
Martensite in Steels

The name *martensite* is after the German scientist Martens. It was used originally to describe the hard microconstituent found in quenched steels. Martensite remains of the greatest technological importance in steels where it can confer an outstanding combination of strength (> 3500 MPa) and toughness (> 200 MPa m^{1/2}). Many materials other than steel are now known to exhibit the same type of solid-state phase transformation, known as a *martensitic transformation*, frequently also called a *shear* or *displacive transformation*. Martensite occurs in, for example, nonferrous alloys, pure metals, ceramics, minerals, inorganic compounds, solidified gases and polymers (Table 1). We shall review first the experimental facts about martensite and then proceed to explain them.

Composition	M_S / K	Hardness HV
ZrO ₂	1200	1000
Fe-31Ni-0.23C wt%	83	300
Fe-34Ni-0.22C wt%	< 4	250
Fe-3Mn-2Si-0.4C wt%	493	600
Cu-15Al	253	200
Ar-40N ₂	30	

Table 1: The temperature M_S at which martensite first forms on cooling, and the approximate Vickers hardness of the resulting martensite for a number of materials.

Diffusionless Character

Martensitic transformations are diffusionless, but what evidence is there to support this?

Martensite can form at very low temperatures, where diffusion, even of interstitial atoms, is not conceivable over the time period of the experiment. Table 1 gives values of the highest temperature at which martensite forms in a variety of materials; this temperature is known as the martensite-start, or M_S temperature. It is obvious that although martensite *can* form

at low temperatures, it need not do so. Therefore, a low transformation temperature is not sufficient evidence for diffusionless transformation.

Martensite plates can grow at speeds which approach that of sound in the metal. In steel this can be as high as 1100 m s^{-1} , which compares with the fastest recorded solidification front velocity of about 80 m s^{-1} in pure nickel. Such large speeds are inconsistent with diffusion during transformation. Note that martensite need not grow so rapidly. For example, in shape-memory alloys or in single-interface transformations, the interface velocity is small enough to observe.

The chemical composition of martensite can be measured and shown to be identical to that of the parent austenite. The totality of these observations demonstrate convincingly that martensitic transformations are diffusionless.

The Habit Plane

This is the interface plane between austenite and martensite as measured on a macroscopic scale (Fig. 1), for example by using one or two-surface crystallographic trace analysis on metallographic samples. For unconstrained transformations this interface plane is flat, but strain energy minimisation introduces some curvature when the transformation is constrained by its surroundings. Nevertheless, the macroscopic habit plane is identical for both cases, as illustrated in Figure 1.

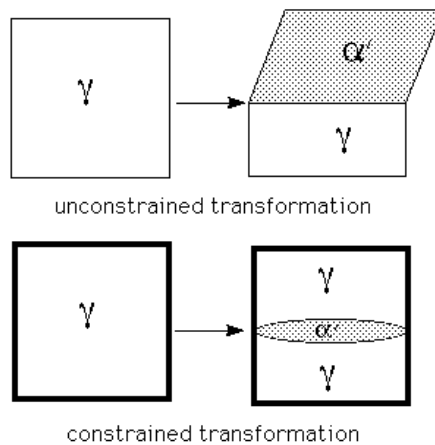


Figure 1: An illustration of the habit plane between austenite (γ) and martensite (α')

Steels of vastly different chemical composition can have martensite with the same habit plane (Table 2), and indeed, other identical crystallographic characteristics.

Composition /wt.%	Approximate habit plane indices
Low-alloy steels, Fe-28Ni	$\{1\ 1\ 1\}_\gamma$
Plate martensite in Fe-1.8C	$\{2\ 9\ 5\}_\gamma$
Fe-30Ni-0.3C	$\{3\ 15\ 10\}_\gamma$
Fe-8Cr-1C	$\{2\ 5\ 2\}_\gamma$
ϵ -martensite in 18/8 stainless steel	$\{1\ 1\ 1\}_\gamma$

Table 2: Habit plane indices for martensite. With the exception of ϵ -martensite, the quoted indices are approximate because the habit planes are in general irrational.

Orientation Relationships

The formation of martensite involves the coordinated movement of atoms. It follows that the austenite and martensite lattices will be intimately related. All martensitic transformations therefore lead to a reproducible orientation relationship between the parent and product lattices. It is frequently the case that a pair of corresponding close-packed[†] planes in the ferrite and austenite are parallel or nearly parallel, and it is usually the case that corresponding directions within these planes are roughly parallel (Fig. 2):

$$\begin{aligned} & \{1\ 1\ 1\}_\gamma \parallel \{0\ 1\ 1\}_\alpha \\ & \langle 1\ 0\ \bar{1} \rangle_\gamma \parallel \langle 1\ 1\ \bar{1} \rangle_\alpha \end{aligned} \quad \text{Kurdjumov-Sachs}$$

$$\begin{aligned} & \{1\ 1\ 1\}_\gamma \parallel \{0\ 1\ 1\}_\alpha \\ & \langle 1\ 0\ \bar{1} \rangle_\gamma \quad \text{about } 5.3^\circ \text{ from } \langle 1\ 1\ \bar{1} \rangle_\alpha \text{ towards } \langle \bar{1}\ 1\ \bar{1} \rangle_\alpha \end{aligned} \quad \text{Nishiyama-Wasserman}$$

$$\begin{aligned} & \{1\ 1\ 1\}_\gamma \quad \text{about } 0.2^\circ \text{ from } \{0\ 1\ 1\}_\alpha \\ & \langle 1\ 0\ \bar{1} \rangle_\gamma \quad \text{about } 2.7^\circ \text{ from } \langle 1\ 1\ \bar{1} \rangle_\alpha \text{ towards } \langle \bar{1}\ 1\ \bar{1} \rangle_\alpha \end{aligned} \quad \text{Greninger-Troiano}$$

[†] The body-centred cubic lattice does not have a close-packed plane but $\{0\ 1\ 1\}_\alpha$ is the most densely packed plane.

Note that these have been stated approximately: the true relations are irrational, meaning that the indices of the parallel planes and directions cannot be expressed using rational numbers (the square root of 2 is not a rational number).

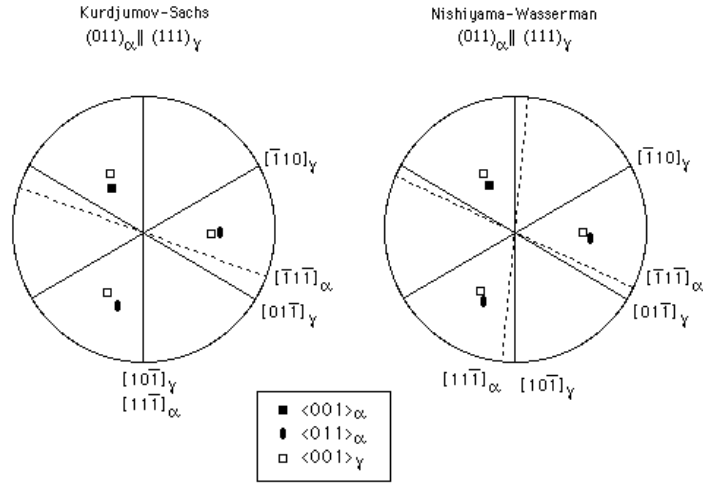


Fig. 2: Stereographic representation of the Kurdjumov–Sachs and Nishiyama–Wasserman orientation relationships. The stereograms are both centred on $(1\ 1\ 1)_{\gamma} \parallel (0\ 1\ 1)_{\alpha}$. It is seen that the NW orientation can be generated from KS by an appropriate small rotation (5.25°) about $[0\ 1\ 1]_{\alpha}$. Only a few of the poles are marked to allow a comparison with the Bain orientation relationship. The neighbouring pairs of poles would superpose exactly for the Bain orientation.

Athermal Nature of Transformation

In the vast majority of cases, the extent of reaction is found to be virtually independent of time:

$$1 - V_{\alpha'} = \exp\{\beta(M_S - T)\} \quad \text{where} \quad \beta \simeq -0.011 \quad (1)$$

$V_{\alpha'}$ is the fraction of martensite and T is a temperature below M_S . This is the Koistinen and Marburger equation; notice that time does not feature in this relation, so that the fraction of martensite depends only on the undercooling below the martensite–start temperature. This athermal character is a consequence of very rapid nucleation and growth, so rapid that the time taken can in normal circumstances be neglected.

Isothermal martensite *is* possible when nucleation is hindered, although the growth rate of individual plates of martensite can still be rapid.

Structure of the Interface

Any process which contributes to the formation of martensite cannot rely on assistance from thermal activation. There must therefore exist a high level of continuity across the interface, which must be coherent and semi-coherent. A stress-free fully coherent interface is impossible for the $\gamma \rightarrow \alpha'$ transformation since the lattice deformation \mathbf{BR} is an invariant-line strain. A semi-coherent interface must be such that the interfacial dislocations can glide as the interface moves (climb is not permitted). It follows that the Burgers vectors of the interface dislocations must not lie in the interface plane unless the dislocations are screw in character.

There is an additional condition for a semi-coherent interface to be glissile. The line vectors of the interfacial dislocations must lie along an *invariant-line*, *i.e.* a line which joins the parent and product crystals without any rotation or distortion. Why is that? If there is any distortion along the dislocation line, then other dislocations are needed to accommodate that misfit. It will then be necessary to have more than one set of non-parallel dislocations in the interface. These non-parallel dislocations can intersect to form jogs which render the interface sessile.

It follows that for martensitic transformation to be possible, the deformation which changes the parent into the product must leave one or more lines invariant (unrotated, undistorted). A deformation which leaves one line invariant is called an 'invariant-line strain'.

The Shape Deformation

The passage of a slip dislocation through a crystal causes the formation of a step where the glide plane intersects the free surface (Fig. 3a,b). The passage of many such dislocations on parallel slip planes causes macroscopic shear (Fig. 3c,d). Slip causes a change in shape but not a change in the crystal structure, because the Burgers vectors of the dislocations are also lattice vectors.

During martensitic transformation, the pattern in which the atoms in the parent crystal are arranged is *deformed* into that appropriate for martensite, there must be a corresponding change in the macroscopic shape of the crystal undergoing transformation. The dislocations responsible for the deformation are in the α'/γ interface, with Burgers vectors such that in addition to deformation they also cause the change in crystal structure. The deformation is such that an initially flat surface becomes uniformly tilted about the line formed by the intersection of the interface plane with the free surface. Any scratch traversing the transformed

region is similarly deflected though the scratch remains connected at the α'/γ interface. These observations, and others, confirm that the measured shape deformation is an invariant-plane strain (Fig. 3e–g) with a large shear component ($\simeq 0.22$) and a small dilatational strain ($\simeq 0.03$) directed normal to the habit plane.

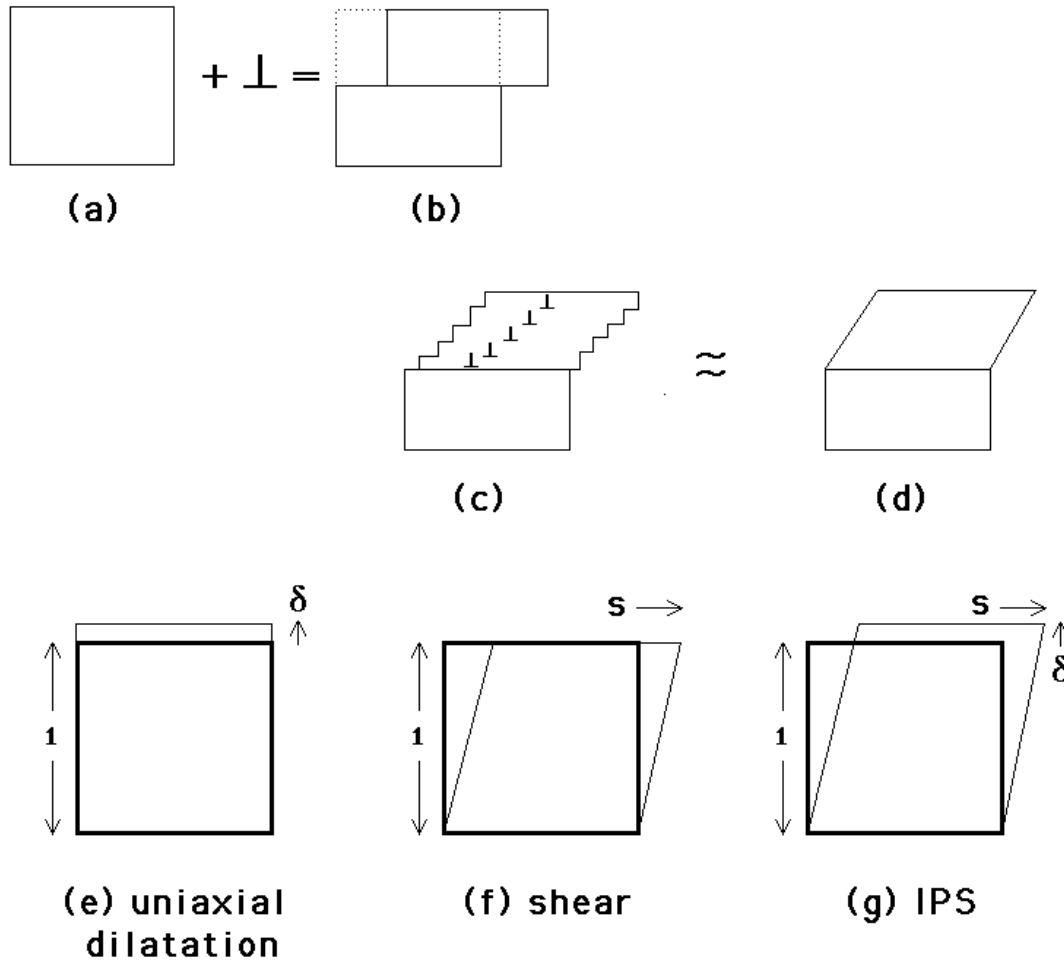


Fig. 3: (a, b) Step caused by the passage of a slip dislocation. (c, d) Many slip dislocations, causing a macroscopic shear. (e) An invariant-plane strain with a uniaxial dilatation. (f) An invariant-plane strain which is a simple shear. (g) An invariant-plane strain which is the combined effect of a uniaxial dilatation and a simple shear.

Bain Strain

We now consider the nature of the strain necessary to transform the c.c.p. lattice of γ into the b.c.c. lattice of α' . Such a strain was proposed by Bain in 1924 and hence is known

as the ‘Bain Strain’ (Fig. 4). There is a compression along the z axis and a uniform expansion along the x and y axes.

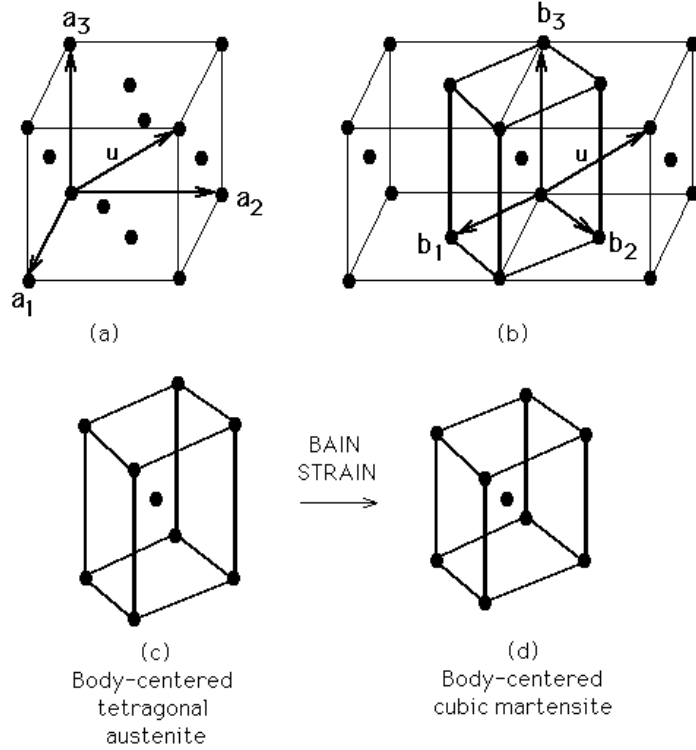


Fig. 4: The Bain strain (not all lattice points illustrated)

The deformation describing the Bain Strain is given by

$$\mathbf{B} = \begin{pmatrix} \epsilon_0 & 0 & 0 \\ 0 & \epsilon_0 & 0 \\ 0 & 0 & \epsilon'_0 \end{pmatrix}$$

$$\epsilon_0 = \frac{\sqrt{2}a_{\alpha'} - a_{\gamma}}{a_{\gamma}} \quad \epsilon'_0 = \frac{a_{\alpha'} - a_{\gamma}}{a_{\gamma}}$$

where $a_{\alpha'}$ and a_{γ} are the lattice parameters of martensite and austenite respectively. The contraction is therefore along the $[0\ 0\ 1]_{\gamma}$ axis and a uniform expansion on the $(0\ 0\ 1)_{\gamma}$ plane.

The Bain strain implies the following orientation relationship between the parent and product lattices:

$$[0\ 0\ 1]_{fcc} \parallel [0\ 0\ 1]_{bcc} \quad [1\ \bar{1}\ 0]_{fcc} \parallel [1\ 0\ 0]_{bcc} \quad [1\ 1\ 0]_{fcc} \parallel [0\ 1\ 0]_{bcc}$$

but in fact, the experimentally observed orientation relationships are irrational, as discussed earlier. We shall deal with this inconsistency later.

Temporarily neglecting the fact that the Bain orientation is inconsistent with experiments, we proceed to examine whether the Bain strain leaves at least one line invariant. After all, this is a necessary condition for martensitic transformation.

In Fig. 5a,b, the austenite is represented as a sphere which, as a result of the Bain strain \mathbf{B} , is deformed into an ellipsoid of revolution which represents the martensite. There are no lines which are left undistorted or unrotated by \mathbf{B} . There are no lines in the $(0\ 0\ 1)_{fcc}$ plane which are undistorted. The lines wx and yz are undistorted but are rotated to the new positions $w'x'$ and $y'z'$. Such rotated lines are not invariant. However, the combined effect of the Bain strain \mathbf{B} and the rigid body rotation \mathbf{R} is indeed an invariant–line strain (ILS) because it brings yz and $y'z'$ into coincidence (Fig. 5c). This is the reason why the observed irrational orientation relationship differs from that implied by the Bain strain. The rotation required to convert \mathbf{B} into an ILS precisely corrects the Bain orientation into that which is observed experimentally.

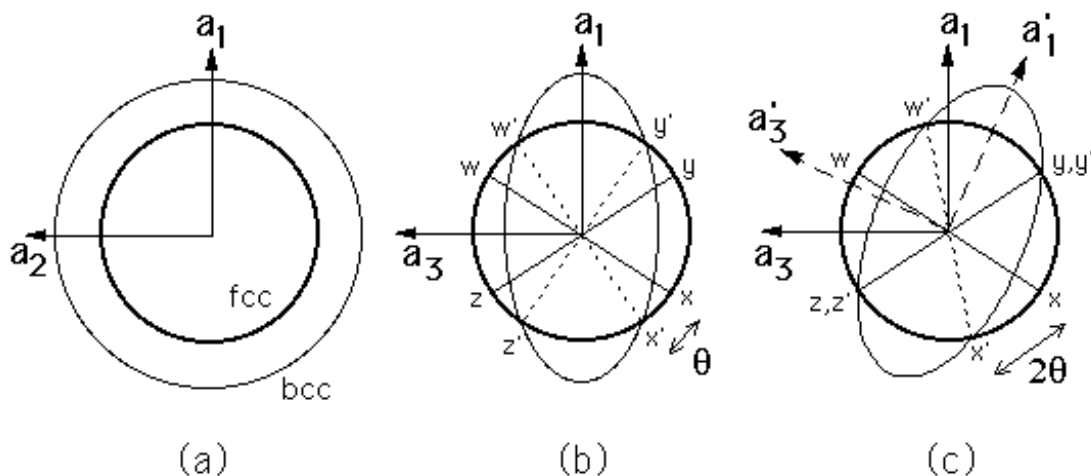


Fig. 5: (a) and (b) show the effect of the Bain strain on austenite, which when undeformed is represented as a sphere of diameter $wx = yz$ in three–dimensions. The strain transforms it to an ellipsoid of revolution. (c) shows the invariant–line strain obtained by combining the Bain strain with a rigid body rotation through an angle θ .

As can be seen from Fig. 5c, there is no rotation which can make \mathbf{B} into an invariant–plane strain since this would require two non–parallel invariant–lines. Thus, for the $fcc \rightarrow bcc$

transformation, austenite cannot be transformed into martensite by a homogeneous strain which is an IPS. And yet, the observed shape deformation leaves the habit plane undistorted and unrotated, *i.e.* it is an invariant–plane strain.

The phenomenological theory of martensite crystallography solves this remaining problem (Fig. 6). The Bain strain converts the structure of the parent phase into that of the product phase. When combined with an appropriate rigid body rotation, the net homogeneous lattice deformation \mathbf{RB} is an invariant–line strain (step *a* to *c* in Fig. 6). However, the observed shape deformation is an invariant–plane strain \mathbf{P}_1 (step *a* to *b* in Fig. 6), but this gives the wrong crystal structure. If a second homogeneous shear \mathbf{P}_2 is combined with \mathbf{P}_1 (step *b* to *c*), then the correct structure is obtained but the wrong shape since

$$\mathbf{P}_1\mathbf{P}_2 = \mathbf{RB}$$

These discrepancies are all resolved if the shape changing effect of \mathbf{P}_2 is cancelled macroscopically by an inhomogeneous lattice–invariant deformation, which may be slip or twinning as illustrated in Fig. 6.

The theory explains all the observed features of the martensite crystallography. The orientation relationship is predicted by deducing the rotation needed to change the Bain strain into an invariant–line strain. The habit plane does not have rational indices because the amount of lattice–invariant deformation needed to recover the correct the macroscopic shape is not usually rational. The theory predicts a substructure in plates of martensite (either twins or slip steps) as is observed experimentally. The transformation goes to all the trouble of ensuring that the shape deformation is macroscopically an invariant–plane strain because this reduces the strain energy when compared with the case where the shape deformation might be an invariant–line strain.

Thermodynamics of Martensitic Transformations

Martensite is not represented on phase diagrams because the latter deal with equilibrium. Martensite deviates from equilibrium in two important ways:

Martensite grows without diffusion, so it inherits the chemical composition of the parent austenite. In an equilibrium transformation the chemical elements partition into the parent and product phases in a manner which leads to a minimisation of free energy.

Secondly, the shape deformation associated with martensitic transformation causes strains; the resulting strain energy has to be accounted for before the transformation can happen.

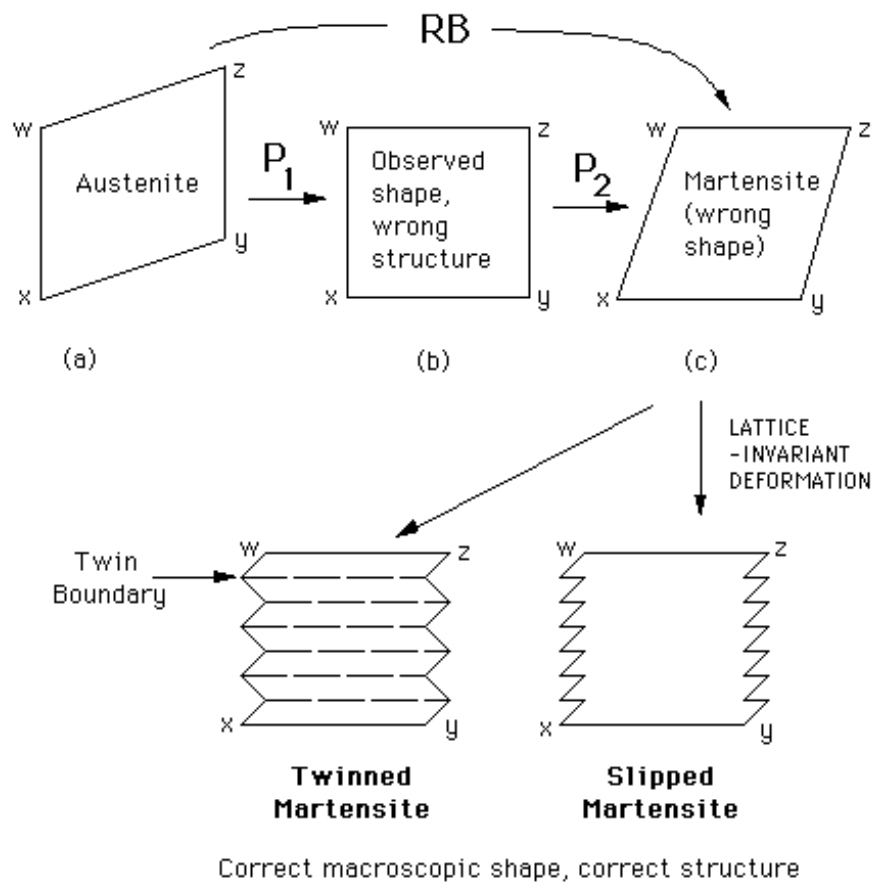


Fig. 6: The phenomenological theory of martensite crystallography

These deviations can be represented on a free energy plot as illustrated in Fig. 7.

The relationship with the phase diagram is illustrated in Fig. 8. Martensitic transformation is only possible below the T'_0 temperature.

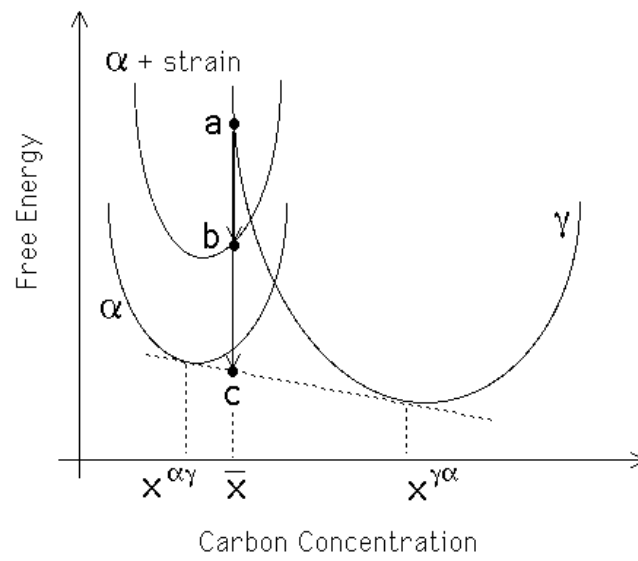


Fig. 7: The distance ac represents the free energy decrease when austenite of composition \bar{x} decomposes into an equilibrium mixture of ferrite and austenite of compositions $x^{\alpha\gamma}$ and $x^{\gamma\alpha}$ respectively. The distance ab is the smaller decrease in free energy when martensite forms without any composition change, taking into account the strain associated with the transformation.

	J mol^{-1}
Strain energy	600
Twin interface energy	100
γ/α' interface energy	1
Stored energy due to dislocations	20

Table 3: Typical energies associated with martensitic transformation.

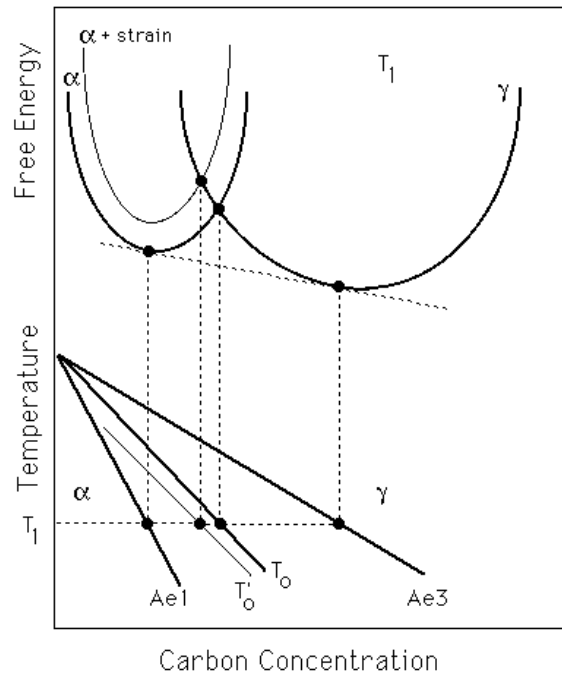


Fig. 8: Schematic illustration of the origin of the T_0 curve on the phase diagram. The T_0' curve incorporates a strain energy term for the ferrite, illustrated on the diagram by raising the free energy curve for ferrite by an appropriate quantity.