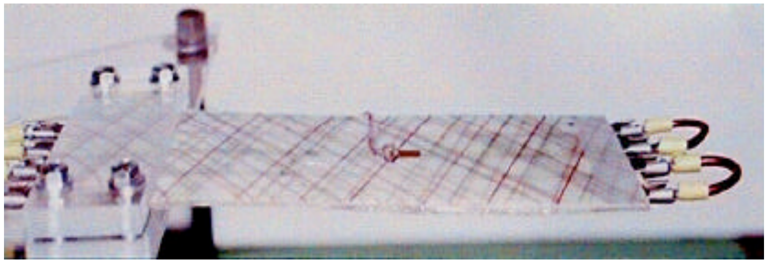
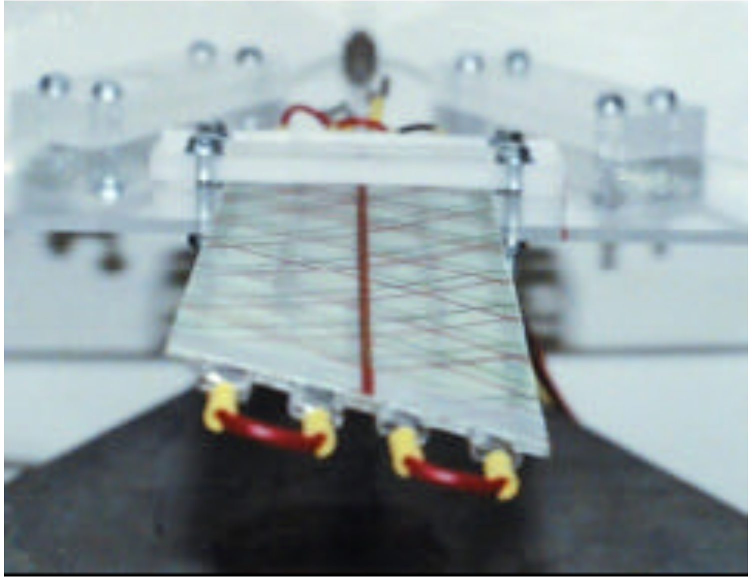
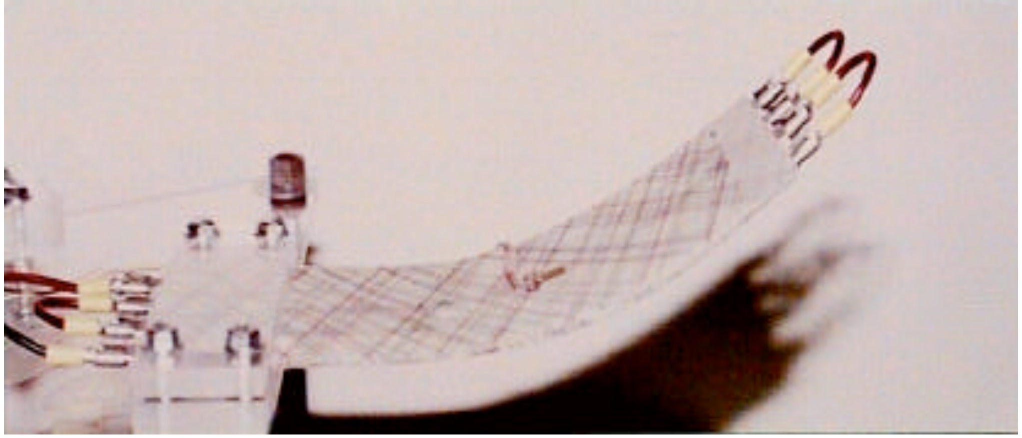
Shape Memory Alloys

Metals are characterized by physical qualities as strength, ductility and conductivity.

Shape memory alloys (SMA) constitute a group of metallic materials with the *ability to recover a previously defined length or a shape when subjected to an appropriate thermo-mechanical load* [1]. *When there is a limitation of shape recovery, these alloys promote high restitution forces.*







[1] Hodgson DE, Wu MH & Biermann RJ (1990). *Shape Memory Alloys, Metals Handbook*. Vol. 2. ASM International, Ohio, 897-902.

Pseudoelastic and ***shape memory effects*** are some of the behaviors presented by these alloys. Although a relatively wide variety of alloys present the shape memory effect, only those that can recover from a large amount of strain or generate an expressive restitution force are of commercial interest. Examples are Ni-Ti, Cu-Zn-Al and Cu-Al-Ni [1].

Basically, SMAs present two well-defined crystallographic phases, i.e., austenite and martensite. The high–temperature phase, austenite is named after English metallurgist William Chandler Austen, and the low–temperature phase, martensite is named after German metallographer Adolf Martens.

The shape memory is a particular manifestation of a crystalline phase transformation known as the *Martensitic Phase Transformation*.

The martensitic phase transformation is a solid-to-solid phase transformation where the lattice or molecular structure changes abruptly at some temperature.

Diffusional transformation	**Diffusionless transformation**
Uncoordinated movement of individual atoms (civilian transformation)	Controlled coordinated movement of individual atoms (military transformation)
Atoms change nearest neighbors as diffusion occurs	Atoms do not change nearest neighbors
Reconstructive transformation	Displacive transformation
Interface not necessarily coherent	Coherence at interface preserved
Relatively slow	Fast
Little strain energy	Large strain energy

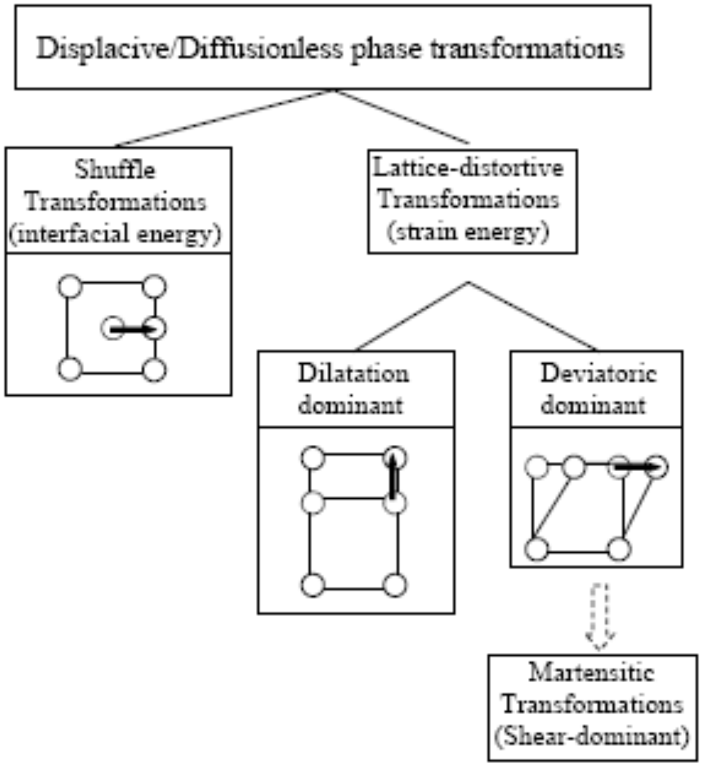
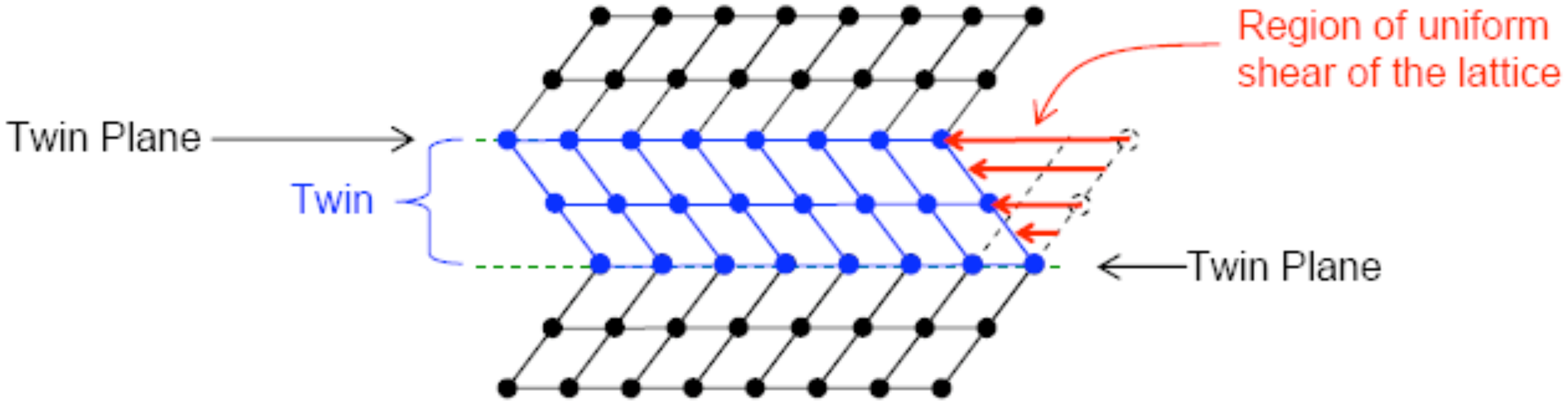


Fig. 1.2 Classification scheme for displacive/diffusionless phase transformations

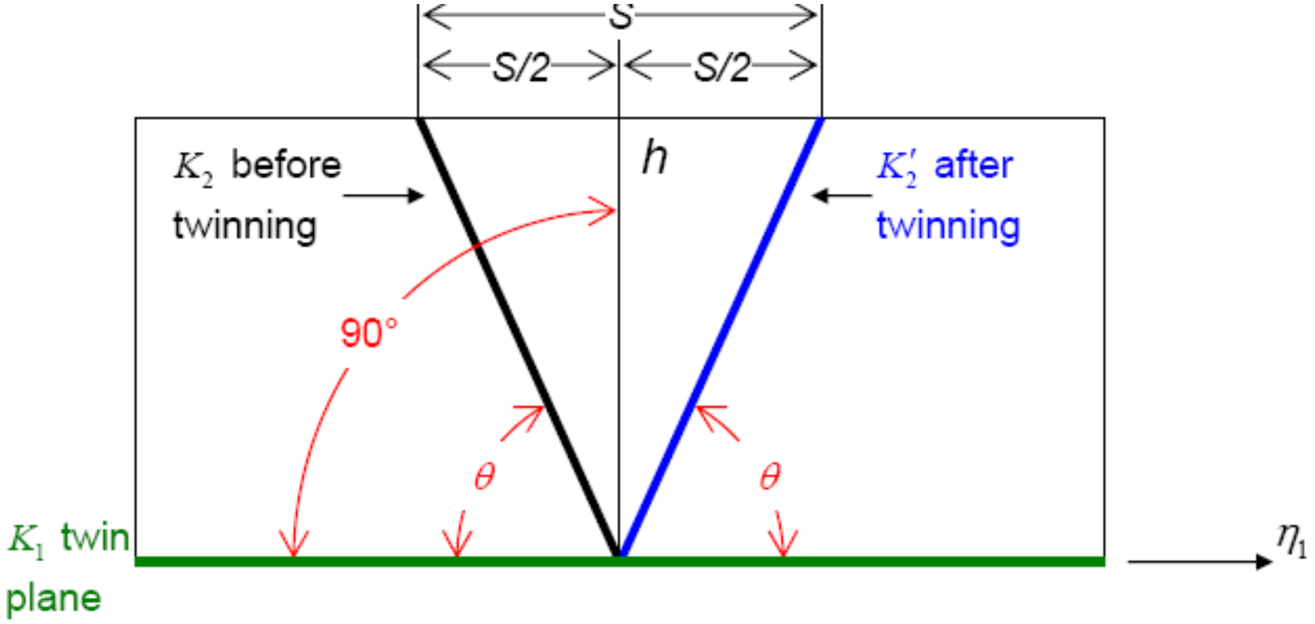
Twinning

Twinning is the coordinated motion of planes of atoms in a lattice parallel to a specific plane (the twinning plane) such that the lattice is divided into two symmetrical parts possessing the same crystal structure, but which are a mirror image of each other.



Crystallography of Twinning

Every structure has its own specific set of twinning elements.



θ = angle between K_1 and K_2

S = the shear displacement of the upper surface relative to the bottom

h = width of the twin

K_1 = the twinning plane (1st undistorted plane)

K'_2 = the 2nd undistorted plane

η_1 = shear direction

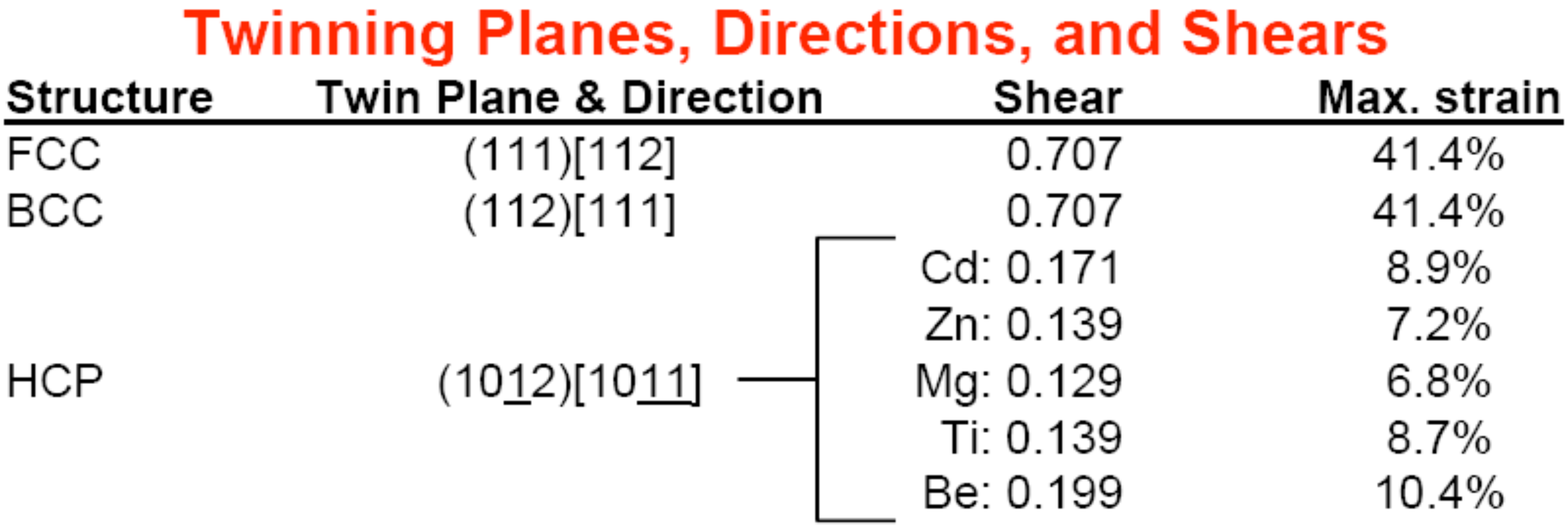
η_2 = direction defined by intersection of shear plane with K_2

$$\gamma = \frac{S}{h} = 2\tan(90^\circ - \theta) = 2\cot\theta$$

Twinning occurs in many structures, for example:

Hexagonal metals such as Zn and Mg twin when they are deformed at ambient temperatures.

BCC metals such as Fe twin when they are deformed at sub-ambient temperatures.



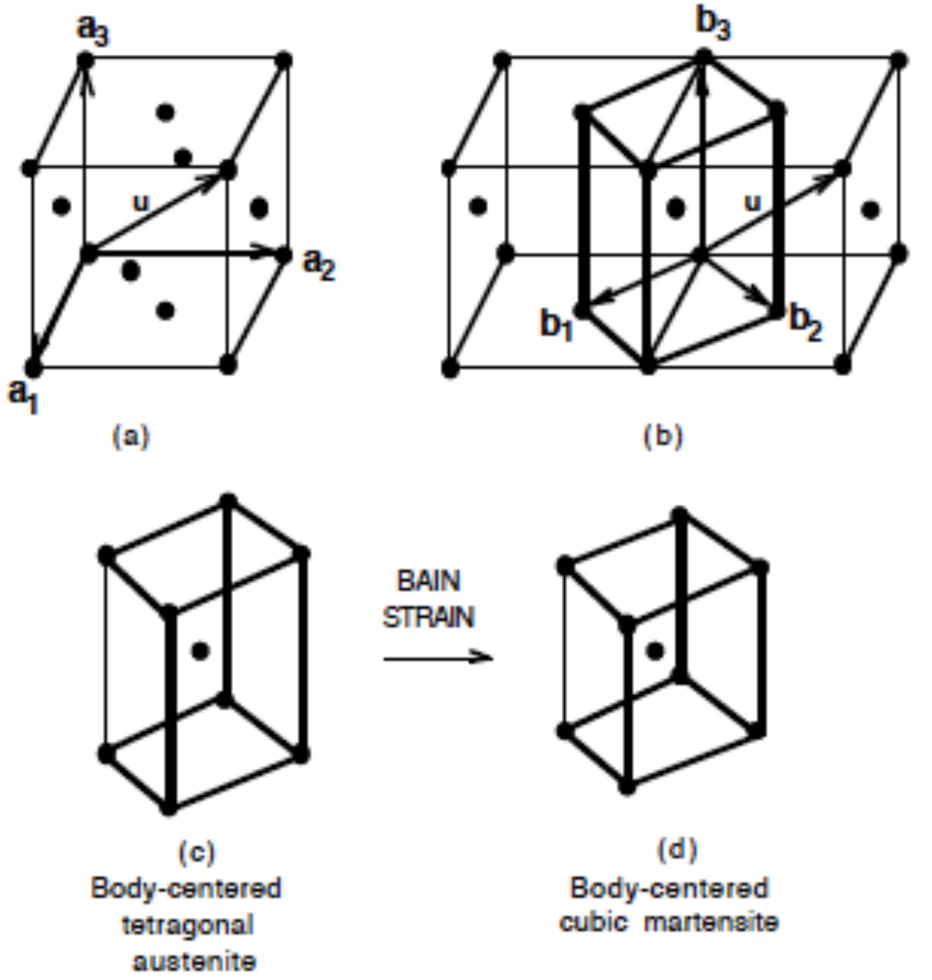
Twinning Planes, Directions, and Shears

Structure	Twin Plane & Direction	Shear	Max. strain
FCC	(111)[112]	0.707	41.4%
BCC	(112)[111]	0.707	41.4%
HCP	$(10\underline{1}2)[10\underline{1}\underline{1}]$	Cd: 0.171	8.9%
		Zn: 0.139	7.2%
		Mg: 0.129	6.8%
		Ti: 0.139	8.7%
		Be: 0.199	10.4%

Mathematical Crystallography

Taken from the book by H. K. D. H. Bhadeshia Professor of Physical Metallurgy University of Cambridge

Transformation:
FCC➔BCT➔BCC



(a)

(b)

(c)
Body-centered
tetragonal
austenite

(d)
Body-centered
cubic martensite

Fig. 1: (a) Conventional FCC unit cell. (b) Relation between FCC and BCT cells of austenite. (c) BCT cell of austenite. (d) Bain Strain deforming the BCT austenite lattice into a BCC martensite lattice.

Consider a vector ***u*** which can be written as a linear combination of the basis vector ***A***

$$\overrightarrow{u} = u_1 \overrightarrow{a_1} + u_2 \overrightarrow{a_2} + u_3 \overrightarrow{a_3}$$

The components of ***u*** can be written as a single-row matrix or as a single-column matrix

$$(u;A) = (u_1\ u_2\ u_3) = (1\ 1\ 1)$$

$$[A;u] = \begin{bmatrix} u_1 \\ u_2 \\ u_3 \end{bmatrix} = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}$$

The row matrix is the transpose of the column matrix

Consider an alternative basis a body-centred tetragonal (BCT) unit cell describing the same austenite lattice.

$$(u;B) = (u_1\ u_2\ u_3) = (0\ 2\ 1)$$

It is obvious that

$$[B;u] = \begin{bmatrix} u_1 \\ u_2 \\ u_3 \end{bmatrix} = \begin{bmatrix} 0 \\ 2 \\ 1 \end{bmatrix}$$

And the equations that relate the transformation of a vector ***u*** are

$$\overrightarrow{a_1} = 1\overrightarrow{b_1} + 1\overrightarrow{b_2} + 0\overrightarrow{b_3}$$
$$\overrightarrow{a_2} = \overline{-1}\overrightarrow{b_1} + 1\overrightarrow{b_2} + 0\overrightarrow{b_3} \quad (a_1\ a_2\ a_3) = (b_1\ b_2\ b_3) \times \begin{pmatrix} 1 & \bar{1} & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$
$$\overrightarrow{a_3} = 0\overrightarrow{b_1} + 0\overrightarrow{b_2} + 1\overrightarrow{b_3}$$

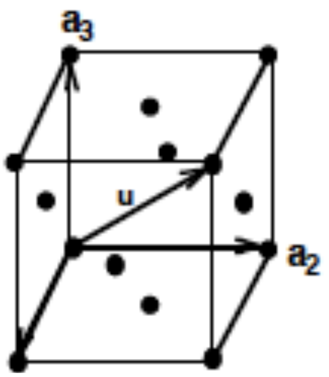
This 3x3 matrix representing the co-ordinate transformation is denoted as (B J A) and transform the components of vector referred to the A basis to those referred to the B basis.

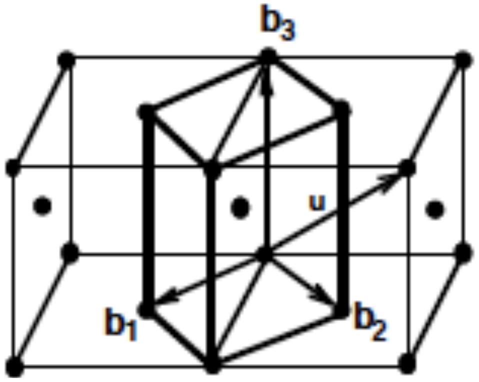
The components of a vector ***u*** can now be transformed between bases using the matrix (B J A) as follows

$$\left[B;\vec{u}\right] = (B\ J\ A)\left[A;\vec{u}\right]$$

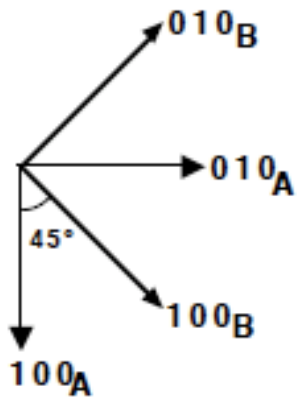
In the example:

$$\begin{bmatrix} 0 \\ 2 \\ 1 \end{bmatrix} = \begin{pmatrix} 1 & \bar{1} & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \times \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}$$





Example 1:



Two adjacent grains of austenite are represented by basis A and B. The grains are oriented such that

$$[001]_A \| [001]_B$$

Angle of 45 degrees as shown

$$[100]_B = [100]_A + [010]_A$$

If a vector in the crystal **A** is given by

$$[A;\vec{u}] = [\sqrt{2}\ 2\sqrt{2}\ 0]$$

Find the same vector in basis **B**

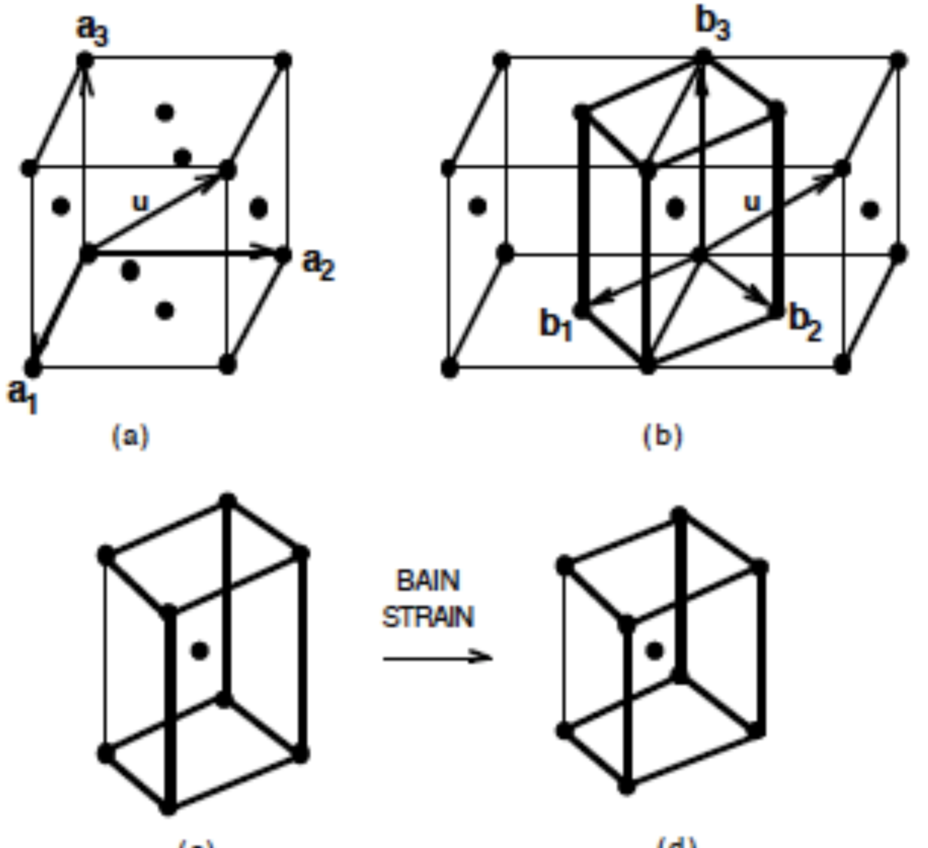
$$\vec{a_1} = \cos 45 \cdot \vec{b_1} - \sin 45 \cdot \vec{b_2} + 0\vec{b_3}$$
$$\vec{a_2} = \sin 45 \cdot \vec{b_1} + \cos 45 \cdot \vec{b_2} + 0\vec{b_3}$$
$$\vec{a_3} = 0\vec{b_1} + 0\vec{b_2} + 1\vec{b_3}$$

$$\Rightarrow (B\ J\ A) = \begin{pmatrix} \cos 45 & \sin 45 & 0 \\ -\sin 45 & \cos 45 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$[B;\vec{u}] = [A;\vec{u}] \times (B\ J\ A) = \begin{pmatrix} \cos 45 & \sin 45 & 0 \\ -\sin 45 & \cos 45 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{bmatrix} \sqrt{2} \\ 2\sqrt{2} \\ 0 \end{bmatrix} = \begin{bmatrix} 3 \\ 1 \\ 0 \end{bmatrix}$$

Note that the components of (B J A) are the cosines of angles between b_i and a_j

We must return to the question of martensite, and how a homogeneous deformation might transform the austenite lattice (parameter aγ) to a BCC martensite (parameter aα). Referring to the figure, the basis **‘A’** is defined by the basis vectors **ai**, each of magnitude aγ, and basis **‘B’** is defined by basis vectors **bi**. Focusing attention on the BCT representation of the austenite unit cell, it is evident that a compression along the [0 0 1]B axis, coupled with expansions along [1 0 0]B and [0 1 0]B would accomplish the transformation of the BCT austenite unit cell into a BCC α cell. This deformation, referred to the basis B, can be written as:



(c) Body-centered tetragonal austenite

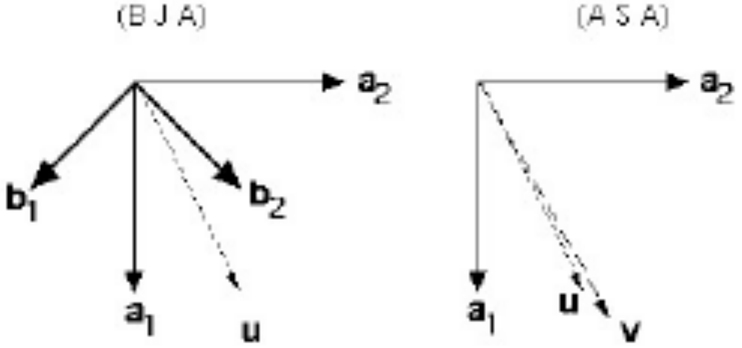
(d) Body-centered cubic martensite

$$\eta_1 = \eta_2 = \sqrt{2}\left(\frac{a_\alpha}{a_\gamma}\right)$$ Along the [100]B and [010]B

$$\eta_3 = \frac{a_\alpha}{a_\gamma}$$ Along the [001]B

Imagine that a part of a single crystal of austenite undergoes the prescribed deformation, allowing us to describe the strain in terms of the remaining (and undeformed) region, which forms a fixed reference basis. Hence, the deformation matrix does not involve a change of basis and the transformation will be given by a 3x3 matrix ***(A S A)***.

(A S A) converts a vector ***u*** in basis ***A*** into a new vector ***v*** still in basis ***A.***



A major advantage of the Mackenzie–Bowles notation is that it enables a clear distinction to be made between 3X3 matrices which represent changes of axes and those which represent physical deformations referred to one axis system.

Fig. 4: Difference between co–ordinate transformation and deformation matrix.

$$(\mathrm{A\ S\ A}) = \begin{pmatrix} \eta_1 & 0 & 0 \\ 0 & \eta_2 & 0 \\ 0 & 0 & \eta_3 \end{pmatrix}$$

$$[\mathrm{A}; \mathbf{v}] = (\mathrm{A\ S\ A})[\mathrm{A}; \mathbf{u}]$$

Vector components before Bain strain	*Vector components after Bain strain*
$[1\ 0\ 0]_A$	$[\eta_1\ 0\ \ 0]_A$
$[0\ 1\ 0]_A$	$[0\ \ \eta_2\ 0]_A$
$[0\ 0\ 1]_A$	$[0\ \ 0\ \ \eta_3]_A$

Example 2:

Given that the principal distortions of the Bain strain (A S A), referred to the crystallographic axes of the FCC γ lattice (lattice parameter aγ), are η1 = η2 = 1.123883, and η3 = 0.794705, show that the vector

[A; **x**] = [−0.645452 0.408391 0.645452]

remains undistorted, though not unrotated as a result of the operation of the Bain strain. Furthermore, show that for **x** to remain unextended as a result of the Bain strain, its components $\mathbf{x}_i$ must satisfy the equation

$$\left(\eta_1^2 - 1\right)x_1^2 + \left(\eta_2^2 - 1\right)x_2^2 + \left(\eta_3^2 - 1\right)x_3^2 = 0$$

Solution:

$$(\mathrm{A\ S\ A}) = \begin{pmatrix} \eta_1 & 0 & 0 \\ 0 & \eta_2 & 0 \\ 0 & 0 & \eta_3 \end{pmatrix}$$

$$[A;\vec{y}] = (A\ S\ A) \times [A;\vec{x}]$$

$$[A;\vec{y}] = \begin{pmatrix} 1.123883 & 0 & 0 \\ 0 & 1.123883 & 0 \\ 0 & 0 & 0.794705 \end{pmatrix} \times \begin{bmatrix} -0.645452 \\ 0.408391 \\ 0.645452 \end{bmatrix}$$

$$[A;\vec{y}] = \begin{bmatrix} -0.725412 \\ 0.458983 \\ 0.512944 \end{bmatrix}$$

As [A;y] is not a multiple of [A;x] then these two vectors are not parallel, hence y rotates due to the Bain strain

Consider the magnitude of the two vectors. If equal the vectors are undistorted due to the Bain strain.

$$|x|^2 = a_\gamma^2\left(x_1^2 + x_2^2 + x_3^2\right) = |y|^2 = a_\gamma^2\left(y_1^2 + y_2^2 + y_3^2\right)$$

$$\Rightarrow \left(\left(y_1^2 - x_1^2\right) + \left(y_2^2 - x_2^2\right) + \left(y_3^2 - x_3^2\right)\right) = 0$$

$$y_1 = \eta_1 x_1$$

$$x_1^2\left(\eta_1^2 - 1\right) + x_2^2\left(\eta_2^2 - 1\right) + x_3^2\left(\eta_3^2 - 1\right) = 0$$

$$x_1^2\left(\eta_1^2 - 1\right) + x_2^2\left(\eta_2^2 - 1\right) + x_3^2\left(\eta_3^2 - 1\right) = 0$$

$$(-0.645452)^2\left(1.123883^2 - 1\right) = 0.10961$$

$$(0.408391)^2\left(1.123883^2 - 1\right) = 0.0438828$$

$$(0.645452)^2\left(0.794705^2 - 1\right) = -0.1534968$$

This process can be illustrated by considering a spherical volume of the original austenite lattice; (A S A) deforms this into an ellipsoid of revolution

Note that the principal axes (**ai**) remain unrotated by the deformation, and that lines such as ***ab*** and ***cd*** which become ***a'b'*** and ***c'd'*** respectively, remain unextended by the deformation (since they are all diameters of the original sphere), although rotated through the angle θ.

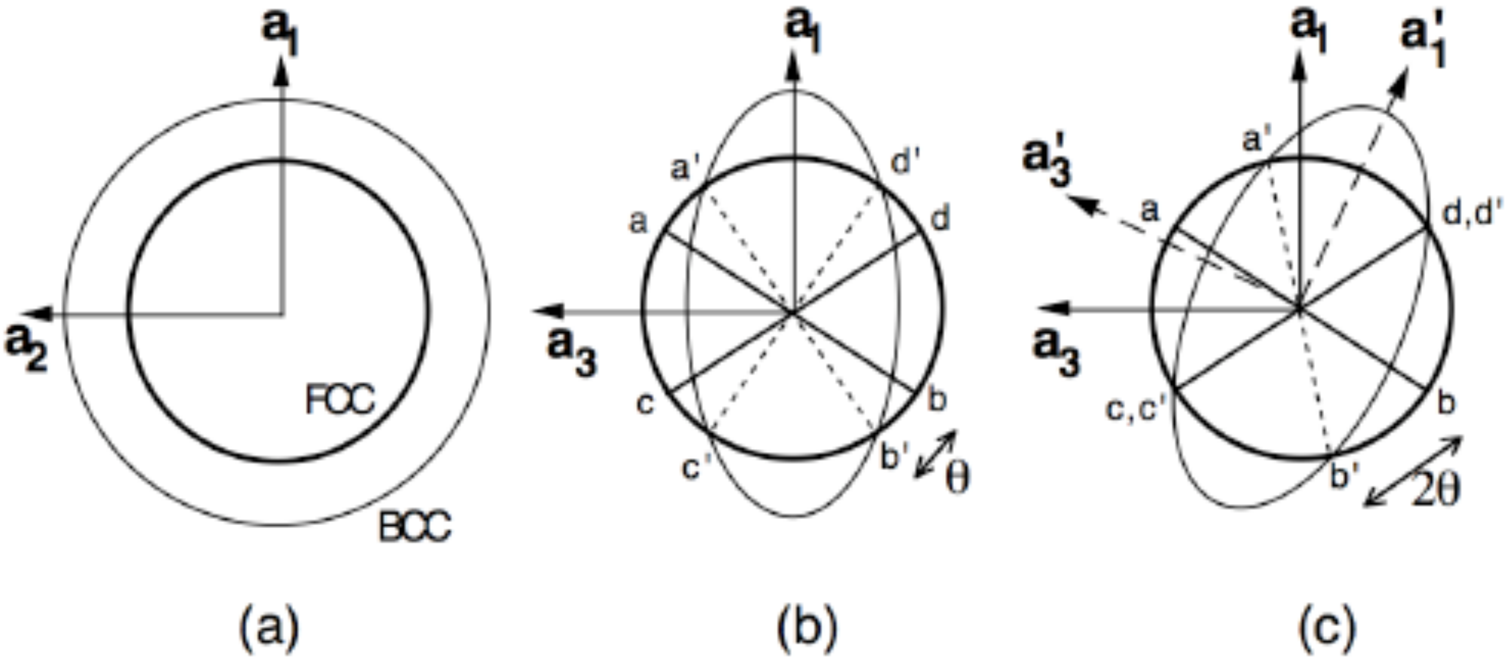
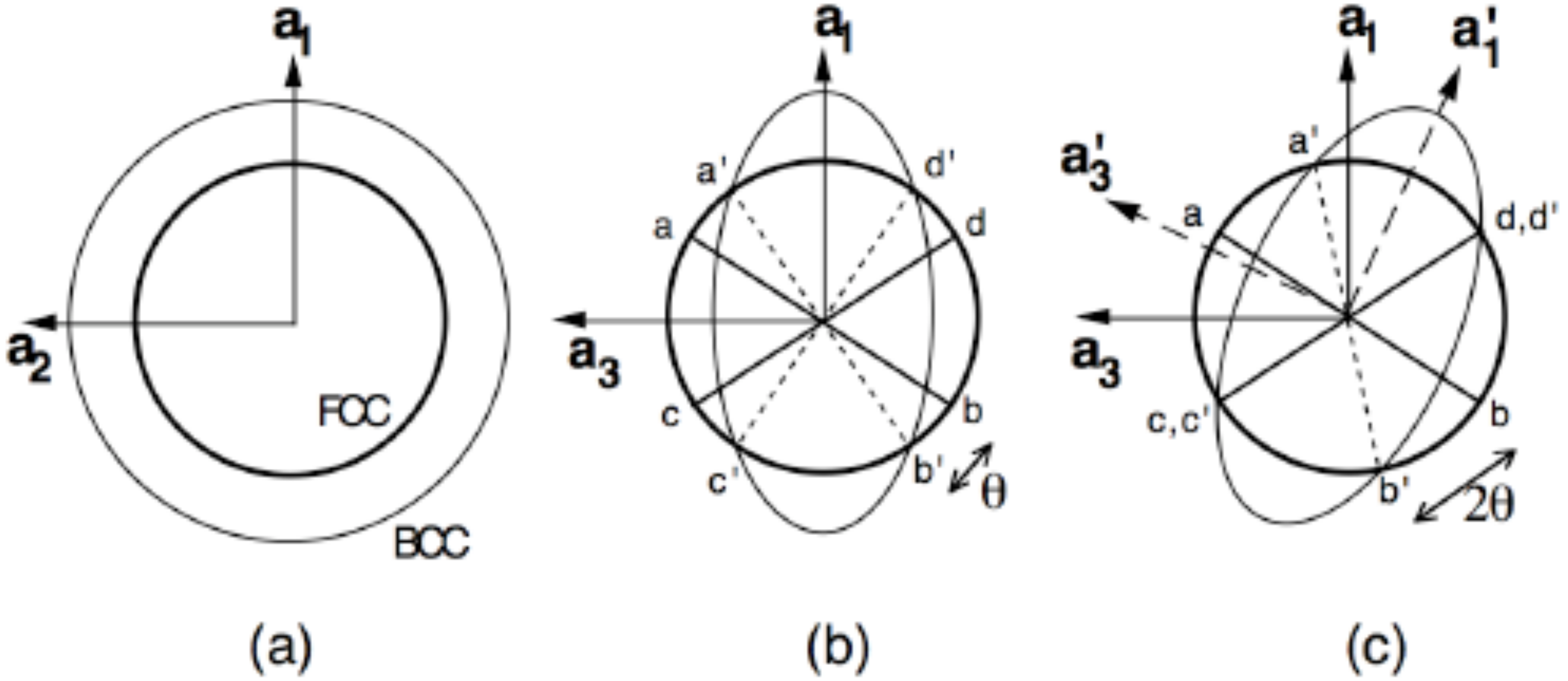


Fig. 5: (a) and (b) represent the effect of the Bain Strain on austenite, represented initially as a sphere of diameter ab which then deforms into an ellipsoid of revolution. (c) shows the invariant–line strain obtained by combining the Bain Strain with a rigid body rotation.



Suppose now, that the ellipsoid resulting from the Bain strain is rotated through a right–handed angle of ***ϑ***, about the axis ***a2***. This rotation will cause the initial and final cones of unextended lines to touch along ***cd***, bringing ***cd*** and ***c'd'*** into coincidence. If the total deformation can therefore be described as (A S A) combined with the above rigid body rotation, then such a deformation would leave the line ***cd*** **both unrotated and unextended**; such a deformation is called **an invariant–line strain**. Notice that the total deformation, consisting of (A S A) and a rigid body rotation is no longer a pure strain, since the vectors parallel to the principal axes of (A S A) are rotated into the new positions ***a'I***. (martensite transformation must contain an invariant line)

Interfaces

The ratio η of its final to initial length is called a principal deformation associated with that principal axis and the corresponding quantity (η−1) is called a principal strain.

When two of the principal strains differ in sign from the third (all non-zero), it is possible to obtain a total strain which leaves one line invariant. When the invariant line is at the interface of the two crystals then their lattices would match exactly along that line.

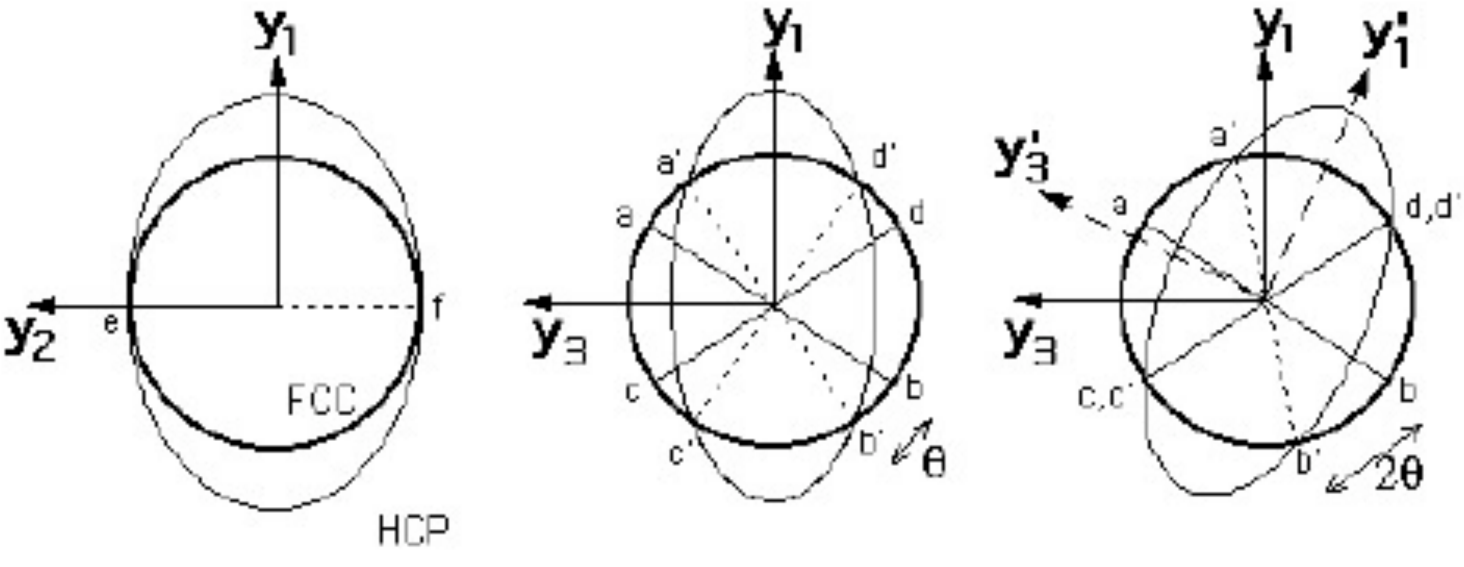
A completely undistorted interface would have to contain two non-parallel directions which are invariant to the total transformation strain (invariant-plane strain → a plane that remains unrotated and undistorted).

Example 3:

A pure strain ***(Y Q Y)***, referred to an orthonormal basis ***Y*** whose basis vectors are parallel to the principal axes of the deformation, has the principal deformations ***η_1 = 1.192281***, ***η_2 = 1*** and ***η_3 = 0.838728***. Show that ***(Y Q Y)*** combined with a rigid body rotation gives a total strain which leaves a plane unrotated and undistorted.

η2 = 1 -> ef//y2
It remains unextended and unrotated

Transform and rotate about ***y2*** (***ef***) then ***cd*** will remain unrotated and undistorted. Any combination of ***ef*** and ***cd*** will also remain invariant



Thus, a pure strain when combined with a rigid body rotation can only generate an invariant–plane strain only if two of its principal strains have opposite signs, the third being zero.

Since it is the pure strain which actually accomplishes the lattice change (the rigid body rotation causes no further lattice change), any two lattices related by a pure strain with these characteristics may be joined by a fully coherent interface.

The (Y Q Y) transformation matrix represents the pure strain part of the total transformation strain required to change a FCC lattice to an HCP lattice, without any volume change, by shearing on the (1 1 1)γ plane in the [1 1 -2]γ direction. The magnitude of the shear being equal to half the twinning shear.

Example 4: The Bagaryatski Orientation Relationship

Cementite (θ) has an orthorhombic crystal structure, with lattice parameters aθ = 4.5241, b = 5.0883 and c = 6.7416 Angstroms along the [1 0 0], [0 1 0] and [0 0 1] directions respectively. When cementite precipitates from ferrite (α, BCC structure, lattice parameter aα = 2.8662°A), the lattices are related by the Bagaryatski orientation relationship, given by:

$$[1\ 0\ 0]_\theta \| [0\ \bar{1}\ 1]_\alpha \quad ; \quad [0\ 1\ 0]_\theta \| [1\ \bar{1}\ \bar{1}]_\alpha \quad ; \quad [0\ 0\ 1]_\theta \| [2\ 1\ 1]_\alpha$$

Derive the co-ordinate transformation matrix **(α J θ)** representing this orientation relationship

Solution:

The orientation relationship denotes parallelism between vectors in the two lattices. To find **(α J θ**) it is necessary to ensure that the magnitudes of the parallel vectors are also equal , since the magnitude must remain invariant to a co-ordinate transformation.

$$[1\ 0\ 0]_\theta \parallel [0\ \bar{1}\ 1]_\alpha \quad ; \quad [0\ 1\ 0]_\theta \parallel [1\ \bar{1}\ \bar{1}]_\alpha \quad ; \quad [0\ 0\ 1]_\theta \parallel [2\ 1\ 1]_\alpha$$

$$k = \frac{\left|[1\ 0\ 0]_\theta\right|}{\left|[0\ \bar{1}\ 1]_\alpha\right|} = \frac{a_\theta}{a_\alpha\sqrt{2}} = \frac{4.5241}{2.8662\sqrt{2}} = 1.116162$$

$$g = \frac{\left|[0\ 1\ 0]_\theta\right|}{\left|[1\ \bar{1}\ \bar{1}]_\alpha\right|} = \frac{b_\theta}{a_\alpha\sqrt{3}} = \frac{5.0883}{2.8662\sqrt{3}} = 1.024957$$

$$m = \frac{\left|[0\ 0\ 1]_\theta\right|}{\left|[2\ 1\ 1]_\alpha\right|} = \frac{c_\theta}{a_\alpha\sqrt{6}} = \frac{6.7416}{2.8662\sqrt{6}} = 0.960242$$

By definition if we multiply the direction **[0 -1 1]α** by **k** then we should obtain the direction **[1 0 0]θ .**

Each column of **(α J θ)** represents the component of a basis vector of **θ** in the **α** basis.

$$(\alpha\, J\, \theta) = \begin{pmatrix} 0.0000 & 1.024957 & 1.920485 \\ -1.11612 & -1.024957 & 0.960242 \\ 1.11612 & -1.024957 & 0.960242 \end{pmatrix}$$

A general expression for finding **(α J θ)** is

$$(\alpha\, J\, \theta) = \begin{pmatrix} 0 & g & 2m \\ \bar{k} & \bar{g} & m \\ k & \bar{g} & m \end{pmatrix} = \begin{pmatrix} J_{11} & J_{12} & J_{13} \\ J_{21} & J_{22} & J_{23} \\ J_{31} & J_{32} & J_{33} \end{pmatrix} \times \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Martensitic Transformations

Suppose that the atoms in the solid are arranged in a square lattice at high temperature. During cooling there will be a thermal contraction, but when a critical temperature is reached, the crystal lattice structure changes abruptly to the rectangular lattice. ***Though the distortion of the cell is significant, there is no diffusion and there is not change in the relative position of the atoms during the transformation***.

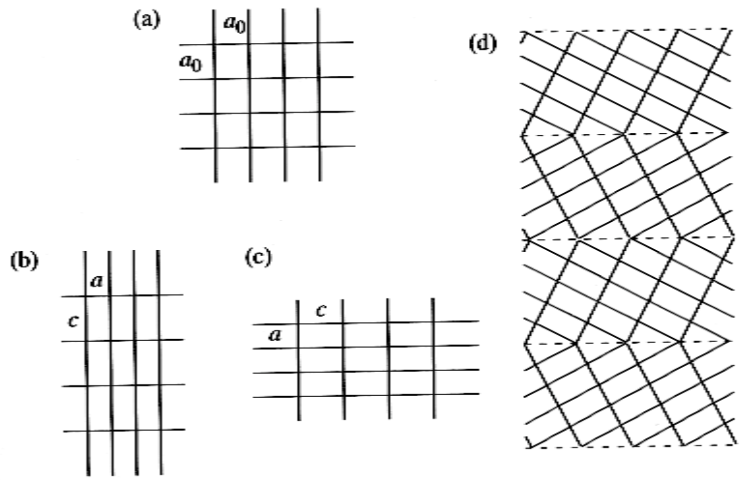


FIG. 1.3. A schematic illustration of the martensitic phase transformation: (a) austenite (b, c) variants of martensite and (d) a coherent arrangement of alternating variants of martensite.

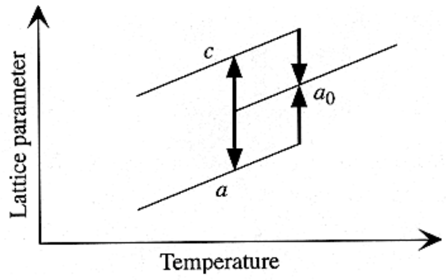


FIG. 1.4. The typical behavior of the lattice parameter as a function of temperature during the martensitic phase transformation.

The martensitic transformation is displacive (no diffusion) and first order (abrupt change in lattice parameter).

When heated back, it reaches another critical temperature and the crystal structure abruptly changes from the rectangular lattice to the square lattice. Therefore the transformation is ***crystallographically reversible.***

The high temperature phase is known as austenite phase and the low temperature phase is the martensite phase.

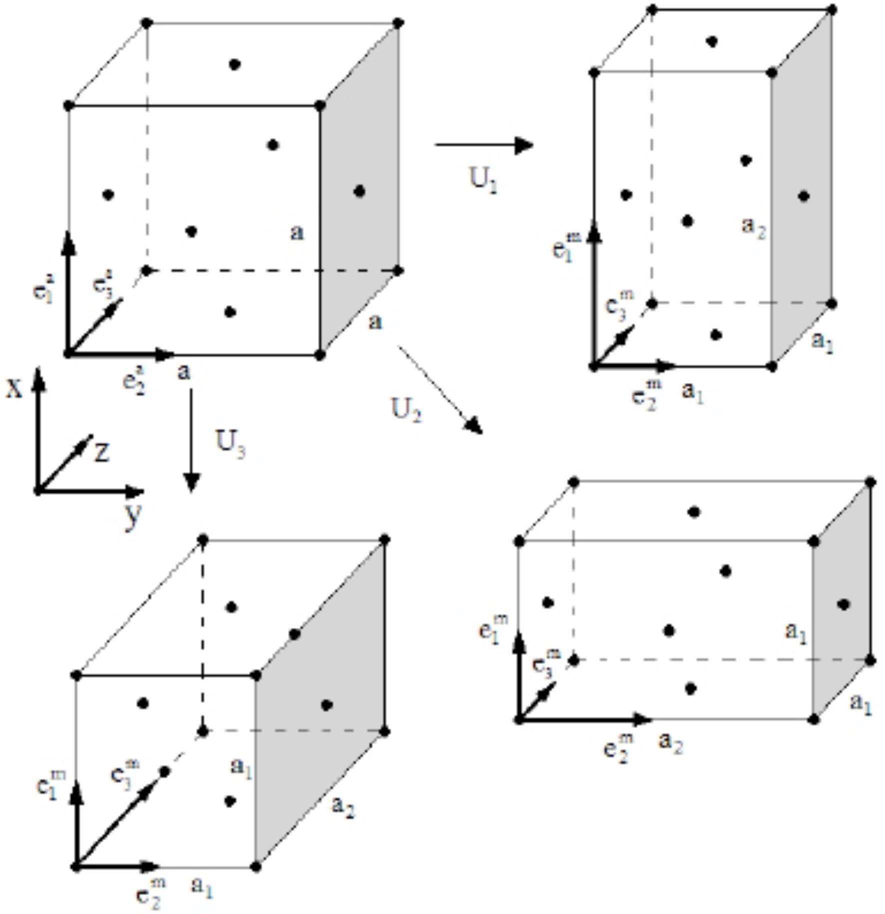
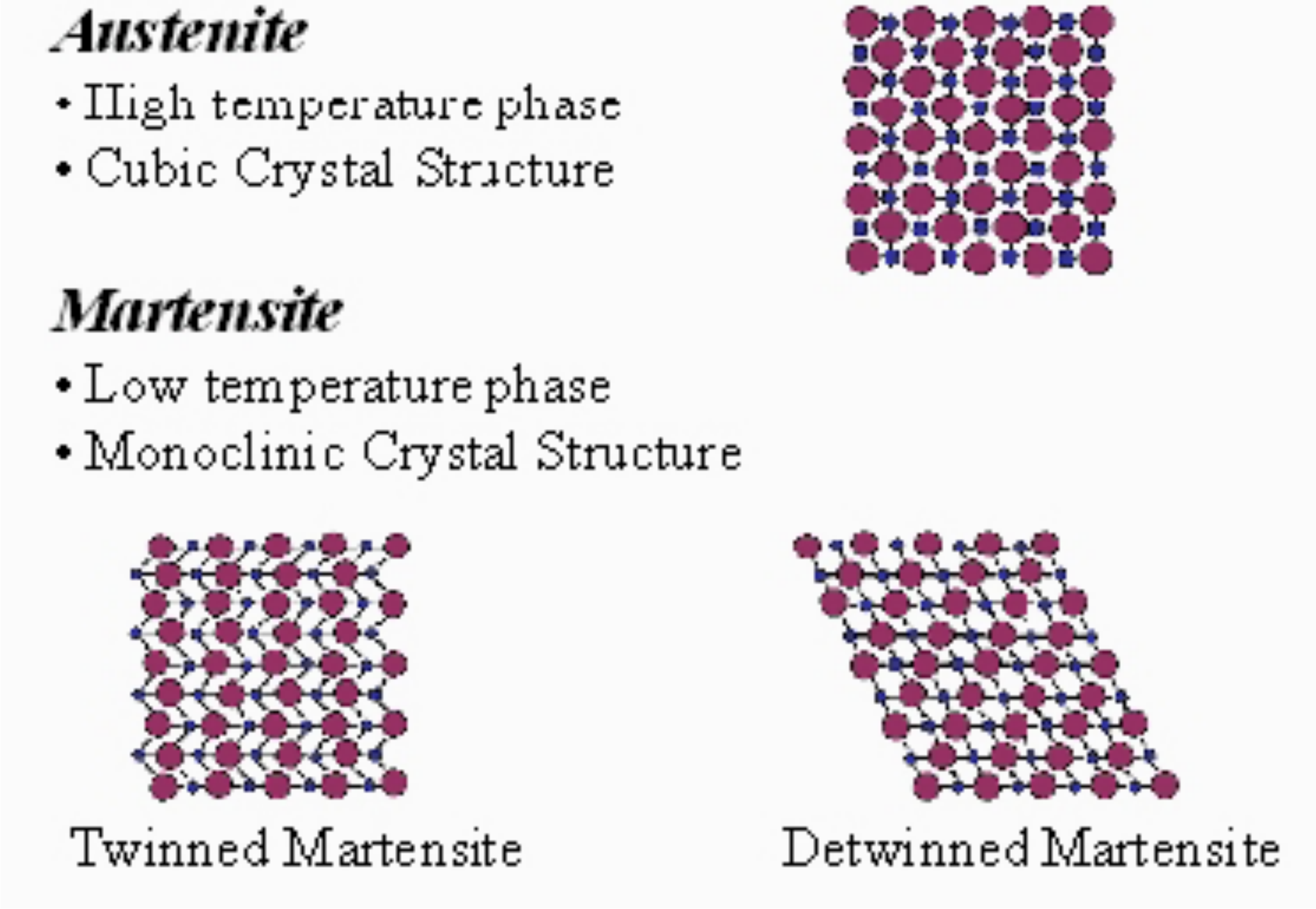


Figure 2.3: The martensitic transformation in Indium-Thallium takes the cubic austenite lattice to the tetragonal martensite lattices. .

Martensite is a phase that, in the absence of stress, is stable only at low temperatures; in addition, it can be induced by either stress or temperature. Martensite is easily deformed, reaching large strains (~8%) [1].



Austenite

- High temperature phase
- Cubic Crystal Structure

Martensite

- Low temperature phase
- Monoclinic Crystal Structure

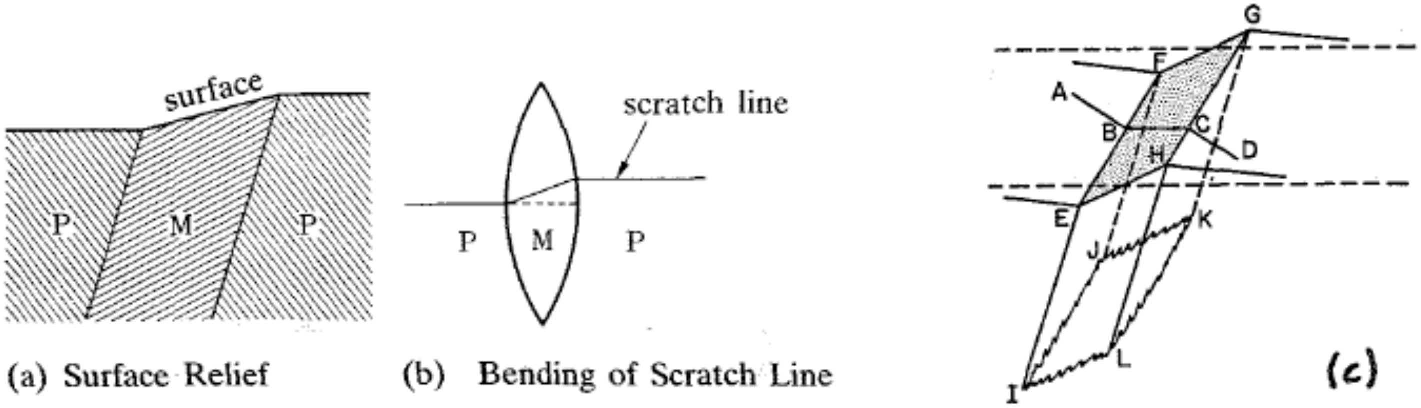
Twinned Martensite

Detwinned Martensite

The martensitic transformation is shear-dominant diffusionless solid-state phase transformation occurring by nucleation and growth of the martensitic phase from the parent austenitic phase [2]

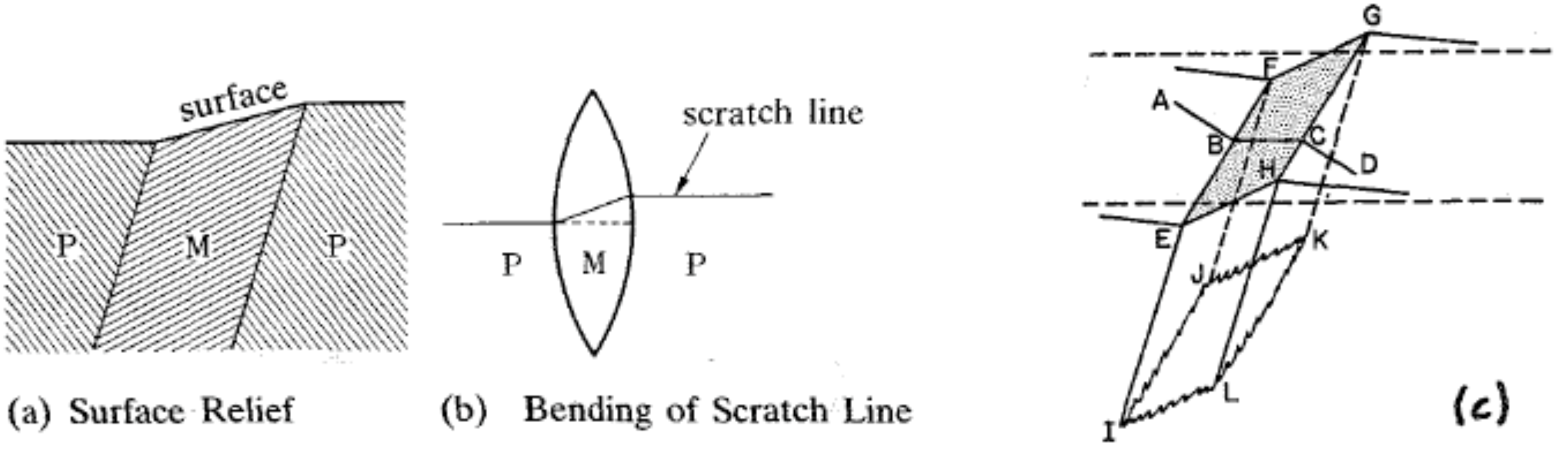
[2} Olson, G.B., Cohen, M., 1982. “Stress assisted isothermal martensitic transformation: application to TRIP steels”; Metall. Trans. A 13, 1907–1914.

Martensitic transformations are displacive, diffusionless transformations during which the atoms execute a small, well-defined and cooperative movement, resulting in a change in lattice structure and a shape change. **The lattice structure of the resulting martensite has an orientation relationship to the lattice structure of the parent phase. The martensite phase is separated from the parent phase by an undistorted plane, called the habit plane.**



(a) Surface Relief (b) Bending of Scratch Line

Figure 3.1: *Formation of surface relief and bending of scratch line accompanying martensitic transformation [15, 9].*



(a) Surface Relief (b) Bending of Scratch Line (c)

Figure 3.1: *Formation of surface relief and bending of scratch line accompanying martensitic transformation [15, 9].*

Habit plane

The martensitic phase takes the form of plates or needles, which appear to be embedded in the matrix along certain well-defined planes. Such a plane, the plane of contact between the two phases or interface plane, is called the *habit plane.* It separates the parent and martensite phases. In the figure above the planes **EFIJ** and **GHKL** are habit planes.

The **habit planes** which occur in a specimen don’t have arbitrary directions, owing to the well-defined movements of atoms during transformation. These directions are specified by indices of planes in the parent phase.

Two important features of habit planes; the habit plane is essentially an undistorted plane and the habit plane must also be unrotated.

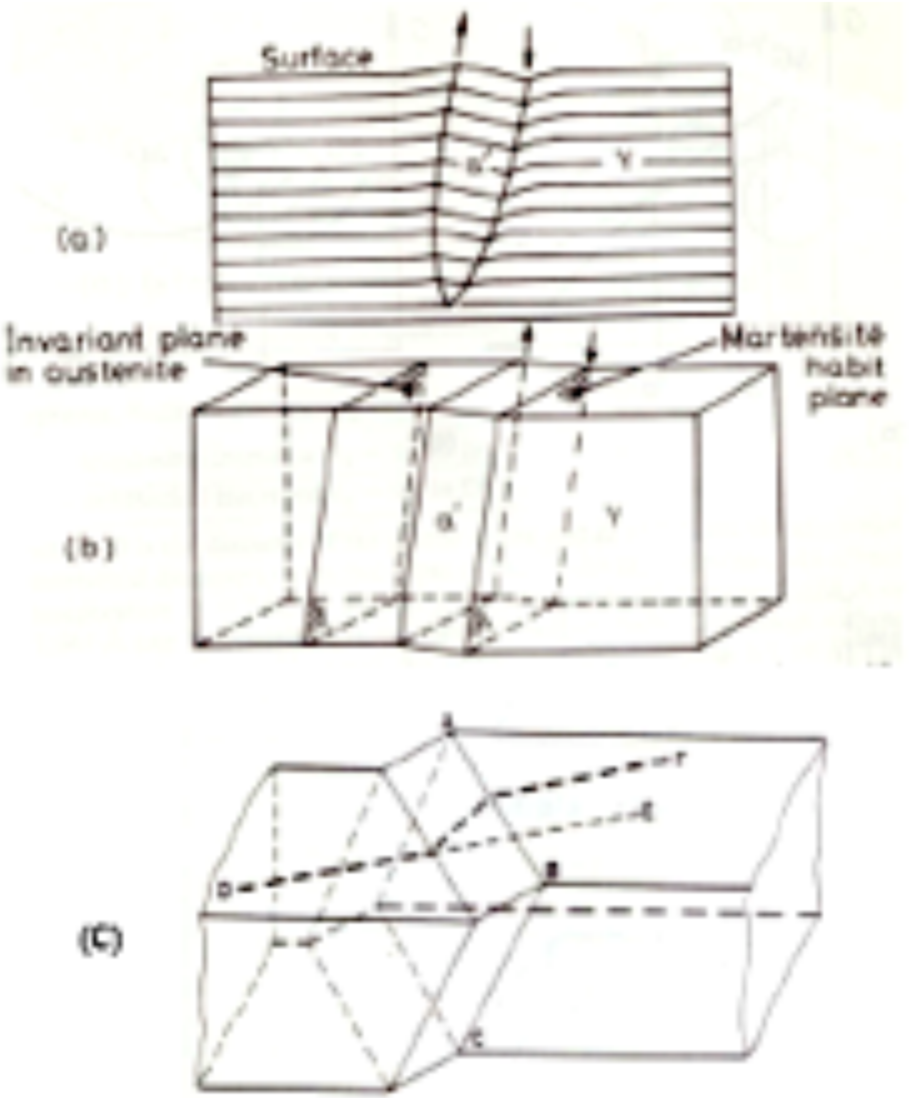


Fig. 1.3 (a) and (b) illustrate how a martensite plate remains (macroscopically) coherent with the surrounding austenite and even the surface it intersects; (c) Schematic representation of the invariant-plane strain shape deformation characteristic of a MT. The initial straight scratch DE is displaced to the position DF when the martensite plate ABC is formed. The plane ABC is invariant (undistorted and unrotated as a result of the MT).

Lattice Correspondence

Since the martensitic transformation occurs diffusionlessly, the lattice of the parent phase deforms to that of the martensite phase maintaining one-to-one correspondence.

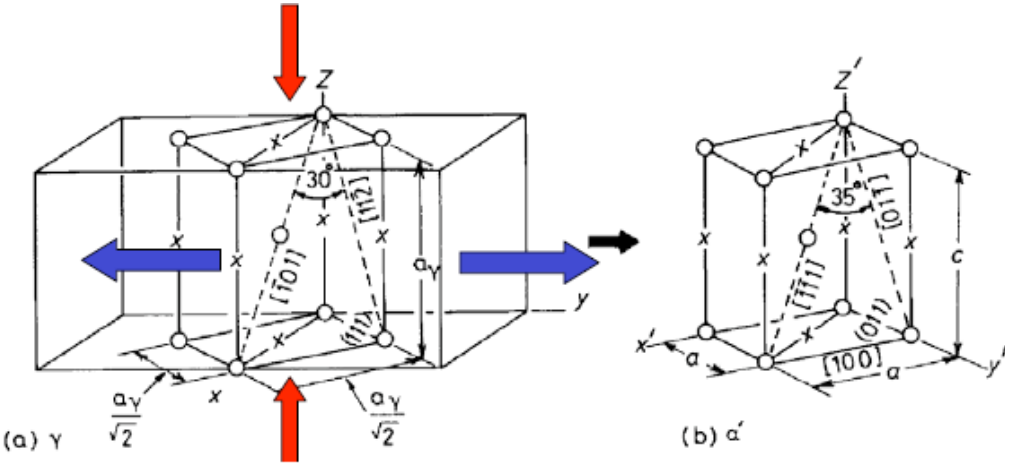


Fig. 1.4 Bain correspondence for the α → α’ transformation. Possible interstitial sites for carbon are shown by crosses. To obtain α’ the γ unit cell is contracted about 20% on the C axis and expanded about 12% on the a axes.

The Bain deformation results in the following correspondence of crystal planes and directions between the parent and the product phase:

$(111)_\gamma \,//\, (011)_{\alpha'}$ $[001]_\gamma \,//\, [001]_{\alpha'}$ $[1\bar{1}0]_\gamma \,//\, [100]_{\alpha'}$ $[110]_\gamma \,//\, [010]_{\alpha'}$

But in fact, the experimental observed orientation relationships are irrational. The relative directions can vary between <101>γ // <111>α’ (the Kurdjumov-Sachs relationship) and <110>γ // <101>α’ (the Nishiyama-Wasserman relationship) and these two orientation differ by ~5° about [111] γ.

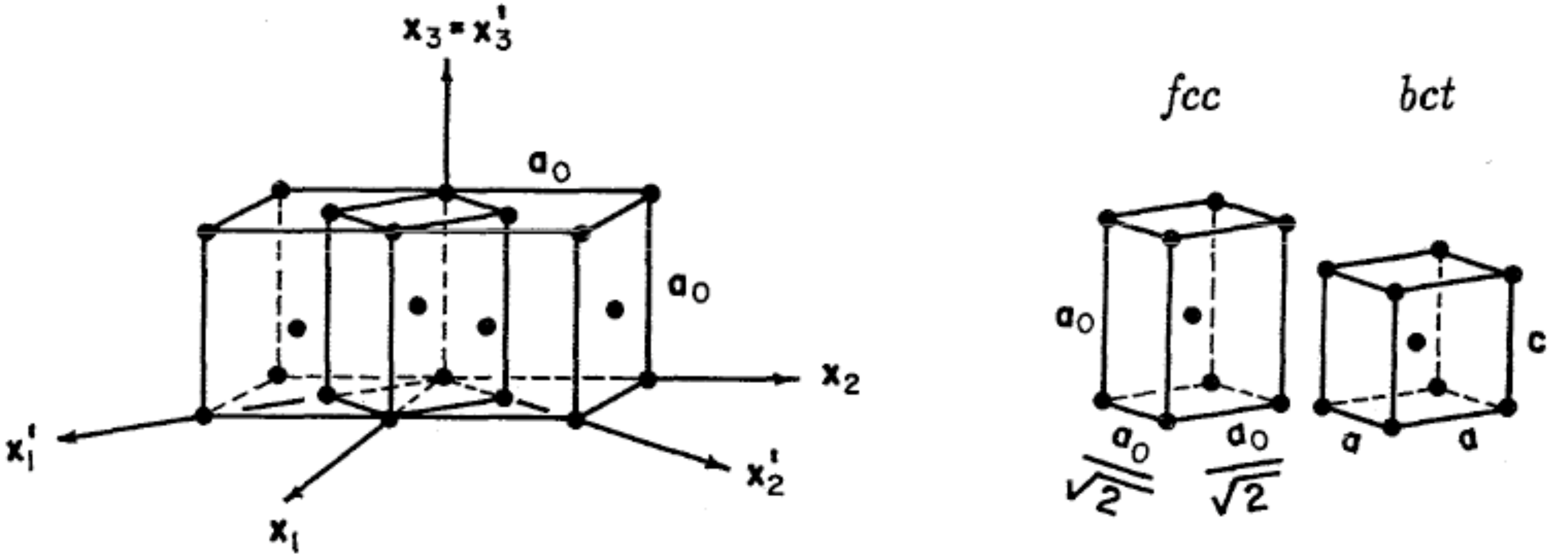


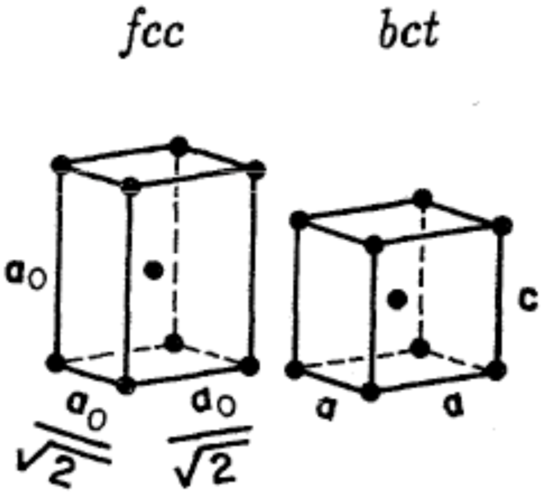
Figure 3.2: *Lattice correspondence and lattice deformation for the fcc to bct transformation in iron alloys [9].*

It can be derived that the direction $[100]_f$ becomes the direction $[110]_b$ (the subscripts f and *b* refer to the fcc and bct structures respectively), $[0l0]_f$ becomes $[-110]_b$ and $[001]_f$ becomes $[001]_b$. This implies that the following lattice correspondence:

$$\begin{bmatrix} x_1' \\ x_2' \\ x_3^1 \end{bmatrix}_b = \begin{bmatrix} 1 & -1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix}_f$$

The matrix is called *correspondence matrix*, and belongs to the described Bain correspondence; if another correspondence is assumed to transform a ***fcc*** into a *bct* lattice, then another correspondence matrix results.

Tetragonal martensite in Fe-Ni alloys has a c/a-ratio of 1.0, while in the parent structure this ratio is √2. If the volume of the structural cell doesn't change during transformation (which is true for NiTi), then the following principal distortions are obtained:



$$FCC \rightarrow \frac{a_0}{\sqrt{2}} \times \frac{a_0}{\sqrt{2}} \times a_0 = a \times a \times c = a^3 \rightarrow BCT$$

$$a_0 = 1.26a$$

$$along\_x_1' = \eta_1 = 1.12$$

$$along\_x_2' = \eta_2 = 1.12$$

$$along\_x_3' = \eta_3 = 0.80$$

$$\mathbf{B} = \begin{bmatrix} \eta_1 & 0 & 0 \\ 0 & \eta_1 & 0 \\ 0 & 0 & \eta_3 \end{bmatrix} = \begin{bmatrix} 1.12 & 0 & 0 \\ 0 & 1.12 & 0 \\ 0 & 0 & 0.80 \end{bmatrix}$$

A clear view of this deformation can be obtained by considering a unit sphere in the parent structure, just as the transformation occurs from cubic to tetragonal to tetragonal then the sphere transforms into an ellipsoid.

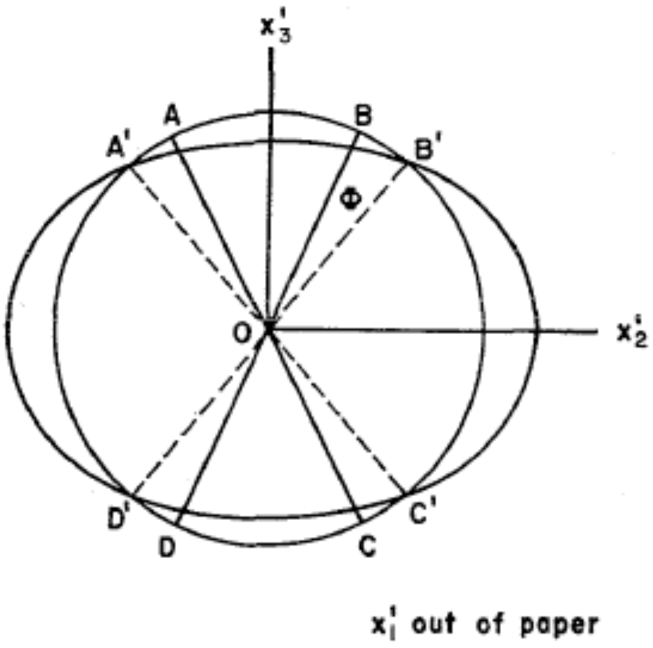


Figure 3.3: *Cones of unextended lines resulting when a unit sphere is homogeneously distorted into an ellipsoid [9].*

The ellipsoid intercepts the sphere in two circles (with x_3 as axis), namely the A'-B' and C'-D'. The cones given by OA, OB, OC, and OD represent positions in the parent and martensite that have no change dimensions.

There is no-plane that it is undistorted only two cone-vectors are unchanged in length. Hence, the Bain model describes the change in lattice structure but it is inconsistent with an important feature of the martensitic transformation an almost undistorted habit plane.

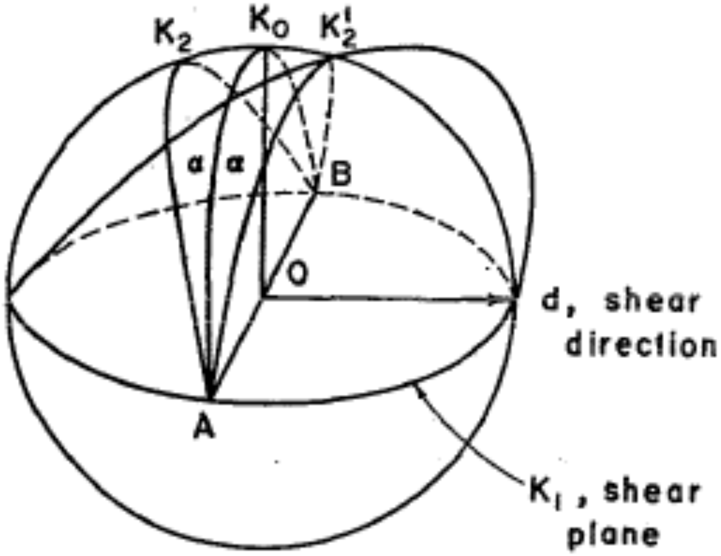


Figure 3.4: *Graphical representation of simple shear, whereby a sphere is sheared on an equatorial plane* $\mathbf{K}_1$ *in the direction* $\vec{d}$ *[9].*

$\vec{d}$

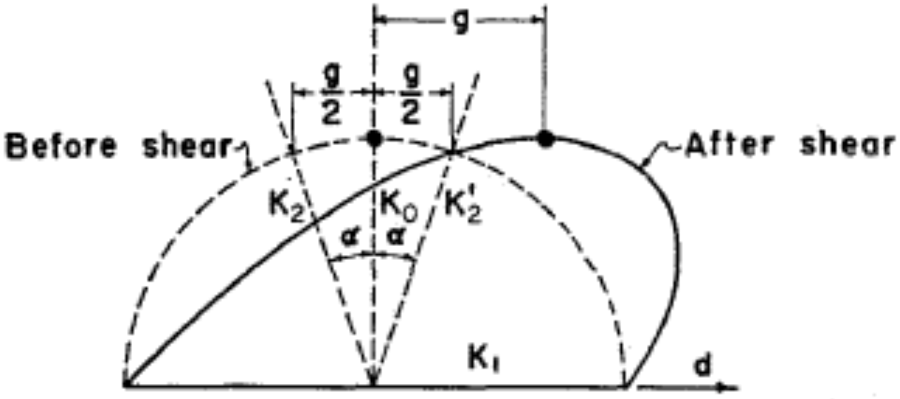


Figure 3.5: *Cross-sectional view of fig. 3.4 [9].*

The condition of an almost undeformed plane, the habit plane is satisfied by a second deformation in the form of a simple shear.

A sphere is sheared on an equatorial plane $\mathbf{K}_1$ in the direction *d.* All points of the structure are displaced in the direction of *d* the distance over which a point is displaced is proportional to the distance of the point to the shear plane $\mathbf{K}_1$.

As a result of the shear, any vector in the plane **AK_2B** is transformed into a vector in the plane **AK'_2B**; its magnitude is unchanged, the vector is only rotated. All vectors on the left of **AK_2B** are decreased in length, those on the right are increased. The plane **AK_2B** represents the initial position of the plane **AK'_2B** which remains undistorted as a result of shear. Obviously, the relative positions of the planes **AK_2B** and **AK'_2B** depend upon the amount of shear: the bigger the shear, the bigger angle α.

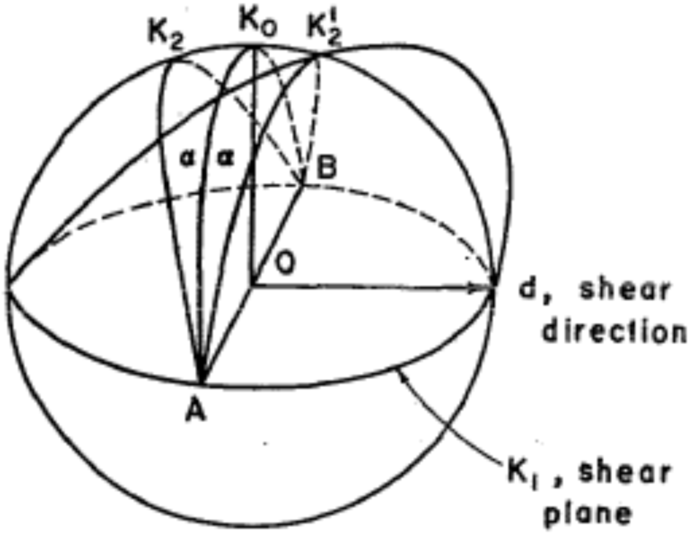


Figure 3.4: *Graphical representation of simple shear, whereby a sphere is sheared on an equatorial plane* $\mathbf{K}_1$ *in the direction* $\vec{d}$ *[9].*

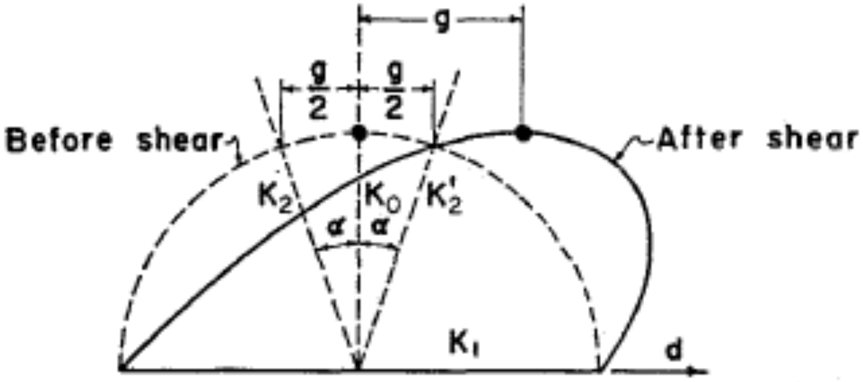


Figure 3.5: *Cross-sectional view of fig. 3.4 [9].*

Combining Bain Distortion and Simple Shear

Combining these two effects leads to the following conclusion: a simple shear (of a unique amount, on a certain plane, and in a certain direction) can be found such that vectors which are increased in length due to the Bain lattice deformation are correspondingly decreased in length by the same amount due to the simple shear, and vice-versa.

Such vectors which remain invariant in length to these operations define potential habit planes. The simple shear can be either a ***slip shear or a twinning shear*** (later more), but in either case, the lattice is left invariant, and the simple shear is thus termed a *lattice invariant shear,* which may be represented by a matrix **P**.

B matrix – deformation due to Bain model

P matrix – deformation due to slip shear or twinning shear

Rigid body rotation: The third additional requirement that the habit plane be unrotated as well has not yet been fulfilled. If in addition to the lattice deformation and the lattice invariant deformation, a rigid body rotation (about a certain axis, over a unique amount θ) is supposed to return the undistorted plane to its original position, then an undistorted and unrotated plane will exist. This rotation can be described by means of a matrix **R**.

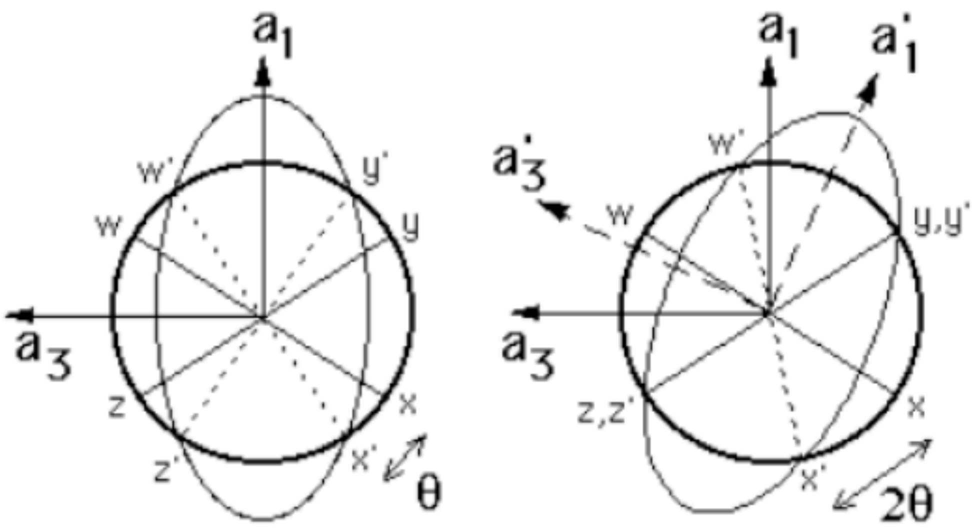


Fig. 1.5 (a) The effect of the Bain strain on austenite, which when undeformed is represented as a sphere of diameter wx=yz in 3D. The strain transforms it to an ellipsoid of revolution. (b) The invariant-line strain obtained by combining the Bain strain with a rigid body rotation through an angle θ.

Total Shape Change:

The features of the total macroscopic shape change, i.e. surface relief and an undistorted and unrotated habit plane, match well to a mathematical model called *invariant plane strain* (IPS). Then, the displacement of any point is in a common direction and proportional to the distance from a fixed (i.e., not moved by the strain) plane of reference, which is the invariant plane. Simple examples are simple shear and uniaxial extension. **A** general IPS can be represented by the combination of these two, where a martensite plate is formed within a single crystal of the parent phase. The invariant plane is of course the habit plane.

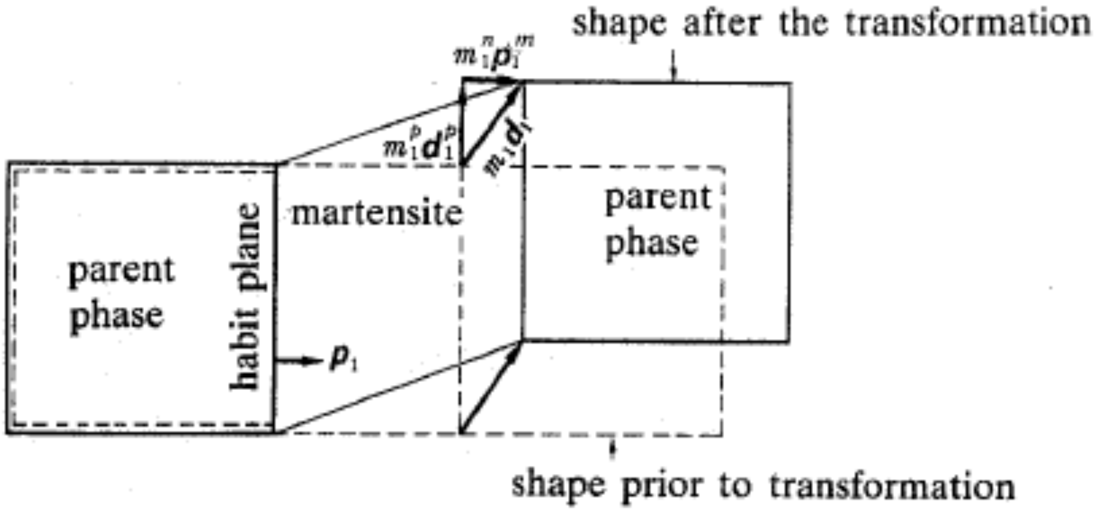
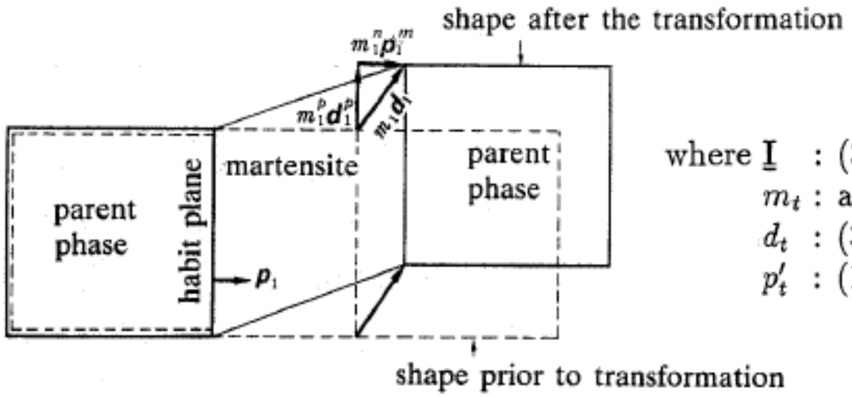


Figure 3.6: *Shape deformation accompanying the formation of a single martensite plate [15].*



$$\underline{P}_t = \underline{I} + m_t d_t p_t'$$

where $\underline{I}$: (3 × 3) unit matrix
m_t : amount of deformation
d_t : (3 × 1) unit vector in the direction of the shape change
p_t' : (1 × 3) unit vector normal to the invariant plane

Figure 3.6: *Shape deformation accompanying the formation of a single martensite plate [15].*

The total shape change may also be described by means of three sub-transformations, with respective matrices ***B, P and R***. Therefore we can write:

$$P_t = \underline{B}\,\underline{P}\,\underline{R}$$

B matrix – deformation due to Bain model
P matrix – deformation due to slip shear or twinning shear
R matrix – Rigid body rotation

B can be determined by XRD by calculating the lattice parameters of the parent and martensite phases.
P can be determined by making assumptions on the direction and shear plane for the lattice invariant strain.

$$\underline{F} = \underline{B}\,\underline{P}$$

The matrix F determines the habit plane. Two possible solutions.

R can be calculated from the condition that the habit plane (with a unit plane normal p_t , is unrotated.

$$\underline{\mathbf{P}}_t = \underline{\mathbf{I}} + m_t d_t p'_t$$

If the equation is applied to p_t

$$\begin{aligned}\underline{\mathbf{P}}_t p_t &= p_t + m_t d_t (p'_t p_t) \\ &= p_t + m_t d_t \Rightarrow \\ \underline{\mathbf{P}}_t p_t - p_t &= m_t d_t\end{aligned}$$

The amount of shear m_t and the shear direction d_t can be calculated.

The ***fcc* + *bct* transformation** that occurs in steel is used as example. However, most SMA's have a ***bcc* structure** in the high temperature state, which transforms into some other structure. The phenomenological theory described above is likewise applicable to any other martensitic transformation.

Martensitic Transformation

Martensitic transformations are diffusionless, the change in crystal structure being achieved by a deformation of the parent phase. As in mechanical twinning, there is an invariant–plane on which there is a shear; the transformation may also involve a volume change which occurs normal to the invariant plane.

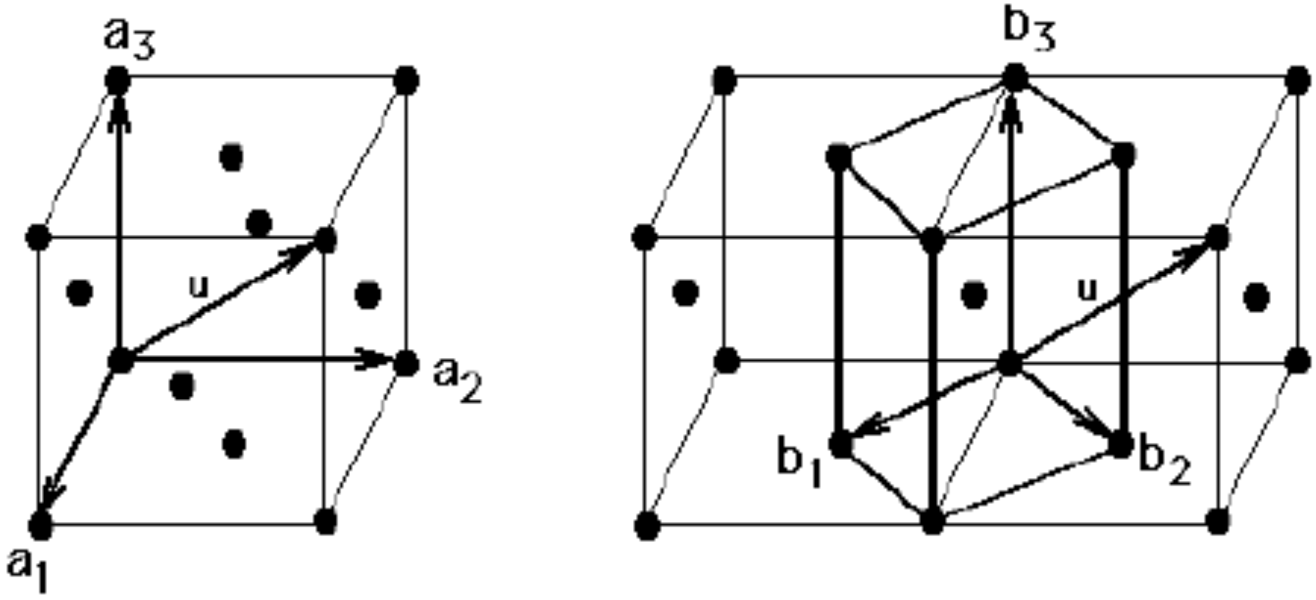
c.c.p.→h.c.p. e.g. cobalt

To transform a c.c.p. structure into h.c.p. requires a displacement of $a/6 < 1\ 1\ 2 >$ on every second $\{1\ 1\ 1\}\mathit{ccp} \equiv (0\ 0\ 0\ 1)\mathit{hcp}$. The latter is the invariant plane.

FCC⇒HCP transformation

c.c.p.→b.c.c. e.g. iron

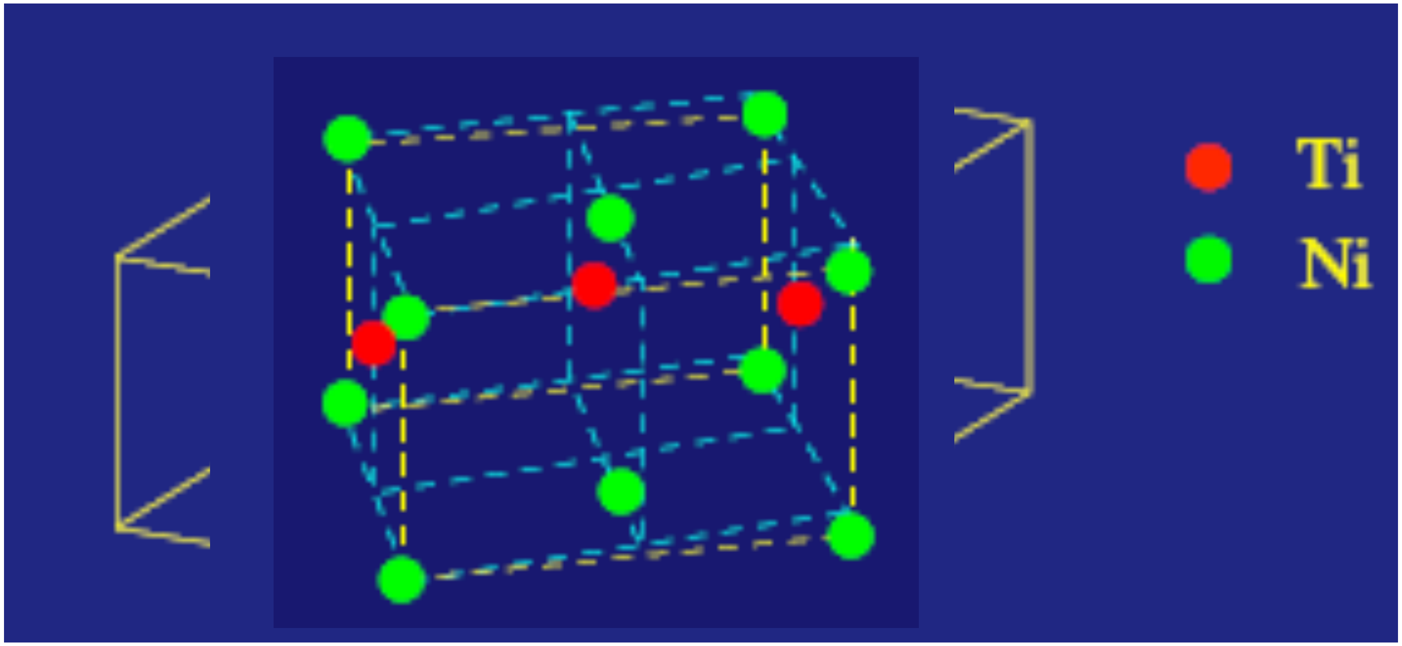
The deformation necessary to convert the c.c.p. structure into b.c.c. is more complicated than the simple shear of the previous example. There is a compression along the *z* axis and a uniform expansion along the *x* and *y* axes.



Bain strain.

What make SMAs different from other materials are primarily the shape memory effect (SME) and pseudoelasticity, which are associated with the specific way the phase transformation occurs.

When a SMA undergoes a martensitic phase transformation, it transforms from its high-symmetry, usually cubic austenitic phase to a low-symmetry martensitic phase, such as the monoclinic variants of the martensitic phase in a NiTi SMA.

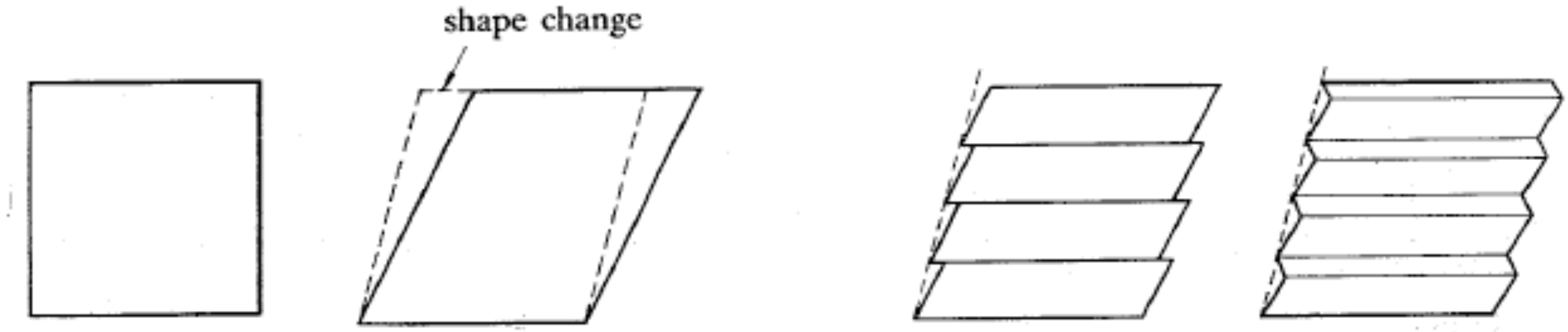


In the absence of applied stresses, the variants of the martensitic phase usually arrange themselves in a self-accommodating manner through twinning, resulting in no observable macroscopic shape change.

By applying mechanical loading, the martensitic variants are forced to reorient (detwin) into a single variant leading to large macroscopic inelastic strains. After heating above certain temperature, the martensitic phase returns to the austenitic phase, and the inelastic strains are recovered. This behavior is known as the SME.

Slip or Twinning

It has been stated that the required shear deformation (matrix P) can be produced by either slip or twinning. Due to the lattice deformation (Bain Distortion), the parent phase lattice is changed to the martensite lattice, resulting in a certain shape change (solid line). The observed shape change of the crystal is different, indicated with the dashed line. The dashed line in (c) and (d) marks the habit plane, the plane which separates the parent and martensite phase. Comparison of (b) with (c) and (d) makes clear that slip or twinning is necessary to connect the parent and martensite phase along the habit plane.



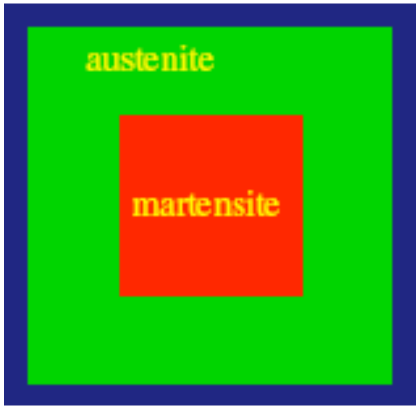
(a) Parent Lattice Prior to Transformation

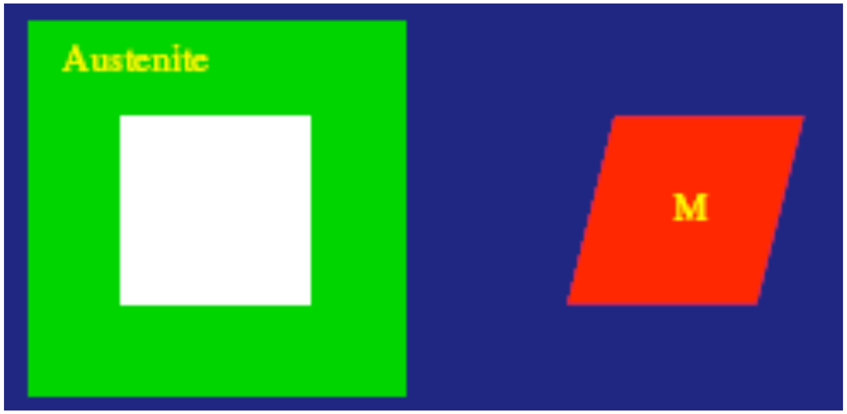
(b) Lattice Deformation Due to Transformation

(c) Lattice Deformation and Slip Shear

(d) Lattice Deformation and Twinning Shear

Figure 3.7: *Slip shear or twinning shear in addition to lattice deformation is necessary to obtain the actual shape change [15].*

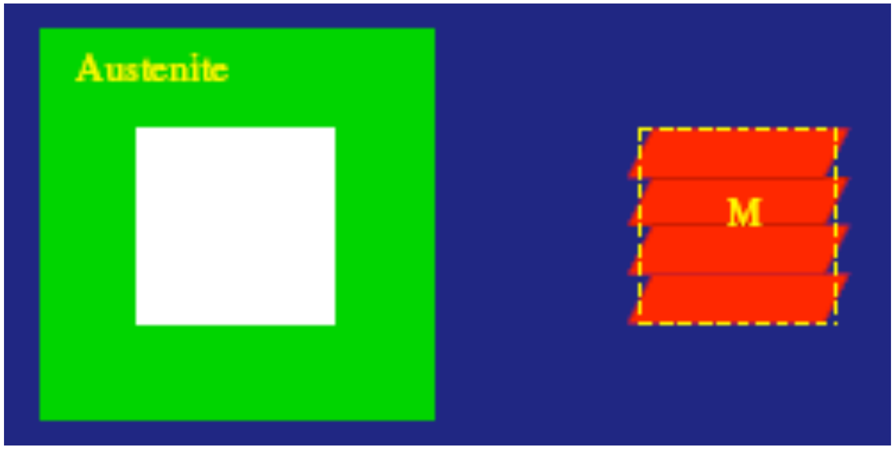




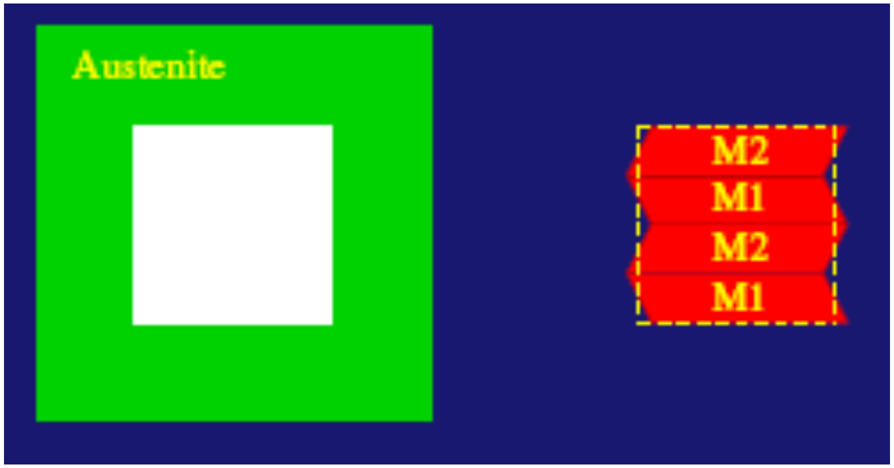
The interface between the austenite and martensite is called the habit plane

How does the martensite grows in an austenitic matrix?

the lattice distortion makes them incompatible.



Single martensite with slip
(irreversible process)

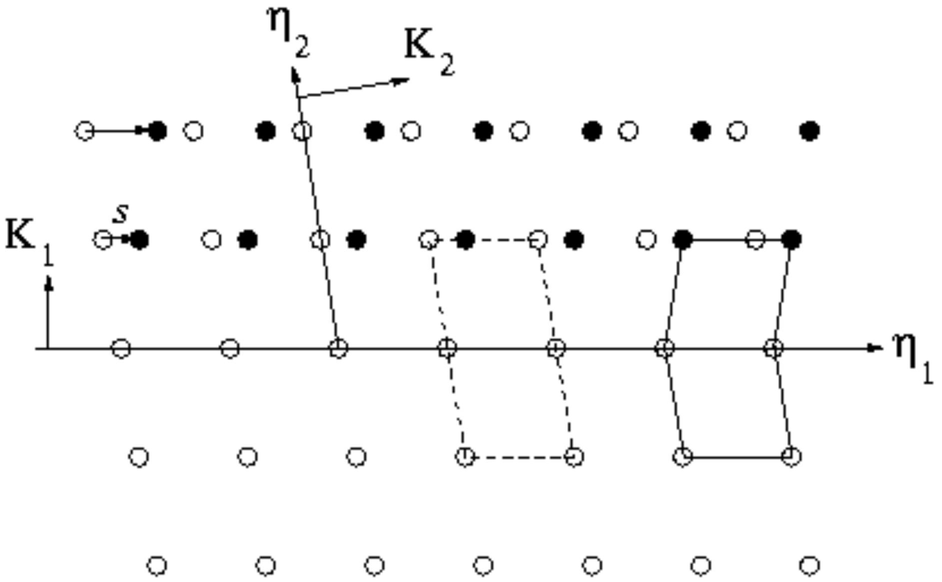


Twin martensite variants (reversible process)

When slip occurs in a crystal, then crystal planes glide over each other (usually close packed planes in close packed directions). This process is irreversible; it is not possible to return the crystal into its exact original configuration. *Martensitic transformations which are accompanied by slip are therefore irreversible transformations and metals or alloys with this property cannot show the SME, since a reversible martensitic transformation is required*.
Crystal structures which possess very little slip possibilities, have a quite different mechanism to react on shear loads: twinning. When twinning occurs, atoms in a thin band move over a distance, which is less than an interatomic distance, in such way, that afterwards the atoms are mirrored-about a mirror plane, called the twinning plane.
The thin band is bounded by two parallel twinning planes. Twins occurring during deformation are found in all metal lattices. They are formed either because the deformation takes place so rapidly that the usual deformation process doesn’t occur or because the normal plastic deformation is difficult to be brought about; this is the case when the stress, needed to cause the turning over, is less than the stress giving rise to plastic deformation by slip.

Twinned Martensite Microstructure

A *twin* in a crystalline solid occurs between two adjacent regions of the same crystal lattice, where one of the regions is related to the other by a simple shear.



The dashed line shows two unit cells of the original lattice before the shear; while, the solid line indicates a unit cell for each of the lattices after the shear. A twin is also defined by its *twinning elements,* η_1, κ_1, η_2 , κ_2 and , some of which are shown. Specifically, the twin plane normal is parallel to κ_1; the direction of the twin shear is parallel to η_1 ; a second undistorted plane has normal κ_2 ; and an undistorted vector in this previous plane is parallel to $\boldsymbol{\eta_2}$. The magnitude of the twin shear is $\boldsymbol{s}$.

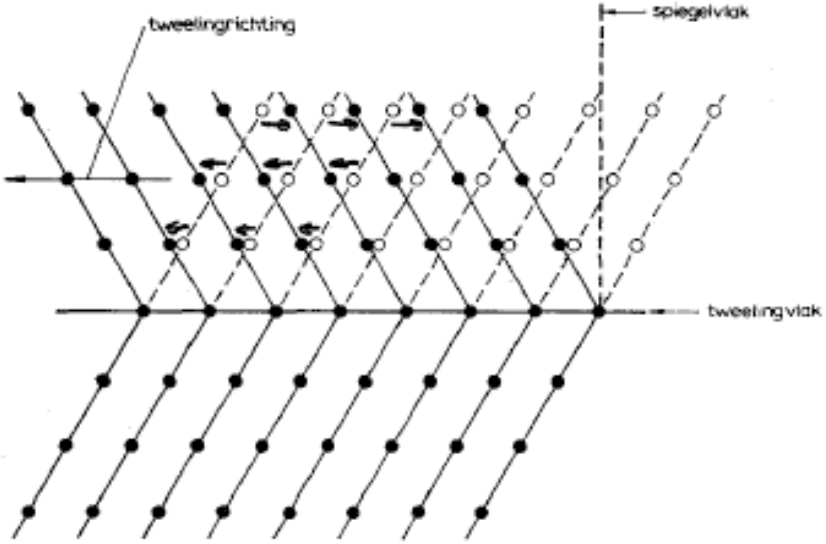


Figure 3.8: *Atom movements during twinning; the dotted lines give the initial situation [7].*

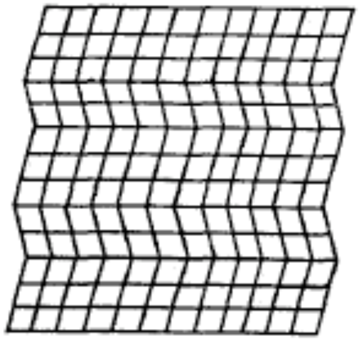
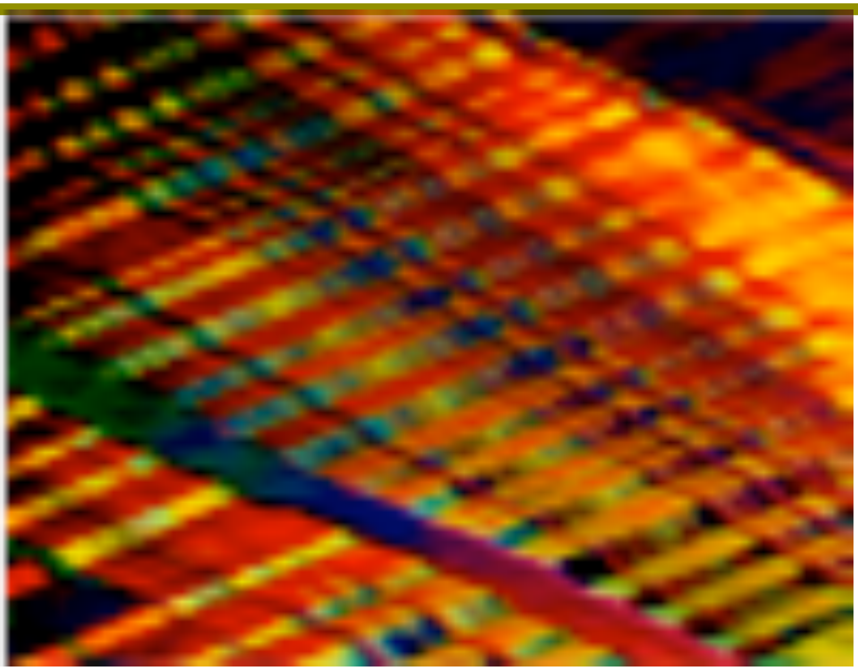
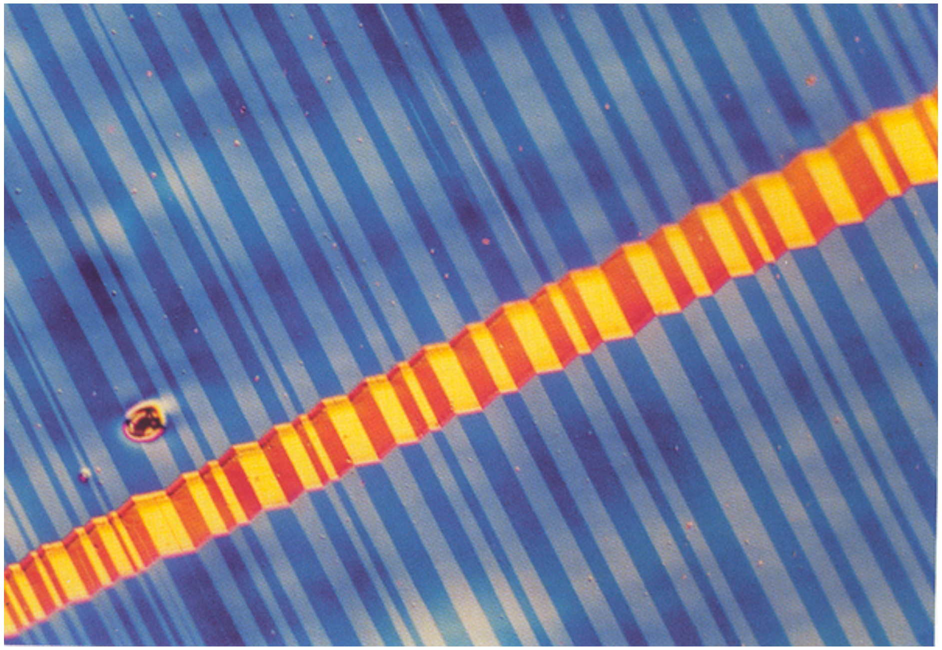
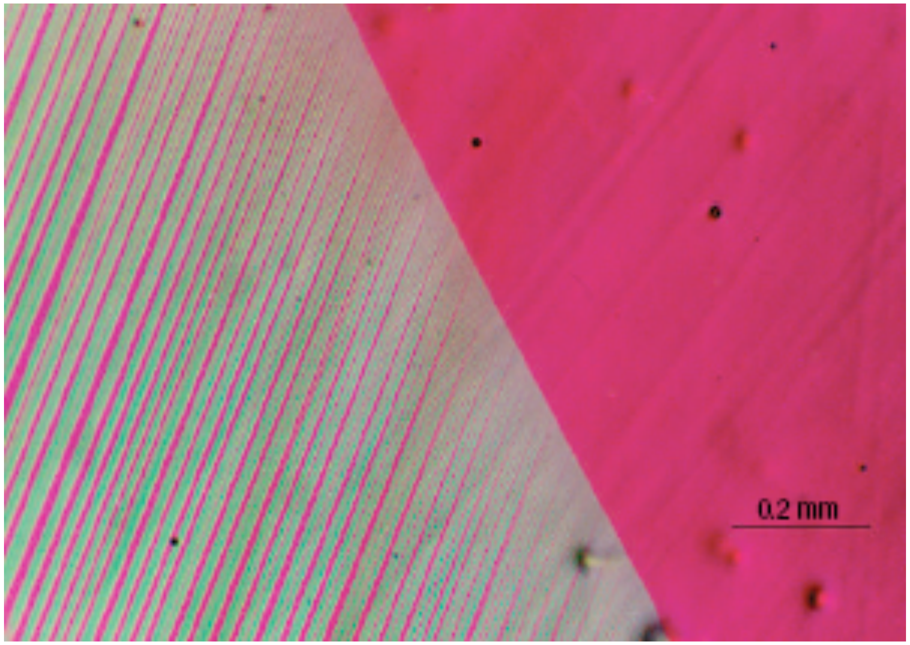


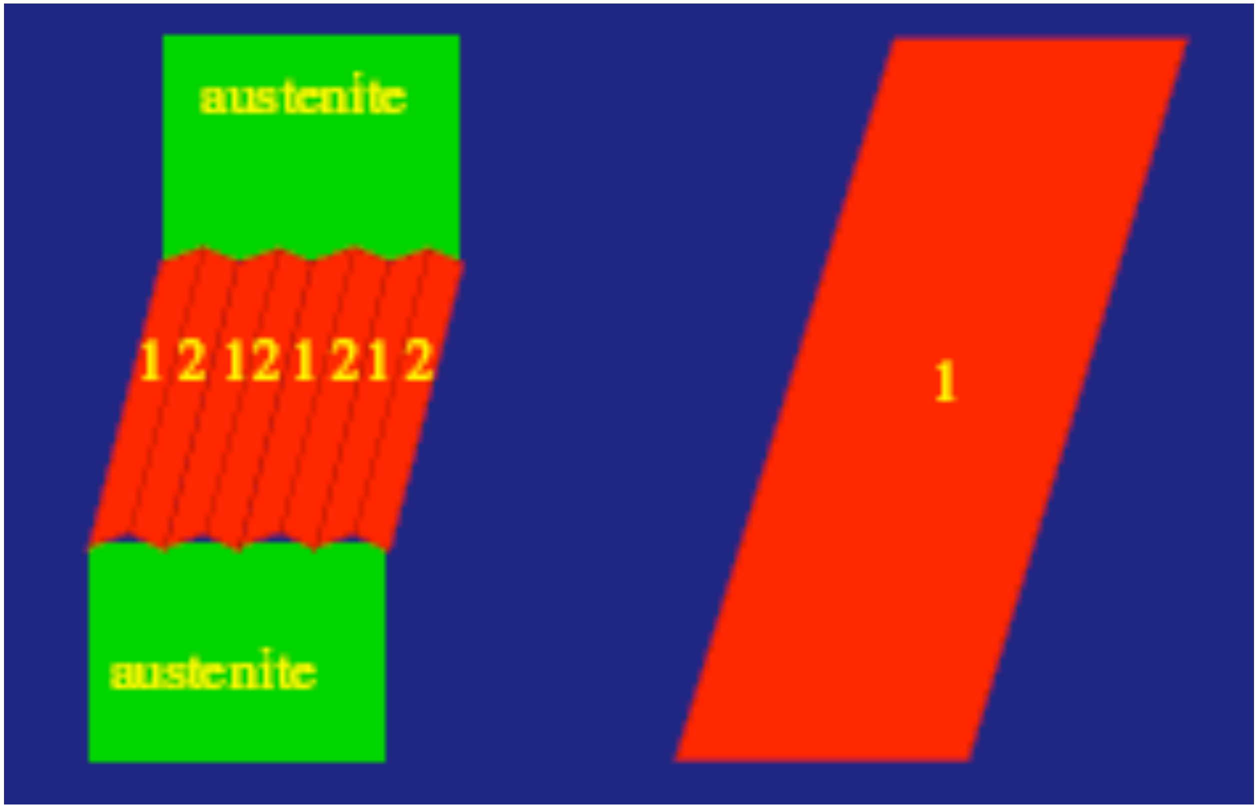
Figure 3.9: *Displacements of crystal parts to the left as a result of twinning [9].*







Twinning is a reversible process. That is why martensites formed in SMA’s are often internally twinned. It should be noted that the important parameter in twinned martensite is the proportion of the twinned volume to the untwinned volume, i.e. the relative thicknesses of the bands determine the amount of macroscopic shear.

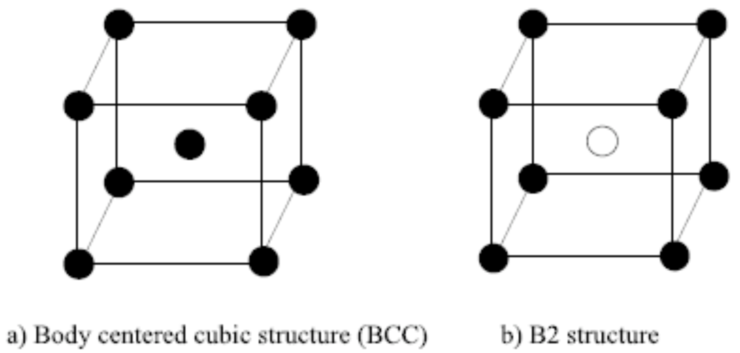


How does martensite grow under an imposed shear like deformation?

Austenite initially transforms to twinned martensite, which in turn gives way to a single variant martensite (detwinning).

Ni-Ti-NOL (Navy Ordinance Laboratory)

The NiTi – Nitinol is a commonly used shape memory alloy. It corresponds to an stoichiometry $Ni_{50}Ti_{50}$.


a) Body centered cubic structure (BCC) b) B2 structure

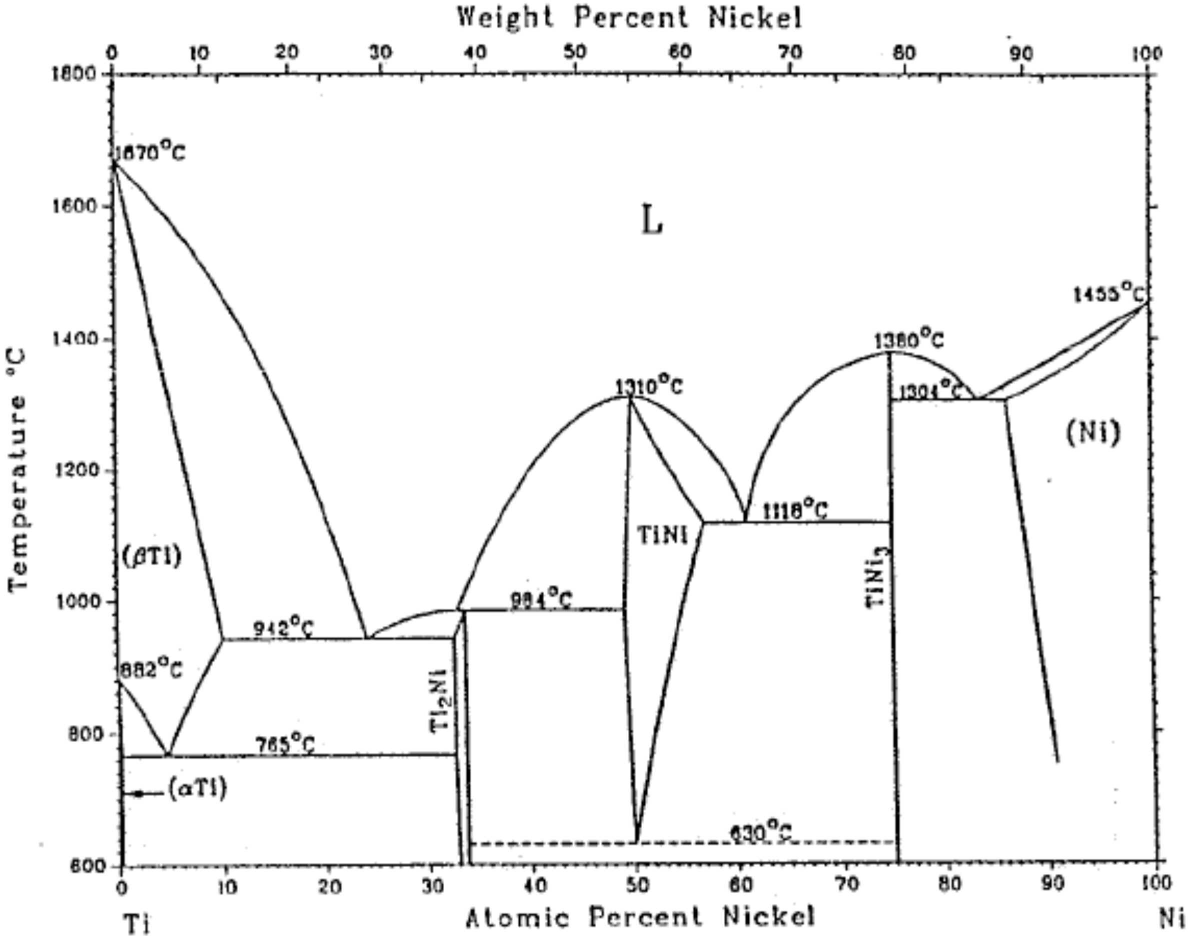


Figure 3.10: *The phase diagram of NiTi [16].*

It has a B2 (CsCl crystal structure) which forms directly from the liquid and it is stable at room temperature. It is an ordered alloy.

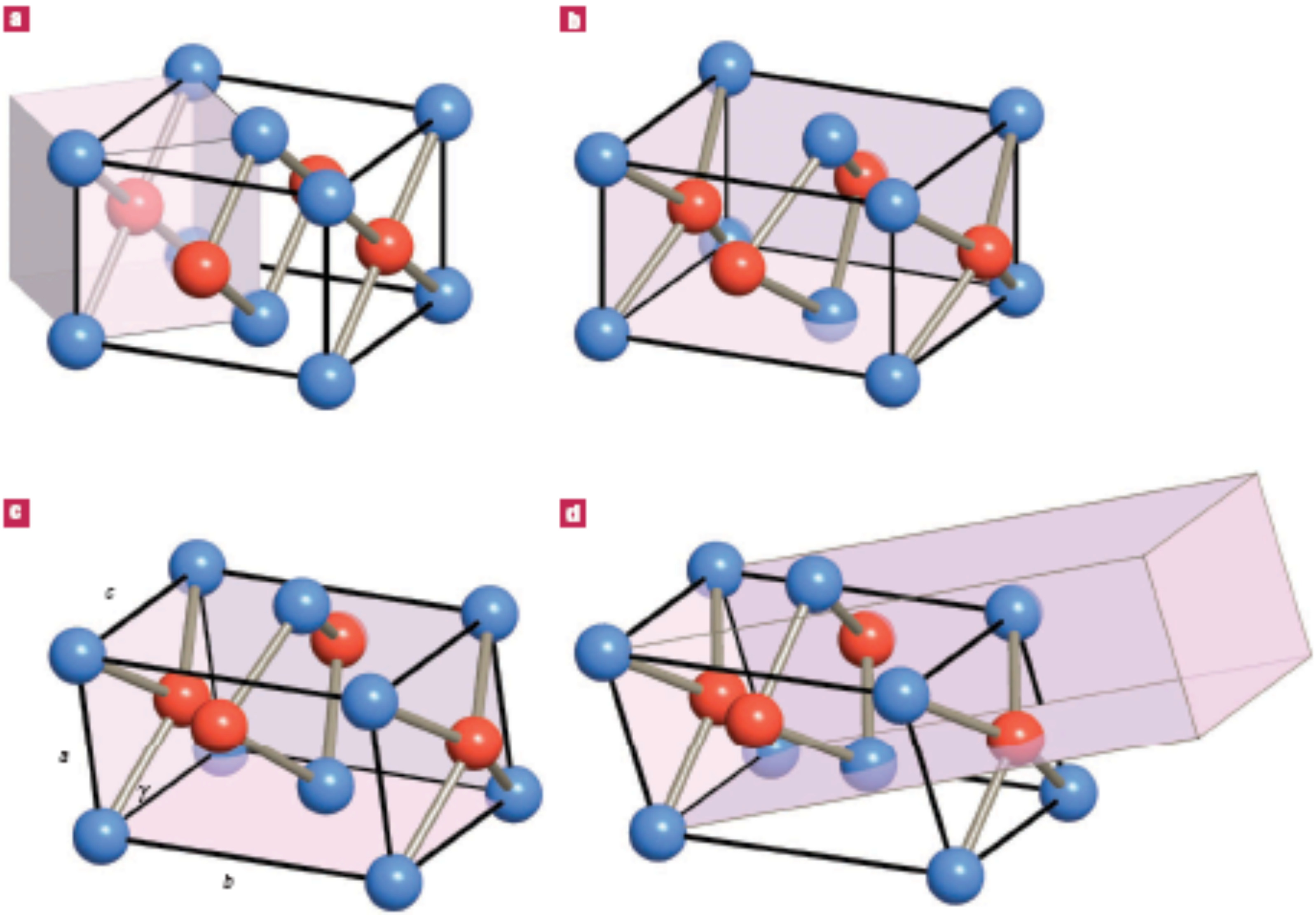


Figure 1 Martensitic distortions of the *B*2 crystal structure of NiTi. a, The relation between the cubic *B*2 cell (shaded box) and the undistorted (tetragonal) *B*19 cell. b, The orthorhombic *B*19 structure. c, The distortion to the stress-stabilized *B*19′ structure. d, The BCO minimum-energy structure with further doubled conventional cell (shaded box). The smaller *B*19′-type primitive BCO cell is shown by thick solid lines. Ni and Ti atoms are represented by red balls and blue balls, respectively. For the metastable R phase (not shown here), we obtain the lattice parameters and Ti positions reported previously[12], but not the internal coordinates of Ni(1b), Ni(1c) and Ni(3d); our calculation gives $z_{1b} = 0.6376$, $z_{1c} = 0.4624$ and $z_{3d} = 0.9091$. The experimentally reported values imply an implausible 2.045 Å bond length[12] between Ni(1c) and Ti(1c); we presume they are in error.

Martensite Variants

When a martensitic transformation occurs, the external shape of the specimen changes significantly. In reality such drastic shape change is not observed at the macro-scale. This is because of the following:

1. The parent phase is often not a single crystal, but polycrystalline. A lot of grains with different orientations exist in a polycrystalline material. This will cause constraining effects at the grain boundaries; if a particular grain wants to change its shape, then the surrounding grains prohibit this shape change to a large extent.
2. Even when we are dealing with a parent phase consisting of a single crystal, still no macroscopic shape change will occur. This is due to the formation of so-called martensite variants.

Formation of Martensite Variants – Crystallographic Features

Most SMA's have basically superlattices with *bcc* structures in the high temperature state. Alloys with *bcc* structures are classified as, β phase alloys. Regardless of the type of alloy, β phases of alloys which have about 50:50 composition ratios (like NiTi) and are ordered like CsCl are denoted by β_2 or B2. β phases of alloys which have about 75:25 composition ratios and are ordered like Fe_3Al are denoted by $\beta_1$or DO_3.

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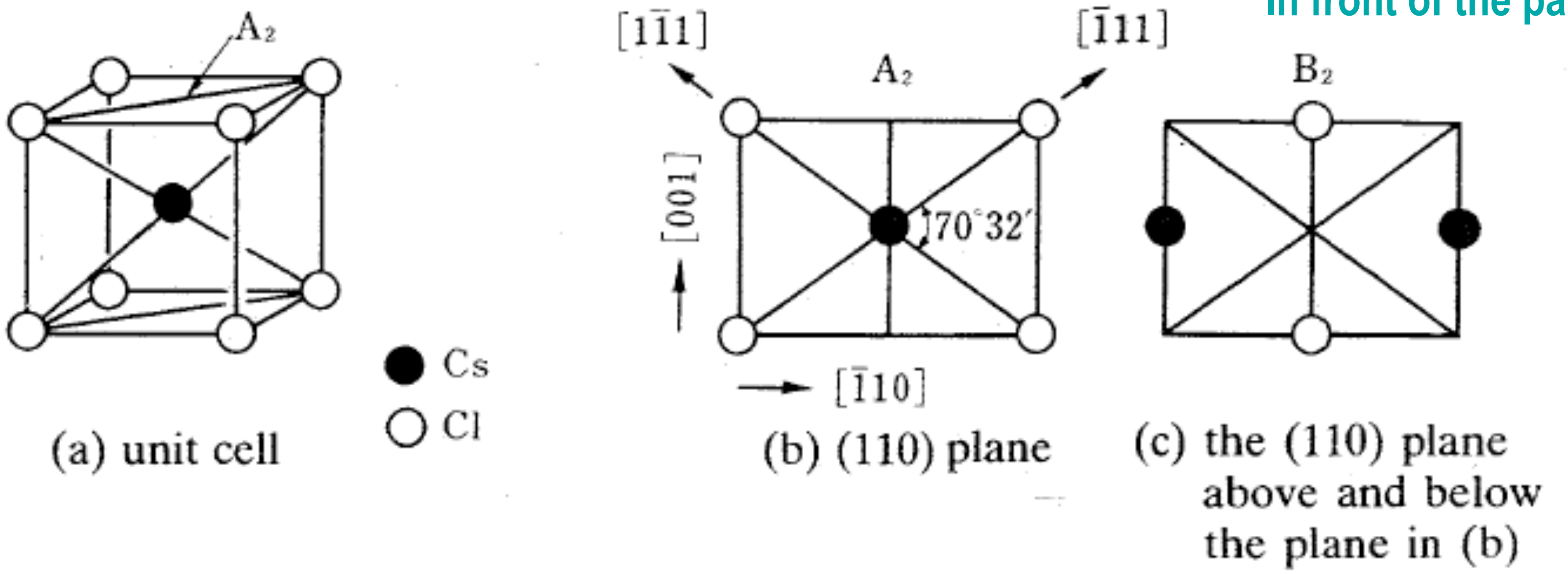


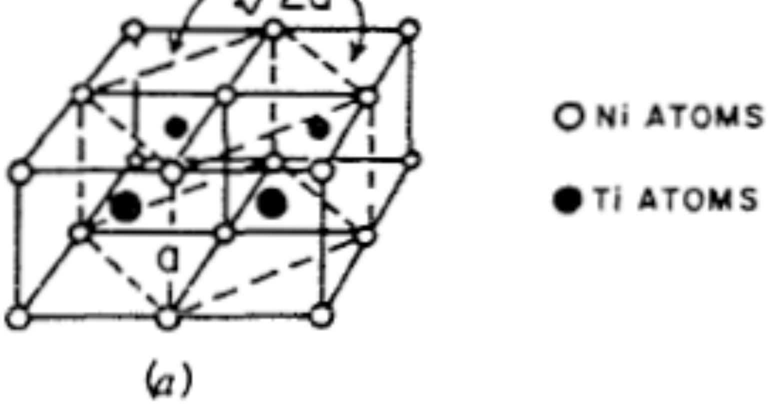
(a) unit cell

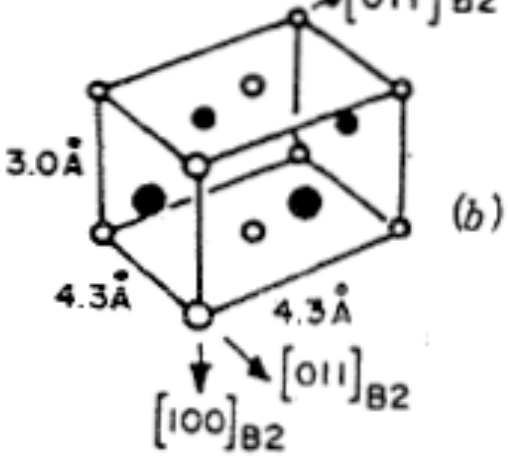
(b) (110) plane

(c) the (110) plane above and below the plane in (b)

Figure 3.13: *Crystal structure of a CsCl-type B2 lattice (a); the planes in (b) and (c) are alternately stacked [15].*

The B2 structure could be viewed as a result of alternatively stacking the planes (b) and (c), giving an FCT cell .





It is thought that the martensitic transformations which occur in B2 phase alloys are due to: (I) an orthorhombic distortion, resulting in different values of the lattice parameters, but still right angles; (II) shearing, which is for NiTi in the [011]B2 direction along the (100)B2 plane, and (III) a planar shuffle: the atoms in alternate (011)B2 planes shift about 1/3 in the [01-1] direction.

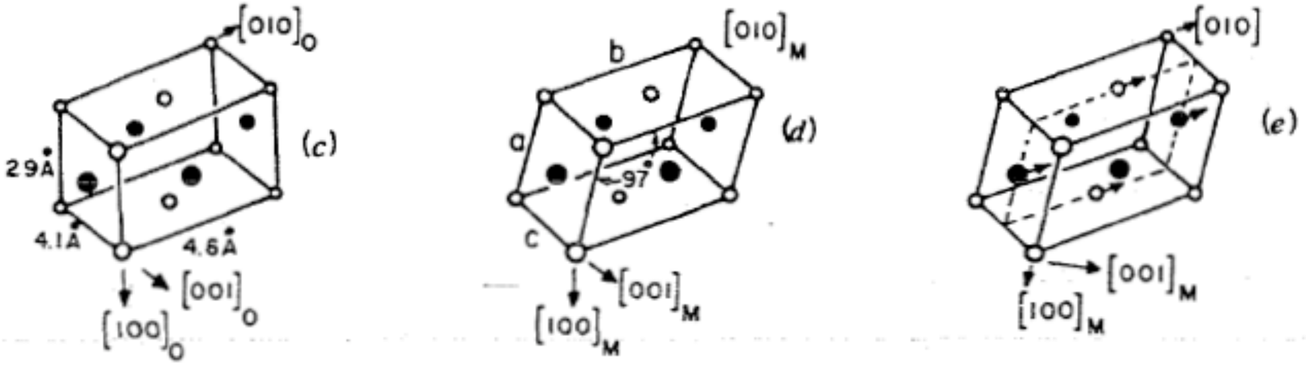


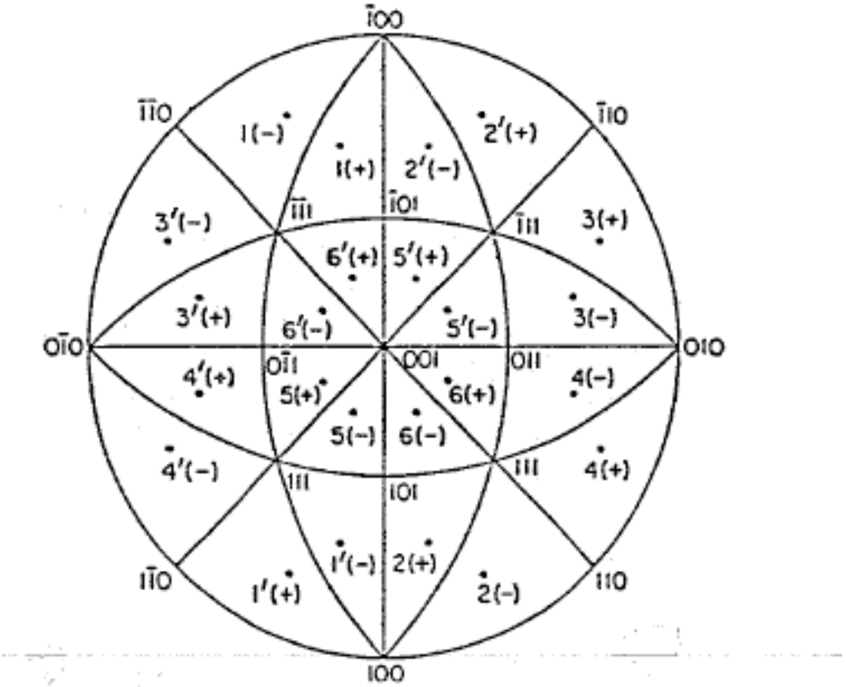
Figure 3.14: *Crystallographic 'steps' for the B2 → B19' transformation in NiTi. (a) B2 cells; (b) B2 ≡ fct cell; (c) orthorombic distortion; (d)* $(100)_{B2}[0\bar{1}\bar{1}]_{B2}$ *shear to monoclinic; (e)* $(011)_{B2}[01\bar{1}]_{B2}$ *planar shuffle.*

Variants in NiTi

Above the (100) plane was taken as the shear plane; however, crystallographically equivalent structures can be obtained by shearing in the (010) and (001) planes. The same holds for the shear directions.

The conclusion is that even though the parent phase consists of a single crystal, a number of different martensites, i.e. with different lattice correspondences and with different habit plane indices (but nonetheless crystallographically equivalent), will appear scattered throughout the specimen.

These martensites with different habit plane indices are called *variants.* In *BCC* SMA's, 24 variants are possible. These 24 variants do not come into existence randomly.



The number designation of each habit plane variant indicates the dominant (major) correspondence variant: variant 1 or **1’** is more dominantly present then variant 2, while variant 6 and *6’* are minor variants. The same number appears with and without a prime (’); this indicates that the pair are variants with oppositely directed shears. Finally, for a given shear plane and direction, there are two possible solutions for the habit plane indices, this is indicated by a (+) and (-).

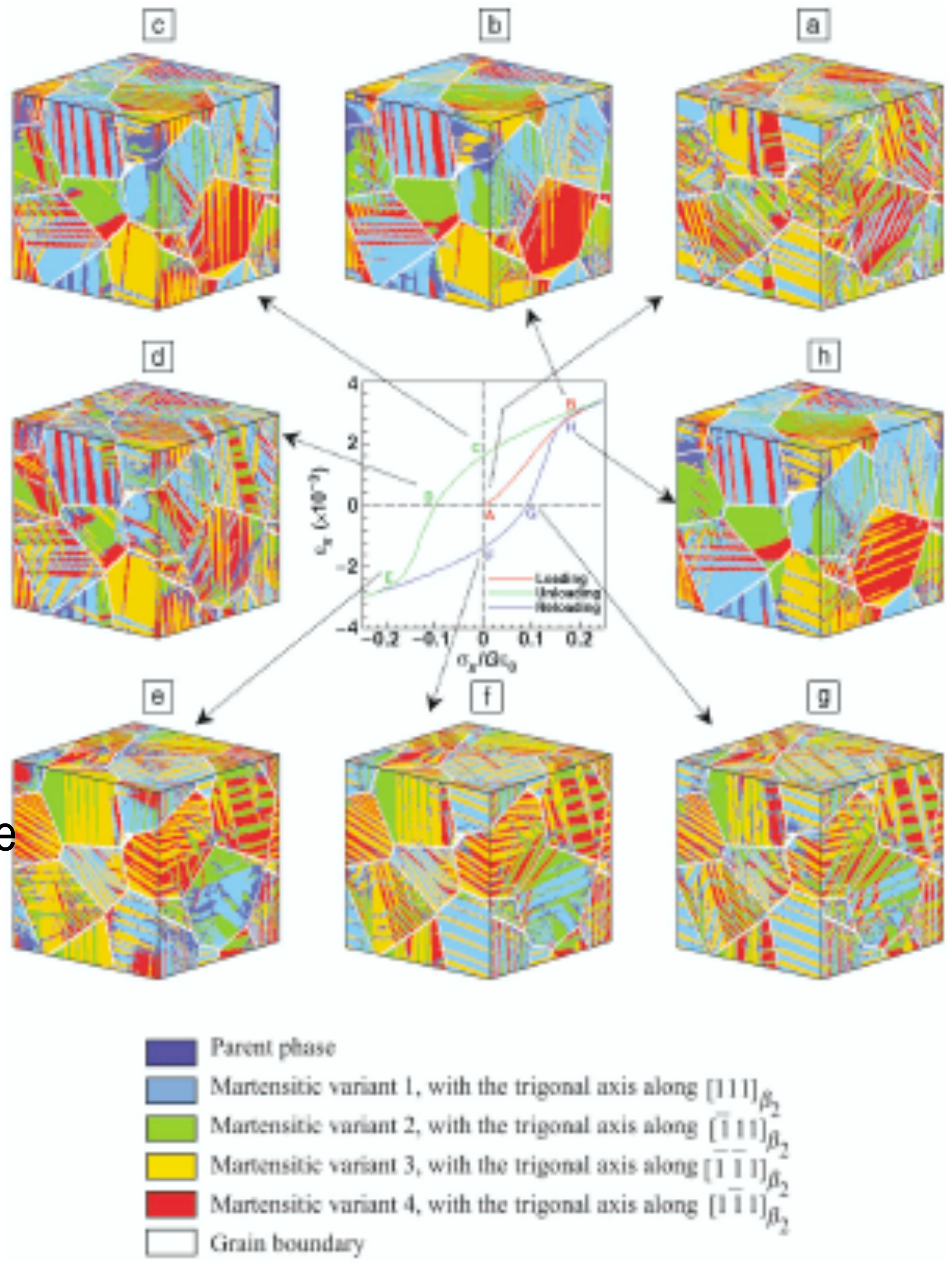


Figure 3. (a)–(h) Hysteresis loop and corresponding three-dimensional microstructures obtained at different stresses with $\zeta = 5$ for a polycrystal of a AuCd alloy consisting of eight randomly oriented grains in the computational cell.

What happens if an external stress is applied?

There are two different situations:

1. the starting material consists of a single twinned martensite plate, i.e. only one variant (dashed lines). By applying a shear stress, the internal interfaces, mostly twin boundaries, will move. One of the two twin variants will shrink (2) while the other (1) is growing resulting in the shown macroscopic shape change. On further stressing, eventually the plate will be totally *detwinned,* and plastic deformation like slip will commence.

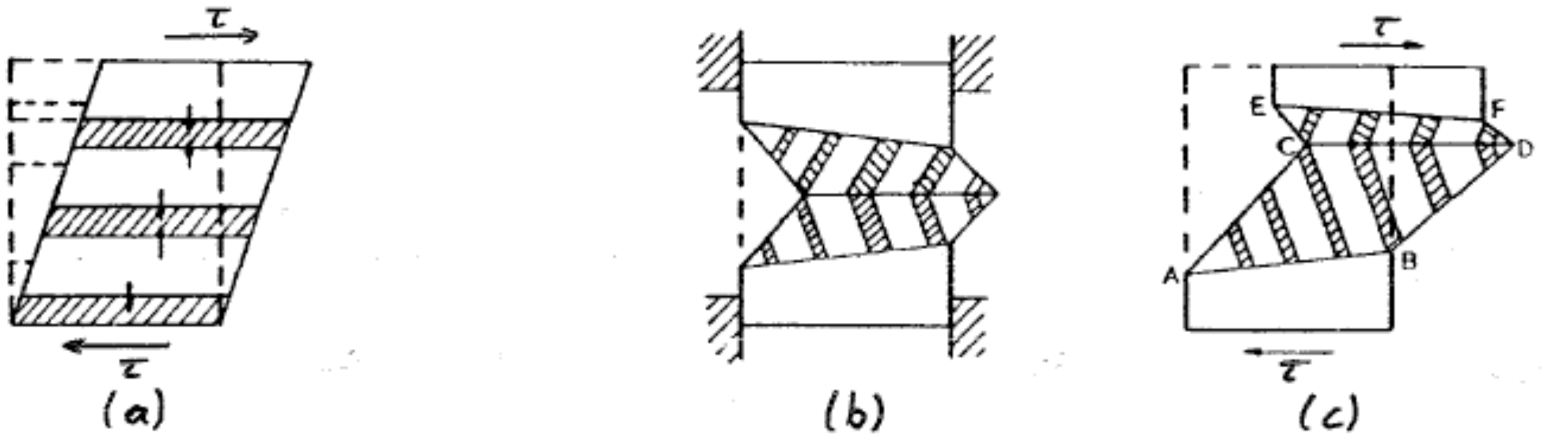
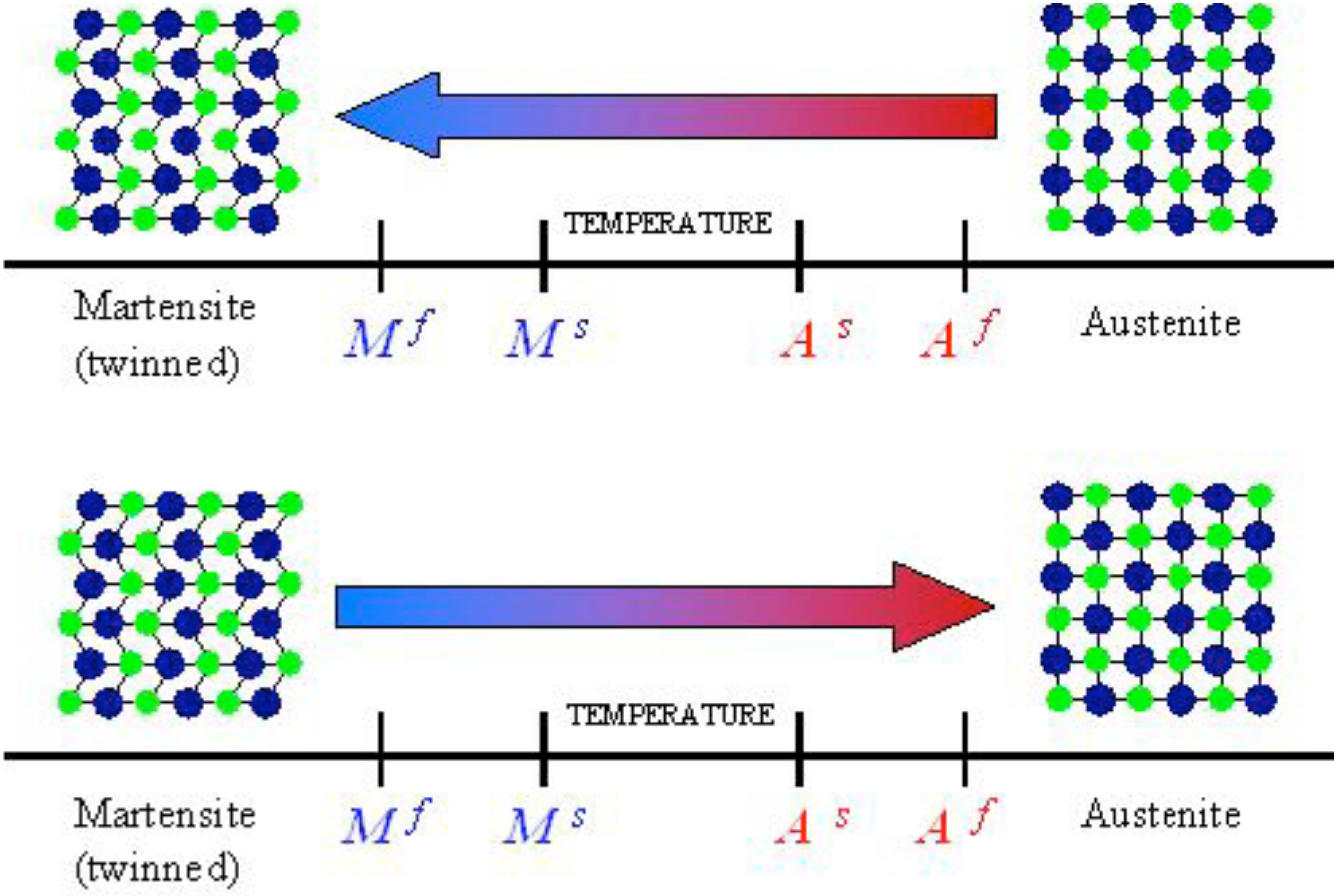


Figure 3.17: *Changes introduced upon application of external stress. (a) movement of the boundaries in between the different twin related variants; (b) two variants formed in a self-accomodating manner; (c) growth of one variant at the expense of the other caused by an external stress [22].*

2. the material consists of several variants, which is an idealized situation, where two out of the twenty-four martensite plate variants have grown together as a self-accommodating martensite plate group in order to minimize the strains and stresses. The parent phase above and below the martensite plates is kept fixed. If the sample is not kept fixed but strained by a shear stress, the martensite plate group tends to minimize the internal stresses by changing the amount of the two variants present. This means that the boundary CD between the two martensite plates moves or that the habit plane **AB** moves faster than the habit plane EF. So in this case certain variants grow at the expense of others by means of moving interfaces, and eventually only one variant persists (after which (1.) may occur).

This process is called *reorientation* of martensite variants.

Reverse Transformation



An important feature of the Shape Memory Effect is that on heating the specimen regains its original macroscopic form.

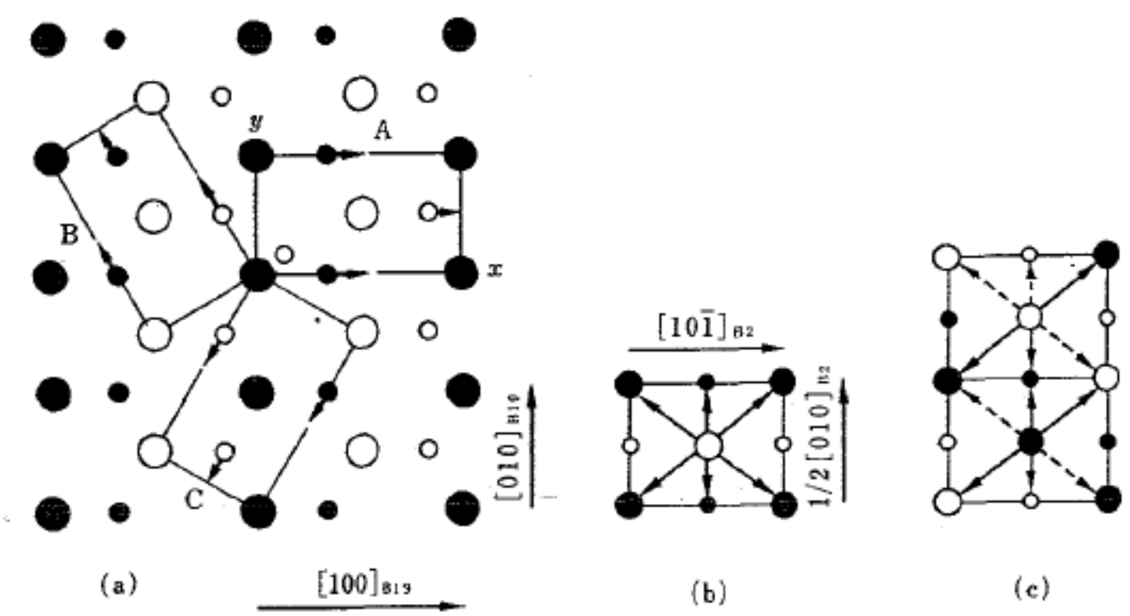


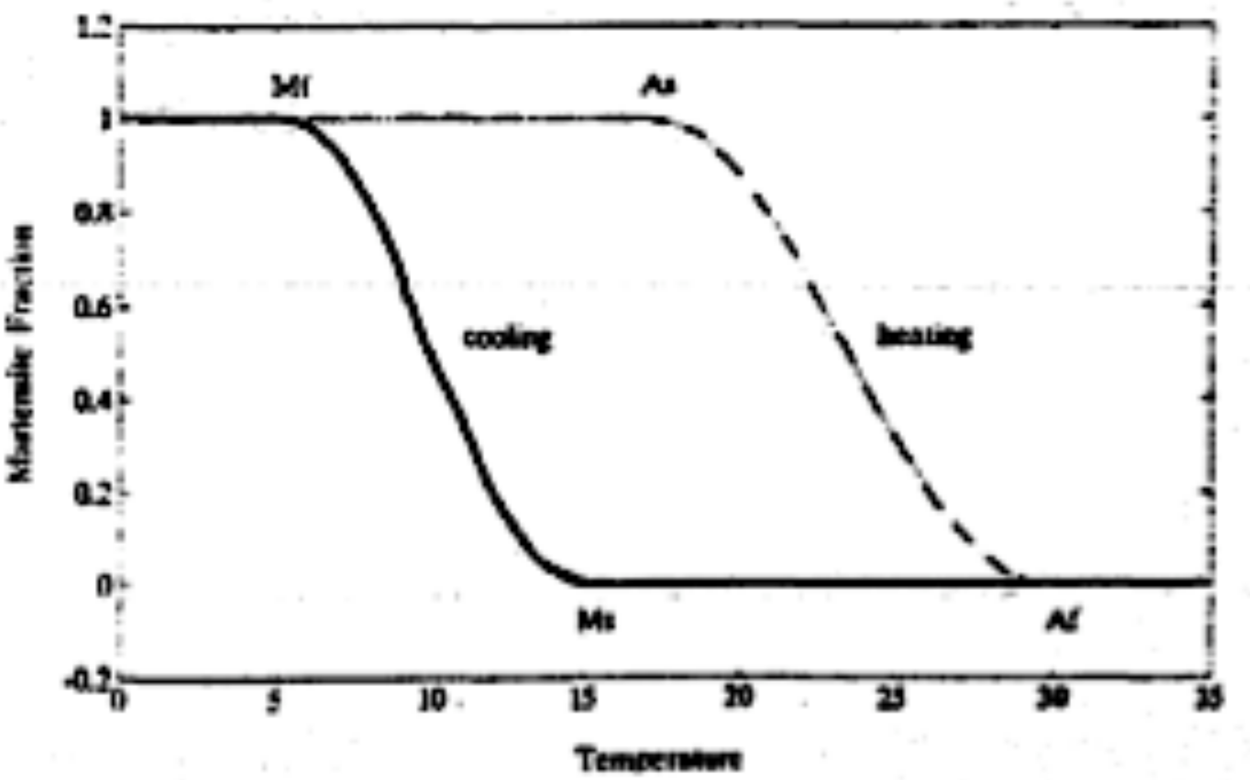
Figure 3.19: *(a) Three possible lattice correspondences in the reverse transformation of the B2 → B19 transformation; (b) parent phase crystal structure resulting from lattice correspondence A: a B2 superlattice the same as the pre-transformation structure; (c) parent phase crystal structure resulting from lattice correspondence B: completely different from a B2 structure [15].*

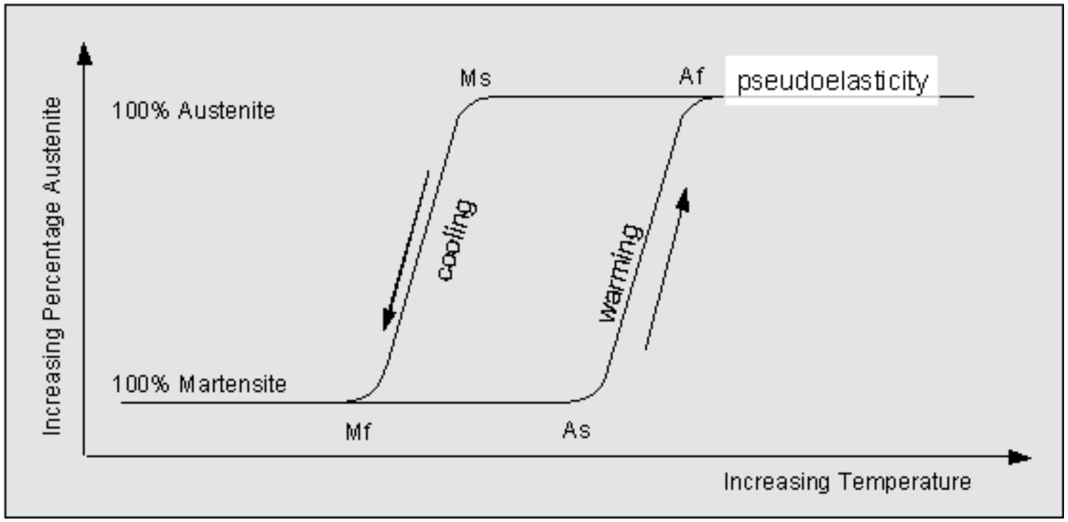
In the figure there are, three equivalent lattice correspondences, represented by the rectangles marked **A**, **B** and ***C***. If the reverse transformation occurs along path **A**, then the crystal structure of the product phase will be as shown in **(b),** and the **B2** superlattice structure of the parent phase will be preserved in both the forward and reverse transformations. However, if it occurs along either the **B** or ***C*** paths, the resultant crystal structure will be as shown in **(c)** **(**markedly differ from the original **B2** structure). The latter structure shown in **(c)** would raise the free energy, ***reverse transformations along path B or C are impossible***. Thus the orientation of the parent phase crystal is automatically preserved by its ordered structure.

Temperature Behavior of the Martensitic Transformation

The transformation temperature is the temperature at which a SMA changes from Austenite to Martensite or vice-versa.

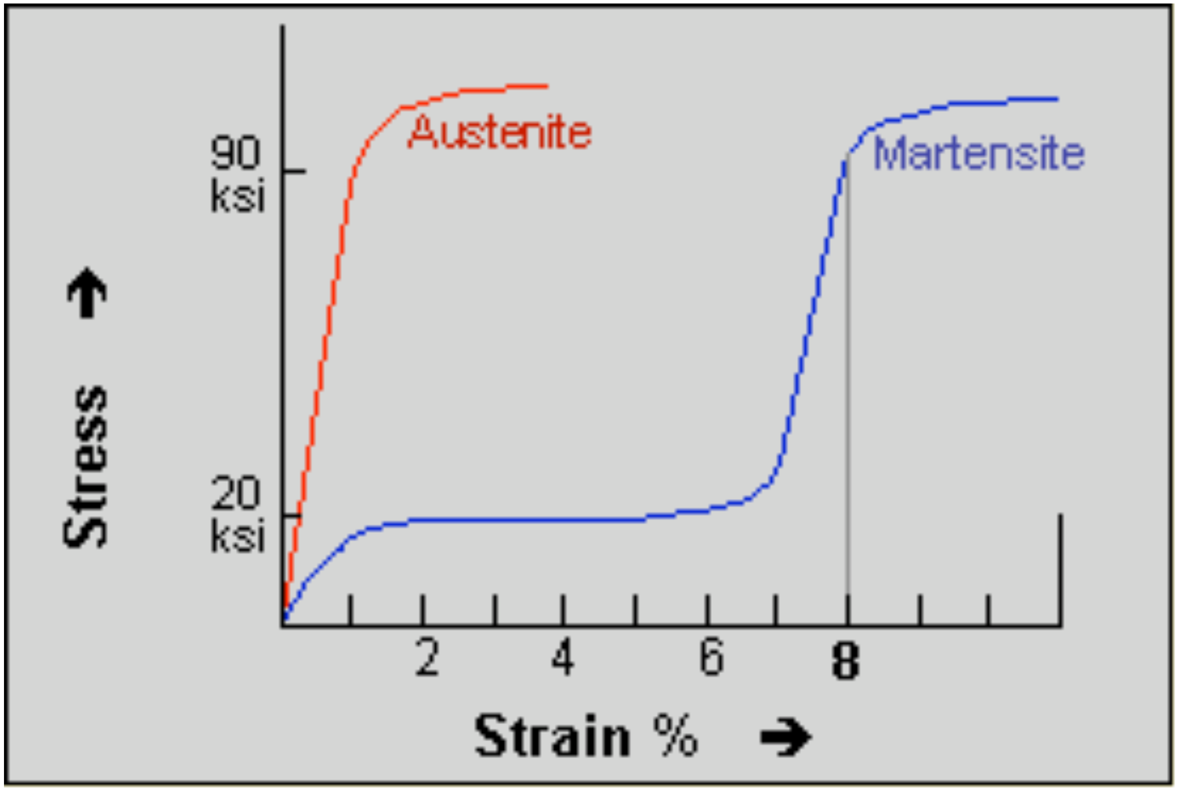
For any particular alloy chemistry, the transformation temperature can be changed by the processing history, and the stress conditions. Although for practical purposes a single transformation temperature can be used, the picture is somewhat complicated by hysteresis.





The higher temperature austenitic structure has the characteristic stress-strain curve of most metals. The lower temperature martensitic structure has a stress-strain curve more like that of an elastomer in which there is a plateau in the stress/strain curve.

All the deformation up to about 8% is *elastic* or in other words it can be recovered, but not by simply relaxing the stress whilst in the martensitic condition.



Martensitic transformations are usually divided into two ***groups—thermoelastic and non-thermoelastic***.

- The ***non-thermoelastic*** transformations occur mainly in ferrous alloys and are associated with non-mobile martensite-parent phase interfaces pinned by permanent defects and proceed by successive nucleation and growth. Due to re-nucleation of austenite during the reverse (martensite to austenite) transformation, these transformations are crystallographically non-reversible in the sense that the martensite cannot revert to the parent phase in the original orientation.

- The ***thermoelastic*** martensitic transformations, on the other hand, are associated with mobile interfaces between the parent and martensitic phases. These interfaces are capable of "backward" movement during the reverse transformation by shrinkage of the martensitic plates rather than nucleation of the parent phase, which leads to a crystallographically reversible transformation (Otsuka and Wayman, 1999). The unique properties of SMAs (i.e., shape memory effect, pseudoelasticity) are the result of thermoelastic martensitic transformation.

Thermoelasticity: The thermoelastic transformation is a transformation in which a given plate or domain of martensite grows or shrinks as the temperature is respectively lowered or raised, and the growth rate appears to be governed only by the rate of change in temperature.

The first observed and most well-known martensitic transformation occurs during the hardening of steel. In pure iron, the austenitic ***fcc*** lattice transforms into a *bcc* lattice. In quenched steel (Fe-C alloy), this transformation is prevented by the carbon atoms dissolved in the ***fcc*** lattice of iron. The structure that results is the martensite *bct* structure. The quenching is essential to prevent diffusion of C atoms out of the ***fcc*** lattice to form cementite (Fe_3C). This clearly shows the diffusionless character of the martensitic transformation. However, short distance diffusions, which always occur, and diffusion during heating cause the irreversibility of the martensitic transformation in steel. This kind of transformation is obviously ***non- thermoelastic.***

NiTi does show thermoelastic behaviour. Quenching is not needed to achieve a martensitic transformation: the transition from a B2 to a B19’ lattice also takes place during slow cooling near room temperature.

Summarized below are the main characteristics of martensitic phase transformations:

•It is associated with an inelastic deformation of the crystal lattice with no diffusive process involved. It results from a cooperative and collective motion of atoms over distances smaller than the lattice parameters. The absence of diffusion makes the martensitic phase transformation almost instantaneous (Nishiyama, 1978).

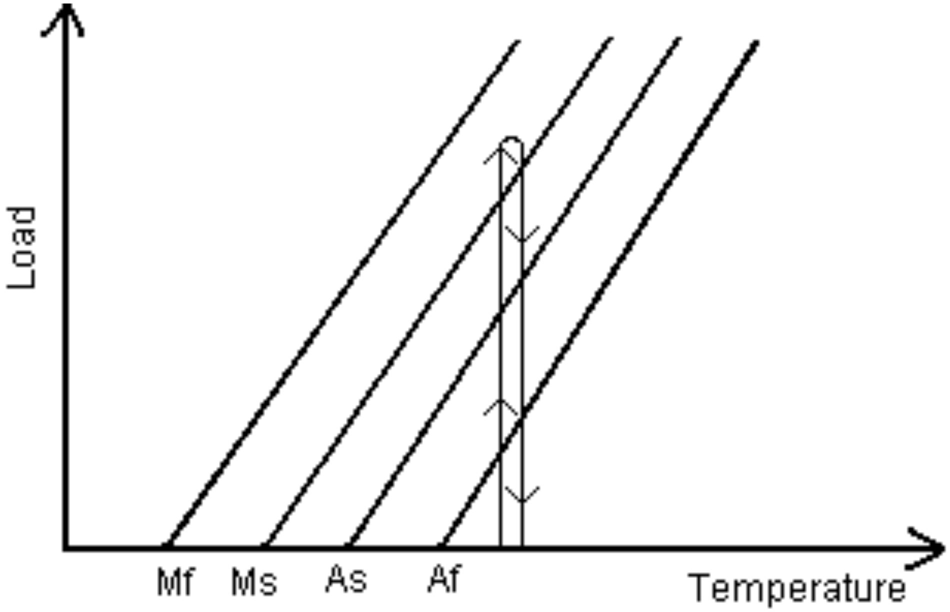
•Parent and product phases coexist during the phase transformation, since it is a first order transition, and as a result there exists an invariant plane, which separates the parent and product phases. The lattice vectors of the two phases possess well defined mutual orientation relationships (the Bain correspondences, see Bowles and Wayman, 1972), which depend on the nature of the alloy.

- Transformation of a unit cell element produces a volumetric and a shear strain along well defined planes. The shear strain is many times larger than the elastic distortion of the unit cell. This transformation is crystallographically reversible (Kaufman and Cohen, 1958).
- Since the crystal lattice of the martensitic phase has lower symmetry than that of the parent austenitic phase, several variants of martensite can be formed from the same parent phase crystal (De Vos et al., 1978).
- Stress and temperature have a large influence on the martensitic transformation. Transformation takes place when the free energy difference between the two phases reaches a critical value (Delaey, 1990).

Pseudo Elasticity or Superelasticity

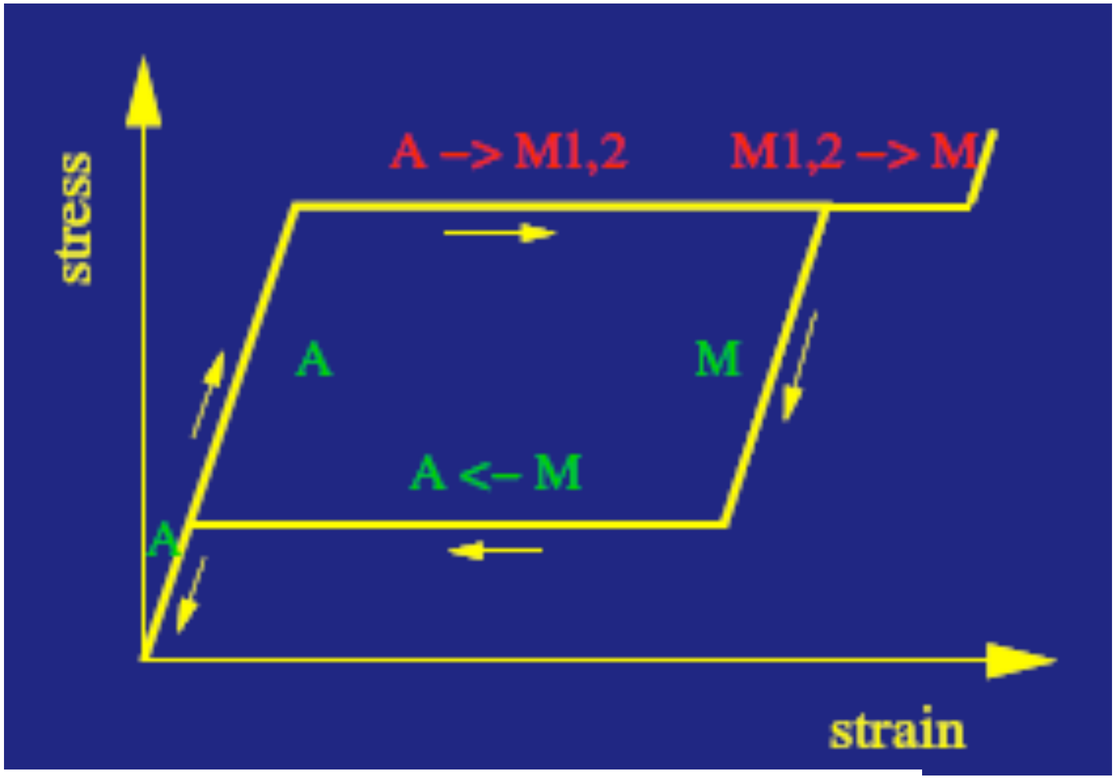
Pseudo-elasticity occurs in SMAs when the alloy is completely composed of Austenite (temperature is greater than ***Af***). Unlike the shape memory effect, pseudo-elasticity occurs without a change in temperature. .

The load on the shape memory alloy is increased until the Austenite becomes transformed into Martensite simply due to the loading. The loading is absorbed by the softer Martensite, but as soon as the loading is decreased the Martensite begins to transform back to Austenite since the temperature of the alloy is still above ***Af***, and the wire springs back to its original shape



Some examples of applications in which pseudo-elasticity is used are:

- Eyeglass Frames
- Brassieres Underwires
- Medical Tools
- Cellular Phone Antennae
- Orthodontic Arches



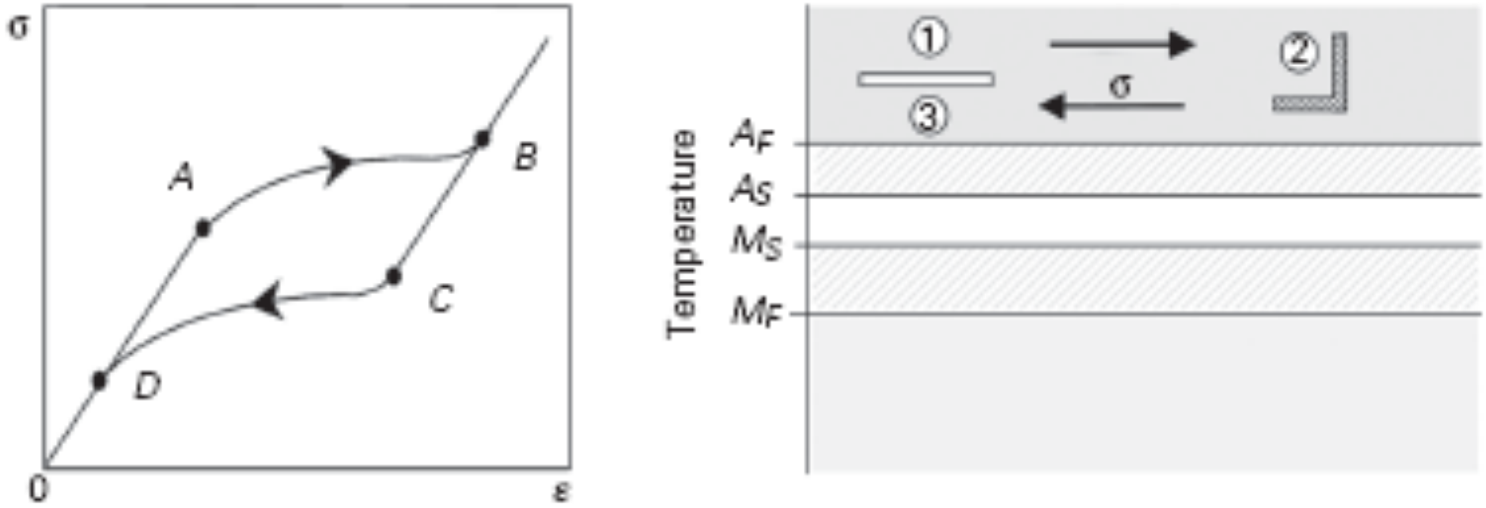
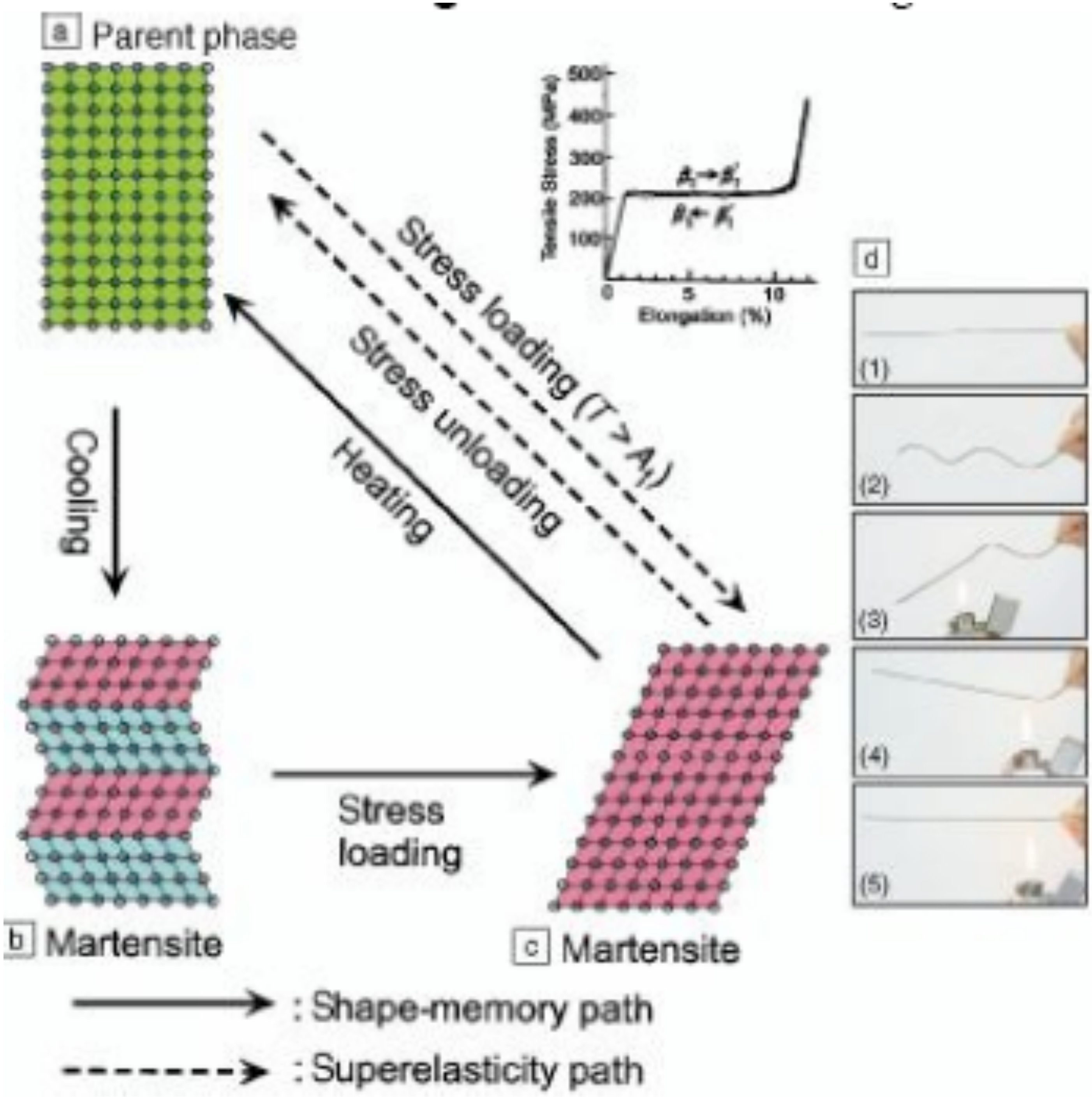
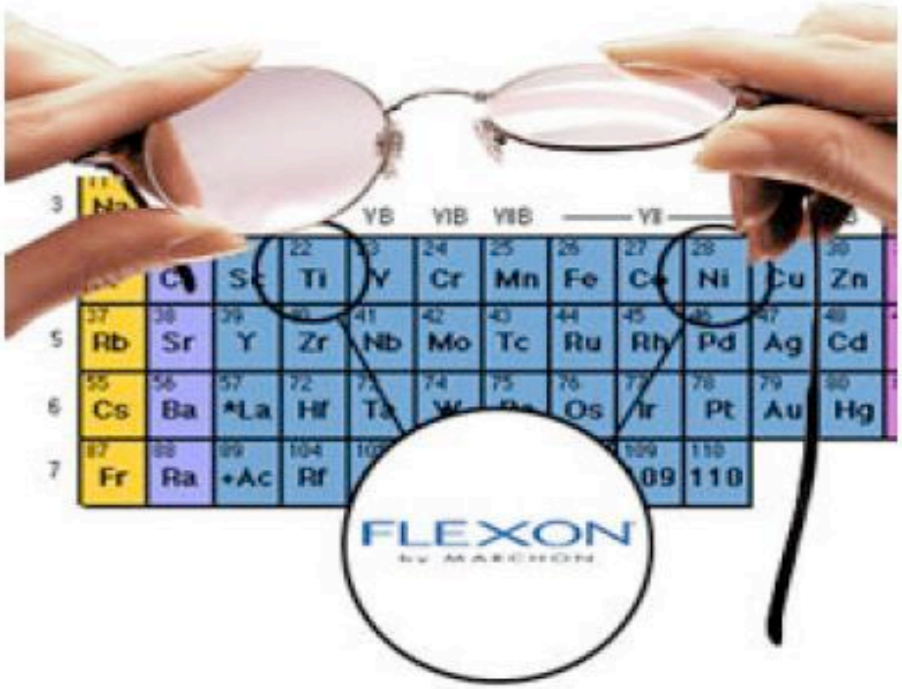


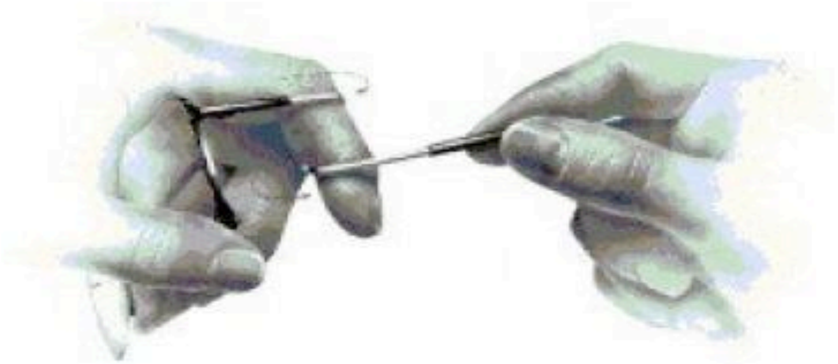
Figure 1. Pseudoelasticity. A_S, A_F and M_S and M_F = temperature at which the formation of austenite and martensite starts and ends, respectively. σ-ε = stress-strain curve. See text

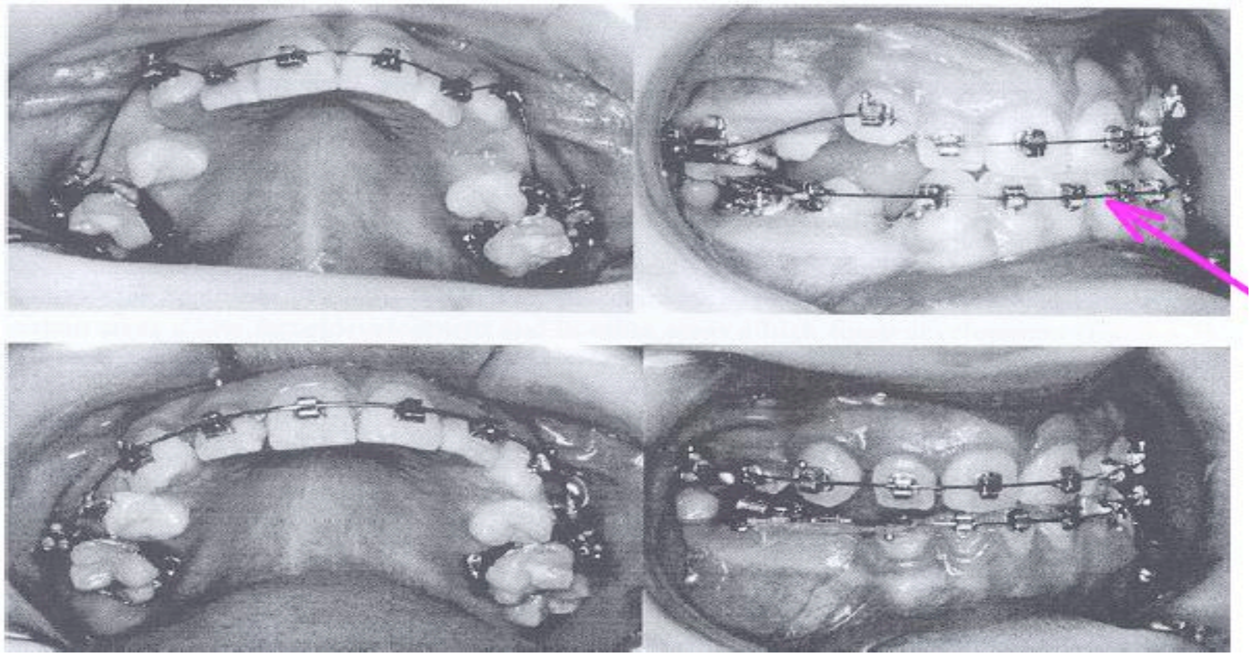

a Parent phase
Tensile Stress (MPa)
500
400
300
200
100
0
5
10
Elongation (%)
$\beta_1 \rightarrow \beta_1'$
$\beta_1 \leftarrow \beta_1'$
Stress loading ($T > A_f$)
Stress unloading
Heating
Cooling
d
(1)
(2)
(3)
(4)
(5)
Stress loading
b Martensite
c Martensite
: Shape-memory path
: Superelasticity path

Pseudoelasticity is observed when the martensitic phase transformation is induced by applied thermomechanical loading of the austenitic phase in which case detwinned martensite is directly produced from austenite.

The process is associated with large inelastic (transformation) strains which are recovered upon unloading due to the reverse phase transformation (Wayman, 1983).







Capability for so called "constant force" action on the strain of up to 6% results in wider and wider application of orthodontic wires made of NiTi.

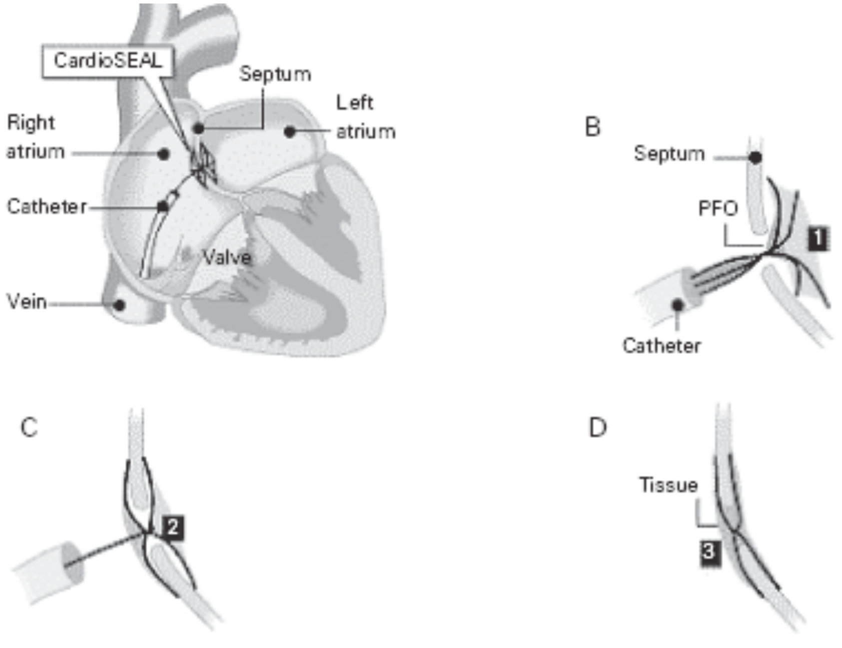
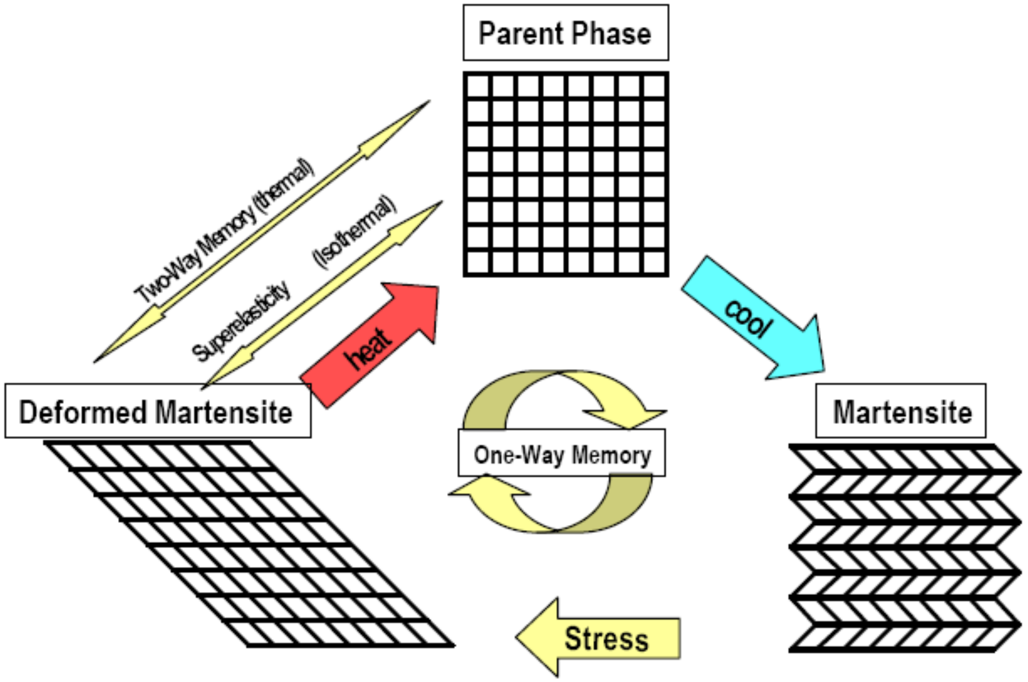
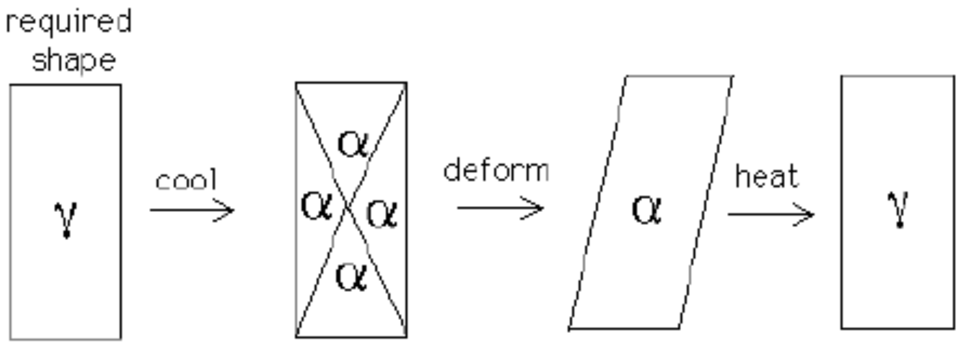


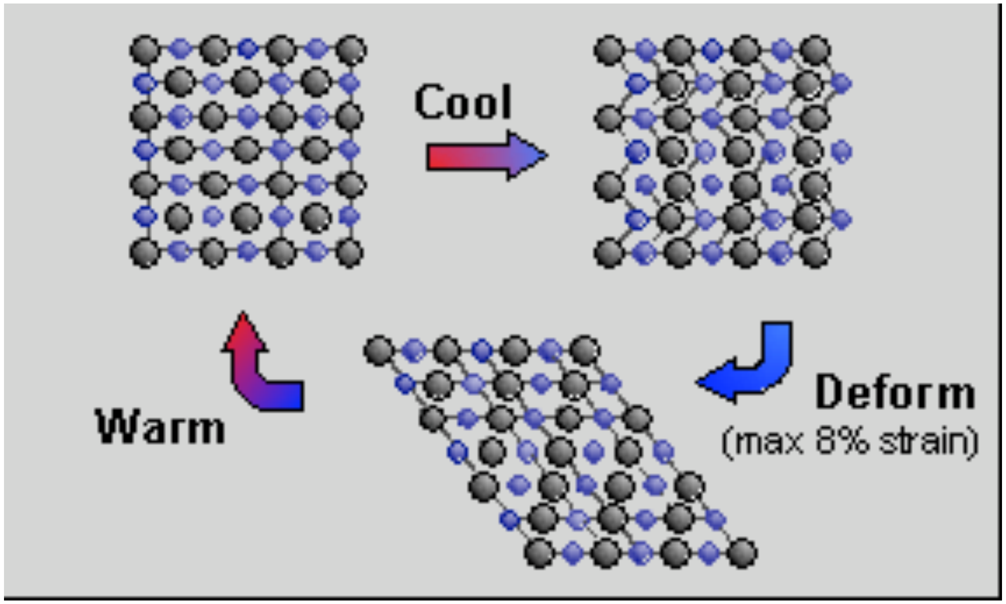
Figure 6. Atrial septal occlusion device. *A*, Scheme of the heart with the device in place. *B*, The first half of the device is placed in the left atrium. *C*, The second half of the device is placed in the right atrium. *D*, The catheter is withdrawn and the tissue begins its recovery. PFO = patent foramen ovale. Taken from Ref. 26 (http://www.nmtmedical.com).



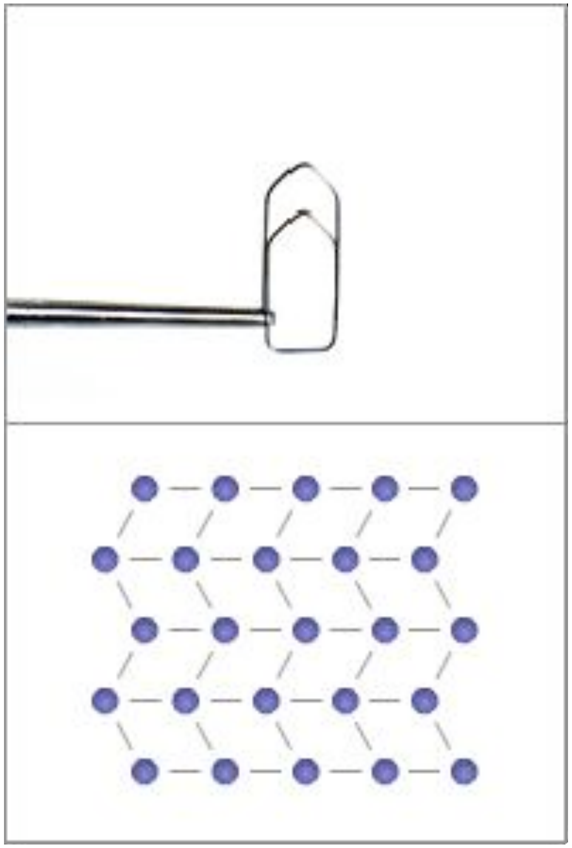
Shape Memory Effect



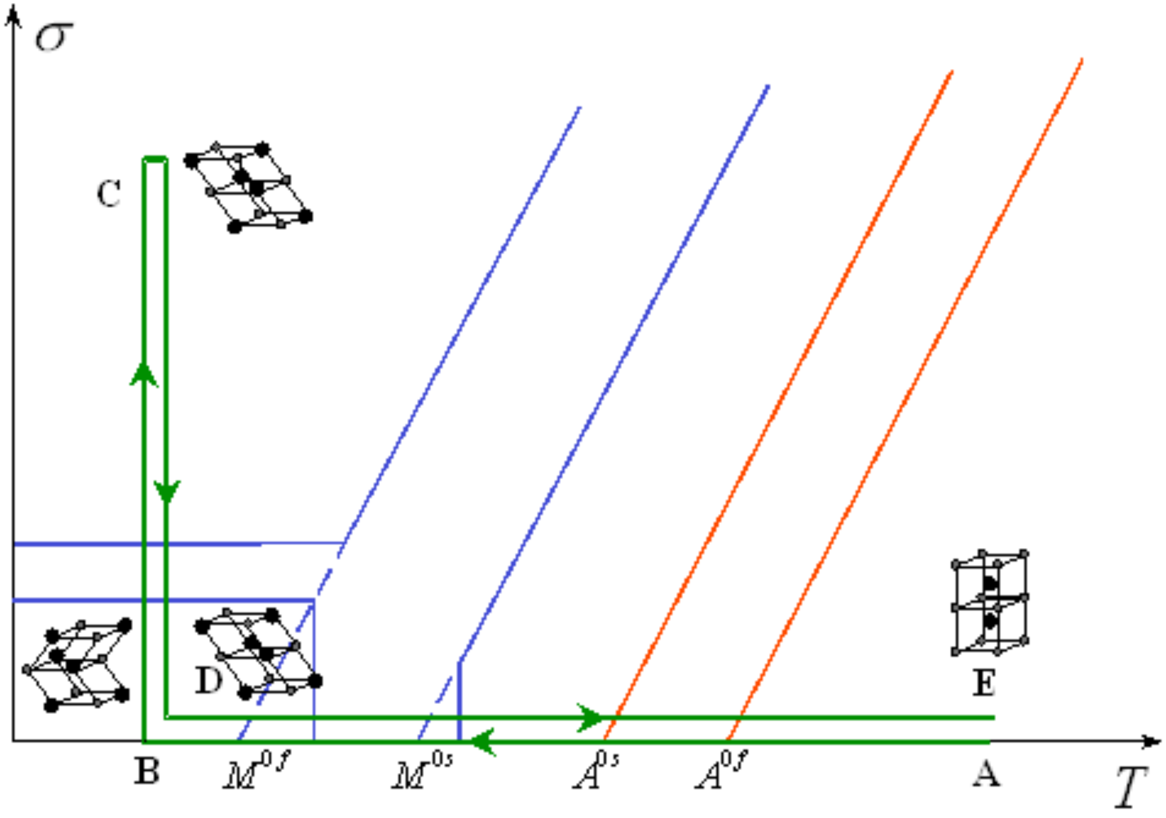
We cool the material and it becomes martensitic. It does not change shape by being cooled, but we can now deform it mechanically.



If it stays cold it will remain deformed, but if we allow it to warm up, the austenitic structure re-appears and the material returns to its original shape.
This cycle from austenitic to martensitic to deformed martensitic and back to austenitic is repeatable indefinitely and is what we call “free recovery”. It is important to note that it is a “One-Way” process, we can only go around clockwise.



DE

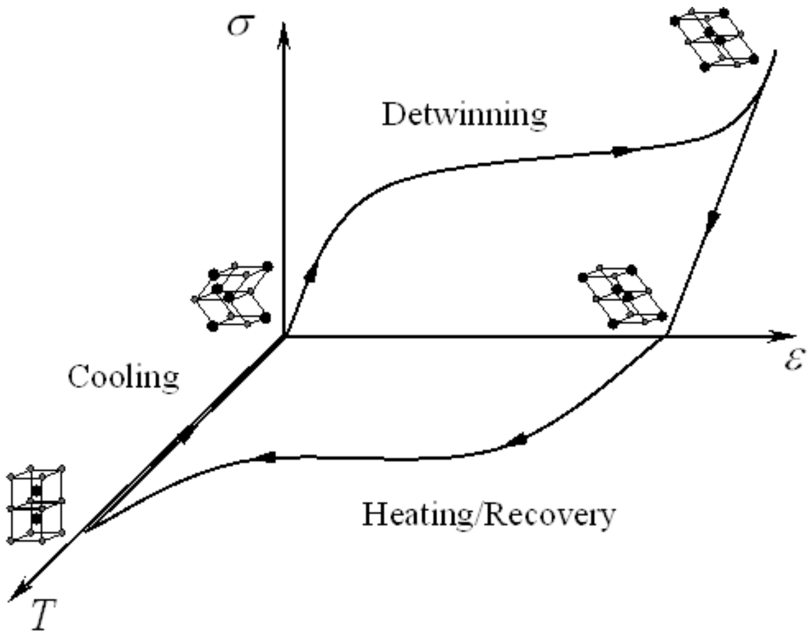


AB – Austenite is cooled and it transform into martensite with many twinning variants.

BC - At low temperature, the material is deformed. The martensite with many variants is detwinned because it is subjected to stresses.

CD – The stresses are eliminated

DE – The detwinned martensite transforms into austenite and it recovers its previous shape.



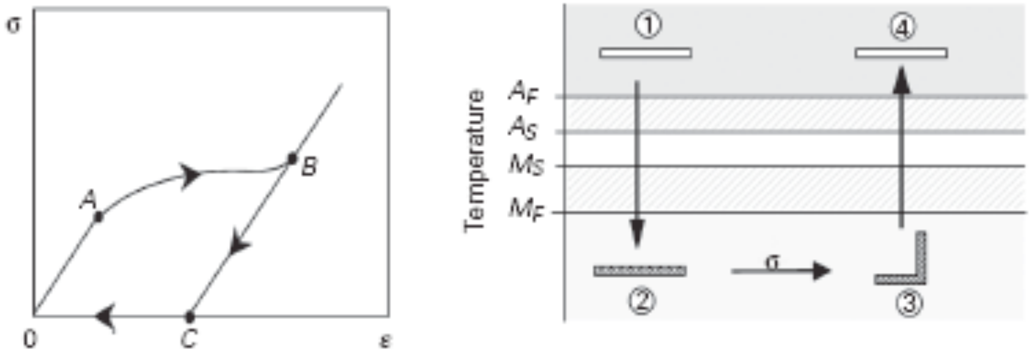


Figure 2. Shape memory effect. For abbreviations, see legend to Figure 1. See text for

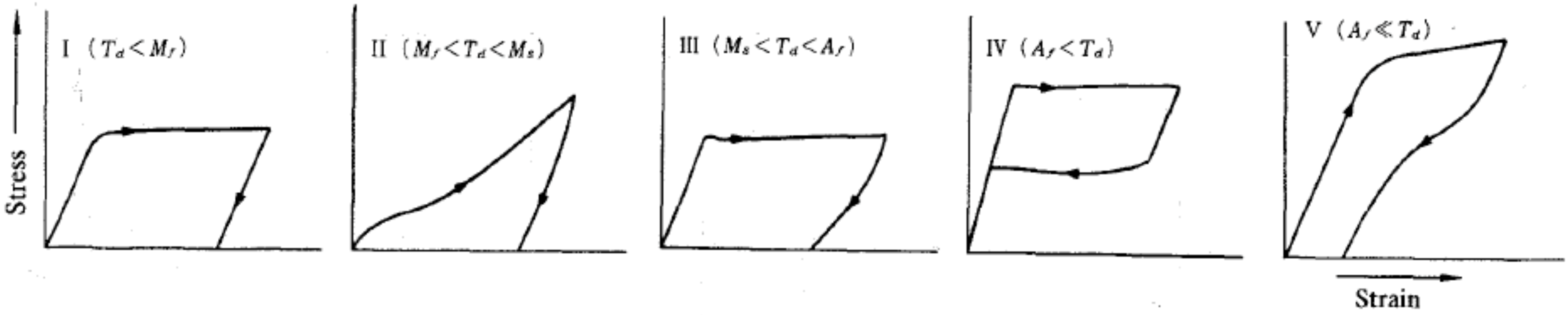


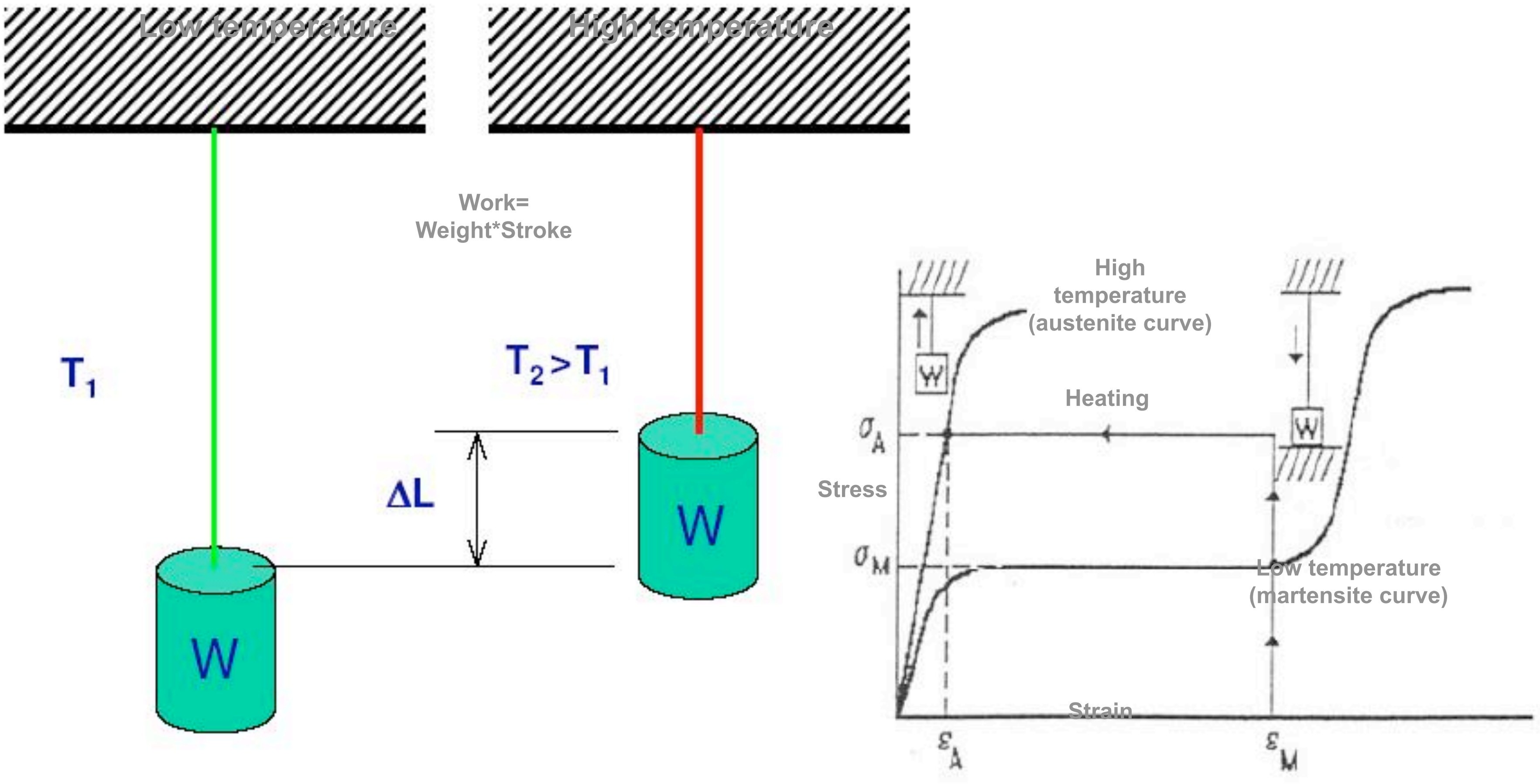
Figure 4.2: *Five types of stress-strain curves for NiTi systems [15].*

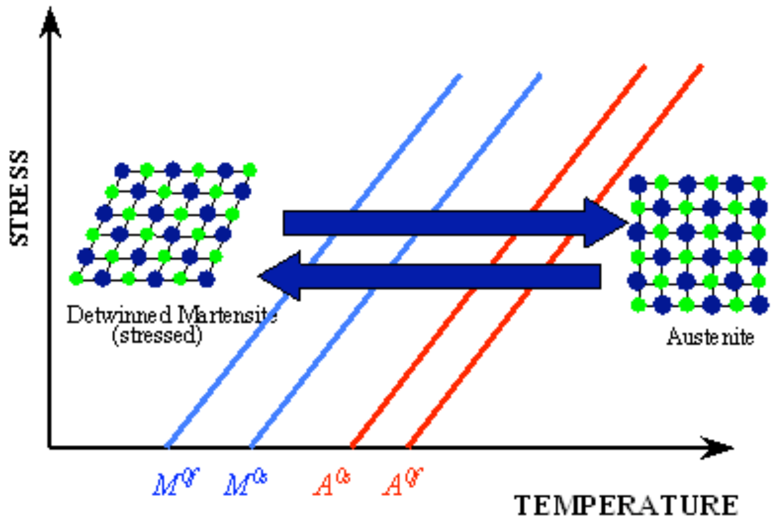
Alloy	Composition	M$_s$ (°C)	Transformation Temperature Hysteresis (°C)	Type of Transformation*	Ordered or Disordered	Volume Change
AgCd	44~49at.%Cd	−190~−50	~15	B2→M2H	ordered	−0.16
AuCd	46.5~50at.%Cd	30~100	~15	B2→M2H	ordered	−0.41
CuAlNi	14~14.5wt.%Al 3~4.5wt.%Ni	−140~100	~35	DO$_3$→2H	ordered	−0.30
CuAuZn	23~28at.%Au 45~47at.%Zn	−190~40	~ 6	L21→M18R	ordered	−0.25
CuSn	~15at.%Sn	−120~30		DO$_3$→2H or18R	ordered	
CuZn	38.5~41.5wt.%Zn	−180~−10	~10	B2→9R or M9R	ordered	−0.5
CuZnX (X=Si, Sn, Al, Ga)	few wt.% ×	−180~100	~10	B2→9R or M9R DO$_3$→18R or M18R	ordered	
InTl	18~23at.%Tl	60~100	~ 4	FCC→FCT	disordered	−0.2
NiAl	36~38at.%Al	−180~100	~10	B2→M3R	ordered	−0.42
TiNi	49~51at.%Ni	−50~100	~30	B2→B19	ordered	−0.34
FePt	~25at.%Pt	~−130	~ 4	L1$_2$→ ordered BCT	ordered	0.8~−0.5
FePd	~30at.%Pd	~−100		FCC→FCT→BCT	disordered	
MnCu	5~35at.%Cu	−250~180	~25	FCC→FCT	disordered	

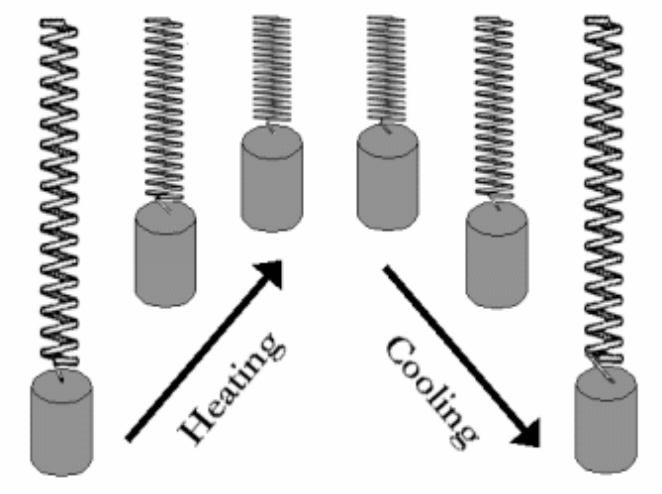
* FCT means face centered tetragonal lattice; BCT means body centered tetragonal. For other symbols see section 1.2.3.

Free recovery mode of operation

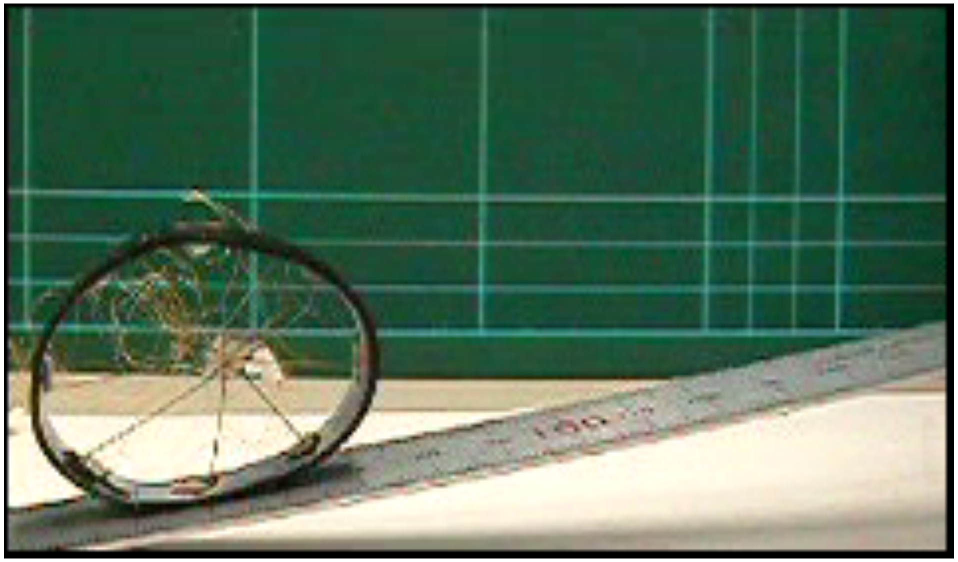
Shape memory alloy materials can perform work similarly to standard heat engines.







Physical Properties	NiTi	Cu Based Alloys
Density	6.4-6.5 gcc^{-1}	7.1-8.0 gcc^{-1}
Melting Point	1250°C	950-1050°C
Thermal Conductivity		
Martensite	8.6-10.0 W m°C^{-1}	- W m°C^{-1}
Parent Phase	18.0 W m°C^{-1}	75-120 W m°C^{-1}
Electrical Resistivity		
Martensite	0.5-0.6 $\times 10^{-6}\Omega$m	0.14 $\times 10^{-6}\Omega$m
Parent Phase	0.82-1.1 $\times 10^{-6}\Omega$m	0.07 $\times 10^{-6}\Omega$m
Coeff' of Thermal Expansion		
Martensite	6.6 $\times 10^{-6}$°C^{-1}	16.0-18.0$\times 10^{-6}$°C^{-1}
Parent Phase	10.0-11.0 $\times 10^{-6}$°C^{-1}	- $\times 10^{-6}$°C^{-1}
Specific Heat Capacity	470-620 J Kg °C^{-1}	390-440 J Kg °C^{-1}
Enthalpy of Transformation	19.0-28.0 JKg^{-1}	7.0-9.0 JKg^{-1}
Transformation Temperature Range	-200-120°C	-200-+200°C
Corrosion Performance	Excellent	Poor
Bio-compatibility	Excellent	Assumed Poor



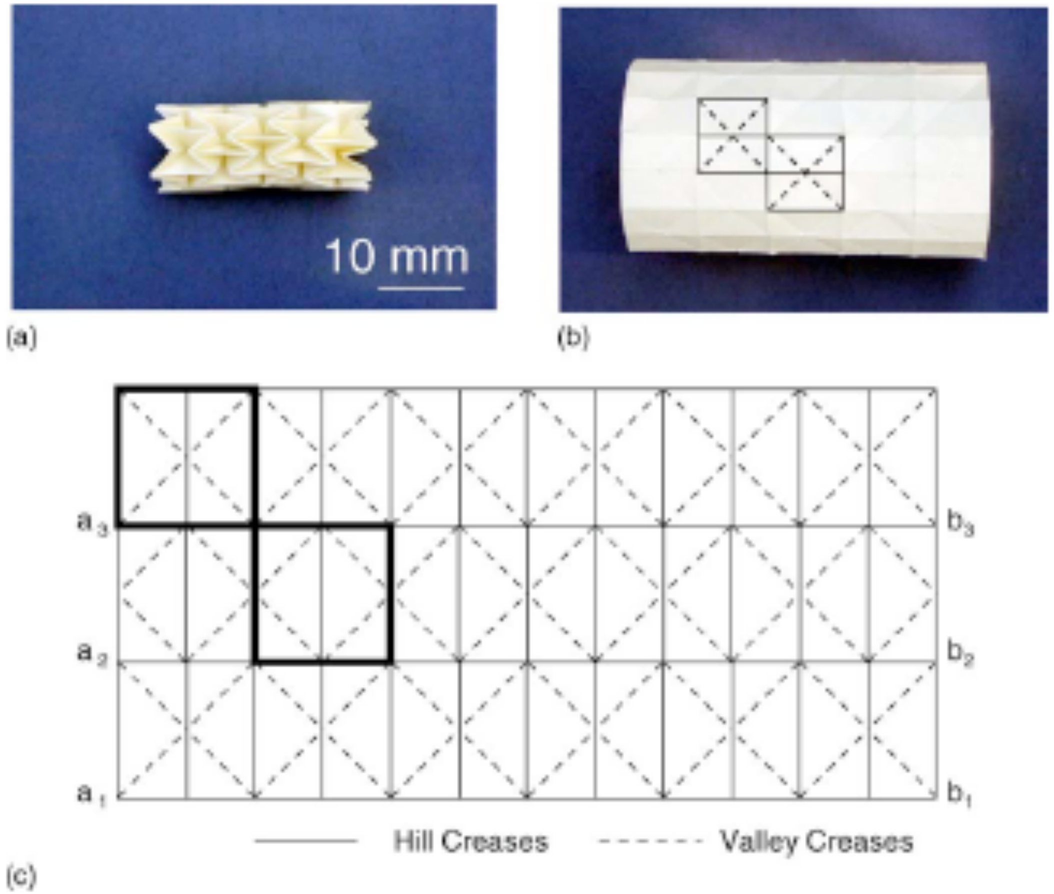


Fig. 1. Photographs of a card model of the origami stent graft in its (a) fully folded, (b) deployed configurations and (c) deployment of the folding pattern. The opposite edge of a sheet, a_1-a_2-a_3 and b_1-b_2-b_3 are joined together to form a cylindrical tube.

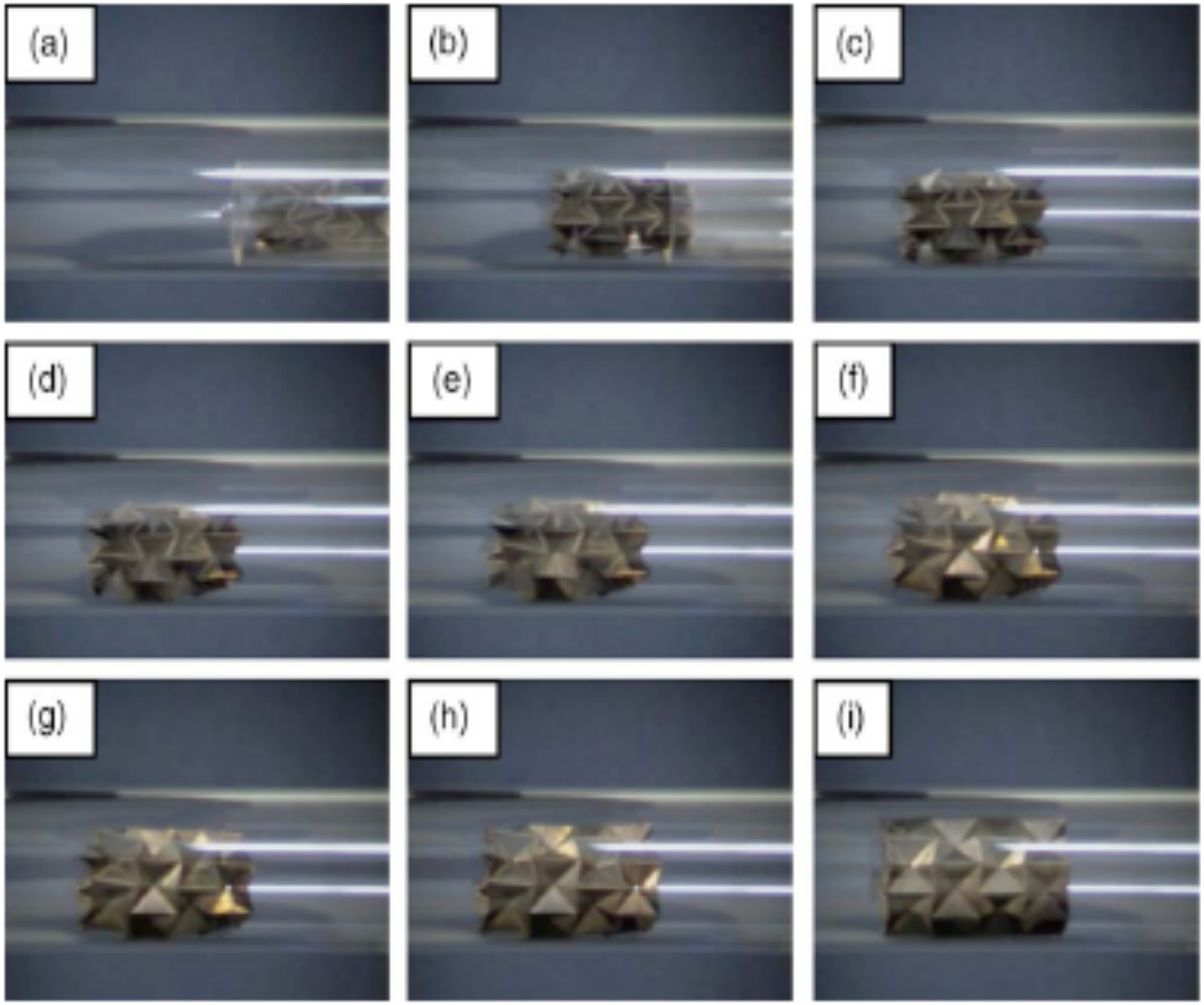


Fig. 6. Series of frames from video recording showing self-deployment of the stent (side view): (a) stent graft which is folded and backed into a small acrylic tube of 13 mm radius was inserted into another acrylic tube of 25 mm radius and (b) the small acrylic tube was removed and (c–i) the stent graft was self-expanding at above A_f (319 K).

Functional Properties of Shape Memory Alloys

SMAs have different shape-memory effects and can be used in different ways.

One-Way Shape-Memory Effect

A shape memory element can be deformed in its martensitic state to almost any “cold shape.” The basic restriction is that the deformations may not exceed a certain limit, typically 8%. These apparent plastic deformations can be recovered completely during heating when the reverse transformation occurs and results in the original “hot shape.” This strain and shape recovery during heating is called the *one-way shape-memory effect* because only the hot shape is memorized.

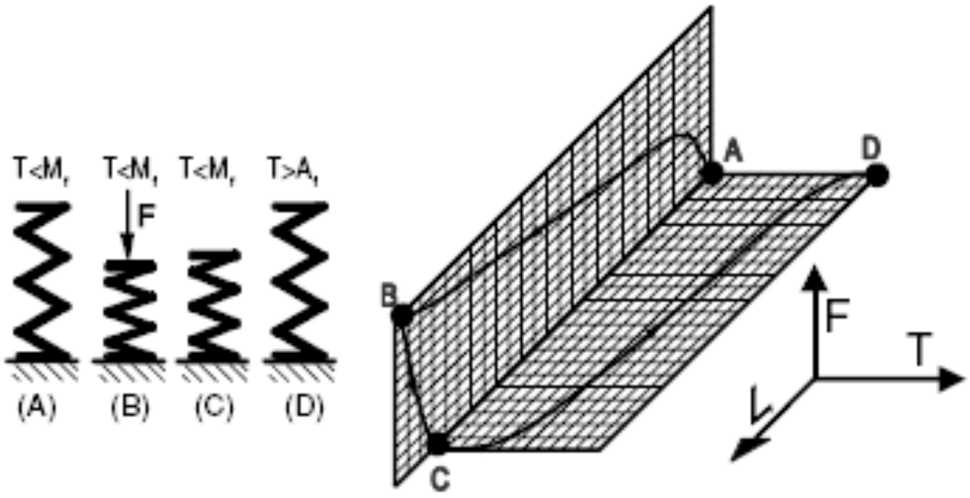
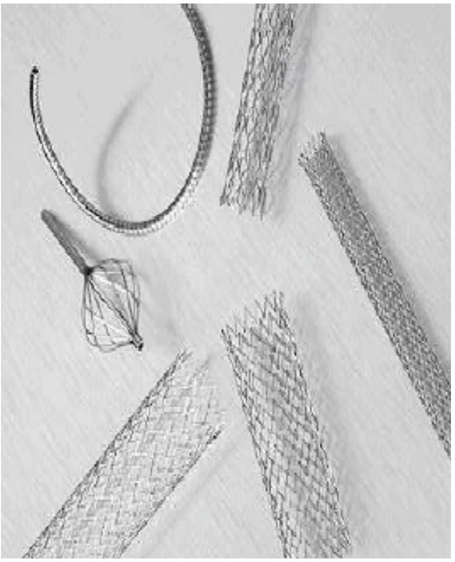


Figure 1. The one-way memory effect. The sample is deformed (A→B) and unloaded (B→C) at a temperature below M_f. The apparent plastic deformation is restored during heating to a temperature above A_f (C→D). Length change, load, and temperature are indicated, respectively, by L, F, and T [from (69)].

Physical basis for this one-way effect (reverse martensitic transformation):

1. The preferential orientation of the martensitic variants originates from the application of stress (below *M*f).
2. The reverse transformation to the parent phase during heating is accompanied by a strain and shape recovery.
3. The one-way shape-memory effect is thus a property *inherent* in the reversible, thermoelastic martensitic transformation.
4. The preferential orientation of the martensitic variants can also be obtained during the forward transformation that causes preferentially oriented formation of martensite. Thus, the apparent plastic strain is caused by the preferential orientation of martensite.



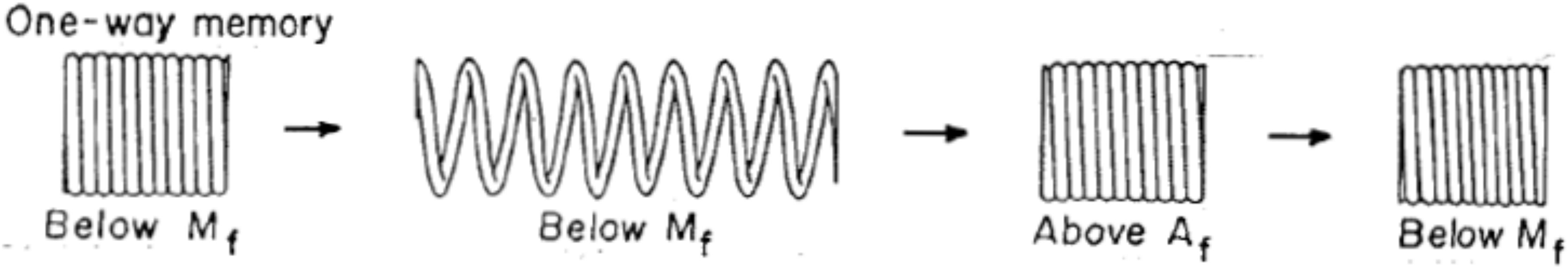


Figure 4.4: *Coil spring example showing the One Way Memory Effect [11].*

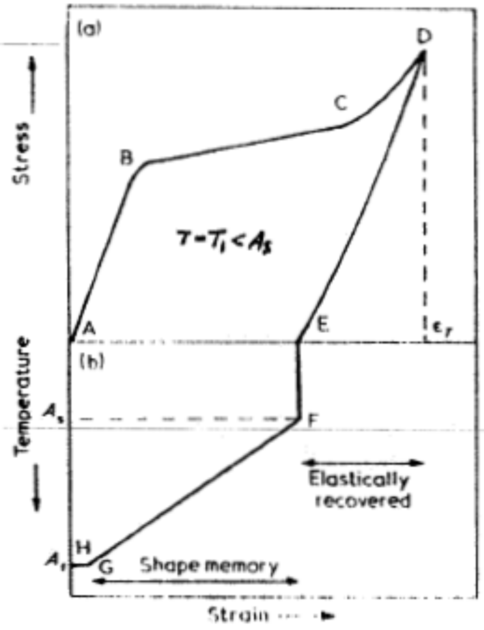


Figure 4.5: *Schematic representation of a stress-strain curve showing the Shape Memory Effect; (a) the deformation stage; (b) the shape recovery while heating the specimen [22].*

Two-way Shape Memory Effect

Shape memory effect normally describes the one-way shape memory effect, where an externally applied load is required to promote de-twinning and/or reorientation of the martensite variants so that a new deformed shape can be obtained and recovered upon heating above Af.

Subsequent cooling from the austenite to the martensite phase does not induce large strains i.e. new shape.

If large transformation strains are generated during both heating and cooling of the material, then this property is known as the two-way shape memory effect and was observed for the first time by Perkins (1974).

The two-way shape memory is not an intrinsic but an acquired characteristic. It can be obtained by cyclic repetition of certain thermomechanical loading paths.

Two-Way Shape-Memory Effect and Training

The two-way memory effect involves memorization of two shapes. The figure shows that a cold shape is obtained spontaneously during cooling. Different from the one-way memory effect, no external forces are required to obtain the “memorized” cold shape. During subsequent heating, the original hot shape is restored. The maximum strains are in general substantially smaller than those of the one-way memory effect. A strain limit of about 2% has been mentioned, although higher TWME strains have been found in specific cases.

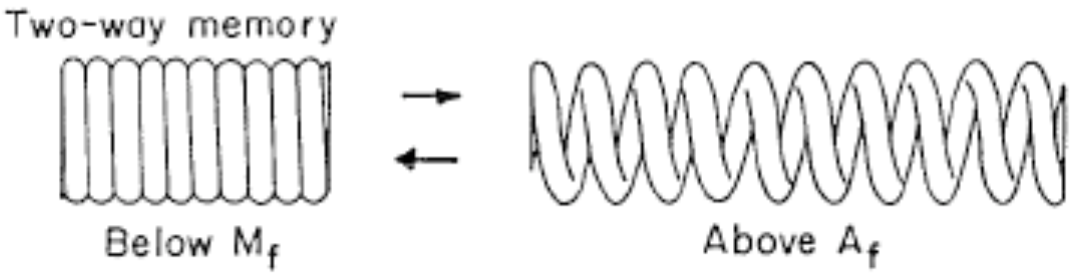


Figure 4.6: *Coil spring example showing the Two Way Memory Effect [11].*

Typically, there are two training procedures (23): thermal cycling with constant stress and thermal cycling with imposed strain. Both induce considerable plastic strains.

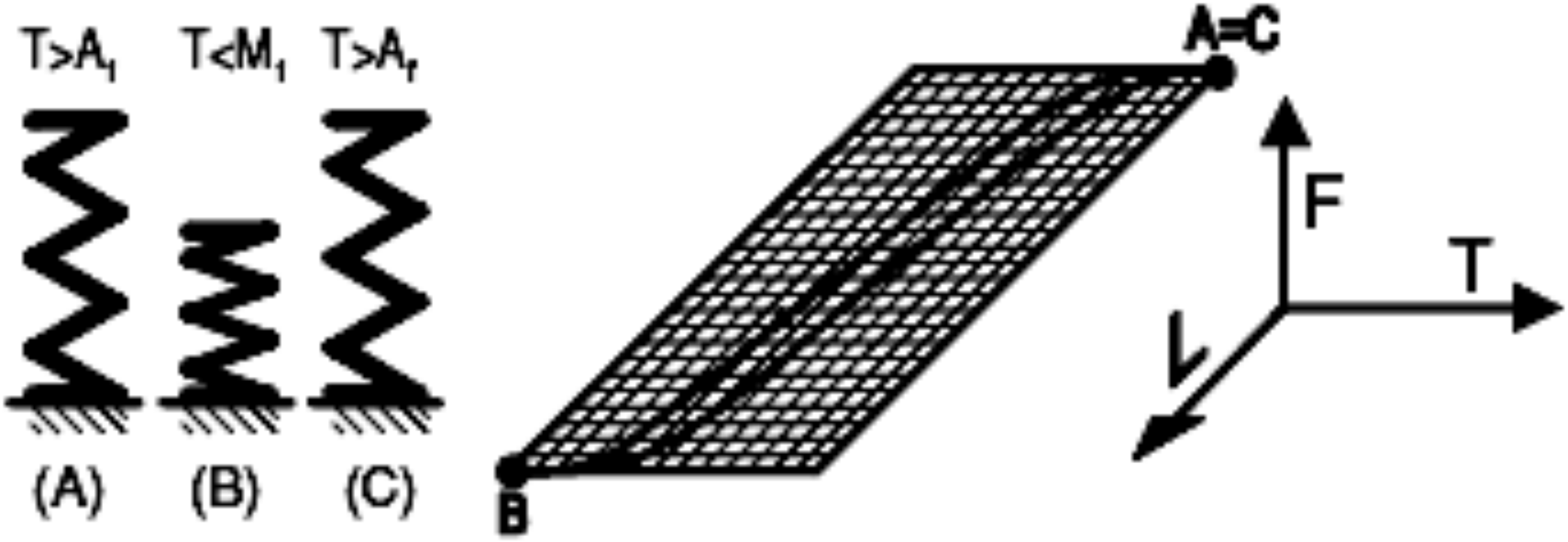


Figure 2. The two-way memory effect. A spontaneous shape change occurs during cooling to a temperature below M_f (A→B). This shape change is recovered during subsequent heating to a temperature above A_f (B→C) [from (69)].

Thermal Cycling with a Constant Stress

When a constant stress (e.g. torsion τ), which is insufficient to induce the martensite, is applied at a temperature ***T >Af***, then during cooling the M***s*** temperature is attained for one particular variant, giving rise to a large strain γ.

On heating the specimen will ordinarily return into its austenitic state. When such thermal cycles are repeated a number of times (N>10 to stabilize the hysteresis loop), it is consequently observed that, without any external applied stress, a spontaneous strain occurs in the same direction as with the stress; its amplitude depends on the number of cycles and on the applied stress during training. This type of training is the most efficient one. It also allows to predict the high and low temperature shapes with good accuracy.

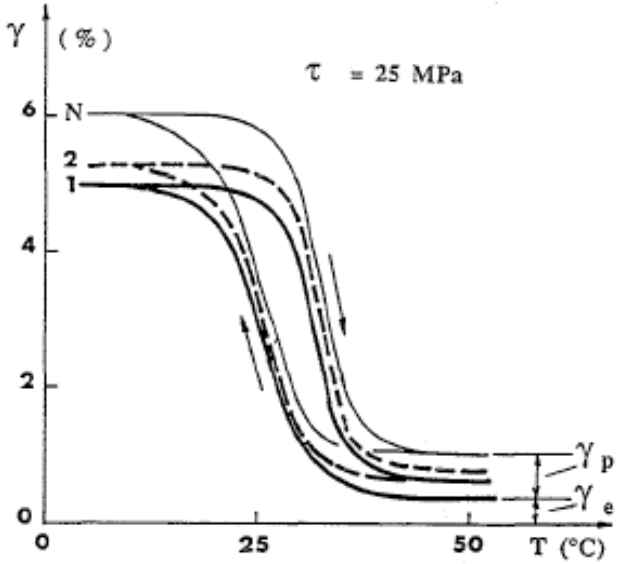


Figure 4.7: *Successive temperature-strain cycles in CuZnAl (torsion). For N>10 the cycles are quasi-closed;* γ_e*=elastic strain induced by the constant stress* τ *in the austenitic state;* γ_p*=plastic strain induced by the training [13].*

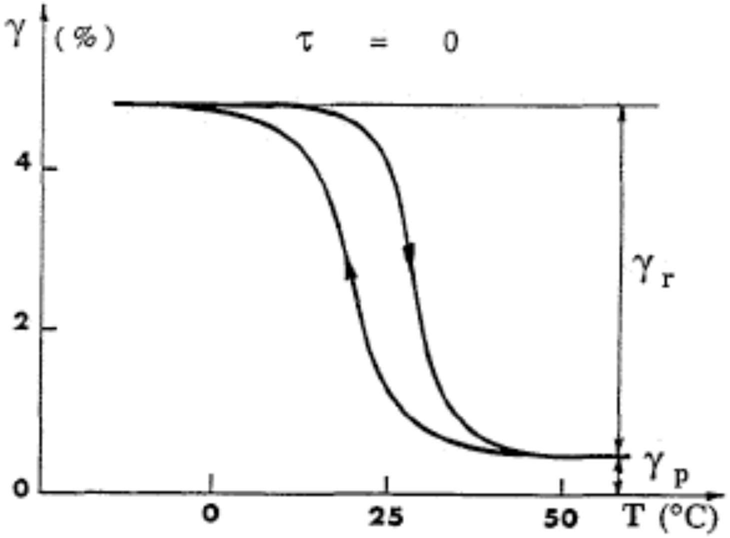


Figure 4.8: *Temperature-strain cycle with zero stress after training with a constant stress of 25MPa;* γ_r *is the reversible part of the strain and the amplitude of the TWME [13].*

Thermal Cycling with Imposed Strain

The sample in the austenite state is submitted to an elastic strain in such a way that the corresponding elastic stress is not enough to generate martensite or plasticity. By cooling the stress induces the favored variants; this relaxes the stress itself because the strain remains constant.

On further cooling the sample strain surpasses the imposed strain, which is a proof that the favored variants, once created, carry on to increase even with zero stress. By heating, the sample recovers its initial shape and stress. When this cycle is repeated a number of times, it will also lead to the TWME, but with less efficiency than the former method.

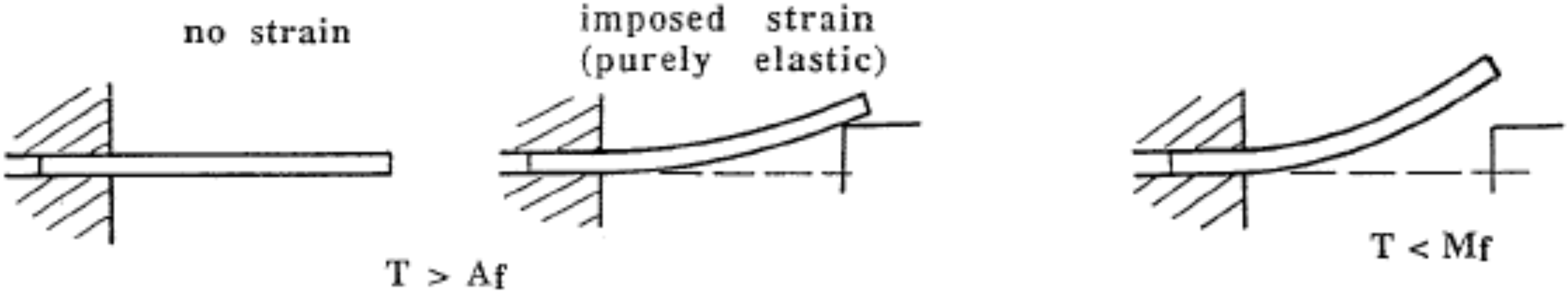
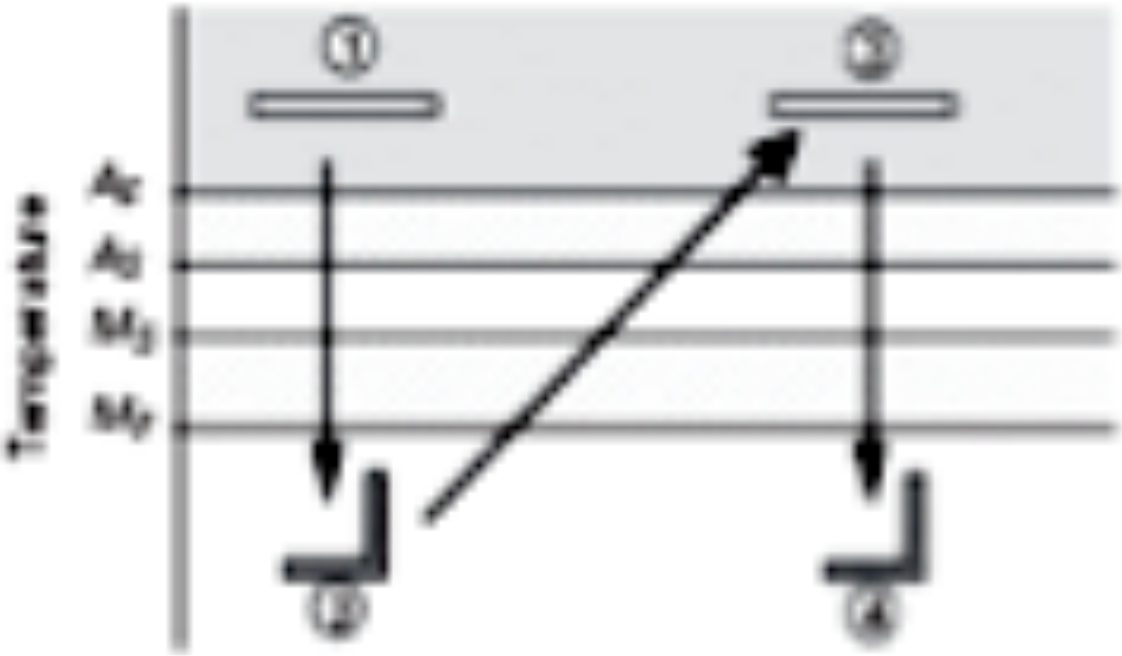


Figure 4.9: *Training process with imposed strain [13].*

Physical basis for the TWME (two-way memory effect):

1. This spontaneous shape change was observed only after particular thermomechanical procedures.
2. These thermomechanical procedures (training) are in general based on the repetition of thermomechanical cycles through the transformation region (73,76,79), that consists of transformation cycles from the parent phase to preferentially oriented martensite.
3. It is generally agreed that cyclic training procedures generate some kind of microstructural asymmetry in the parent phase (texture), so that preferential martensitic variants are formed in subsequent thermal cycles, thus causing the TWME (76,82).
4. The one-way shape-memory effect is thus a property *inherent* in the reversible, thermoelastic martensitic transformation.
5. The preferential orientation of the martensitic variants can also be obtained during the forward transformation that causes preferentially oriented formation of martensite. Thus, the apparent plastic strain is caused by the preferential orientation of martensite.

Figure 3. Two-way shape memory effect. For abbreviations, see legend to Figure 1. See text for explanation of process.



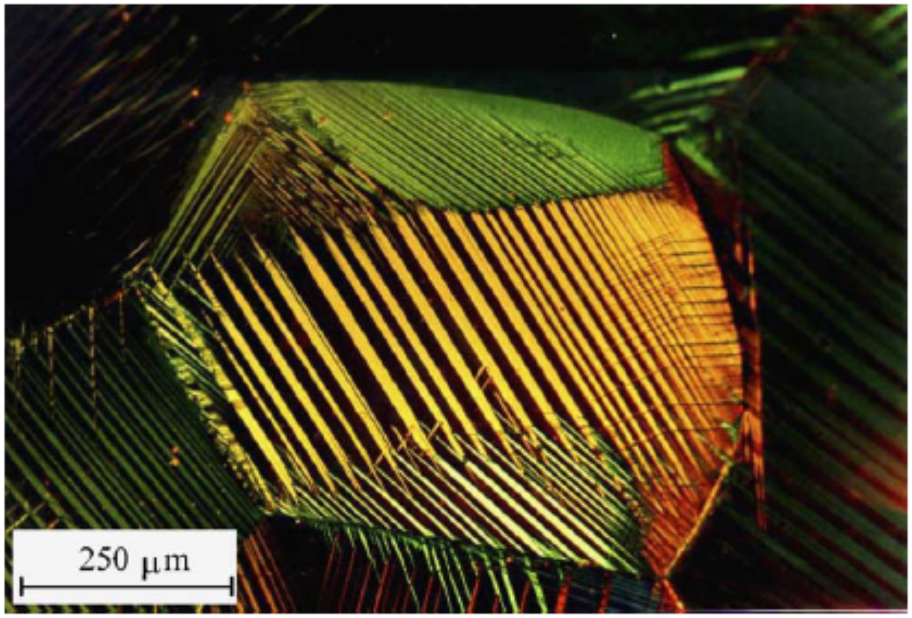
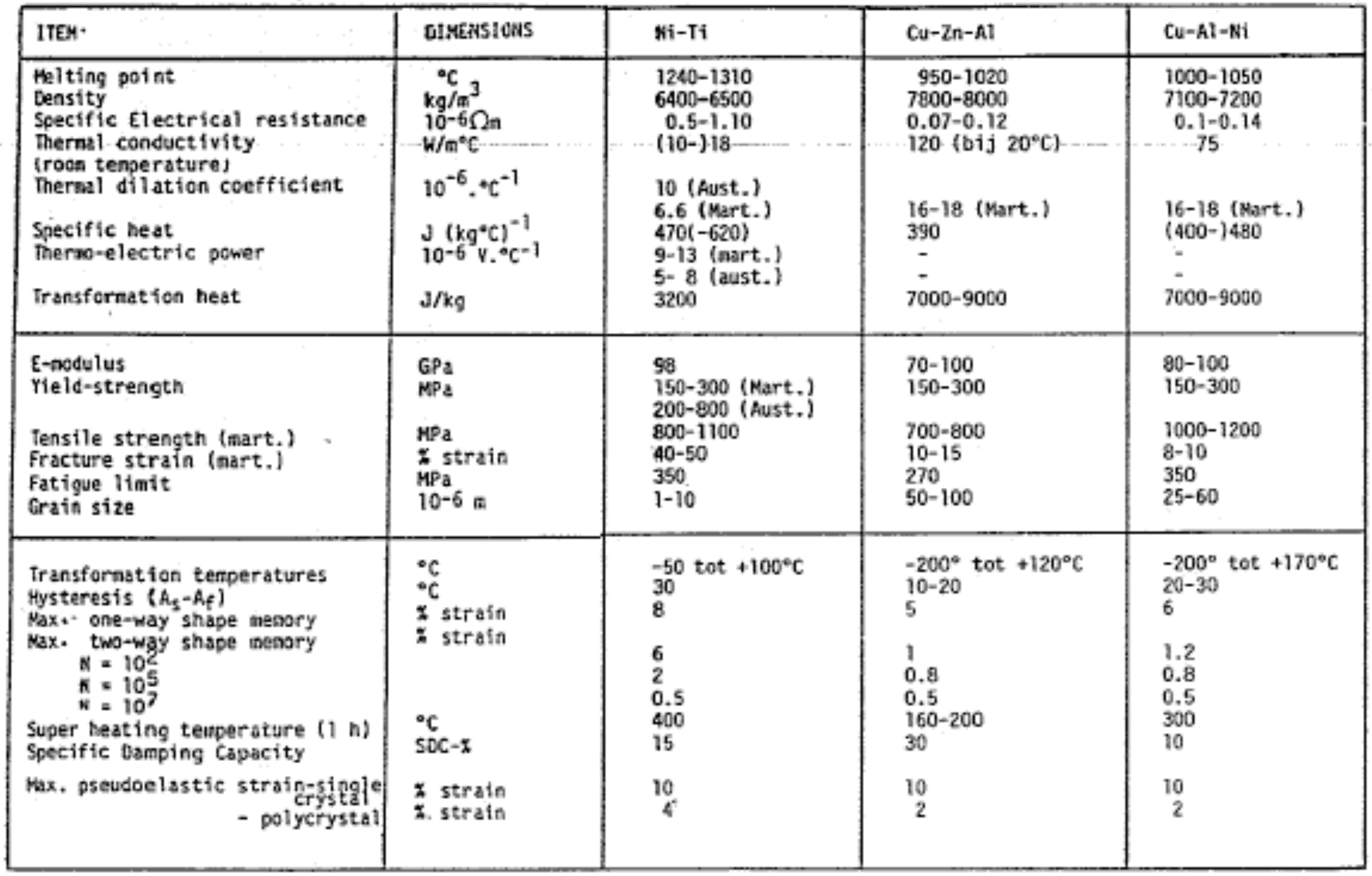


Fig. 10. Formation of different martensitic variants in a single grain of a polycrystalline Cu66.9Zn23.7Al9.4 (at.%) alloy during uniaxial tensile loading (Patoor et al., 1996).

Applications

Despite great scientific efforts to understand, improve and practically use Shape Memory Alloys, only two alloys presently suitable enough for wide spread applications: NiTi and CuZnAl.



ITEM·	DIMENSIONS	Ni-Ti	Cu-Zn-Al	Cu-Al-Ni
Melting point	°C	1240-1310	950-1020	1000-1050
Density	kg/m^3	6400-6500	7800-8000	7100-7200
Specific Electrical resistance	$10^{-6}\Omega m$	0.5-1.10	0.07-0.12	0.1-0.14
Thermal conductivity (room temperature)	W/m°C	(10-)18	120 (bij 20°C)	75
Thermal dilation coefficient	$10^{-6}.°C^{-1}$	10 (Aust.) 6.6 (Mart.)	16-18 (Mart.)	16-18 (Mart.)
Specific heat	$J\ (kg°C)^{-1}$	470(-620)	390	(400-)480
Thermo-electric power	$10^{-6}\ V.°C^{-1}$	9-13 (mart.) 5- 8 (aust.)	- -	- -
Transformation heat	J/kg	3200	7000-9000	7000-9000
E-modulus	GPa	98	70-100	80-100
Yield-strength	MPa	150-300 (Mart.) 200-800 (Aust.)	150-300	150-300
Tensile strength (mart.)	MPa	800-1100	700-800	1000-1200
Fracture strain (mart.)	% strain	40-50	10-15	8-10
Fatigue limit	MPa	350	270	350
Grain size	10^{-6} m	1-10	50-100	25-60
Transformation temperatures	°C	-50 tot +100°C	-200° tot +120°C	-200° tot +170°C
Hysteresis (A_s-A_f)	°C	30	10-20	20-30
Max. one-way shape memory	% strain	8	5	6
Max. two-way shape memory	% strain			
$N = 10^2$		6	1	1.2
$N = 10^5$		2	0.8	0.8
$N = 10^7$		0.5	0.5	0.5
Super heating temperature (1 h)	°C	400	160-200	300
Specific Damping Capacity	SDC-%	15	30	10
Max. pseudoelastic strain-single crystal	% strain	10	10	10
- polycrystal	% strain	4	2	2

Table 5.1: *Comparison between NiTi and Cu-based alloys [13].*

Constrained recovery applications

Industrial applications in which the SME is used only once are for instance tubing or pipe couplings. In these products a NiTi (or ~ Cu-based) alloy which has a transformation temperature far lower than room temperature (about -150°C) is formed into tubing with an inner diameter about **4%** smaller than the nominal outer diameter of the pipes to be joined. When the connection is to be made, the coupling is first immersed in liquid nitrogen and maintained in a low (martensite) state; then a tapered plug is forced inside the coupling so that its inner diameter is expanded by about 7-8%. While keeping the coupling at the low temperature, the two pipes are inserted at both ends of the coupling. When the coupling's temperature rises to room temperature, its inner diameter reverts to the size before the expansion, and the ends of the two pipes are strongly bound together.

Figure 5.1: *Shape Memory Alloy pipe coupling [15].*

Figure 5.2: *Shape Memory Alloy fastener; (a) original shape; (b) straighten ends; (c) insert; (d) heating and fastening [15].*

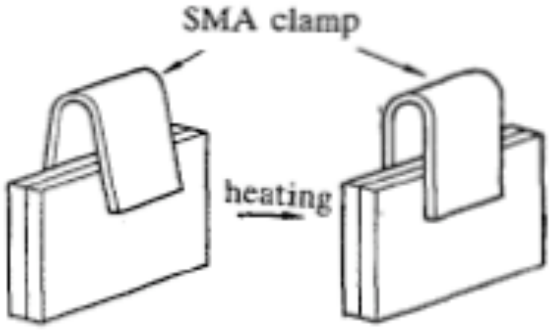


Figure 5.3: *Shape Memory Alloy clamp [15].*

Actuators

For actuators a two way operation is needed. There are two methods for achieving two-way operation properties: - induce the TWME by training processes; since this is still a rather difficult matter, it has not been used yet extensively. - combine a OWME alloy with springs, weights, or other parts so that the component as a whole has two way characteristics.

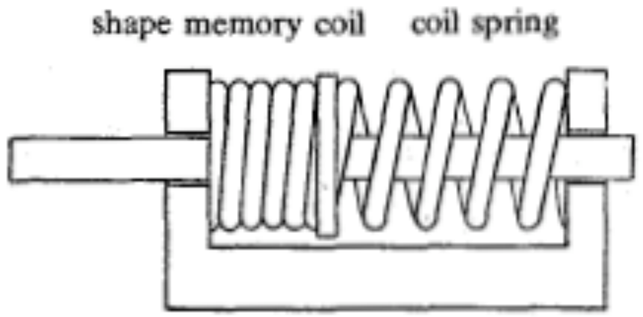


Figure 5.4: *Bias-type Two Way Shape Memory component (a spring is used for the bias force) [15].*

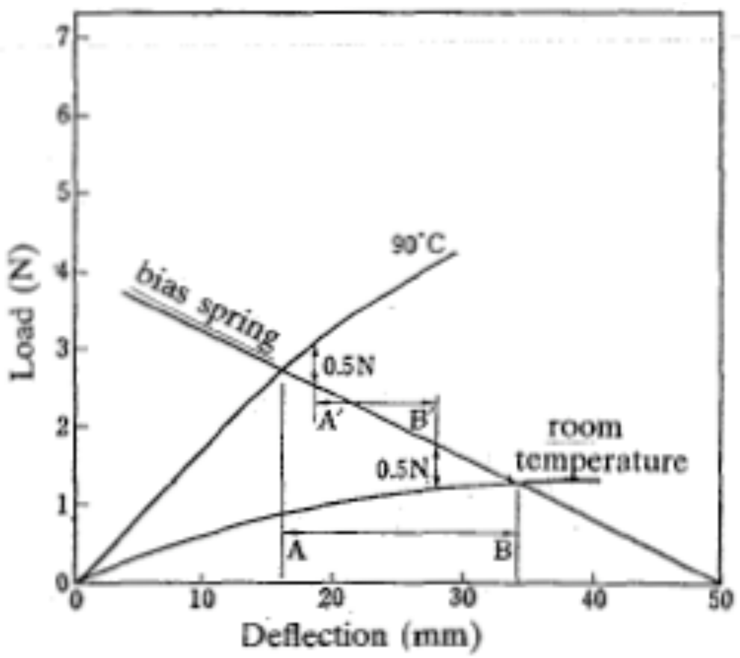


Figure 5.5: *Principles of a Two Way Shape Memory component using a bias spring [15].*

A simplified actuator shown is of the so-called **bias-type**: it consists of a shape memory coil and an ordinary coil spring. The point where the load on the SMA coil is zero is the origin; the zero load point of the coil spring is 50 mm to the left. At room temperature, the SMA follows the lower force-deflection curve and an equilibrium sets in at **34**mm from the origin. When the SMA coil is heated above ***Af,*** it stiffens so that the upper graph is valid: the equilibrium is disturbed and a displacement of **18mm** is obtained. If the actuator is used to perform external work, the stroke length is effectively shortened; if for example a force of **0.5N** works opposite to the displacements at both high and low temperatures, the stroke length would be reduced to **10mm**. The stroke may be extended by utilizing rotational movements and moments.

Heat engines

A special application which uses the ability to do work by means of recovery forces is the heat engine. The principle is as follows: below *Mf* the martensitic specimen is deformed by means of a relatively small force. This force is replaced by a large force. On heating large recovery stresses occur doing external work. The large force is again replaced by the smaller one, after which the temperature is lowered; the cycle is completed.

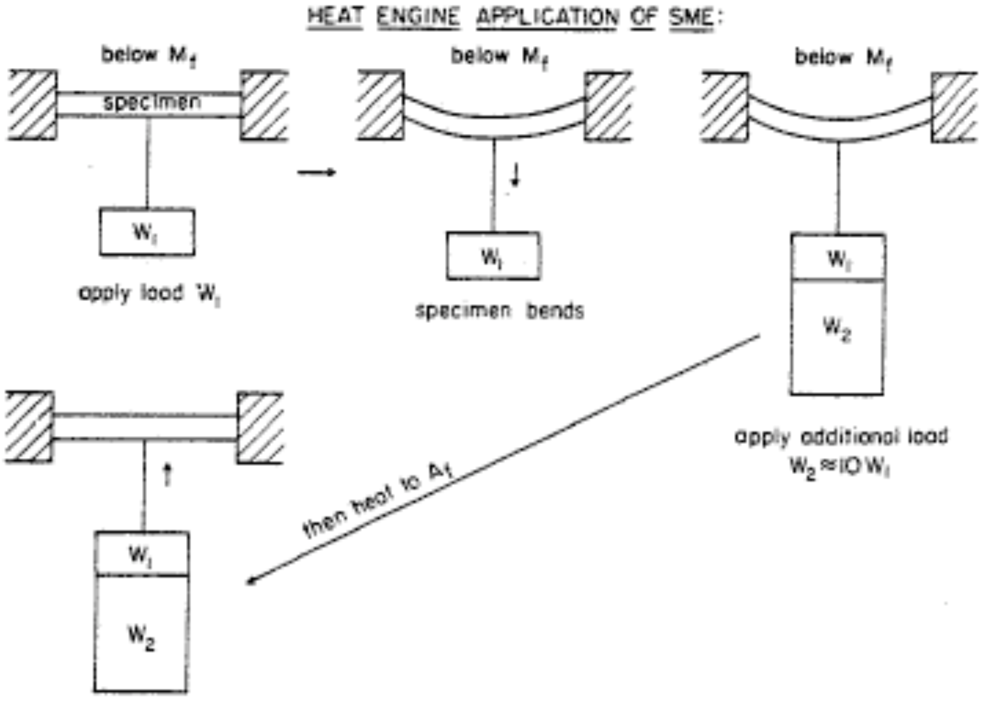


Figure 5.8: *Schematic of heat engine application of a SMA [21].*