Phase transformations in solids

Martensitic transformations

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Martensitic transformation

Rapid quenching of steels from the austenite field results in a metastable phase: martensite.

Its formation is known to occur via atomic movements of less than one atomic spacing. Atoms move fast and cooperatively (military transformation).

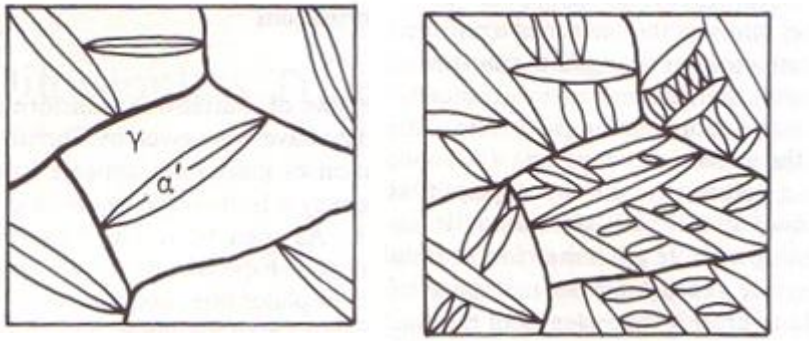
Martensites occur in several materials: steels, Co, SMA,…. although deriving the name from ferrous alloys.

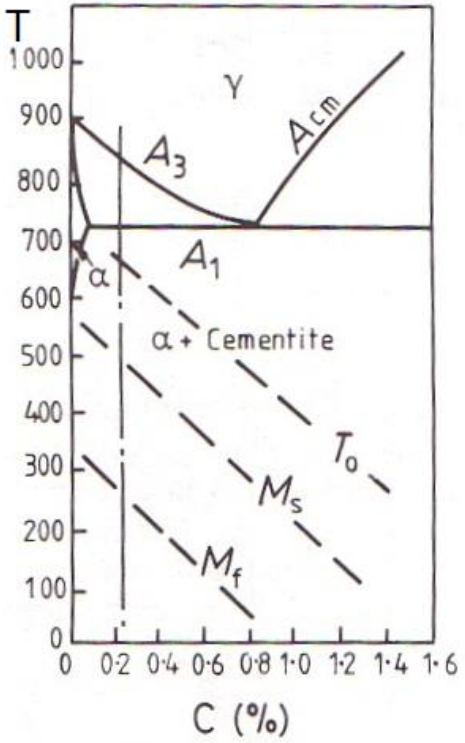
In steels martensite (α') has the same composition as the original austenite (γ): it can be defined as a supersaturated solid solution of C in distorted α-Fe. The distortion results in a tetragonal (bct) phase having peculiar nucleation and growth mechanisms.

Phenomenology of the transformation

Lens shaped plates spanning original γ grains. Density of new grains unrelated to γ grain size; limited number of orientations. High speed of formation: close to sound velocity. First plates form at M_S, start temperature. Volume fraction increases steadily with decreasing temperature. No further transformation below finish temperature M_F. Both temperatures decrease with increasing C %.

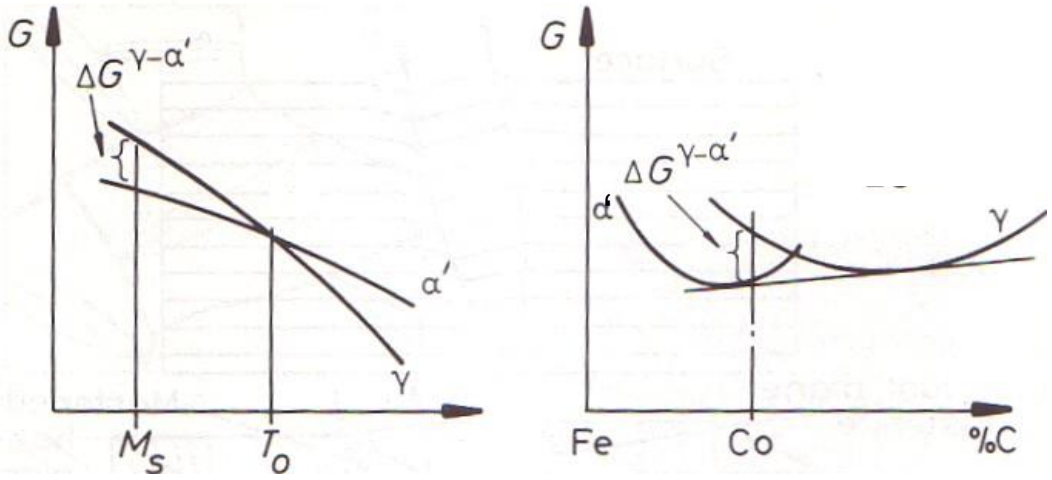
Some retained austenite most often present because of elastic stresses imposed by transformation.

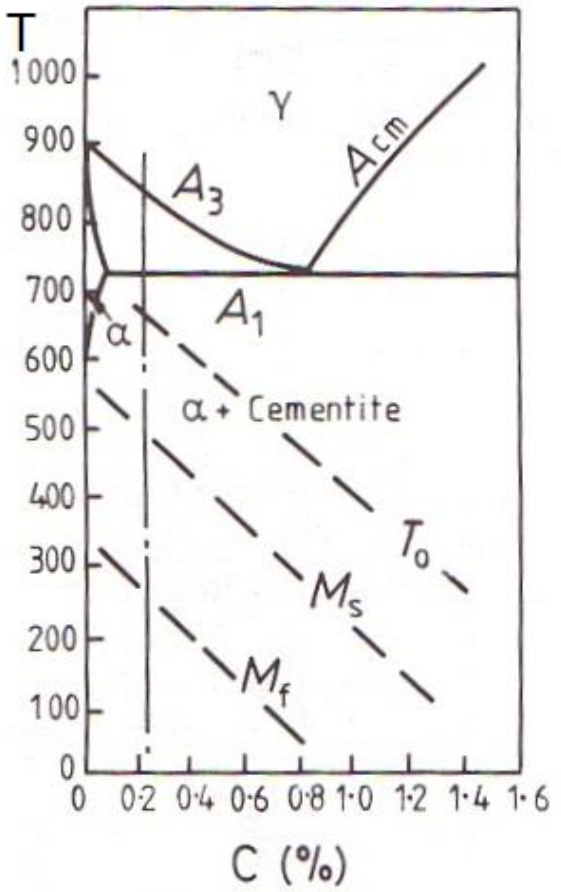




Phenomenology of the transformation

The free energy of γ and α' is equal at T_0 for each C_0 content. M_S occurs on undercooling with respect to T_0. The free energy difference changes with C content. Equilibrium phases are α + Fe_3C anyway.





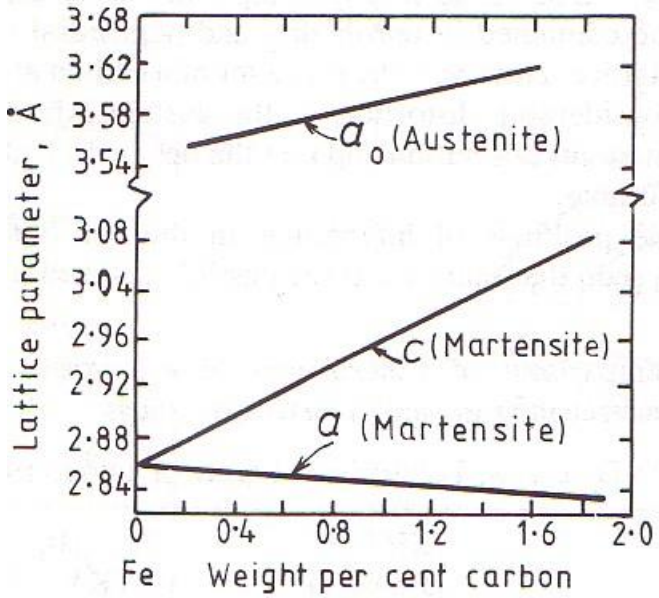
The driving force for nucleation at M_S is

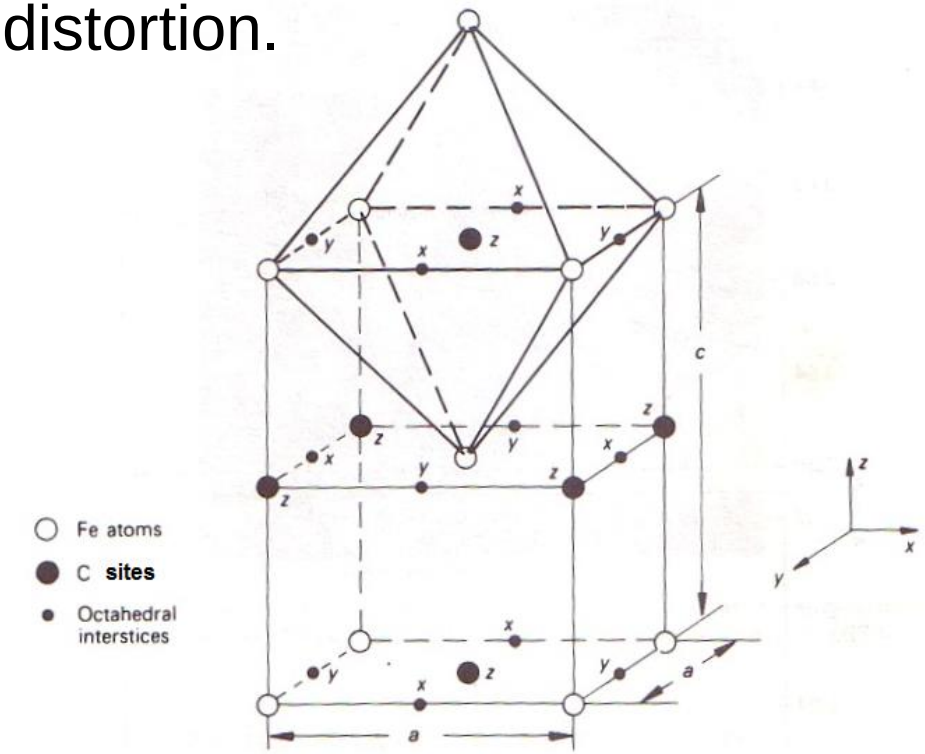
$$\Delta G^{\gamma\rightarrow\alpha'} = \Delta H^{\gamma\rightarrow\alpha'} \frac{(T_0 - M_S)}{T_0}$$

The enthalpy difference between γ and α' is of the order 1/10-1/20 of heat of fusion. It is higher if austenite is ordered (e. g. SMA).

The crystallography of martensite

Austenite contains C in octahedral interstices (size 0.414*~3.6 Å) being stressed (see increase in lattice spacing). C is retained in octahedral interstices in α' (*z* site size in bcc 0.155 *~2.86 Å) causing distortion to bct. *x*, *y* sites: less distortion.



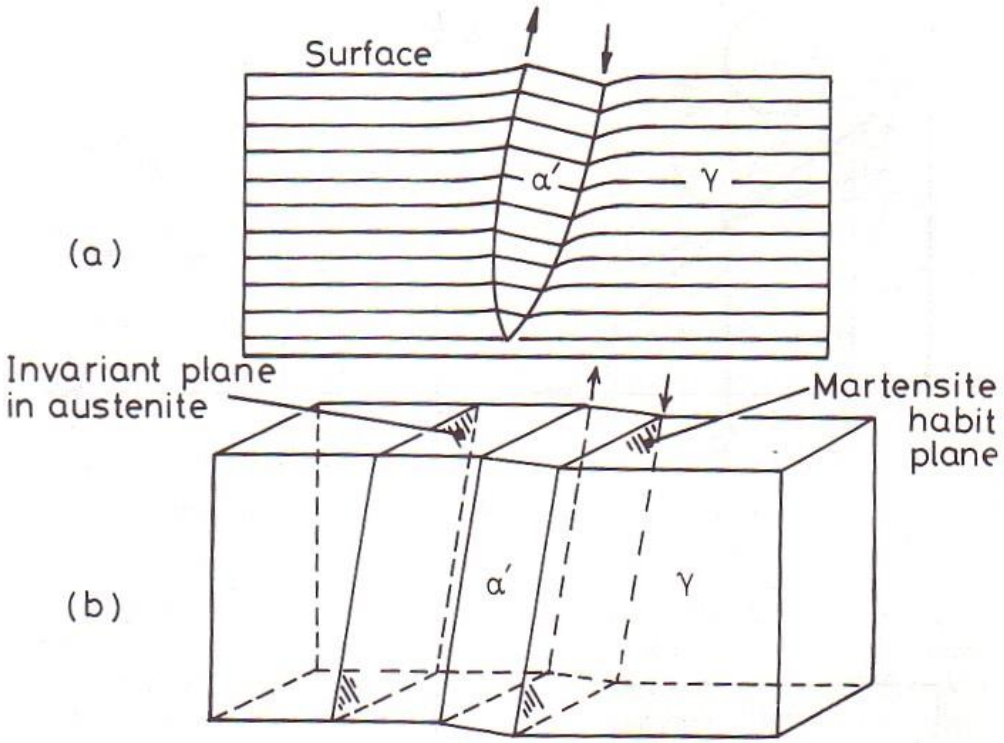


c lattice constant increases while *a* decreases with C%.

Lattice constants trend and number of C atoms (from 1 every ~50 cells to 1 every ~5 cells) suggest cooperativity at long range.

The crystallography of martensite

The α' plates giving relief on the surface of a polished specimen testify elastic deformation of surface. Phases appear continuous with coherent interfaces which move fast independent of thermal activation. Martensite grows on undistorted *habit plane*, common also to austenite.

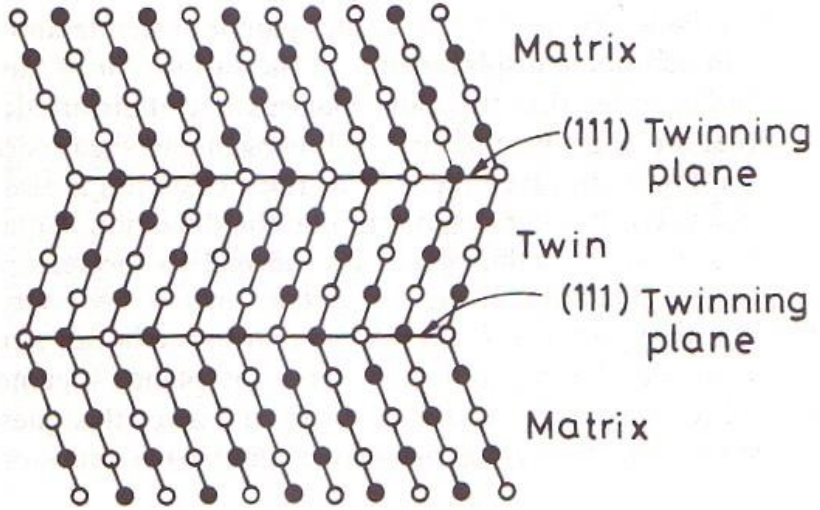


Orientation variants and plate morphology depend on alloy content.

To move fast, planes where growth occurs should be assisted by mobile dislocation interface. How?

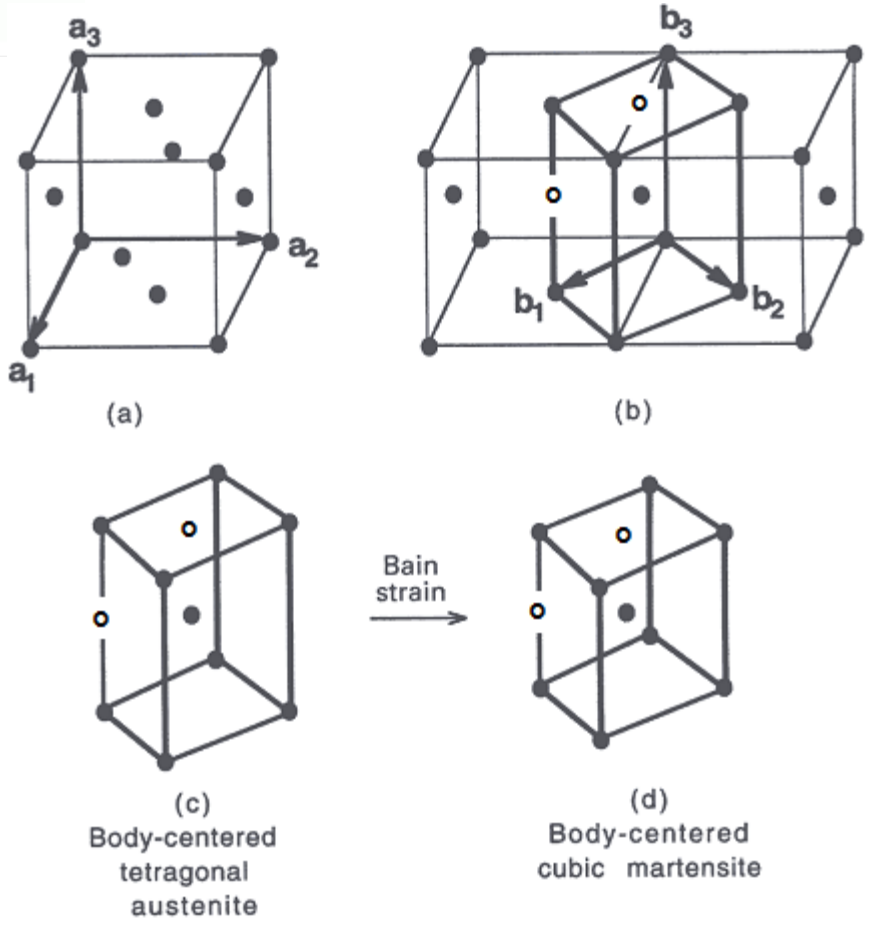
The crystallography of martensite

$\gamma \rightarrow \alpha'$ transformation also implies ~ 4 % expansion which takes place normal to habit plane. Since habit plane is not distorted, martensite must be generated by shear parallel to habit plane. This is called *invariant plane strain* as in conventional twinning.



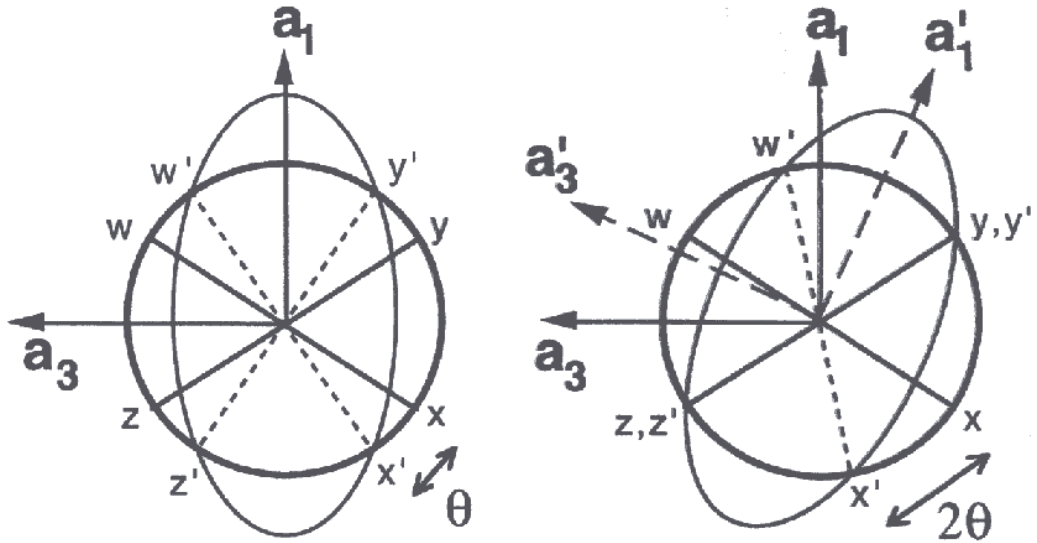
Note this is an example to illustrate invariant planes in twinning, it does not imply a mechanism for martensitic transformation.

Bain strain



Lattice correspondence between austenite and bct martensite: ~ 20% contraction along **a**$_3$, ~ 12 % expansion along **a**$_1$ and **a**$_2$.

- Fe atoms; ○ C atoms



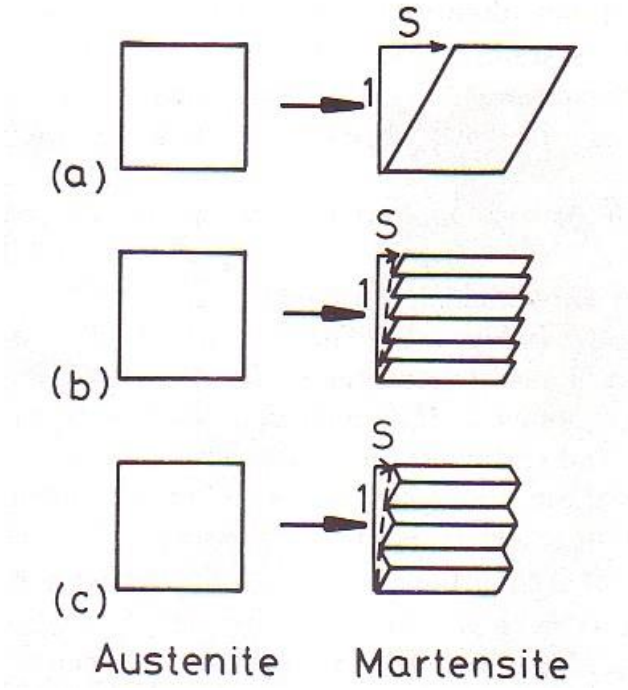
Contraction and expansion seen on a sphere: to have invariant plane further rotation is needed.

Martensitic transformation

pure lattice deformation →

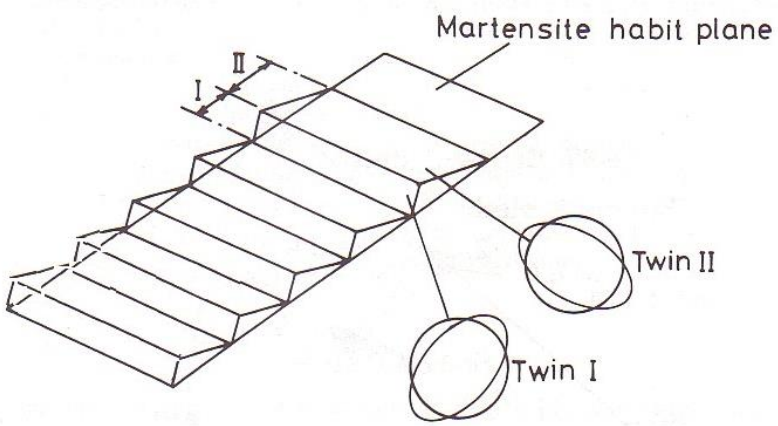
deformation accomodated by slip (up to 0.5 %C) →

deformation accomodated by twinning (higher C content) →



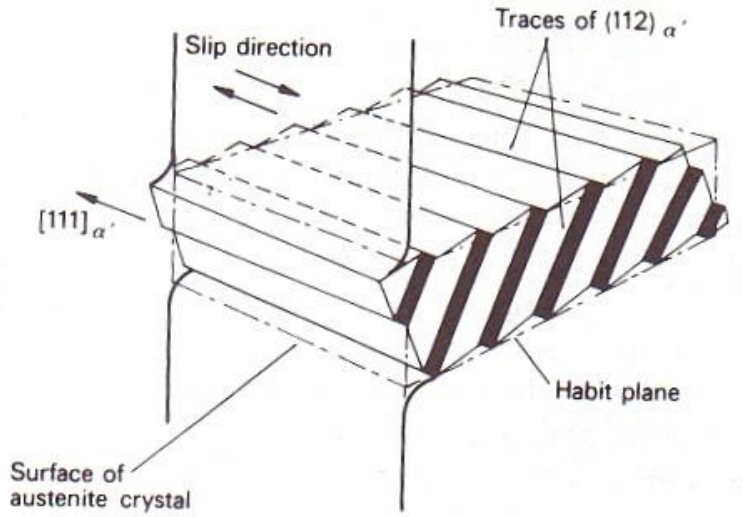
Martensite habit plane → plane in austenite with no net macroscopic distortion.

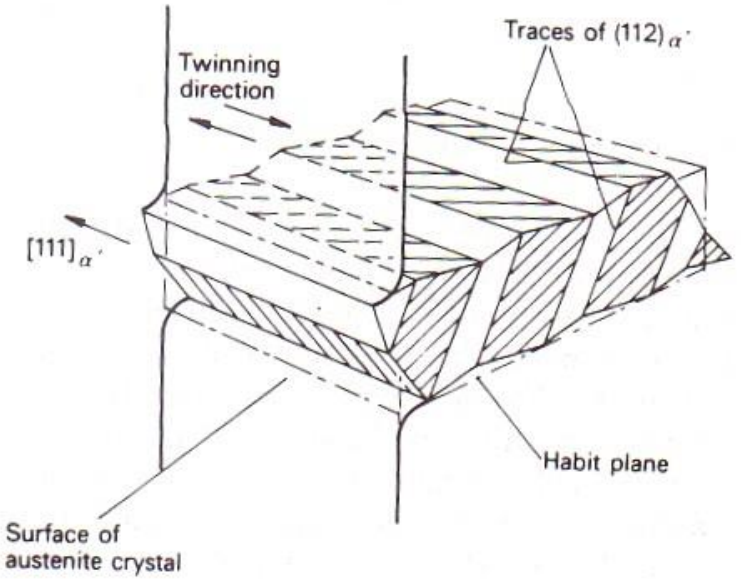
Averaging over series of dislocations or twins reduces distortion to zero.



Martensitic transformation

Further images of lattice invariant deformation showing slip/twinning planes and direction.





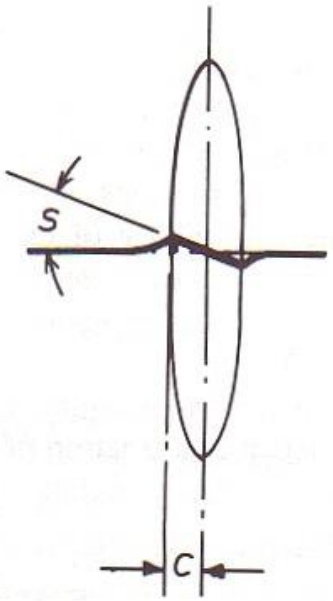
Martensite nucleation

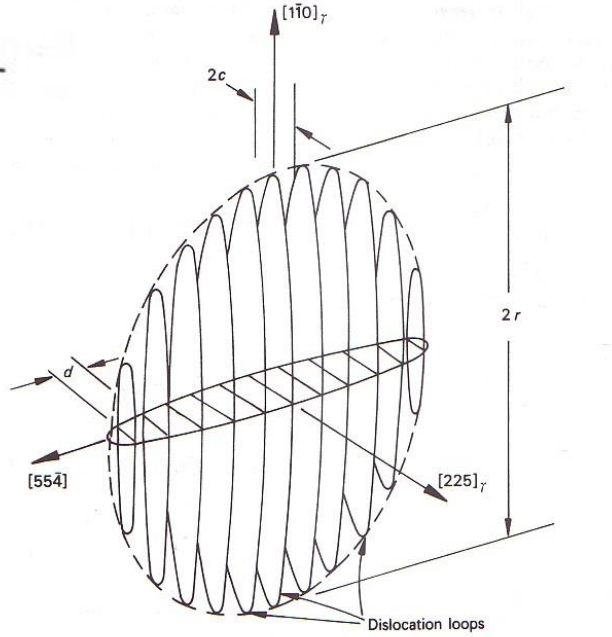
Nucleation determines form and size of plates (growth is too fast to be controlled). The free energy of nucleus formation contains an elastic strain energy term (Bain strain, *s*)

$$\Delta G = -V\Delta G_V^{\gamma\rightarrow\alpha'} + A\sigma + V\Delta G_{el.str}$$

which is accomodated by interfacial dislocation loops providing semi-coherent interface with matrix. Dislocations orientation and grouping may determine site potency.

Nucleation is heterogeneous possibly on pre-existing embryos.



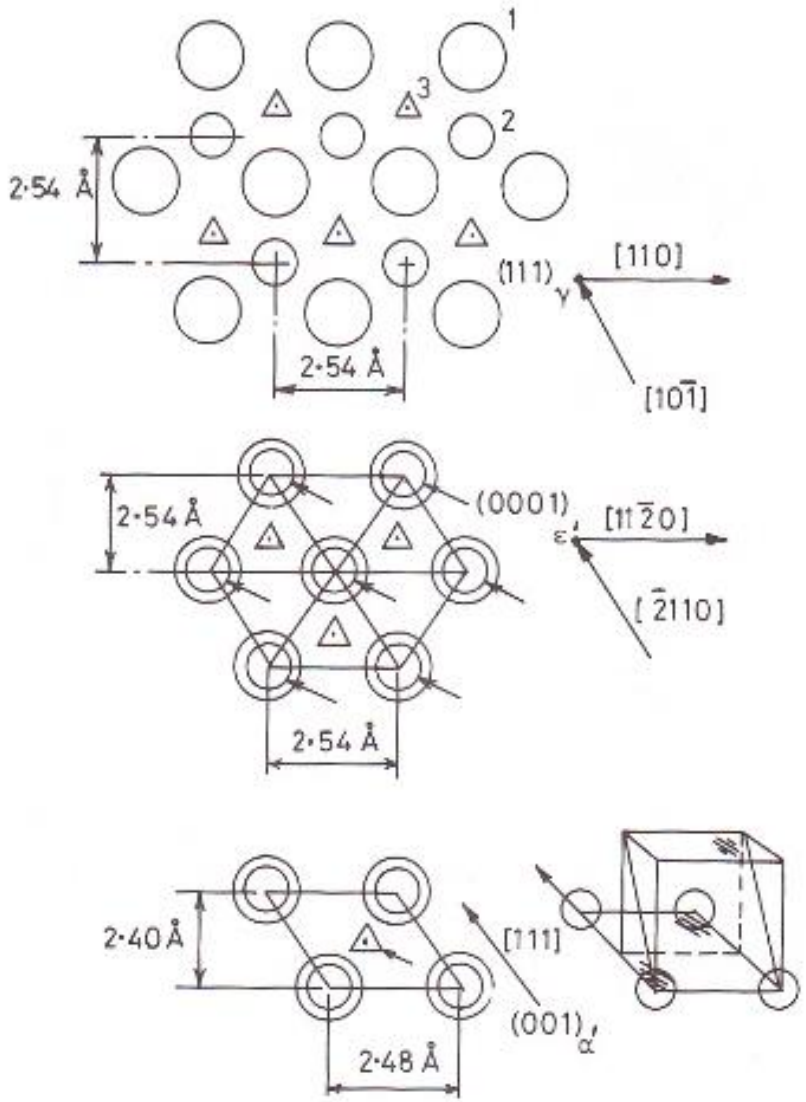


Martensite nucleation

In high-Mn steels (low stacking fault energy) an hexagonal martensite nucleates on stacking faults.

Here a model for this nucleation (also in stainless steels) via a stacking fault + twinning shear.

No unique model possible (various martensites in different steels).



Martensite growth

Lath growth on $\{111\}_\gamma$ (low Carbon steels) supposed to occur via formation and glide of interfacial dislocations.

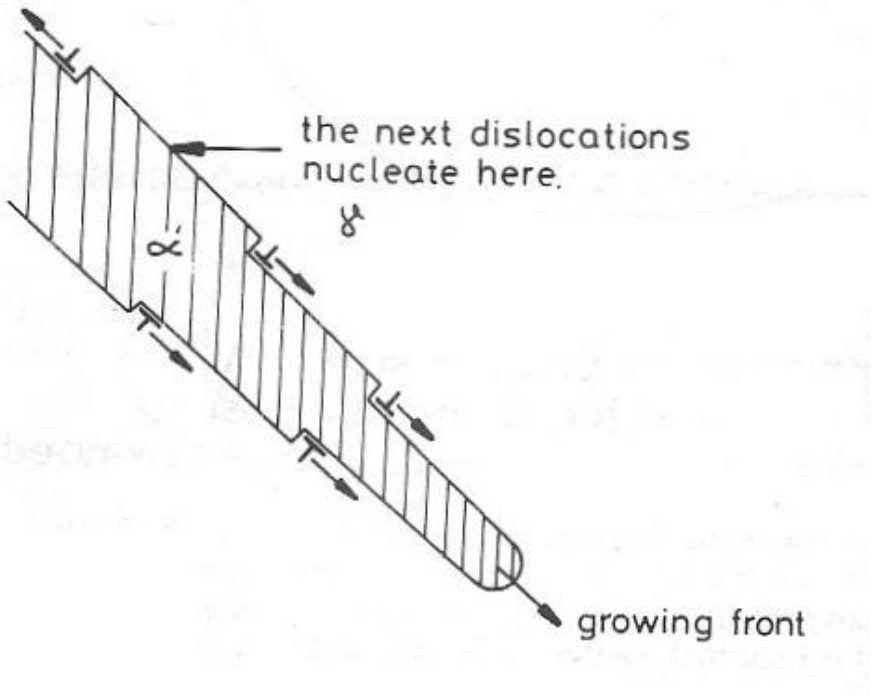


Plate growth on $\{225\}_\gamma$ and $\{259\}_\gamma$ (high C steels, Fe-Ni alloys) is thought to occur mostly via twinning. Lower M_S temperatures favour twinning over slip.

Martensitic transformation

Orientation Relationships and Habit Planes of some Martensites

Alloy	Transformation	Orientation relation	Habit plane	Defect structure
Fe–(0–0.4 wt% C)	fcc → bct	$(111)_\gamma // (011)_{\alpha'}$ $[10\bar{1}]_\gamma // [\bar{1}1\bar{1}]_{\alpha'}$	$\{111\}_\gamma$	needles or laths, high dislocation density
Fe–(0.5–1.4 wt% C)	fcc → bct	$(111)_\gamma // (011)_{\alpha'}$ $[10\bar{1}]_\gamma // [\bar{1}1\bar{1}]_{\alpha'}$	$\{225\}_\gamma$	mixed twins and dislocations
Fe–(1.5–1.8 wt% C)	fcc → bct	$(111)_\gamma // (011)_{\alpha'}$ $[10\bar{1}]_\gamma // [\bar{1}1\bar{1}]_{\alpha'}$	$\{259\}_\gamma$	mainly twinned
Fe–(27–34 wt% Ni)	fcc → bcc	$(111)_\gamma // (011)_{\alpha'}$ $[10\bar{1}]_\gamma // [111]_{\alpha'}$	$\{259\}_\gamma$	mainly twinned
Fe–(11–29% Ni)–(0.4–1.2% C)	fcc → bct	$(111)_\gamma // (011)_{\alpha'}$ $[10\bar{1}]_\gamma // [111]_{\alpha'}$	$\{259\}_\gamma$	mainly twinned
Fe–(7–10% Al)–2% C	fcc → bct	$(111)_\gamma // (011)_{\alpha'}$ $[10\bar{1}]_\gamma // [111]_{\alpha'}$	$\{3\ 10\ 15\}_\gamma$	twinned
Fe–(2.8–8% Cr)–(1.1–1.5% C)	fcc → bct	probably as for Fe–C alloys	$\{225\}_\gamma$	mixed twins and dislocations
Fe–4.5 wt% Cu	fcc → bcc	as for Fe–C alloys	$\{112\}_\gamma$	laths, dislocations
Co	fcc → hcp	$(111)_\gamma // (0001)_{\alpha'}$ $[11\bar{2}]_\gamma // [1\bar{1}00]_{\alpha'}$ or $[1\bar{1}0] // [11\bar{2}0]_{\alpha'}$	$\{111\}_\gamma$	stacking faults
Ti	bcc → hcp	$(110)_\gamma // (0001)_{\alpha'}$	$\{89,12\}_\gamma$, $\{133\}_\gamma$	mixed twins and dislocations
Zr	bcc → hcp	$(110)_\gamma // (0001)_{\alpha'}$	$\{569\}_\gamma$, $\{145\}_\gamma$	—
Li	bcc → hcp	$(110)_\gamma // (0001)_{\alpha'}$	$\{441\}$	—

Martensitic transformation

Tempering of martensites in steels (diffusional)

Heat treatment of martensites is needed to improve toughness.

Martensite is supersaturated in C and other elements → precipitation with various steps possible.

Retained austenite transforms too.

Table 6.3 Transformations Occurring During Tempering of Ferrous Martensites

Temperature/°C	Transformation	Remarks
25–100	Carbon segregation to dislocations and boundaries; pre-precipitation clustering and ordering	Clustering predominant in high-carbon steels
100–200	Transition-carbide precipitation, diam. 2 nm (first stage of tempering)	Carbides may be η(Fe_2C) or ε($Fe_{2.4}C$)
200–350	Retained austenite transforms to ferrite and cementite (second stage)	Associated with tempered martensite embrittlement
250–350	Lath-like Fe_3C precipitation (third stage)	
350–550	Segregation of impurity and alloying elements	Responsible for temper embrittlement
400–600	Recovery of dislocation substructure. Lath-like Fe_3C agglomerates to form spheroidal Fe_3C	Lath structure maintained
500–700	Formation of alloy carbides. (secondary hardening or fourth stage)	Occurs only in steels containing Ti, Cr, Mo, V, Nb, or W; Fe_3C may dissolve
600–700	Recrystallization and grain growth; coarsening of spheroidal Fe_3C	Recrystallization inhibited in medium-carbon and high-carbon steels; equiaxed ferrite formed