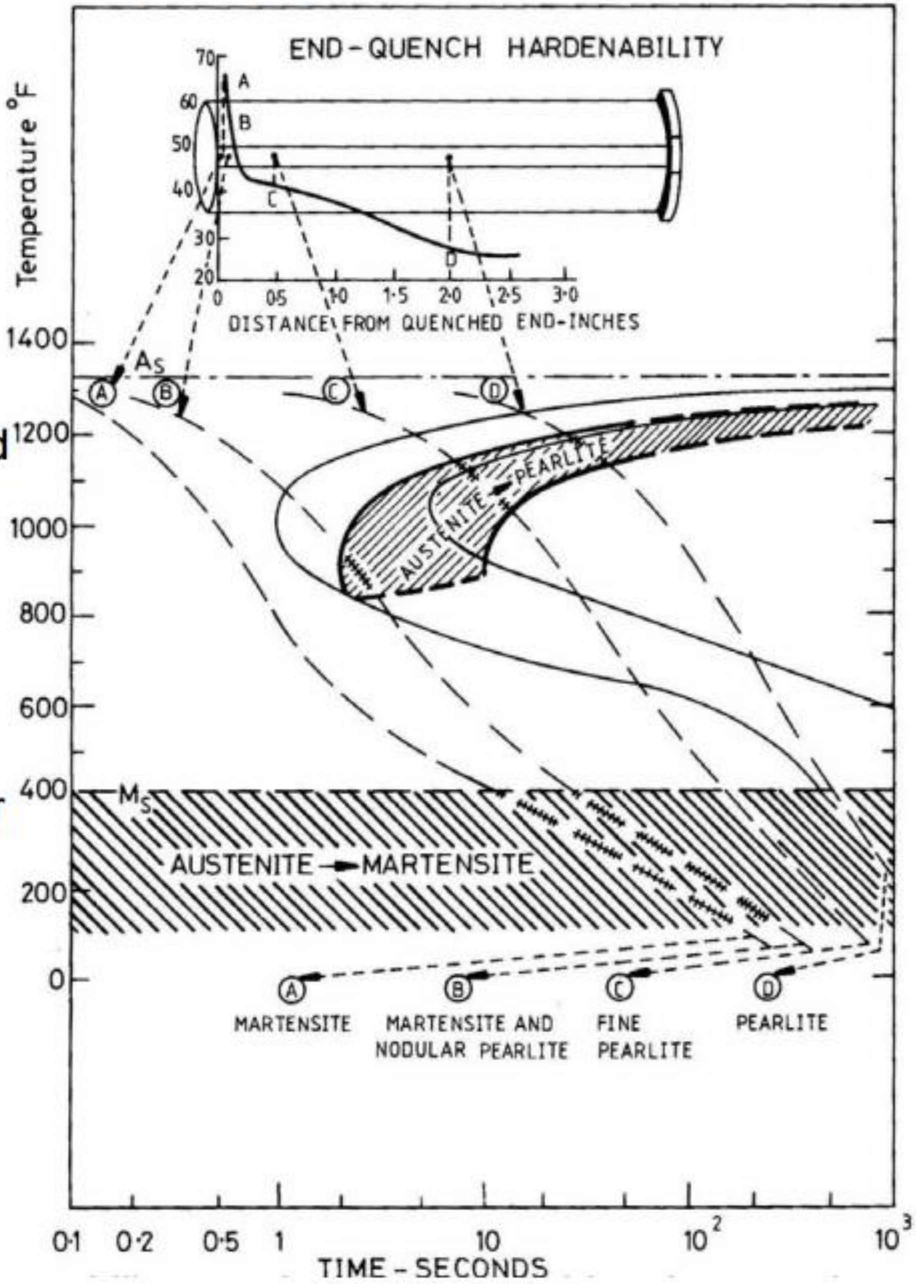
Continuous Cooling Diagrams

Isothermal transformation (TTT) diagrams are obtained by rapidly quenching to a given temperature and then measuring the volume fraction of the various constituents that form as a function of time at that temperature. Practical heat treatments, however, are usually concerned with transformations that occur during continuous cooling, and under these conditions TTT diagrams cannot be used to give the times and temperatures of the various transformations. A continuous cooling transformation (CCT) diagram must be used instead.

TTT diagram is interpreted by reading from left to right at a constant temperature the CCT diagram is read along the cooling curves from the top left to bottom right.

Continuous Cooling Diagram

- Practical heat treatments are usually concerned with transformation that occur during continuous cooling. A continuous cooling transformation (CCT) diagram must be used instead of TTT diagrams.
  1. The CCT diagram is the TTT diagram shifted to lower temperatures and longer times.
  2. The end of reaction will be displaced to lower temperatures and longer times.
- In practical heat treatments the cooling curves will not be linear but will depend on the transfer of heat from the specimen to the quenching medium and the rate of release of latent heat during transformation.



Continuous Cooling Diagram

- Unique features of CCT diagrams

1. A depress of the M_S temperature at slow cooling rates.
2. The tempering of martensite that takes place on cooling from M_S to about 200°C.
3. A greater variety of microstructures.

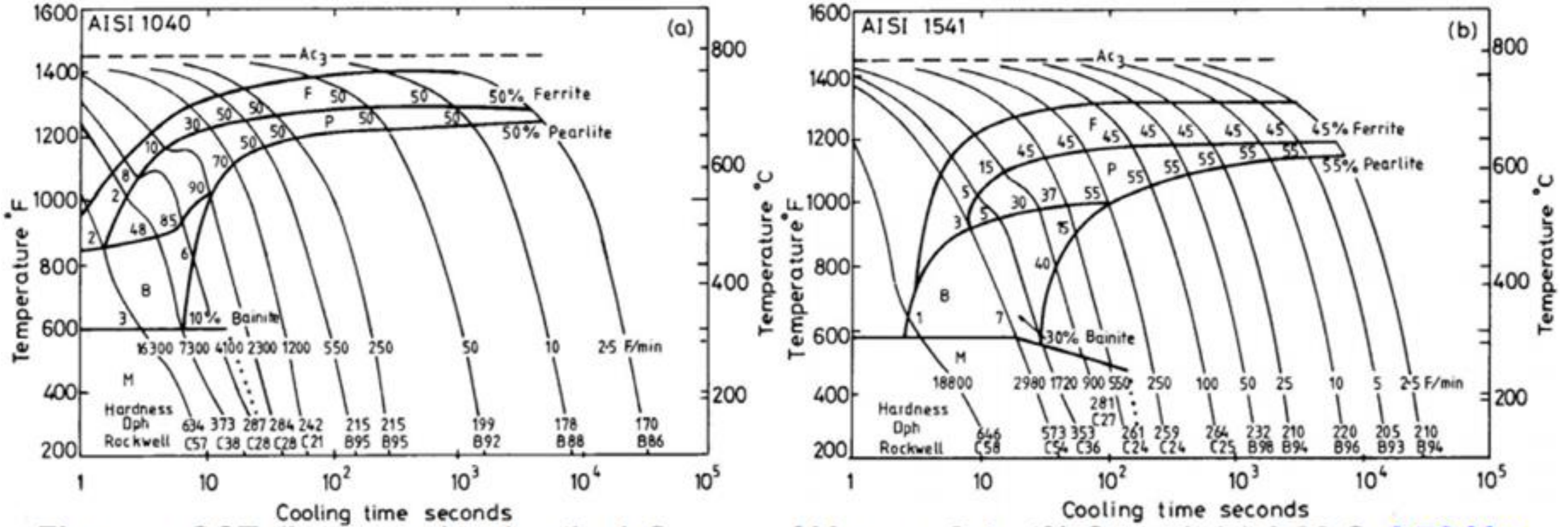


Fig. CCT diagrams showing the influence of Mn on a 0.4 wt% C steel. (a) 0.39 C, 0.72 Mn, 0.23 Si, 0.018S, 0.010P, A_{C1} = 728°C, A_{C3} = 786°C. Grain Size: ASTM No. 7-8. (b) 0.39 C, 1.56 Mn, 0.21 Si, 0.024 S, 0.010 P. A_{C1} = 716°C, A_{C3} = 788°C, Grain size: ASTM No. 8. (F: ferrite, P: pearlite, B: bainite, M: martensite)

Massive Transformations

- **Cu-Zn alloys**
  - Consider the Cu-Zn alloys containing approximately 38 at% Zn. The most stable state for such alloys is β above ~800℃, α below ~600℃ and a mixture of $\alpha+\beta$ with compositions given by the equilibrium phase diagram in between.
  - The transformation of β phase depends on the cooling rate.
    1. Slow cooling favors transformation at small under-cooling and the formation of equiaxed α.
    2. Higher cooling rates result in transformation at lower temperatures and Widmanstätten α needles precipitate.
  - Metastable phases can also form massively. It is not even necessary for the transformation product to be a single phase: two phases, at least one of which must be metastable, can form simultaneously provided they have the same composition as the parent phase.

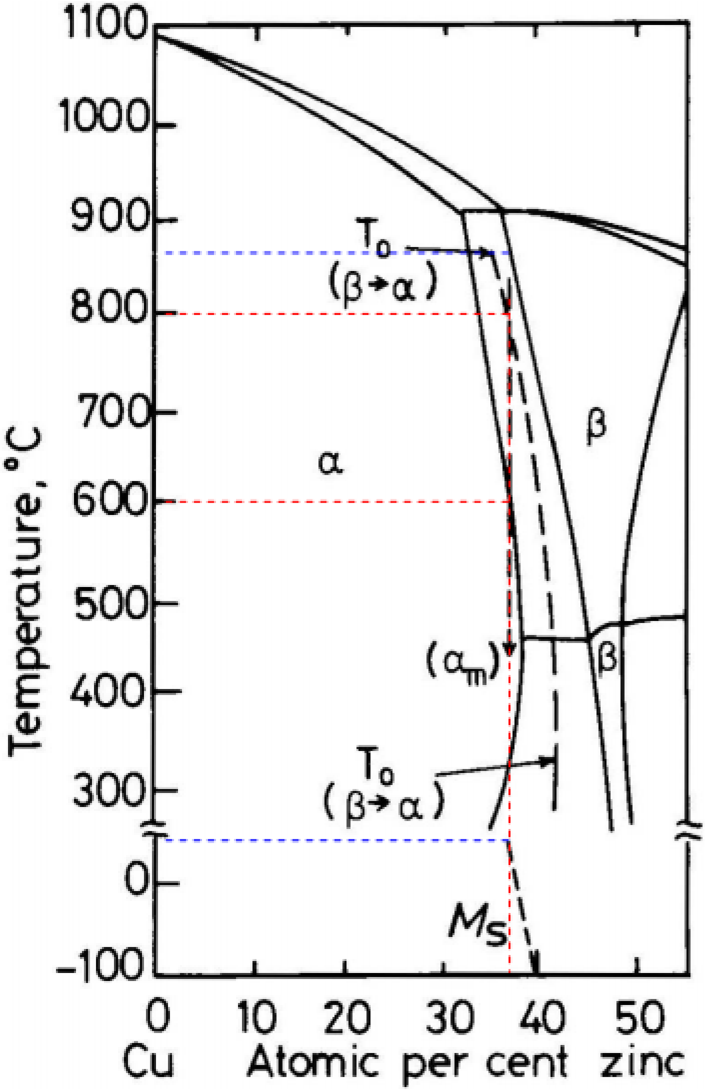


Fig. A part of the Cu-Zn phase diagram showing the α/β equilibrium. The temperature at which $G^{\alpha} = G^{\beta}$ is marked as T_0. M_S marks the beginning of the martensite transformation in rapidly quenched specimens.

Massive Transformations

- The α that precipitates will be richer in Cu than the parent β phase, and the growth of the α phase requires the long-range diffusion of Zn away from the advancing α/β interfaces. This process is relatively slow, especially since the Cu and Zn form substitutional solid solutions, and consequently the C curve for the α precipitate on a TTT or CCT diagram will be located at relatively long times.

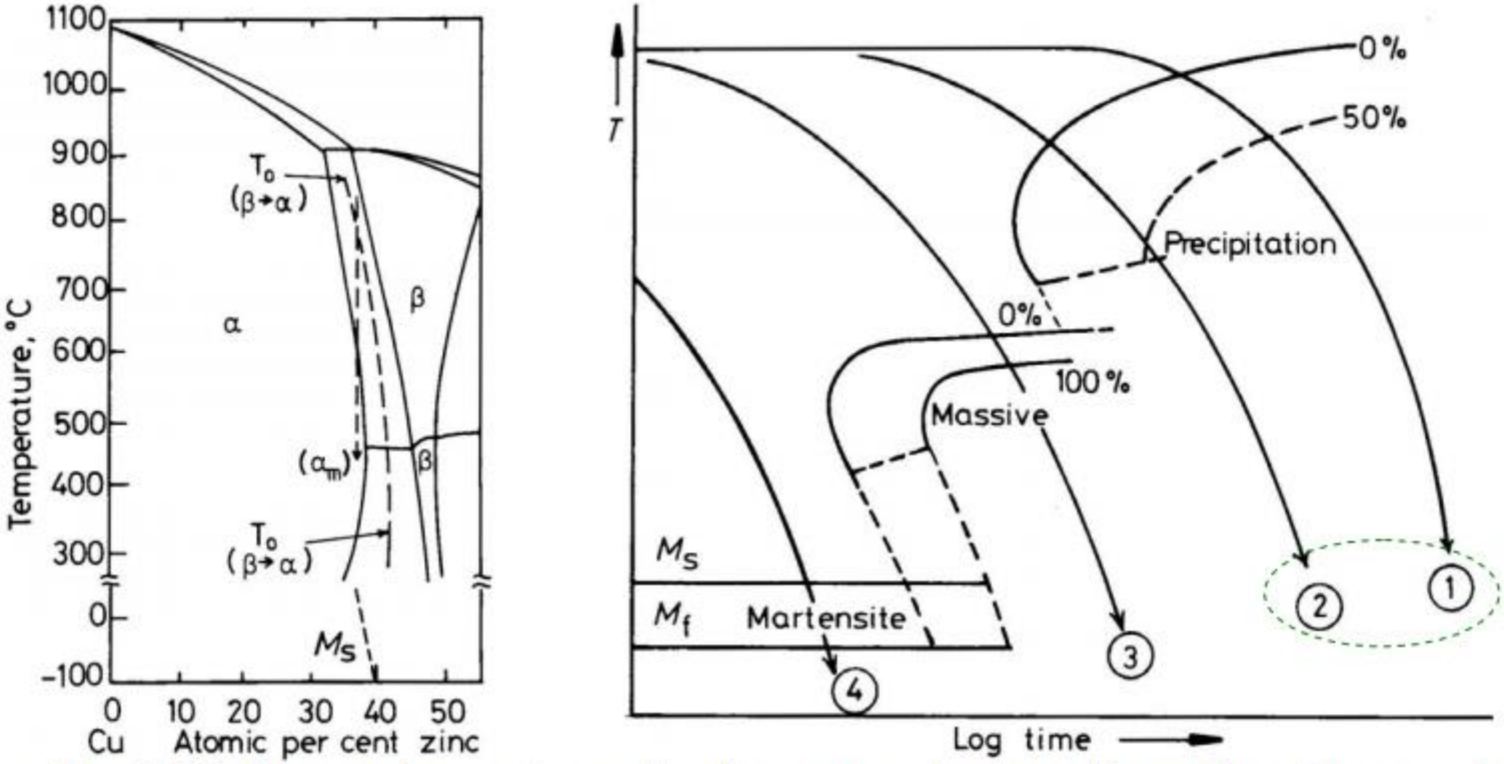


Fig. A possible CCT diagram for systems showing a massive transformation. Slow cooling (1) produces equiaxed α. Widmanstätten morphologies result from faster cooling (2). Moderately rapid quenching (3) produces the massive transformation, while the highest quench rate (4) leads to a martensite transformation.

Massive Transformations

Cu-Zn alloys

- If the alloy is cooled fast enough, there is no time for the precipitation of α, and the β phase can be retained to temperature below 500°C where it is possible for β to transform into α with the same composition. The result is a new massive transformation product.
- Because of the rapid growth the α/β boundaries have an irregular appearance.
- Since both the α and β phases have the same composition, massive α (α_m) can grow as fast as the Cu and Zn atoms can cross the α/β interface, without the need for long-range diffusion.

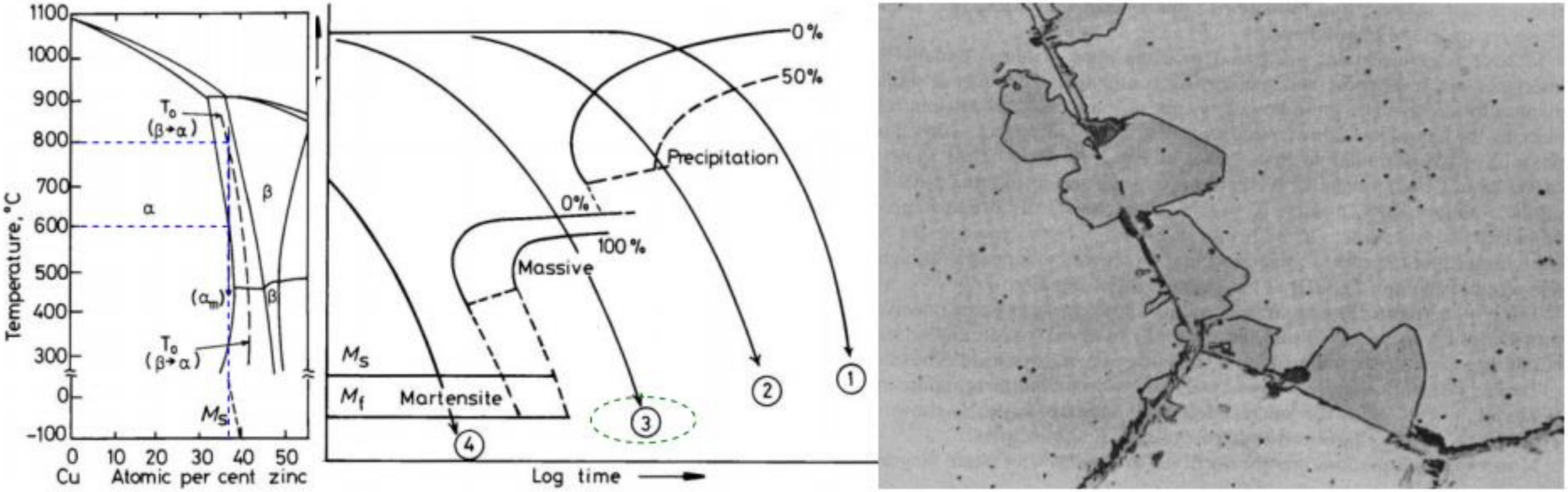


Fig. Massive α formed at the grain boundaries of β in Cu-38.7 wt% Zn quenched from 850°C in brine at 0°C. Some high temperature precipitation has also occurred on the boundaries.

Massive Transformations

- The migration of the α/β interfaces is very similar to the migration of grain boundaries during recrystallization of single-phase material. However, in the massive transformation the driving force is orders of magnitude greater than for recrystallization, which explains why the transformation is so rapid.
- It will transform martensitically if sufficiently high quench rates are used to supress the nucleation of the massive product.
- The condition that must be satisfied for a massive transformation is that the free energy of the new phase must be lower than the parent phase, both phases having the same composition.
- In Cu-38 at% Zn, there is a temperature ~700°C below which G^{α} becomes less than G^{β}.
- Massive transformations usually occur only within the single-phase region of the phase diagram.

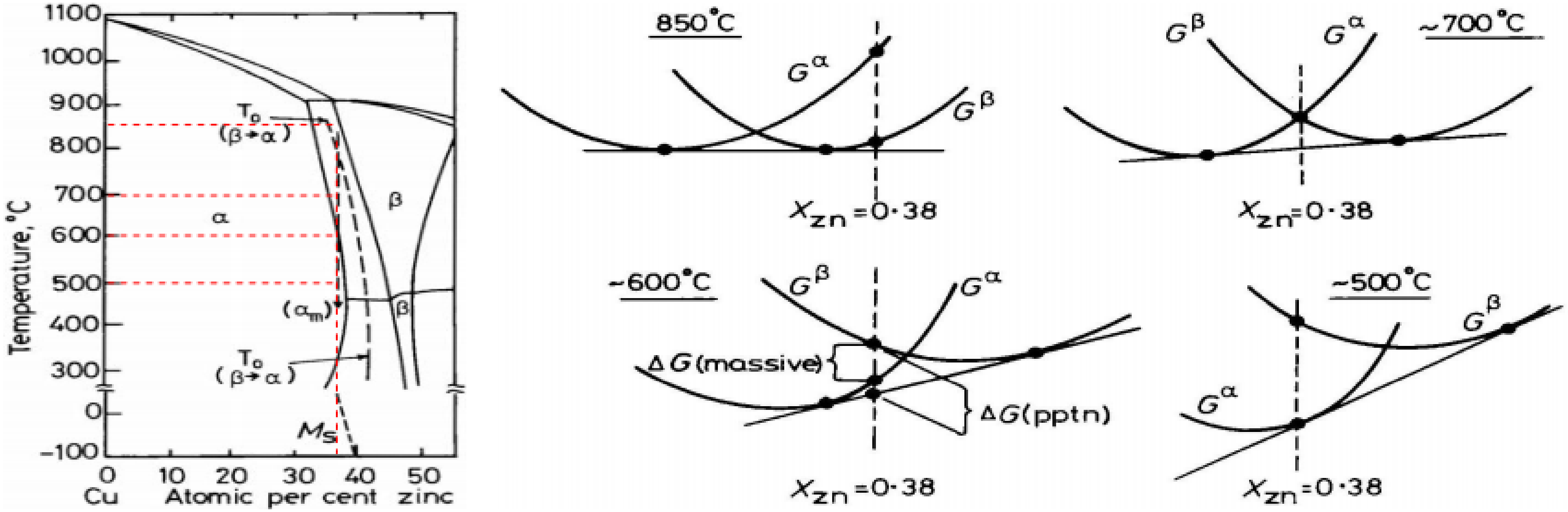


Fig. A schematic representation of the free energy-composition curves for α and β in the Cu-Zn system at various temperatures.

Massive Transformations

- **Massive transformations pure iron**
  - The $\gamma \rightarrow \alpha$ transformation in iron and its alloys can occur massively provided the γ is quenched sufficiently rapidly to avoid transformation near equilibrium, but slow enough to avoid the transformation of martensite.
  - Note the characteristically irregular grain boundaries.
- **Massive v.s. martensitic transformation**
  - Both transformations produce a change of crystal structure without a change in composition.
  - Martensite growth is a diffusionless military transformation, i.e. β is sheared into α by the cooperative movement of atoms across a glissile interface, whereas the growth of massive α involves thermally activated interface migration.

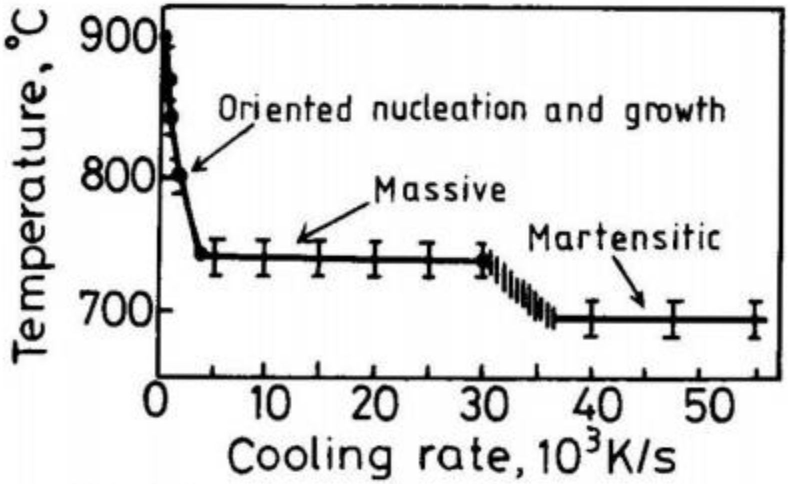


Fig. The effect of cooling rate on the transformation temperature of pure iron.

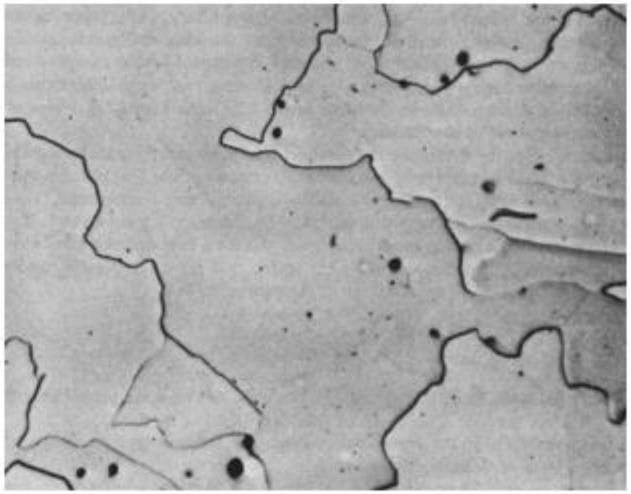


Fig. Massive α in an Fe-0.002 wt% C quenched into iced brine from 1000°C. Note the irregular α/α boundaries.

Diffusionless Transformations

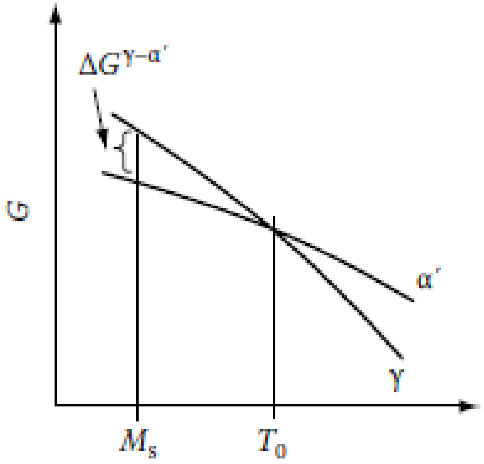
Martensitic Transformations

Martensite is formed in carbon steels by the rapid cooling of austenite at such a high rate that carbon atoms do not have time to diffuse out of the crystal structure in large enough quantities to form cementite (Fe_3C). As a result, the FCC austenite transforms to a highly strained body-centered tetragonal form of ferrite that is supersaturated with carbon. The shear deformations that result produce large numbers of dislocations, which is a primary strengthening mechanism of steels. The highest hardness of a pearlitic steel is 400 Brinell whereas martensite can achieve 700 Brinell. The martensitic reaction begins during cooling when the austenite reaches the martensite start temperature (M_s) and the parent austenite becomes mechanically unstable. As the sample is quenched, an increasingly large % of the austenite transforms to martensite until the lower transformation temperature M_f is reached, at which time the transformation is completed.

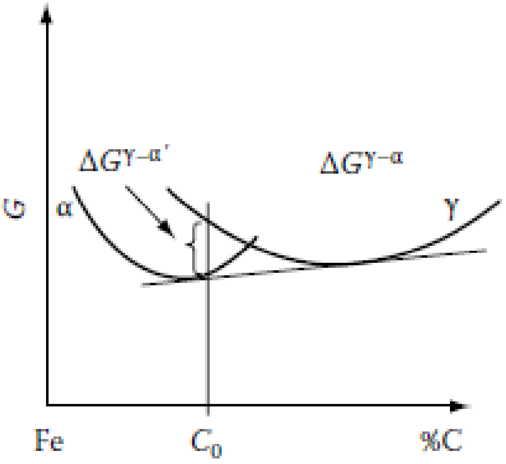
Diffusionless Transformations

Martensitic Transformations

It has been shown that a fully grown plate spanning a whole grain may form within $\sim 10^{-7}$s which means that the α'/γ interface reaches almost the speed of sound in the solid. The first plates form at the M_s temperature. This temperature is associated with a certain driving force for the diffusionless transformation of γ into α' as shown in Fig-a and b.



(a)

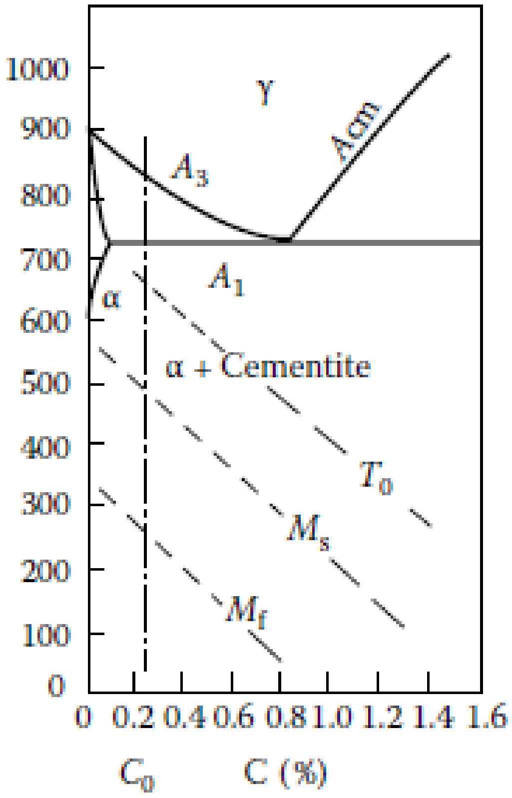


(b)

Diffusionless Transformations

Martensitic Transformations

In low-carbon steels, M_s ~ 500°C (Fig), but increasing C contents progressively decrease the M_s temperature as shown. The M_f temperature corresponds to that temperature below which further cooling does not increase the amount of martensite. In practice the M_f may not correspond to 100% martensite, and some retained austenite can be left even below M_f. The retention of austenite in such cases may be due to the high elastic stresses between the last martensite plates to form, which tend to suppress further growth or thickening of existing plates. As much as 10–15% retained austenite is a common feature



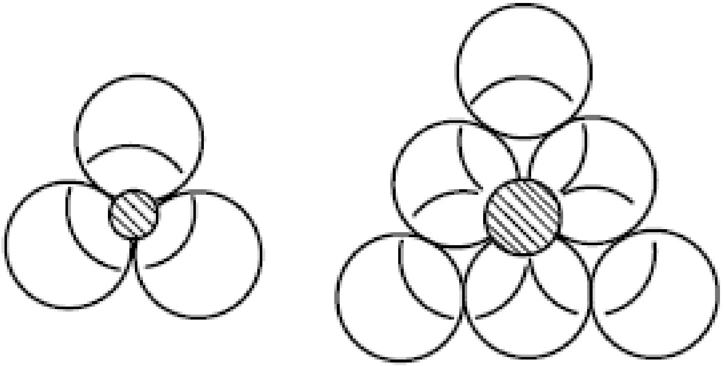
Diffusionless Transformations

Martensitic Transformations

The Solid Solution of Carbon in Iron

In an fcc (or hcp) lattice structure, there are two possible positions for accommodating interstitial atoms as shown in Fig. These are: the tetrahedral site which is surrounded by four atoms and the octahedral site which has six nearest neighbours. The sizes of the largest atoms that can be accommodated in these holes without distorting the surrounding matrix atoms can be calculated if it is assumed that the atoms are close-packed hard spheres. Such a calculation gives:

tetrahedral interstice $d_4 = 0.225D$
octahedral interstice $d_6 = 0.414\mathrm{D}$



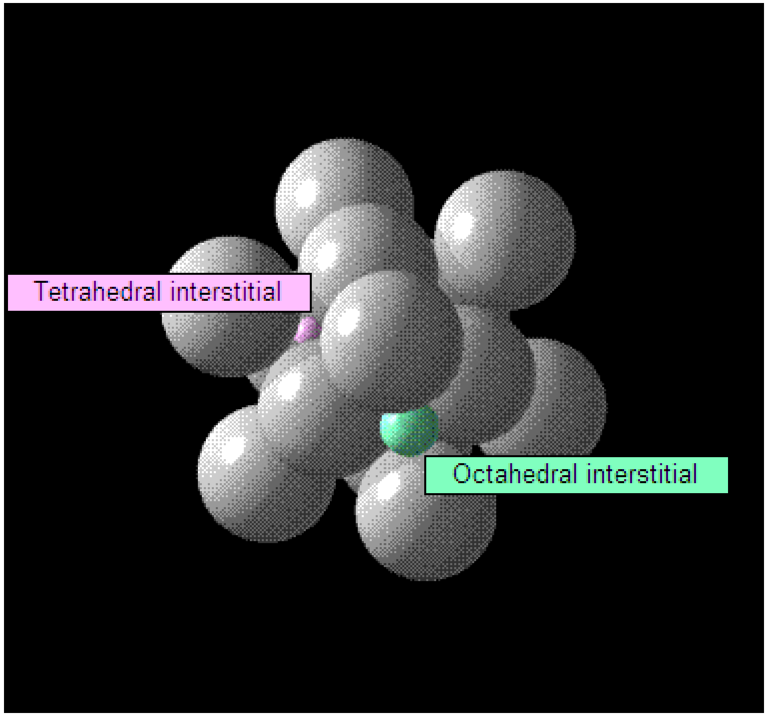
(a) Tetrahedral (b) Octahedral

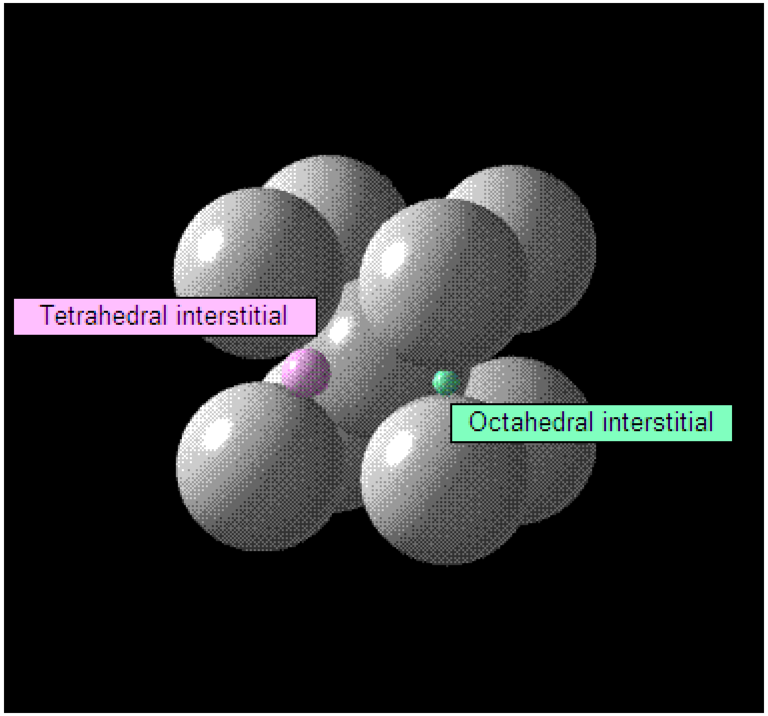
Diffusionless Transformations

Martensitic Transformations

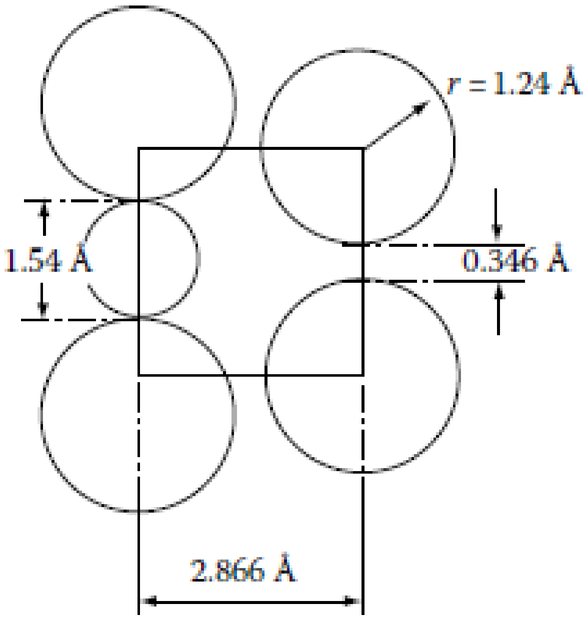
The Solid Solution of Carbon in Iron

However, the diameter of a carbon atom is 1.54 Å. This means that considerable distortion of the austenite lattice must occur to contain carbon atoms in solution and that the octahedral interstices should be the most favourable.



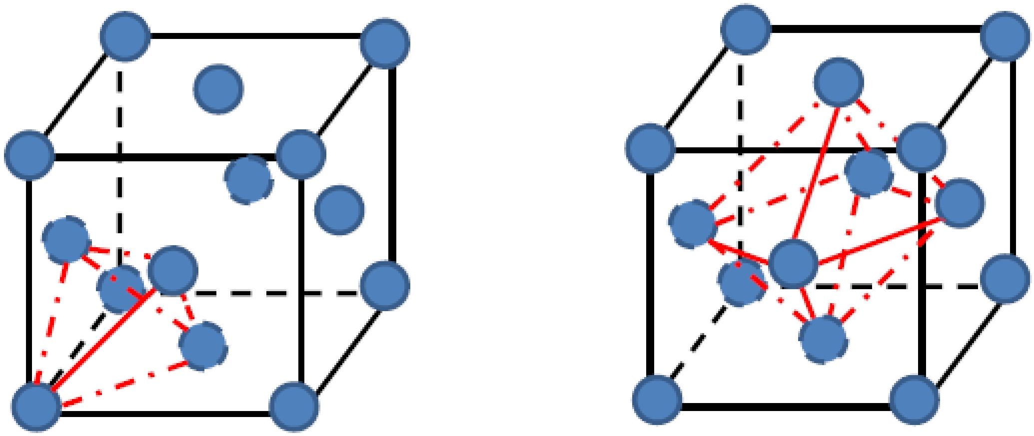


carbon and nitrogen in solution in iron show that these interstitials in fact prefer to occupy the octahedral positions in the bcc lattice. This causes considerable distortion to the BCC lattice as illustrated in Fig. It is assumed that the BCC lattice is weaker in the ⟨100⟩ directions due to the lower number of near and next nearest neighbours compared to the tetrahedral interstitial position.



Why concentration of carbon in α-Fe with BCC structure is less than γ-Fe with FCC structure?

- First let us consider FCC structure (γ-Fe)



- Packing factor of FCC lattice 0.74
- This indicates the presence of voids. Let us discuss it more elaborately.
- In a FCC crystal there are mainly two types of voids:

Tetrahedral: coordination number (CN) is 4. That means the void is surrounded by 4 atoms.

Octahedral: CN is 6. That means the void is surrounded by 6 atoms.

- There are 8 tetrahedral voids in a unit cell. That means 2 voids per atom.

- There are 4 octahedral voids in a unit cell. That means 1 void per atom.

- However, impurities prefer to occupy octahedral voids.

- Because the ratio of the radius of the tetrahedral void to atom is 0.225 and the same for the octahedral void is 0.414.

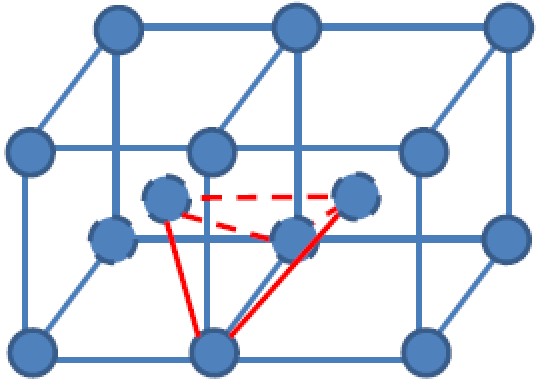
- The ratio of the radius of the carbon atom (size is 77 pm) to Fe (when it has FCC crystal) is 0.596.

- So when a carbon atom occupies any void, lattice will be distorted to increase the enthalpy.

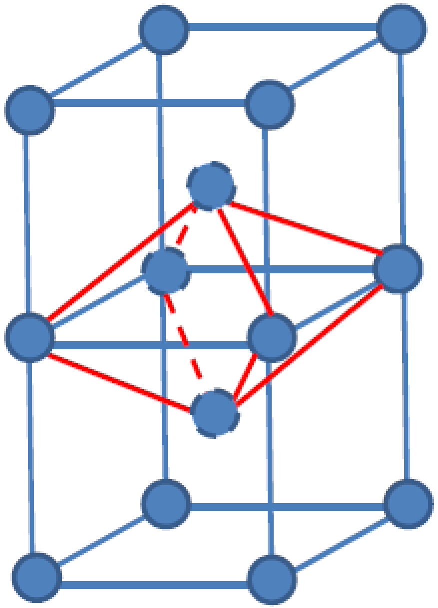
- Distortion will be less if it occupies the octahedral voids.

- Although it increases the enthalpy, carbon atoms will be present up to a certain extent because of the gain in entropy, as explained previously, which decreases the free energy.

Now let us consider the BCC unit cell (α - Fe)



Tetrahedral void



Octahedral void

- Packing factor of BCC lattice 0.68
- So total void in a BCC unit cell is higher than FCC cell.
- However, there are 12 (6 per atom) tetrahedral and 6 (3 per atom) octahedral voids present.
- This number is higher than the number of voids present in a FCC unit cell.

- Unlike voids in FCC lattice, in a BCC lattice the voids are distorted. That means if an atom sits in a void, it will not touch all the host atoms.

- The ratio of the radius of tetrahedral void to atom is 0.29 and the radius of octahedral void to atom is 0.155.

- The ratio of the radius of the C atom (size is 77 pm) to Fe (when it has BCC crystal) is 0.612.

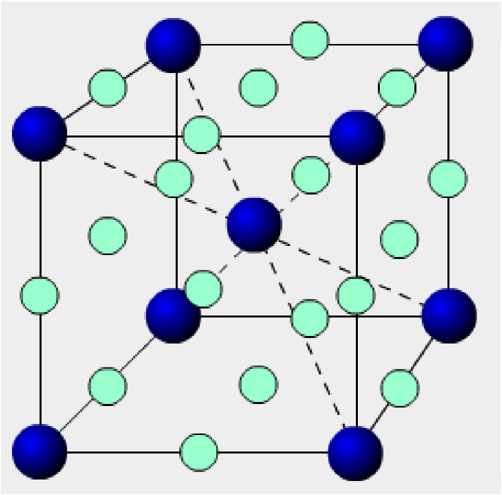
- So it is expected that in a BCC unit cell, impurities should prefer tetrahedral voids.

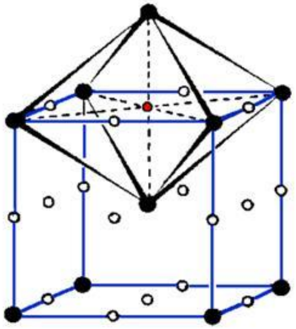
- However, although the octahedral void size is small, planar radius which has 4 atoms on the same plane is 79.6 pm, which is larger that the C atom size. That means it needs to distort only other two atoms.

- On the other hand if C sits in the tetrahedral void it has to distort all four atoms.

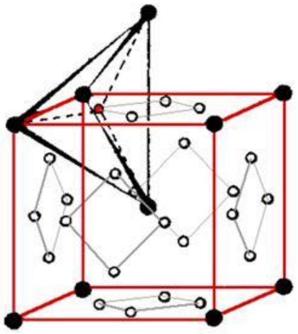
- So in $\alpha -$ Fe with BCC unit cell C occupies the octahedral voids

Octahedral sites in BCC



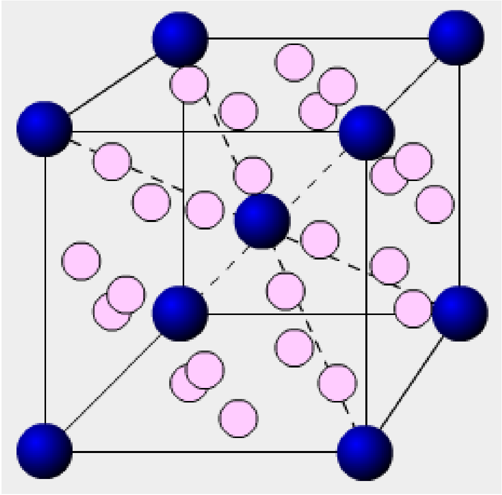


Octahedral Site

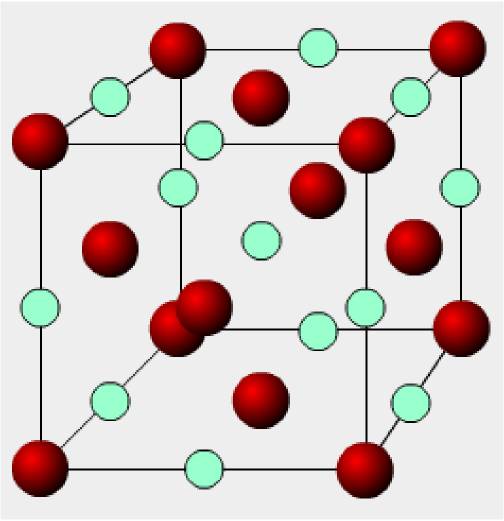


Tetrahedral Site

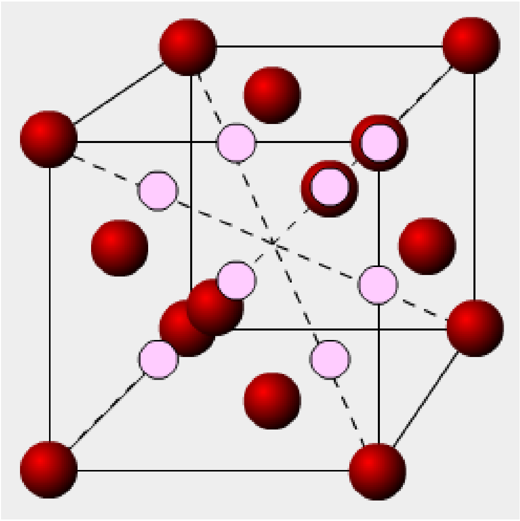
Tetrahedral sites in BCC



Octahedral sites in FCC



Tetrahedral sites in FCC



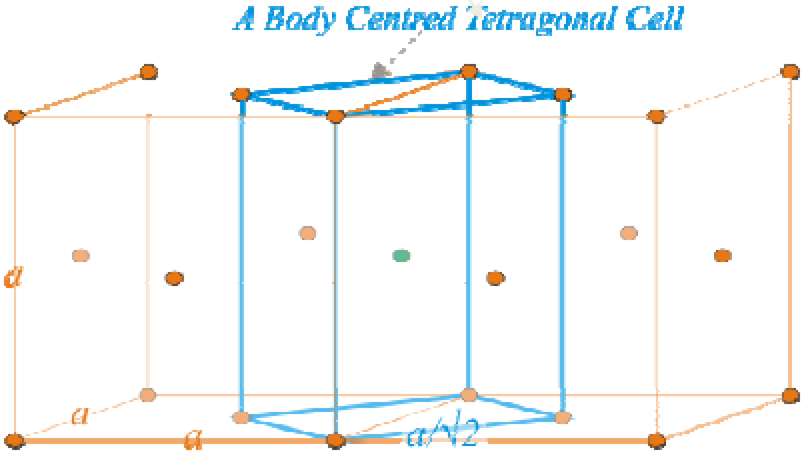
Characteristics of Martensitic Transformations

Martensitic transformation can be understood by first considering an alternate unit cell for the Austenite phase as shown in the figure below.

If there is no carbon in the Austenite (as in the schematic below), then the Martensitic transformation can be understood as a ~20% contraction along the c-axis and a ~12% expansion of the a-axis → accompanied by no volume change and the resultant structure has a BCC lattice (the usual BCC-Fe) → c/a ratio of 1.0.

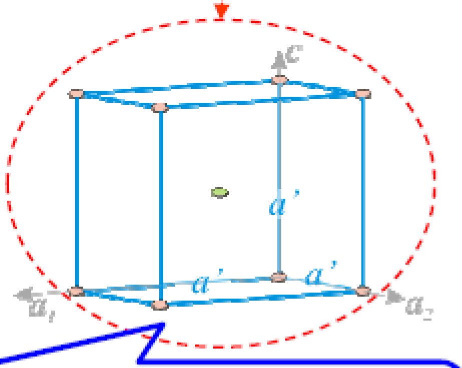
$$\underset{0.8\,\%C}{\gamma\,(FCC)} \xrightarrow{Quench} \underset{0.8\,\%C}{\alpha'\,(BCT)}$$

FCC Austenite alternate choice of Cell



FCC → BCC

In Pure Fe after
the Martensitic transformation
$c = a$



~20% contraction of *c-axis*
~12% expansion of *a-axis*

Diffusionless Transformations

Martensitic Transformations

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 $m^{1/2}$).

Martensitic transformation is the name for any transformation that takes place in a diffusionless and military manner - that is, these transformations take place through atomic movements which are less than one atomic spacing; and in these transformations atoms change their positions in a coordinated manner (unlike thermally activated diffusional, or, so-called, civilian processes).

In shape memory alloys such as Ni-Ti (nitinol), it is the martensitic transformation that is responsible for the shape memory effect.

In this topic, we describe some characteristic features of the martensitic transformations (with specific reference to steels in which, this transformation is repsonsible for hardening by quenching).

Since martensitic transformations are diffusionless, necessarily, the composition does not change during the transformation. It is only the crystal structure that changes. For example, in Fe-C alloys, the austenite (fcc) transforms into martensite (bct);

in Ni-Ti, an ordered bcc transforms to another ordered CsCl type structure. Note that since martensitic transformation is diffusionless, if the austenitic phase is ordered, the martensitic phase is also ordered.

Characteristics of Martensitic Transformations

Occur at high supersaturations, without change in composition

No long range diffusion → Movement of atoms a fraction of the inter-atomic distance

Nearest neighbour configuration remains unchanged

Cooperative movement of a large group of atoms → transformation proceeds at the speed of sound in the material

Thermal activation does not play a role in the growth of the martensitic phase
Thermal activation may play a role in the nucleation of martensite

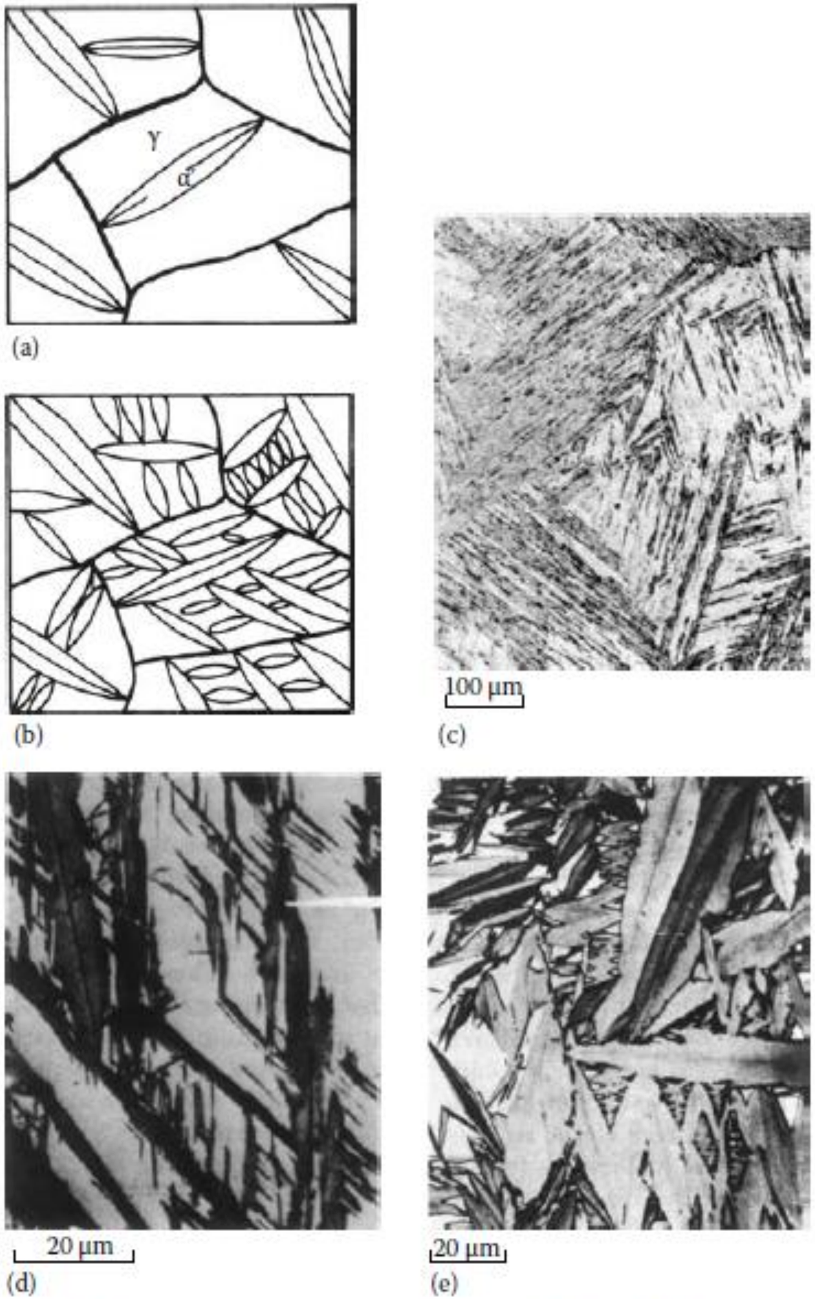
Usually martensite crystals nucleate and grow across the whole grain (in some cases this growth is a function of temperature)

Martensitic crystals have a specific orientation relationship with the parent phase

Interface between Martensite and parent phase → Coherent or Semi-coherent

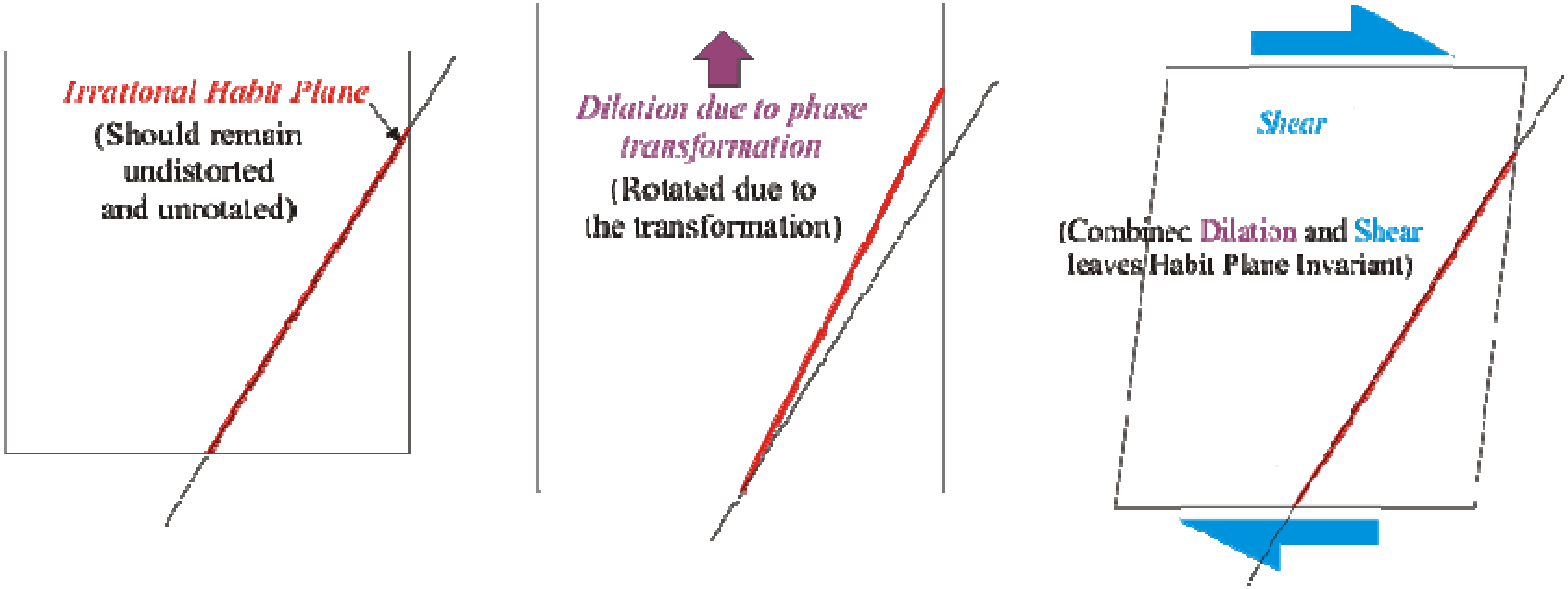
At a given temperature (between M_s and M_f) the fraction transformed ↑ with plastic deformation

With prior plastic deformation the transformation temperature can be increased to M_d



(a), (b) Growth of martensite with increasing cooling below M_s (c)-(e) Different martensite morphologies in iron alloys: (c) low C (lath), (d) medium C (plate), (e) Fe–Ni (plate).

Characteristics of Martensitic Transformations



Irrational Habit Plane

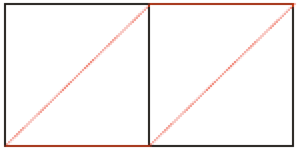
(Should remain undistorted and unrotated)

Dilation due to phase transformation

(Rotated due to the transformation)

Shear

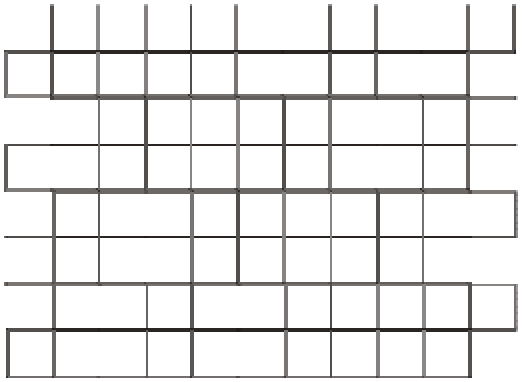
(Combined Dilation and Shear leaves Habit Plane Invariant)



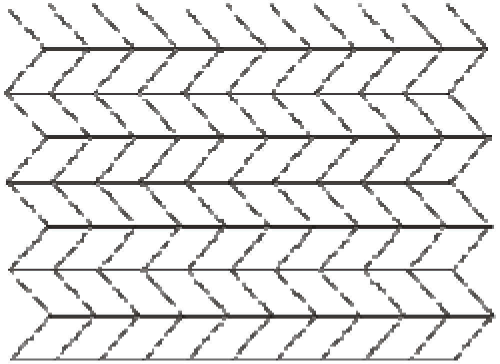
But shear will distort the lattice!

Slip

Twinning



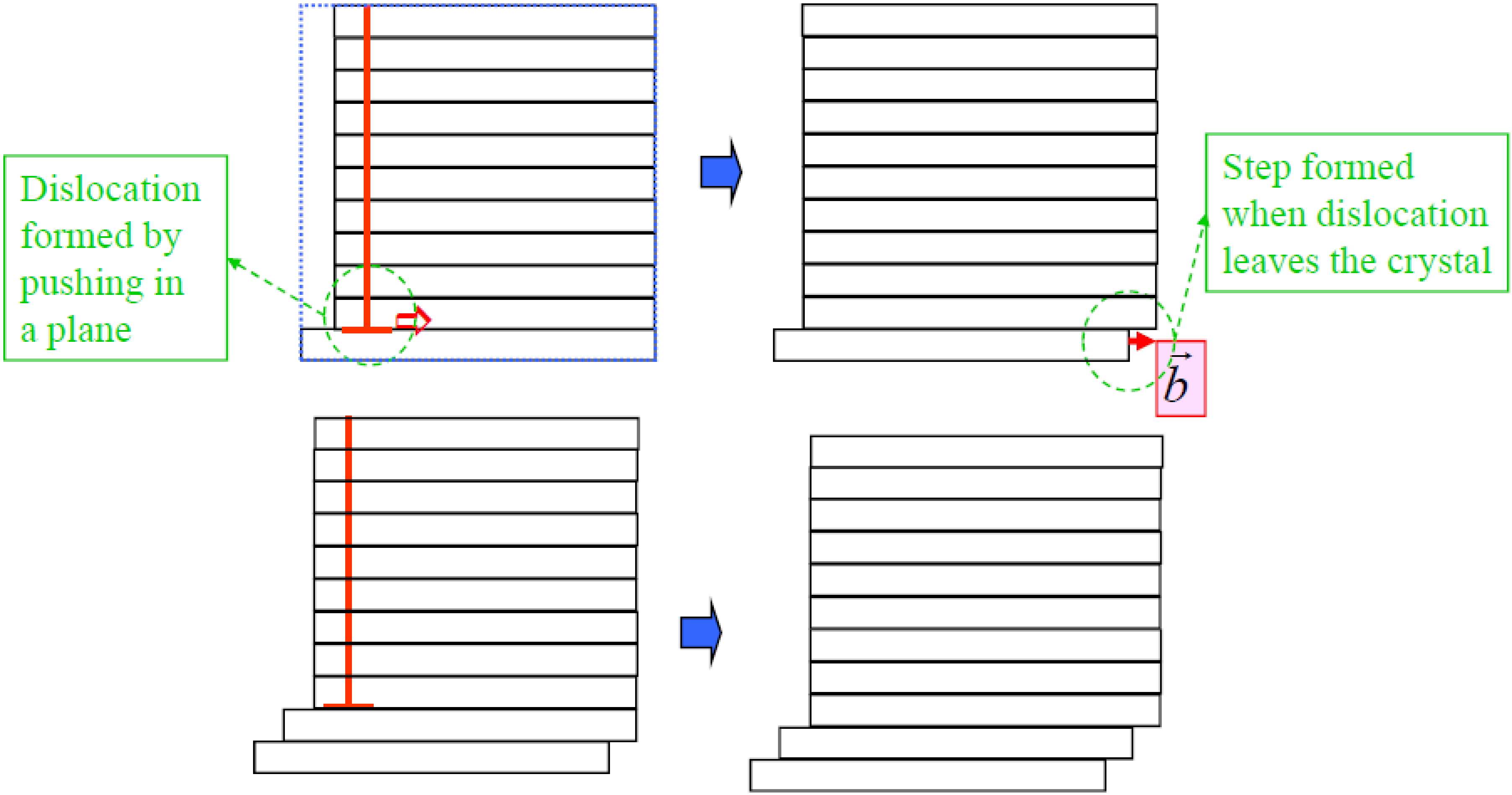
Average shape remains undistorted



Characteristics of Martensitic Transformations

How does the motion of dislocations lead to a macroscopic shape change?

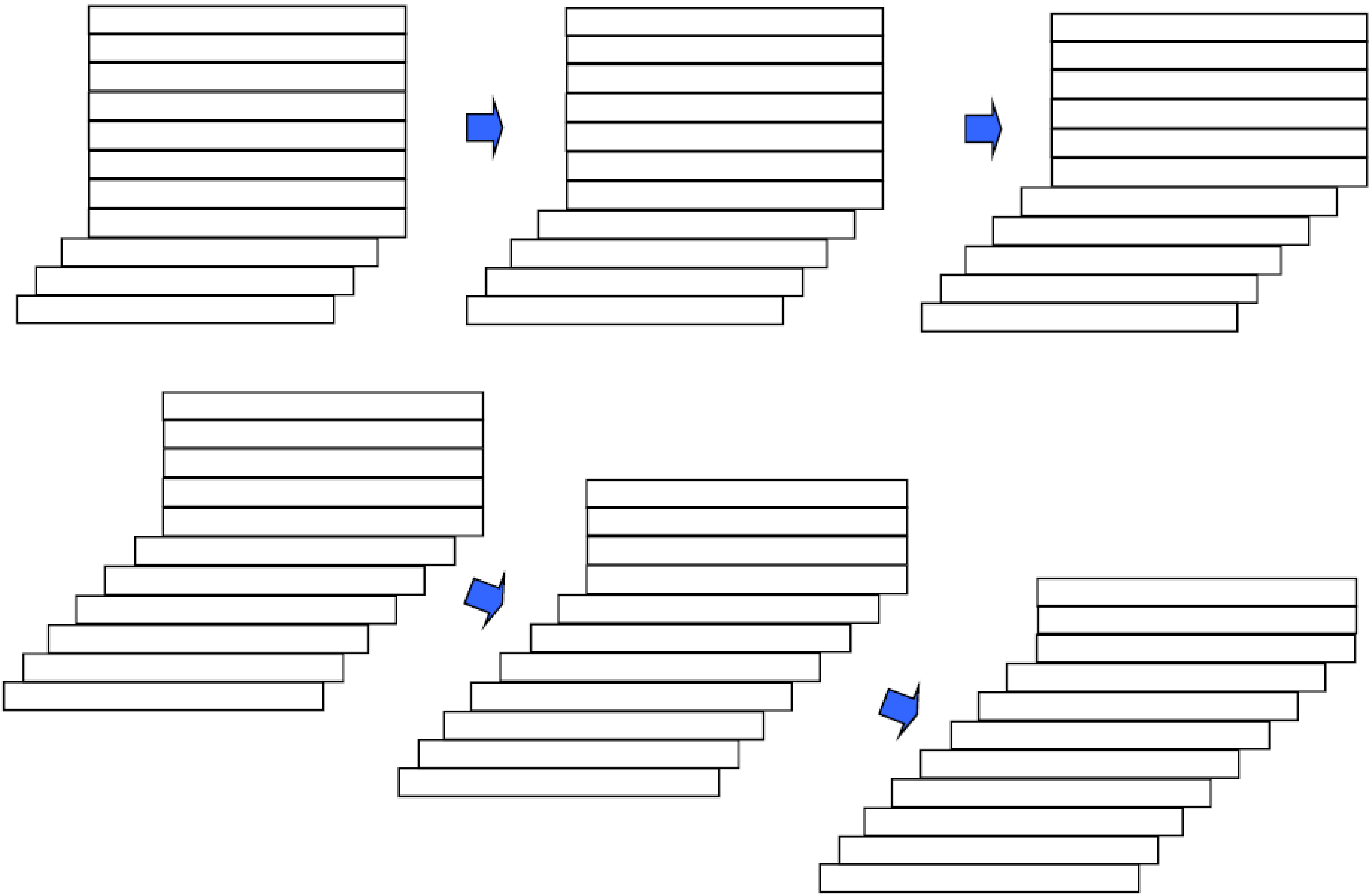
From microscopic slip to macroscopic deformation



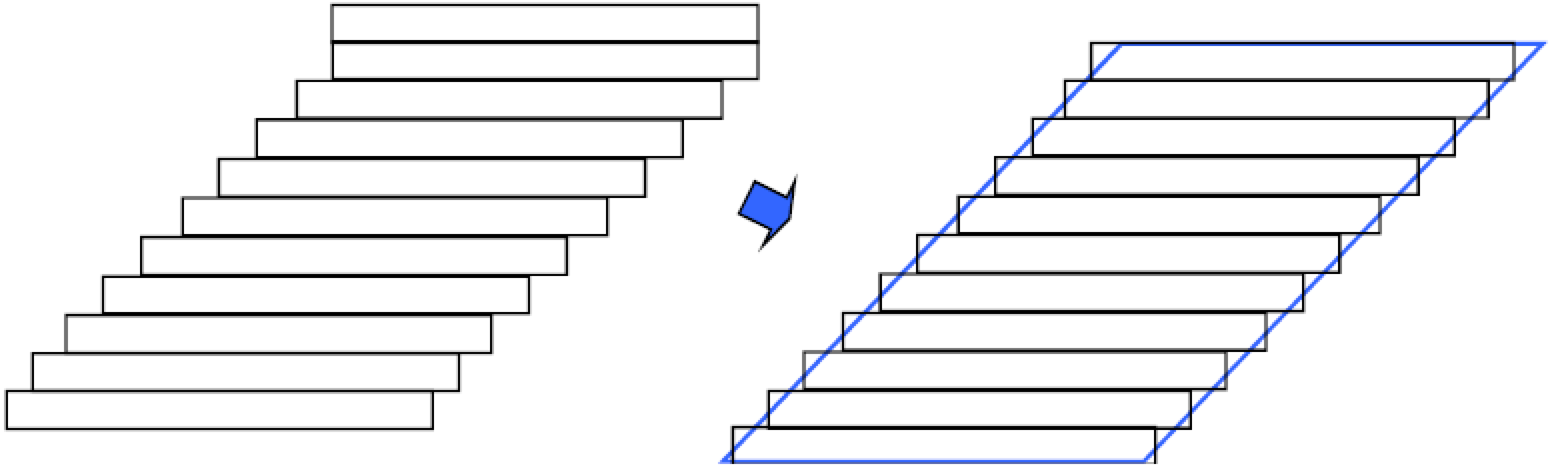
Dislocation formed by pushing in a plane

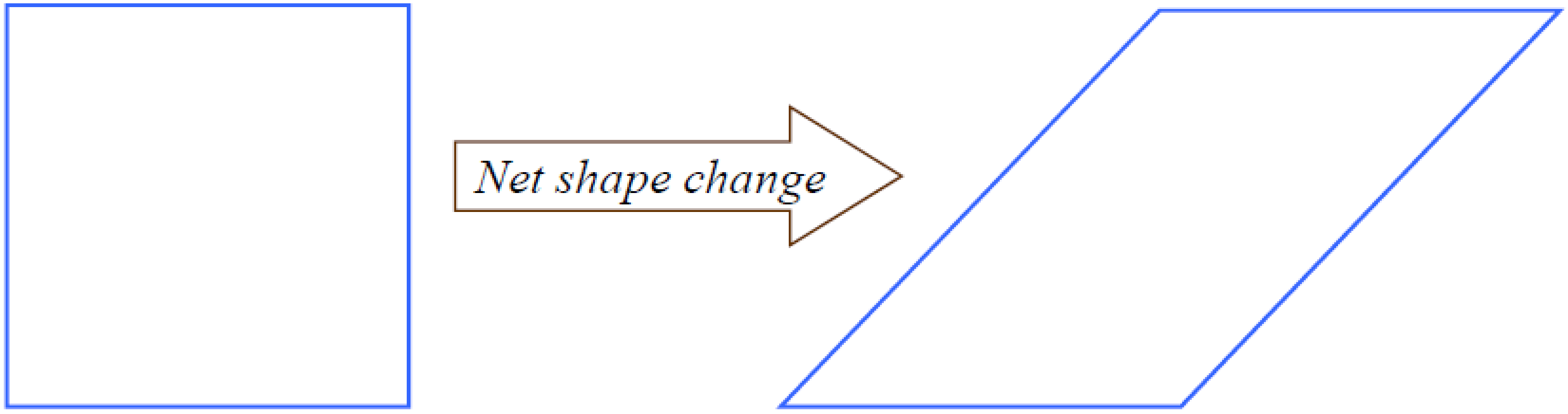
Step formed when dislocation leaves the crystal

Characteristics of Martensitic Transformations

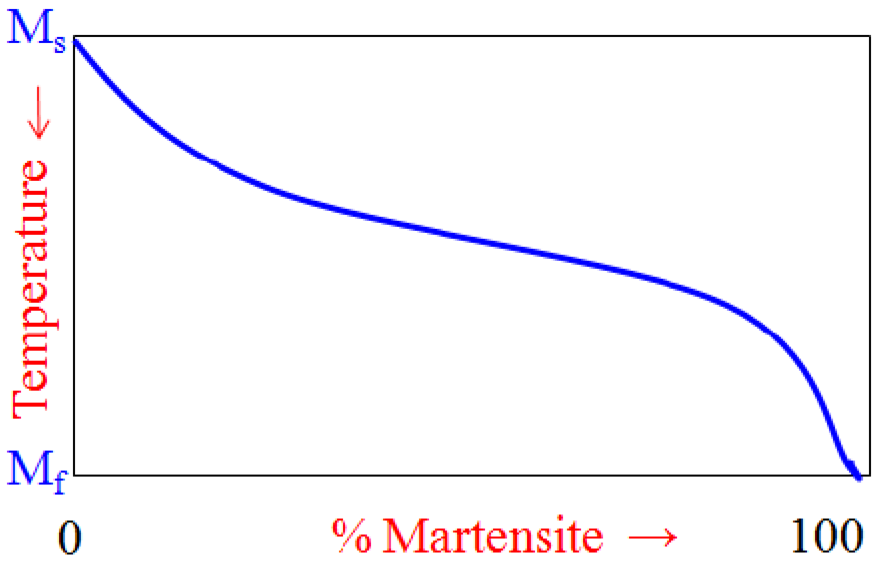


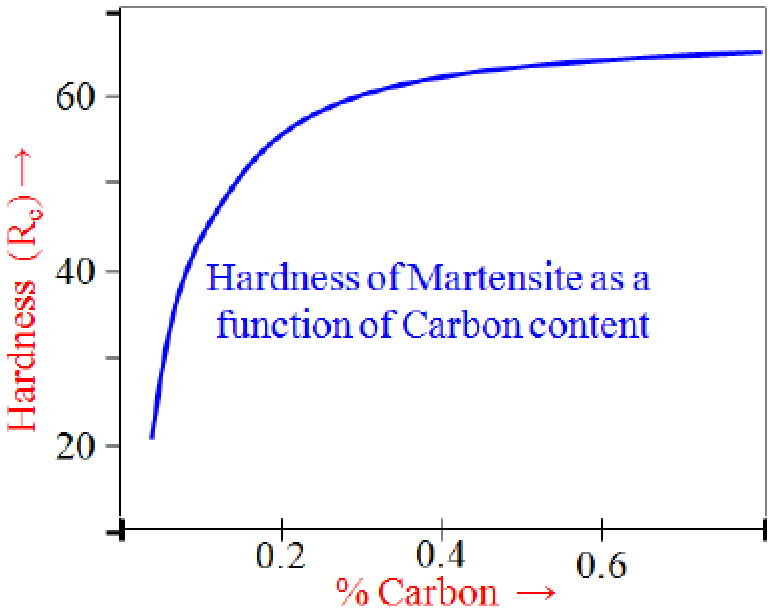
Characteristics of Martensitic Transformations





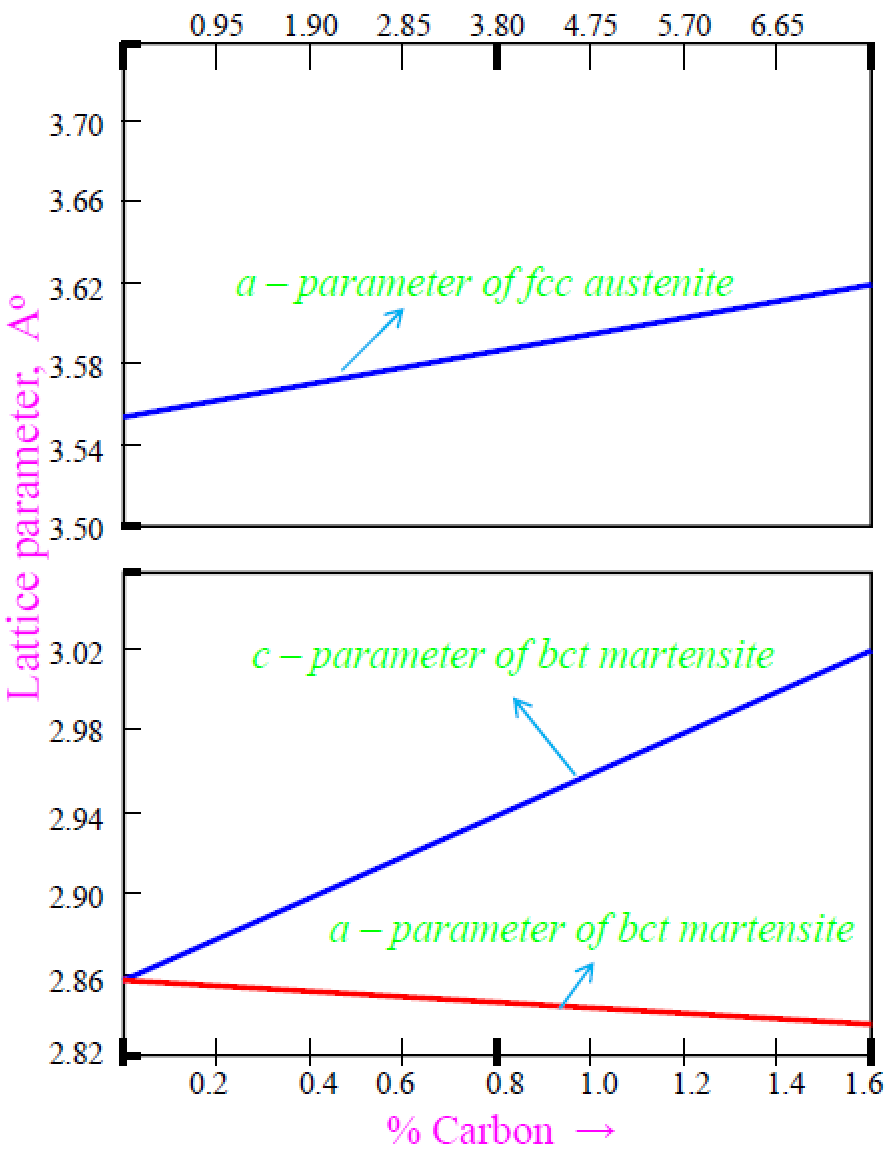
Characteristics of Martensitic Transformations

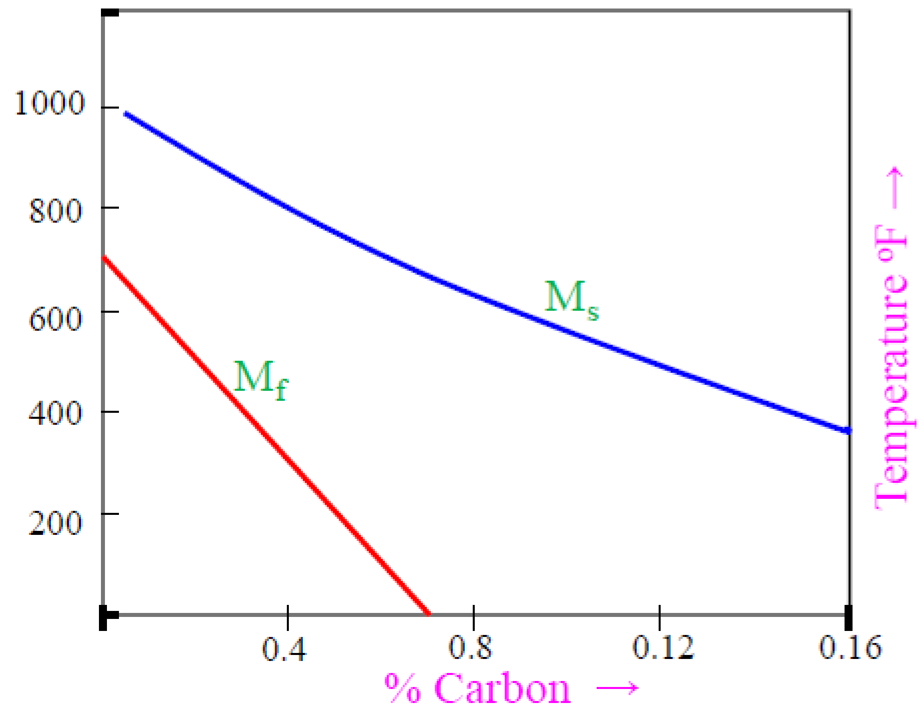




Properties of 0.8% C steel		
Constituent	Hardness (R_c)	Tensile strength (MN / m^2)
Coarse pearlite	16	710
Fine pearlite	30	990
Bainite	45	1470
Martensite	65	-
Martensite tempered at 250 °C	55	1990

Characteristics of Martensitic Transformations





Influence of carbon on the martensite range

Effect carbon on lattice parameters of austenite and martensite

Driving Force for Martensitic Transformations

Diffusionless transformations require larger driving forces than for diffusional transformations

In order for a transformation to occur without long range diffusion, it must take place *without a change in composition*

This leads to the so-called T_0 concept, which is the temperature at which the new phase can appear with a net decrease in free energy *at the same composition as the parent (matrix) phase*.

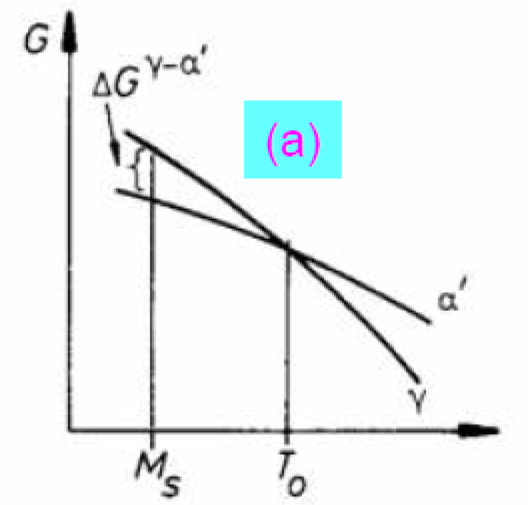
As the following diagram demonstrates, the temperature, T_0, at which segregation-less transformation becomes possible (i.e. a decrease in free energy would occur), is always less than the solvus (liquidus) temperature.

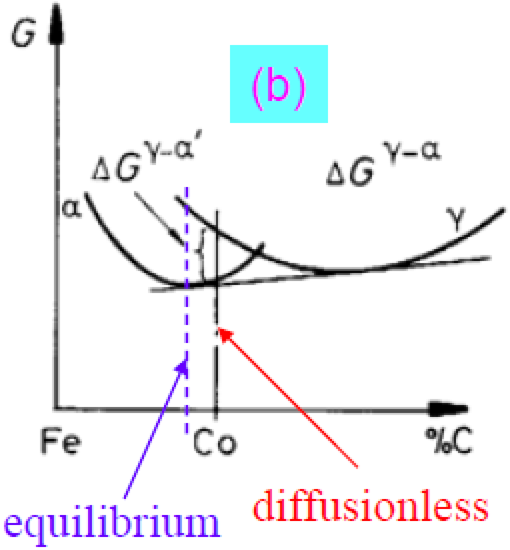
The driving force for a martensitic transformation can be estimated in exactly the same way as for other transformations such as solidification.

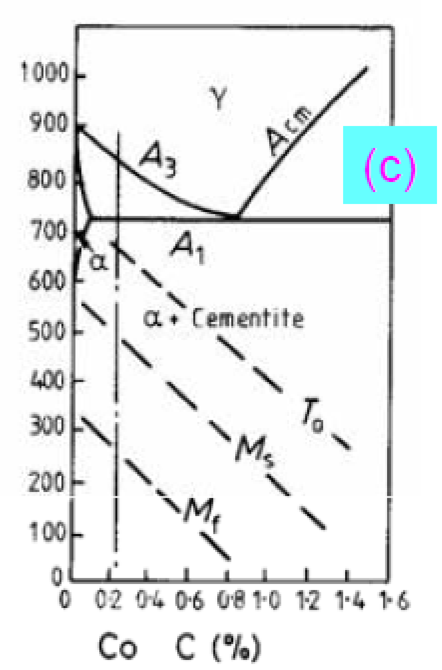
Provided that an enthalpy (latent heat of transformation) is known for the transformation, the driving force can be estimated as proportional to the latent heat and the undercooling below T_0.

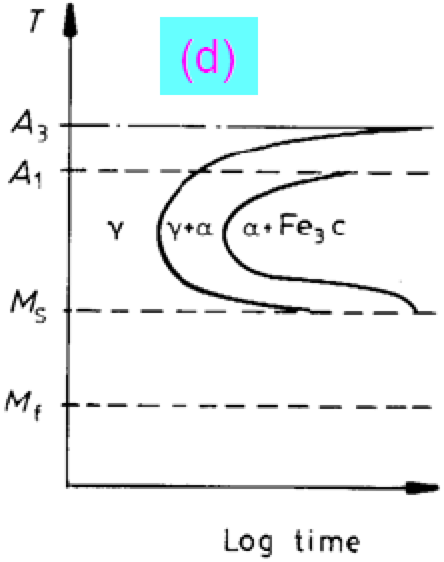
$$\Delta G^{\gamma \to \alpha'} = \Delta H^{\gamma \to \alpha'} \frac{T_0 - M_S}{T_0}$$

Various Ways of Showing Martensitic Transformations









(a) Free energy – temperature diagram for Austenite and martensite of fixed carbon concentration

(b) Free energy – composition diagram for the austenite and martensite phases at the M_s temperature.

(c) Iron-carbon phase diagram with T_0 as defined in (a), M_s and M_f superimposed.

(d) M_s and M_f in relation to the TTT diagram for alloy C_0 in C

Role of Grain Size on Martensite Growth

Since martensite growth relies on maintaining a certain coherency with the surrounding austenite, a high-angle grain boundary is an effective barrier to plate growth. Thus while grain size does not affect the number of martensite nuclei in a given volume, the final martensite plate size *is* a function of the grain size. Another important feature of grain size is its effect on residual stress after transformation is completed. In large grain sized material the dilatational strain associated with the transformation causes large residual stresses to be built up between adjacent grains and this can even lead to grain-boundary rupture (quench cracking) and substantially increase the dislocation density in the martensite. Fine grain-sized metals tend to be more self-accommodating and this, together with the smaller martensite plate size, provides for stronger, tougher material.

Massive vs. Martensitic Transformations

There are two basic types of *diffusionless* transformations.

One is the *massive transformation*. In this type, a diffusionless transformation takes place without a definite orientation relationship. The interphase boundary (between parent and product phases) migrates so as to allow the new phase to grow. It is, however, a civilian transformation because the atoms move individually.

The other is the *martensitic transformation*. In this type, the change in phase involves a definite orientation relationship because the atoms have to move in a coordinated manner. There is always a change in shape which means that there is a strain associated with the transformation. The strain is a general one, meaning that all six (independent) coefficients can be different.

	CIVILIAN	MILITARY
Diffusion Required	Precipitation, Spinodal Decomposition	-
Diffusionless	Massive Transformations	Martensitic Transformations

Effect of Retained Austenite

In most steels, especially those containing more than 0.4% C, austenite is retained after quenching. On ageing in the range 200–300°C this austenite decomposes to bainite. In some high-alloy steels austenite can be stabilized to such low temperatures that the martensite partially reverts into austenite on heating. Very thin regions of retained austenite may even be present between laths in low-carbon steel, and this is thought to improve the toughness of these steels independently of tempering treatments.