloys.

Type	Forming	Cold Working	Machinability	Transformation (°C)
Au-based	Good	Poor to very poor	Fair to good	-50 to 100
Ni-Ti	Poor to very poor	Fair to poor	Poor	-100 to 100
Cu-based	Very good to good	Poor	Good	-200 to 200
Fe-based	Very good to good	Good to poor	Fair to good	-200 to 150

## 26. One-way & Two-way memory effects

We have discussed the shape memory effects and various terminologies used in it. However, there are two more terminologies which are of interest and we would like to throw light on them. They are (1) One-way shape memory effect and (2) Two-way shape memory effect.

### 26.1. One-way shape memory effect:

When a shape memory alloy is in its cold condition (below Austenite start temperature  $A_s$ ), the metal can be bent or stretched and will hold those shapes until heated above the transition temperature. When it is heated, the shape changes to its original shape. When the metal cools again, it remains in the hot shape, under deformed again.

The one-way effect, cooling from high temperature does not produce a macroscopic shape change. You must cause a deformation to create the low-temperature shape. On reheating, the transformation starts at  $A^s$  and is completed at  $A^f$ . Austenite finish temperature, (typically 2 to 20 °C higher, depending on the composition of the alloy or the deformation conditions).  $A^s$  is controlled by the alloy type and its composition and can vary below -150 °C to 200 °C. In this case only the higher temperature shape is memorized by the material. As a matter of fact there is no change in the shape taking place upon cooling under no applied load. This one way SME is an intrinsic character of SMAs [54].

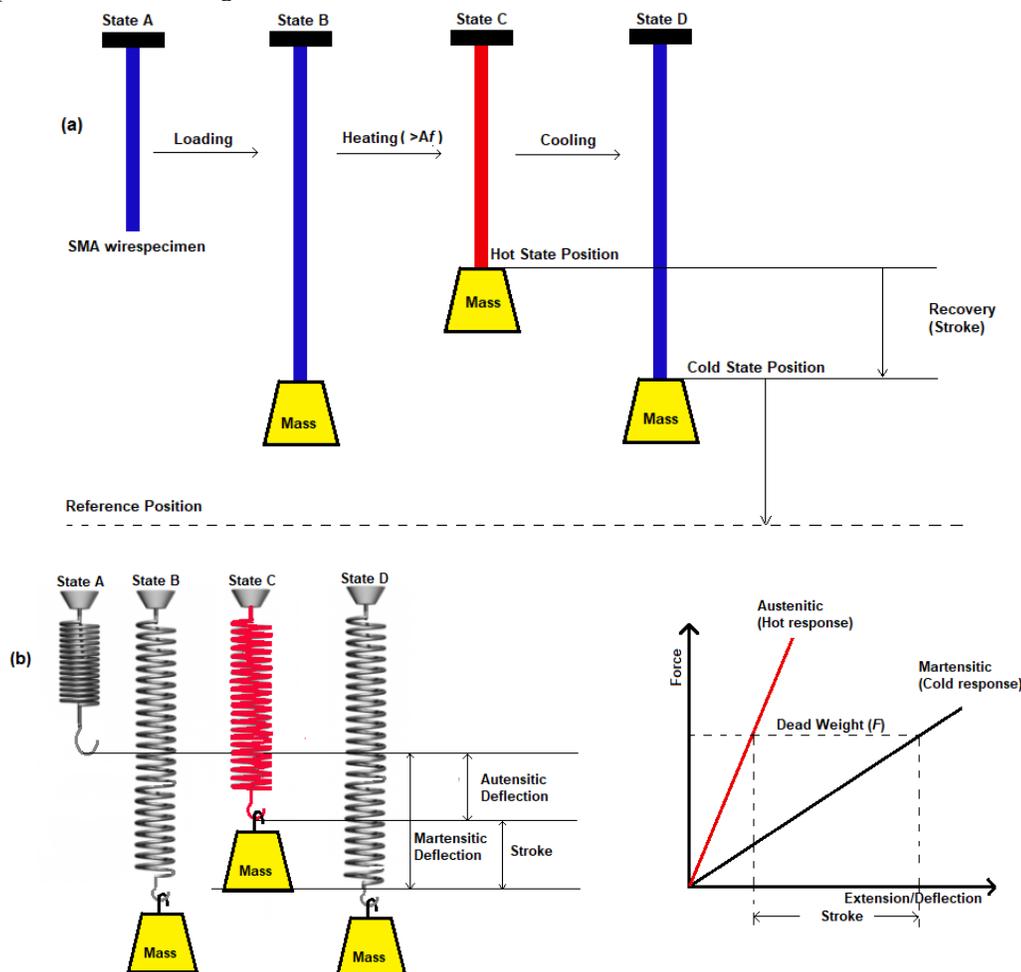


Fig. 30: SMA wire/spring in its martensitic state A is deformed to state B under external load. Upon heating above temperatures  $A_f$ , the SMA wire/spring contracts back to its austenitic state denoted by state C or hot state position. Upon cooling, the SMA wire/spring reached state D. Removal of external load in state D results in SMA wire/spring returning back to state A in an ideal case. Complete cycle A $\leftrightarrow$ D is termed as shape memory effect (SME). (a) SMA wire –shape memory effect. (b) SMA spring-shape memory effect (figure adapted from [57]).

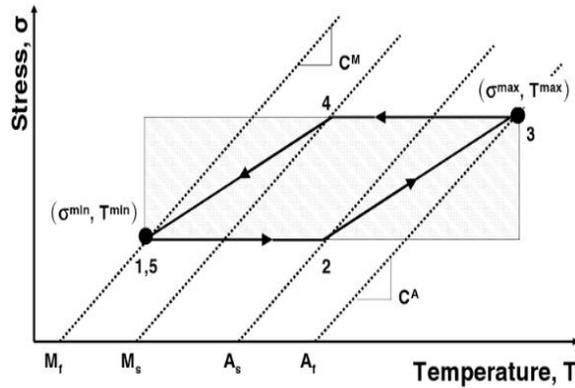


Fig. 31: Example of SMA application design space. [24].

### 26.2. Two-way shape memory effect:

“Shape memory metallic alloys can show a two-way SME (shape memory effect) after a certain thermal treatment. The material does not only remember the external shape in the parent austenitic phase, but also the external shape in the martensitic phase. As a matter of fact, the two-way memory effect is related to the ability of the material to remember two different shapes in the cold and hot phase. This property allows it to move between the two different shapes by simply changing the temperature, with no need to apply force. The two-way memory requires to be induced by specific treatments, such as training. Training consists of different repeated temperature cycles that are also useful to stabilize the SMA properties [55]. Fig. 30 [54] and Fig. 31 [23] represent the one-way and two-way shape memory effect.

## 27. Shape memory alloys

Manufacturing processes and practical applications:

### 27.1. Manufacturing processes:

Shape memory alloys are manufactured by casting, using vacuum arc remelting or induction melting. These processes are special as they keep the impurities in the material to a minimum and ensure the component metals are properly mixed. The ingot is then hot rolled into longer sections and then drawn to turn into wire. Rao, Srivivasa and Reddy [56] have discussed in detail the various manufacturing techniques for shape memory alloys. For instance, in addition to casting (using vacuum arc remelting or induction melting). They pointed out that casting techniques were popular with large scale production

of NiTi alloys that require melting and then hot working and then machining to desired shapes. Vacuum Induction Melting (VIM) and Vacuum arc melting (VAR) and Electronic Beam Melting (EBM) are quite popular production technologies, sintering, laser sintering, hot isotactic pressing, spark plasma sintering, selective laser melting, metal injection molding etc etc have also been mentioned Rao et al. [56] with application to relevant materials.

One can imagine post treatments (like cold and hot working, joining, heat treatments, surface treatments etc. They are used for specific desired properties. The authors [56] have great details of all techniques. Users can consult their excellent brief treatment. Their work is mostly confined to NiTi alloys. Fig. 32 is an interesting and useful illustration showing a wire/spring under various conditions [57].

### 27.2. Applications

Most of the books, proceedings of the many conferences contain not only the production methods of the shape memory alloys but also their applications. Most of the work is on NiTi alloys. Rao et al. [56] have given an overview of shape memory alloy applications. They have mentioned Biomedical Applications, Civil Engineering Applications, Robotics Telecommunication, Aerospace and Automotive Applications and Electrohydraulic and Hydraulic System, Vibration damping and as pointed out above, Biomedical, Auto-motive and aerospace systems and Actuators for various functions in many systems. These materials are also used in Piping, Medicine, Optometry, Orthopedic Surgery, Dentistry, Electronic Circuits, Engines, Crafts etc. Shortage of space does not allow us to detailed description of these applications. They are available in many books and articles.

It must be remembered that Shape Memory Alloys have many advantages over traditional actuators, but they do suffer from a series limitations that may impede practical applications.

Dister Stoekel [58] has also given quite a few examples of application of shape memory Alloys.

Dimitri C. Lagoudas (with D. J. Hartl) [24] in their paper, “Thermo-mechanical Characterization of Shape Memory Alloy Materials” has discussed the applications Design and Empirical I-D Analysis and given quite a few practical application for industrial use (pages 53-0117) and has proposed a diagram for it (Fig.33).

## 28. Shape Memory Polymers

Like many metals and alloys, some polymers also exhibit shape memory properties. The best reference book on this topic is 'Advances in Shape Memory Polymers, Woodhead Publishing Series in Textiles: No. 146 by Jianlian Hu [59], published by Woodhead Publishing, Oxford, Cambridge, Philadelphia, New Delhi (2013).

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