Athermal Phase Transformations in Micromechanics

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Micromechanics of Materials
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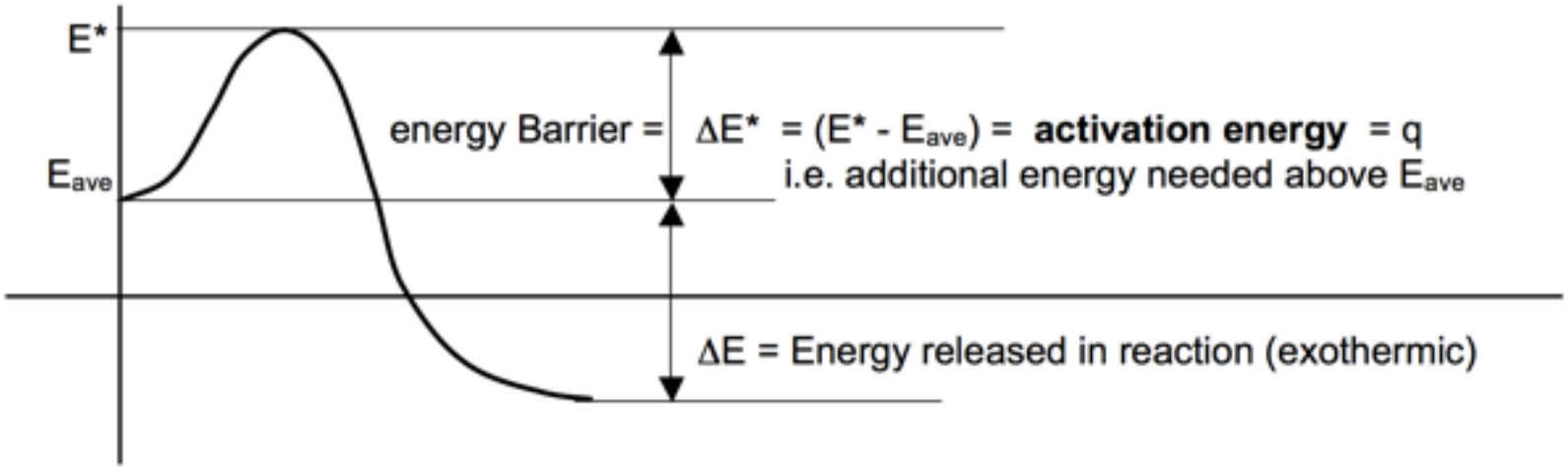
Overview

- Definition: Athermal phase transformations
- Overview: Martensitic phase transformations
- Diffusional vs diffusionless transformations
- Martensite
  - Microstructure
  - Crystallography
  - Bain model
  - Orientation relationships
  - Invariant line strain
  - Habit plane
- Driving forces for martensitic transformations
  - Quenching
    - Martensitic steel
    - Applications
  - External stress
    - TRIP steel
    - Applications

Athermal phase transformations

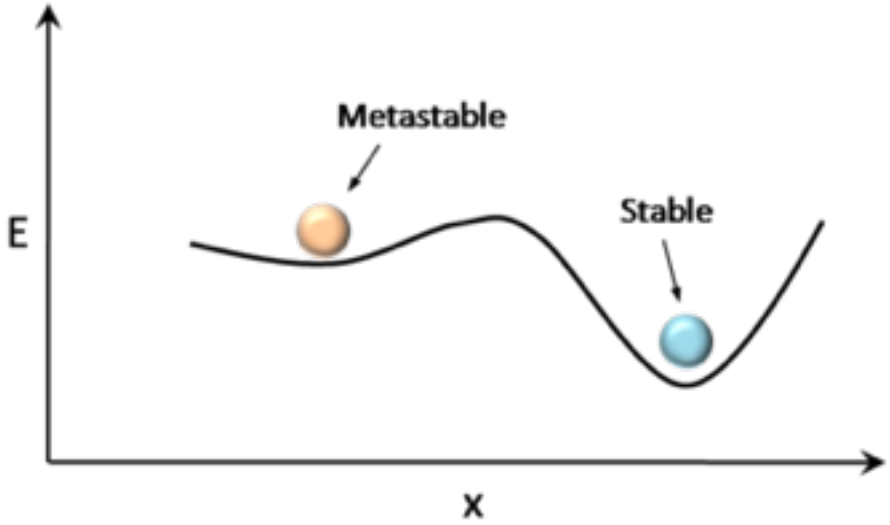
- Athermal does not mean "no temperature dependence", instead it means ***no thermal activation***.

- Processes with no thermal activation do not depend on time, as there is no need to wait for sufficient statistical fluctuations in some specific order parameter to overcome an activation barrier to initiate the process.



Athermal phase transformations

- The stability of a particular state is determined by the correspondence of this state to the minimum (absolute or relative) Gibbs energy and is separated from all neighboring states by an energy barrier.



- At T → 0, energy fluctuations disappear and thermally activated overcoming of barriers become impossible.

However, many processes in reality occur at low temperatures:
- plastic deformation
- fracture
- martensitic transformations

Mechanism that does not require thermal activation: Athermal process

Athermal phase transformations

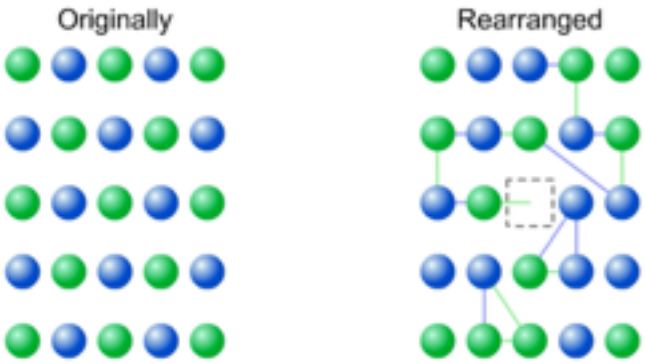
- One of the most important types of athermal transformations is **martensitic transformations**.
- Occurs at a very high rate, close to the speed of sound even at low temperatures
- Martensitic transformations can occur within the whole temperature range
- But the fact that it still occurs as $T \rightarrow 0$, is evidence that it is an athermal process.

Martensitic transformations

- athermal transformation ✓
- solid-solid phase transformation
- involves a change in crystal structure
- diffusionless transformation (displacive, military) ←
- transforms from parent phase to product phase (austenite → martensite)
- shear dominant
- lattice distortive
- metastable phase

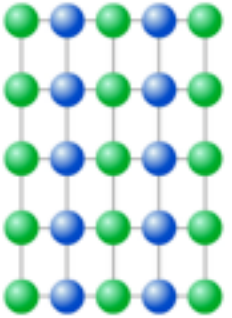
Phase transformations

Diffusional transformations



Diffusionless transformations

The transformation involves, in this case, rows of many atoms moving cooperatively



Examples:
Melting/solidification
Recrystallization
Eutectoid transformations

Examples:
Martensitic transformations
Shape memory alloys

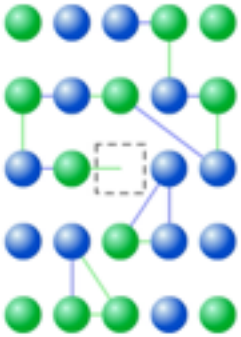
http://www.doitpoms.ac.uk/tlplib/superelasticity/displacive.php

Phase transformations

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

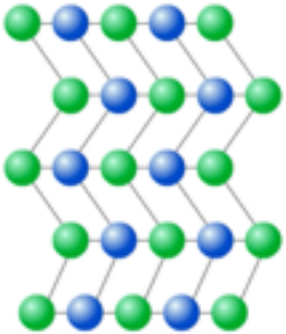
Originally

Transformed

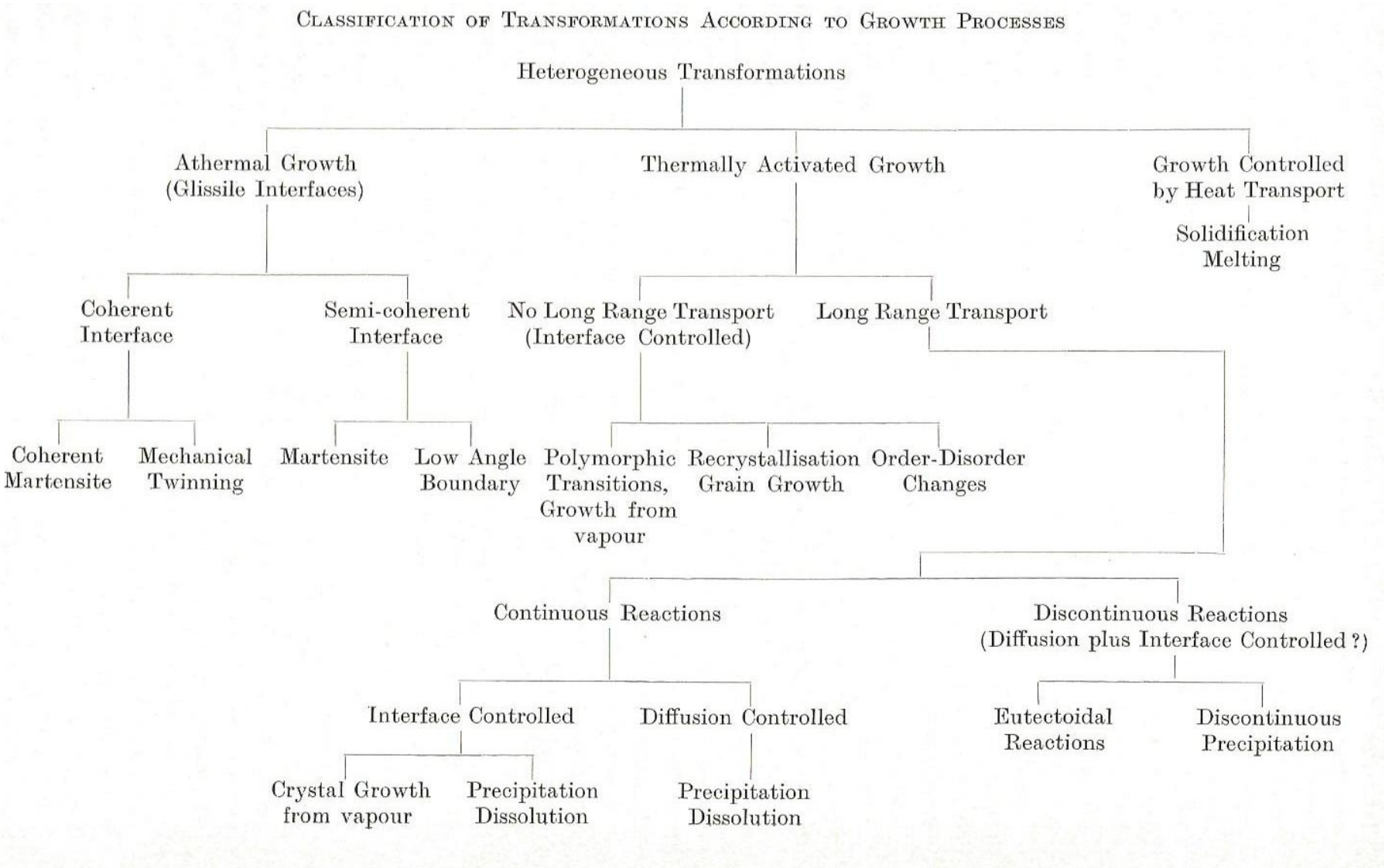


Originally

Transformed

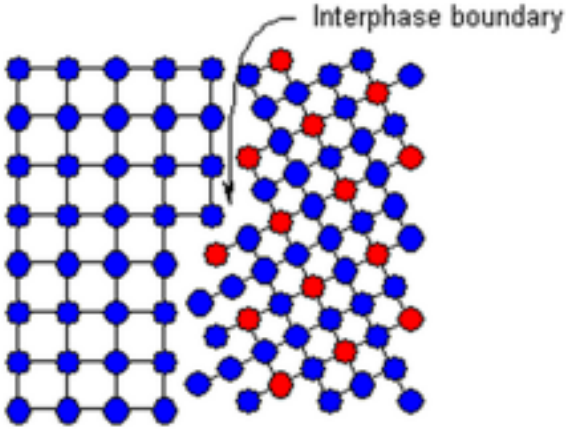


Phase transformations

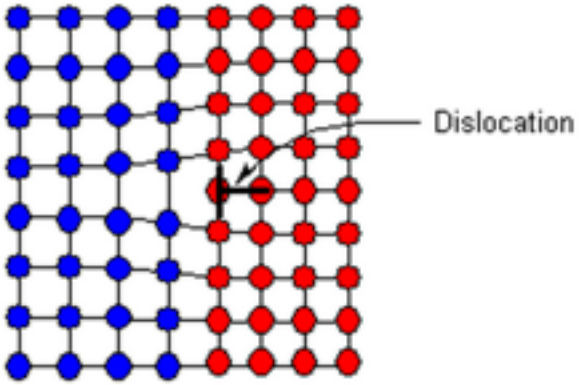


Phase transformations

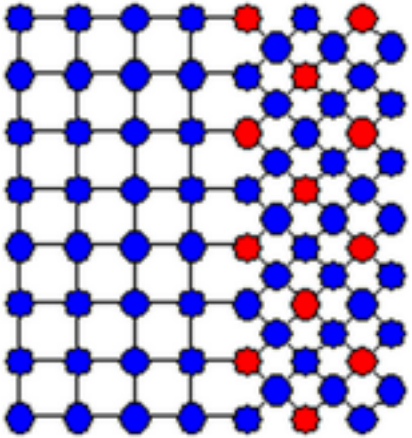
Incoherent interface



Semi-coherent interface

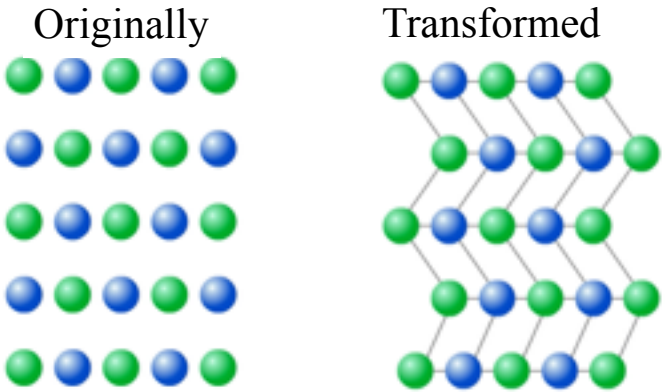


Coherent interface



Martensitic transformations

- The term “martensitic transformation” is used as a generic name to describe a **solid state, diffusionless, athermal phase transformation**.
- The local composition does not change during the transformation.
- The transformation takes place through atomic movements which are less than one atomic spacing.
- The atoms change their positions in a coordinated manner.
- Transformation can occurs at speeds approaching the speed of sound in the material.



Martensite

- Named after the German metallurgist Adolf Martens (1850–1914)
- Originally, the term martensite was used to denote the microstructure of quenched steels, but the term has been extended to other alloys.
- Can now refer to **any crystal structure** that is formed by **diffusionless transformation**.
- The product phase (martensite) has a well defined crystallographic relationship with the parent phase (austenite).
- Martensite can occur as lath or plate-shaped grains.

Types of martensite in steels

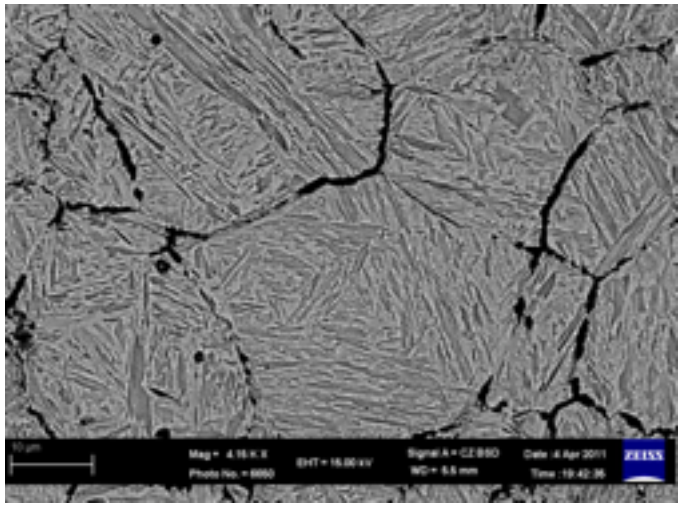
Lath martensite

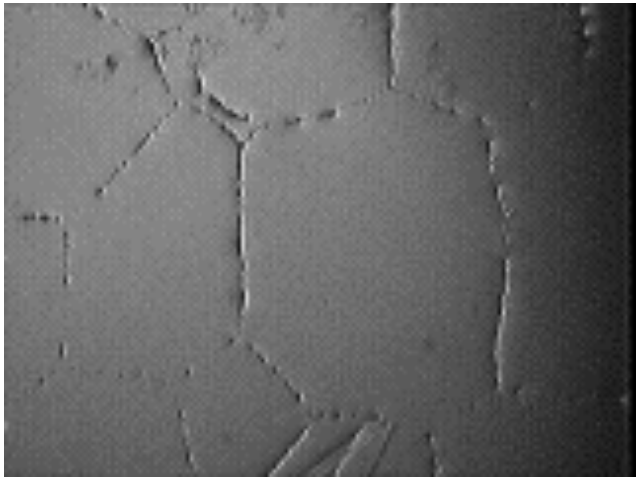
- Many similar sized laths arranged in a parallel fashion to make up a packet.
- Produced from low carbon austenite.
- Higher toughness and ductility, but lower strength.

Plate martensite

- Develops in a non-parallel fashion and neighbouring plates vary considerably in size.
- Produced from high carbon austenite.
- Much higher strength, but may be brittle and non-ductile.

Martensite microstructure





http://www.youtube.com/watch?v=OQ5lVjYssko

Martensitic transformations

Some alloy systems where martensitic transformations are known to occur

Alloy(s)	Transformation
Co, Fe-Mn, Fe-Cr-Ni	FCC ↔ HCP
Fe-Ni	FCC ↔ BCC
Fe-C, Fe-Ni-C, Fe-Cr-C, Fe-Mn-C, etc.	**FCC ↔ BCT**
In-Tl, Mn-Cu	FCC ↔ FCT
Au-Cd	BCC ↔ Orthorhombic
ZrO_2	Tetragonal ↔ Monoclinic
Ti-Al-Nb, Ti-Al-Ta, etc	B2 ↔ Ordered HCP
TiNi (Nitinol)	B2 ↔ Monoclinic

Martensitic transformations strengthen steels significantly. Strengthening is not as significant in other materials.

Crystallography of martensitic transformations

In steels, these martensitic transformations are possible:

a) γ austenite (fcc) → α' martensite (bcc/bct)

b) γ austenite (fcc) → ε martensite (hcp)

c) γ austenite (fcc) → ε martensite (hcp) → martensite α' (bcc)

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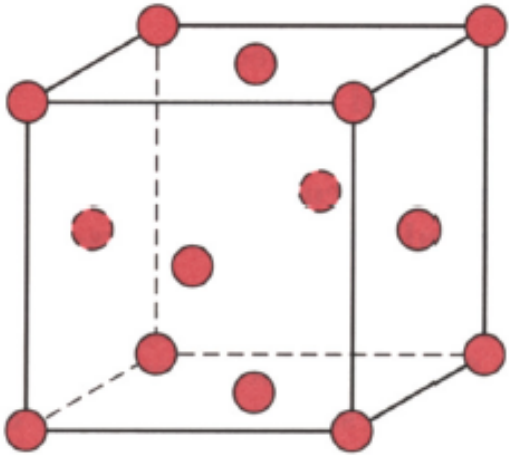
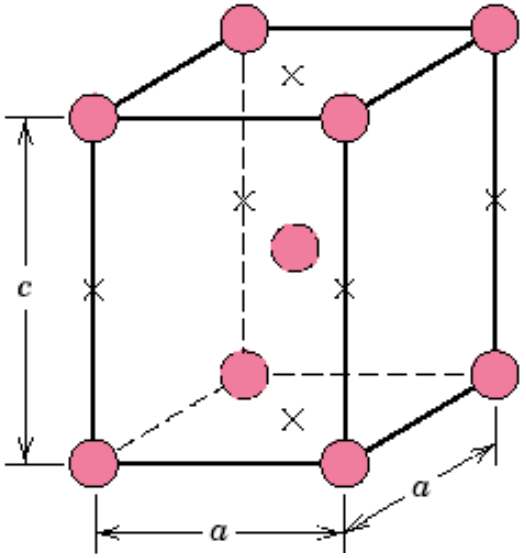
Bain model



fcc austenite
(γ phase)



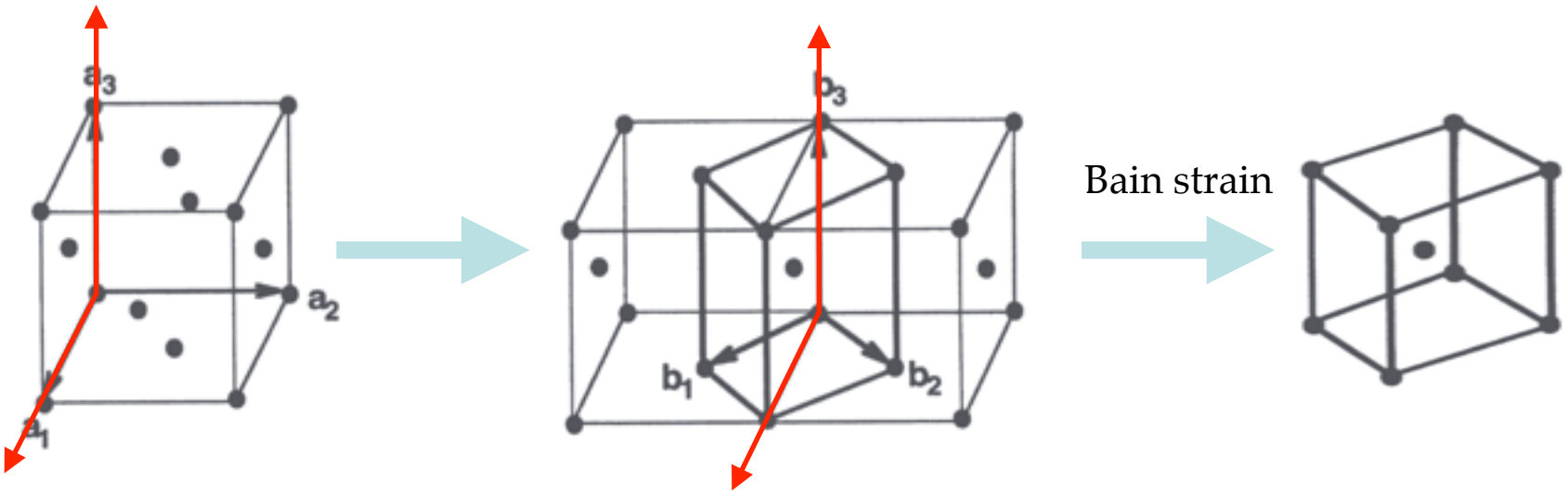
bct martensite
(α' phase)

Circles: Iron atoms

Crosses: Sites that may be occupied by carbon atoms

For this bct unit cell, c > a.

Bain model



Austenite (fcc) Martensite (bct) Martensite (bcc)

Bain orientation relationship (OR):

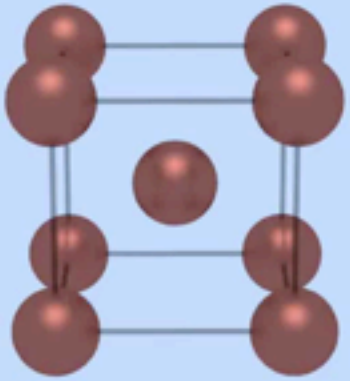
$(001)_{\mathrm{fcc}} \parallel (001)_{\mathrm{bct}}$

$[100]_{\mathrm{fcc}} \parallel [110]_{\mathrm{bct}}$

Bain model

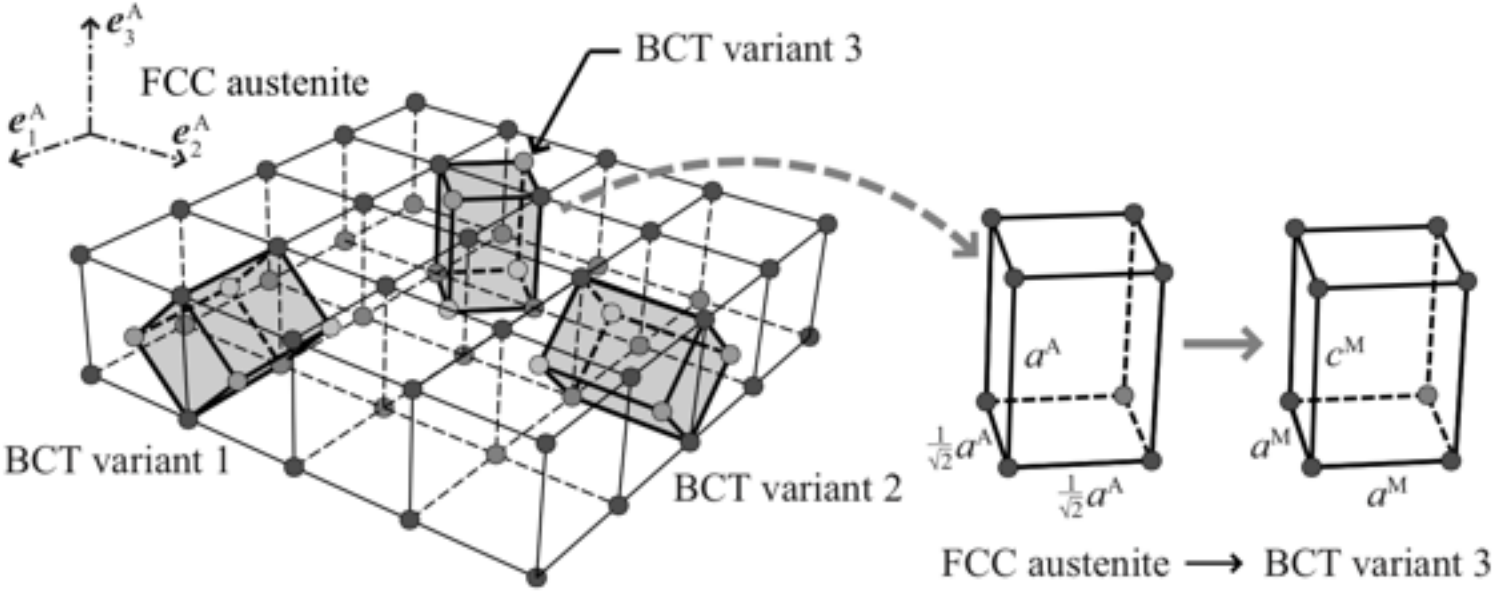
This is the most basic cell of an iron crystal at room temperature.

This atom configuration is called body-centered cubic



http://www.youtube.com/watch?v=mndgs3YJGCU

Bain strain variants (FCC to BCT)

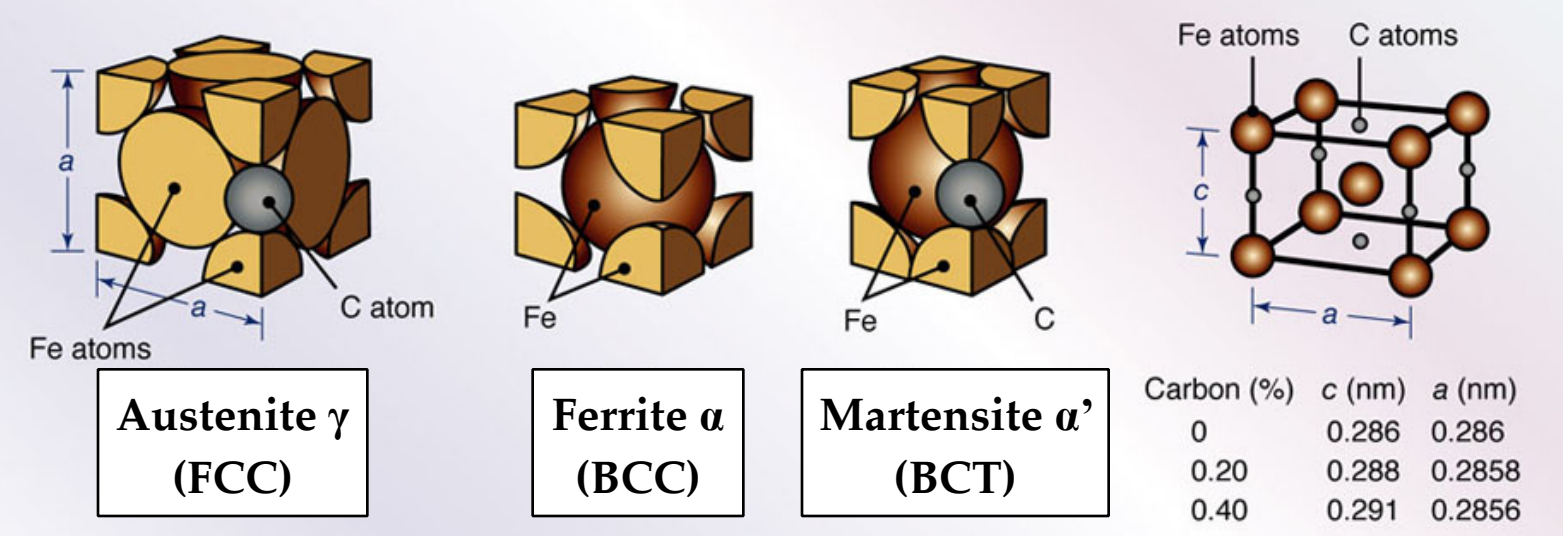


Bain deformation variants:

$$U_1 = \frac{1}{a^A}\begin{pmatrix} c^M & 0 & 0 \\ 0 & \sqrt{2}a^M & 0 \\ 0 & 0 & \sqrt{2}a^M \end{pmatrix} \qquad U_3 = \frac{1}{a^A}\begin{pmatrix} \sqrt{2}a^M & 0 & 0 \\ 0 & \sqrt{2}a^M & 0 \\ 0 & 0 & c^M \end{pmatrix}$$

$$U_2 = \frac{1}{a^A}\begin{pmatrix} \sqrt{2}a^M & 0 & 0 \\ 0 & c^M & 0 \\ 0 & 0 & \sqrt{2}a^M \end{pmatrix}$$

Martensitic transformation in steels



Increasing carbon content increases the lattice dimension ***c*** for martensite

Orientation relationships

The Bain model is the simplest model for the fcc → bcc transformation with minimal atomic movement and minimal strain in the parent phase.

In reality, orientation relationships (OR) that are observed in fcc → bcc/bct transformations are:

- Kurdjumov-Sachs (K-S)
- Nishiyama-Wasserman (N-W)
- Greninger-Troiano (G-T)
- Pitsch

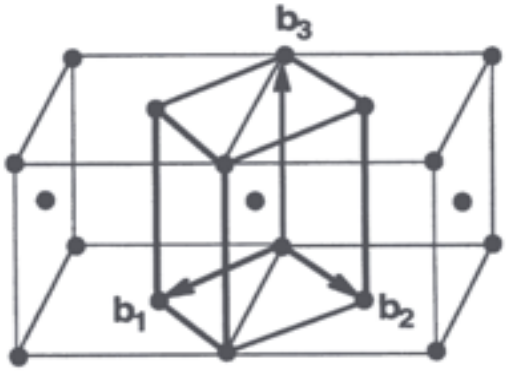
OR	plane	direction
Bain	$\{010\}_\gamma \parallel \{010\}_\alpha$	$\langle 001\rangle_\gamma \parallel \langle 101\rangle_\alpha$
K–S	$\{111\}_\gamma \parallel \{110\}_\alpha$	$\langle 1\bar{1}0\rangle_\gamma \parallel \langle 1\bar{1}1\rangle_\alpha$
N–W	$\{111\}_\gamma \parallel \{110\}_\alpha$	$\langle 0\bar{1}1\rangle_\gamma \parallel \langle 001\rangle_\alpha$
G–T	$\{111\}_\gamma \sim 1°$ to $\{110\}_\alpha$	$\langle \bar{1}2\bar{1}\rangle_\gamma \sim 2°$ to $\langle 1\bar{1}0\rangle_\alpha$
Pitsch	$\{001\}_\gamma \parallel \{\bar{1}01\}_\alpha$	$\langle 110\rangle_\gamma \parallel \langle 111\rangle_\alpha$

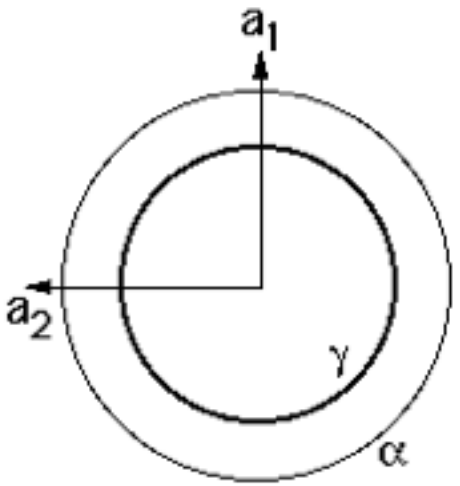
Invariant line strain

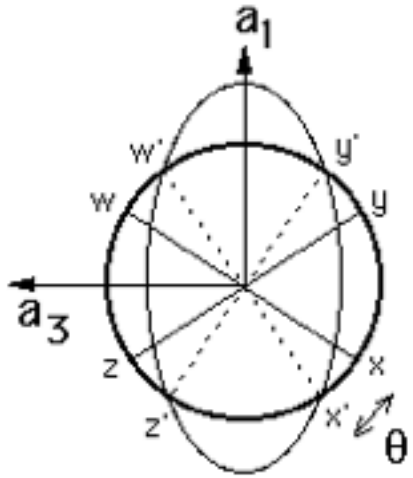
For a martensitic transformation to be possible, the deformation which changes the parent into the product must leave one or more lines invariant (unrotated, undistorted). A deformation which leaves one line invariant is called an 'invariant–line strain'.

Bain deformation, ***B***, followed by a rigid-body rotation, ***R***, to obtain a total deformation that is an invariant line strain:

$$\boldsymbol{F} = \boldsymbol{R}\,\boldsymbol{B}$$



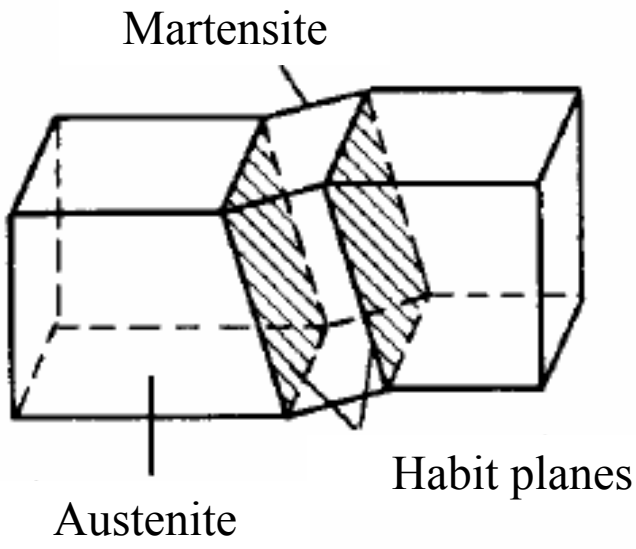


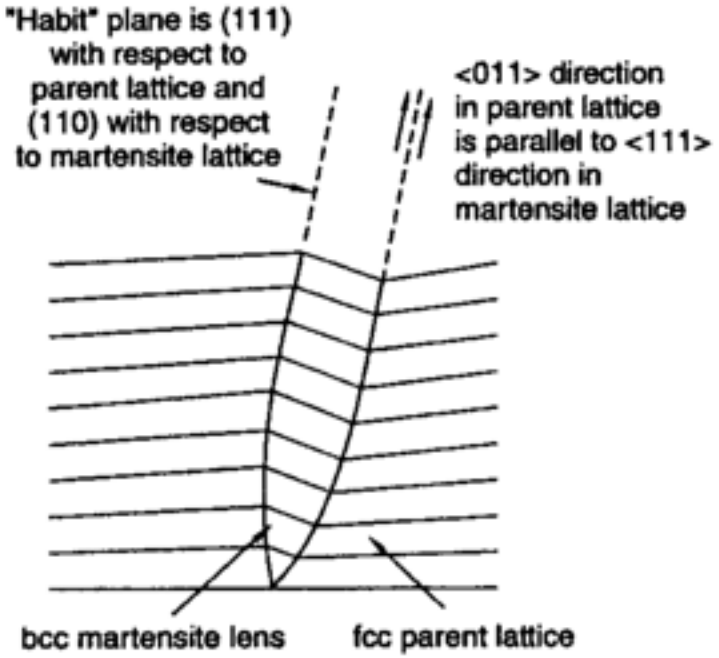


Bain model does not produce an invariant line strain!

Habit planes

The common plane, between the austenite and martensite, on which martensite nucleates is called the habit plane.





Invariant plane strain (observed experimentally) → Interface plane between martensite and parent remains undistorted and unrotated

Crystallography of martensitic transformations

In steels, these martensitic transformations are possible:

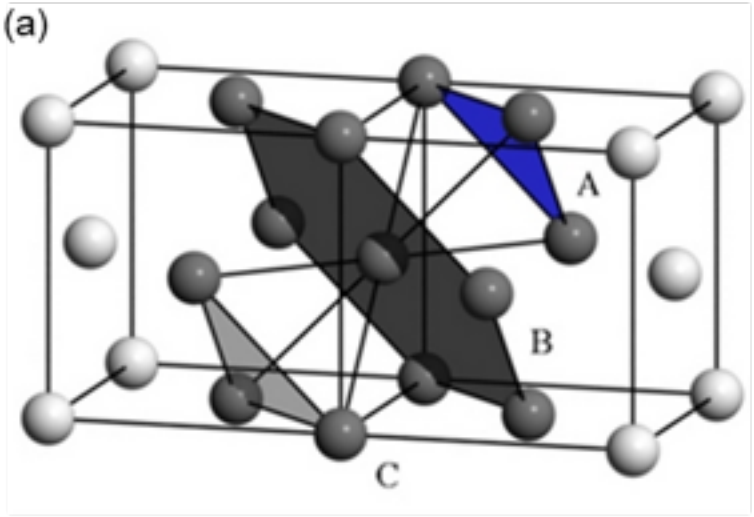
a) γ austenite (fcc) → α' martensite (bcc/bct)

γ austenite (fcc) → ε martensite (hcp)

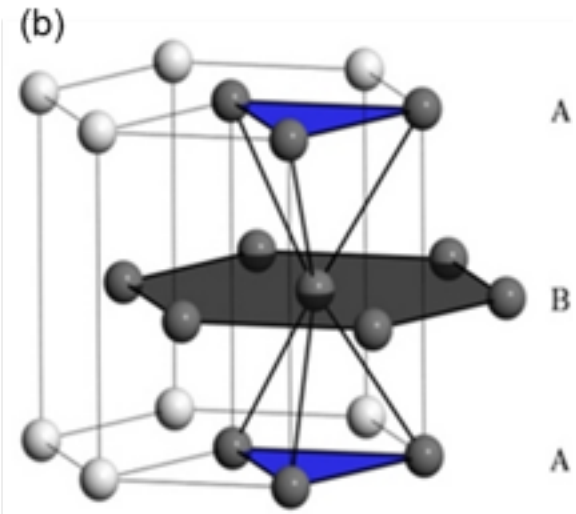
c) γ austenite (fcc) → ε martensite (hcp) → martensite α' (bcc)

ε martensite

- α' martensite (bct) is typically observed in steels.
- In high Mn steels (Mn wt% > 18%), ε martensite forms.
- ε martensite (hcp) is often an intermediate step in the formation of α' martensite.



fcc: ABCABC stacking



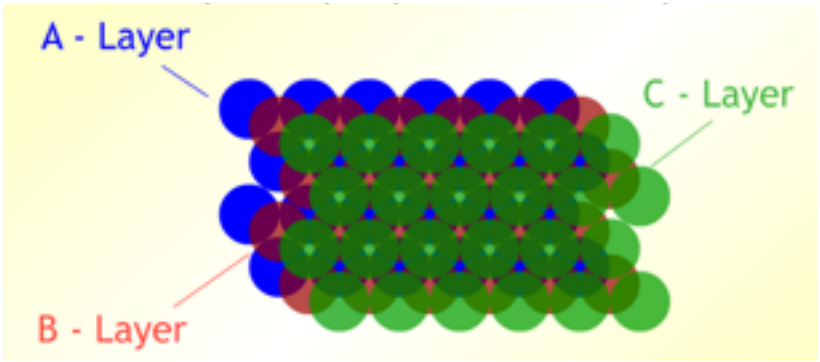
hcp: ABABAB stacking

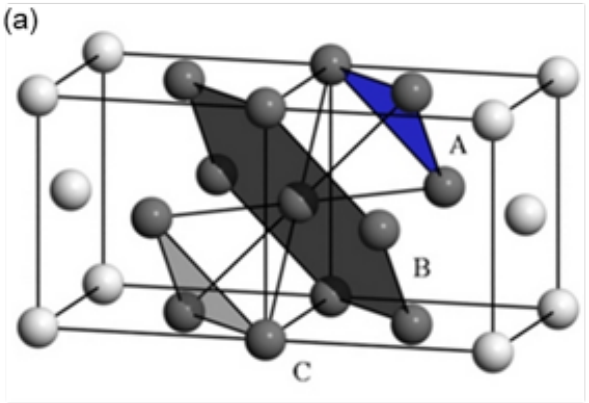
http://abinitio.iehk.rwth-aachen.de/glossar/?text_id=115

ε martensite

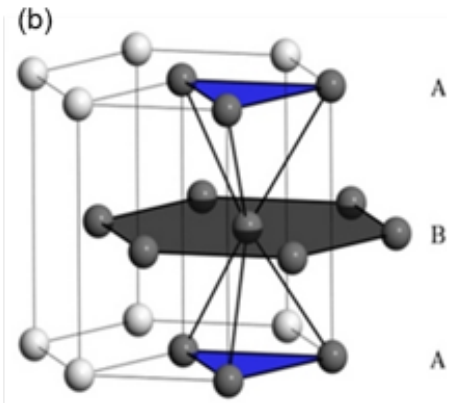
Closed packed planes can be characterized into three types of layers: A, B and C.

Closed packed plane in fcc: {111}
Closed packed plane in hcp: (0001)





fcc: ABCABC stacking



hcp: ABABAB stacking

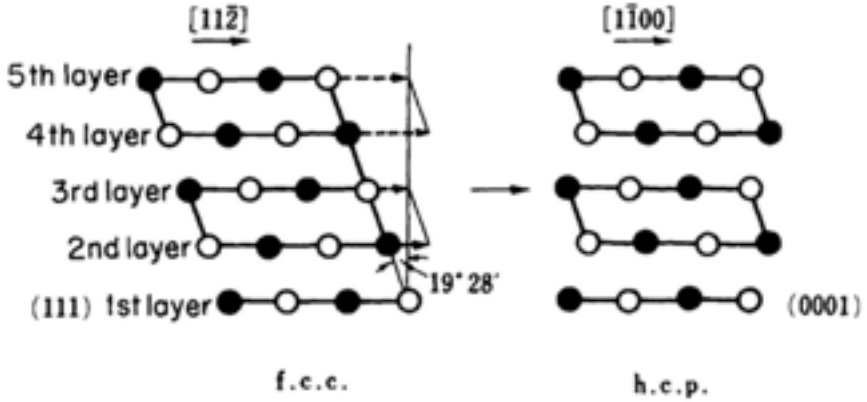
ε martensite

fcc → hcp orientation relationship:

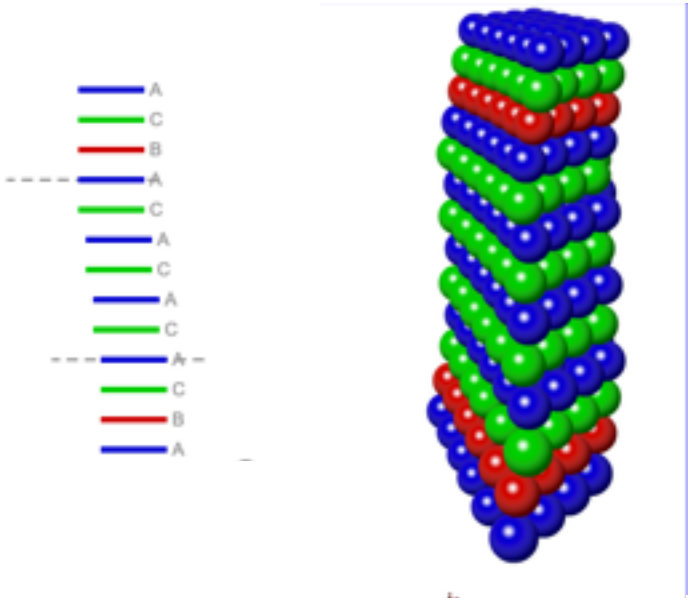
Shoji-Nishiyama OR:

$(111)_{\mathrm{fcc}} || (0001)_{\mathrm{hcp}}$

$[11\bar{2}]_{\mathrm{fcc}} || (1\bar{1}00)_{\mathrm{hcp}}$



fcc → hcp transformation



http://www.doitpoms.ac.uk/tlplib/superelasticity/martensitic_crystallography.php

Crystallography of martensitic transformations

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b) γ austenite (fcc) → ε martensite (hcp)

γ austenite (fcc) → ε martensite (hcp) → martensite α' (bcc)

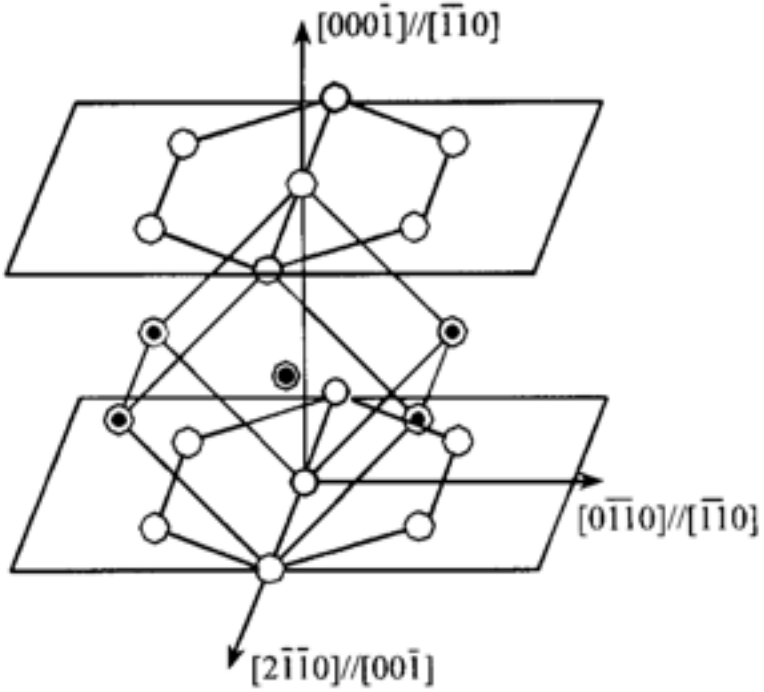
hcp → bcc orientation relationship:

Pitsch-Schrader OR:

$(0001)_{\mathrm{hcp}} \parallel (110)_{\mathrm{bcc}}$

$[\bar{2}110]_{\mathrm{hcp}} \parallel [001]_{\mathrm{bcc}}$

$[0110]_{\mathrm{hcp}} \parallel [1\bar{1}0]_{\mathrm{bcc}}$



Deformation tensor:

$$\boldsymbol{B} = \begin{pmatrix} a_{\mathrm{bcc}}/a_{\mathrm{hcp}} & 0 & 0 \\ 0 & \sqrt{\frac{2}{3}}(a_{\mathrm{bcc}}/a_{\mathrm{hcp}}) & 0 \\ 0 & 0 & \sqrt{2}a_{\mathrm{bcc}}/c_{\mathrm{hcp}} \end{pmatrix}$$

Martensitic transformations

Martensitic transformations can be induced by:

- changing the temperature (quenching)
- applying an external stress

Martensitic transformations

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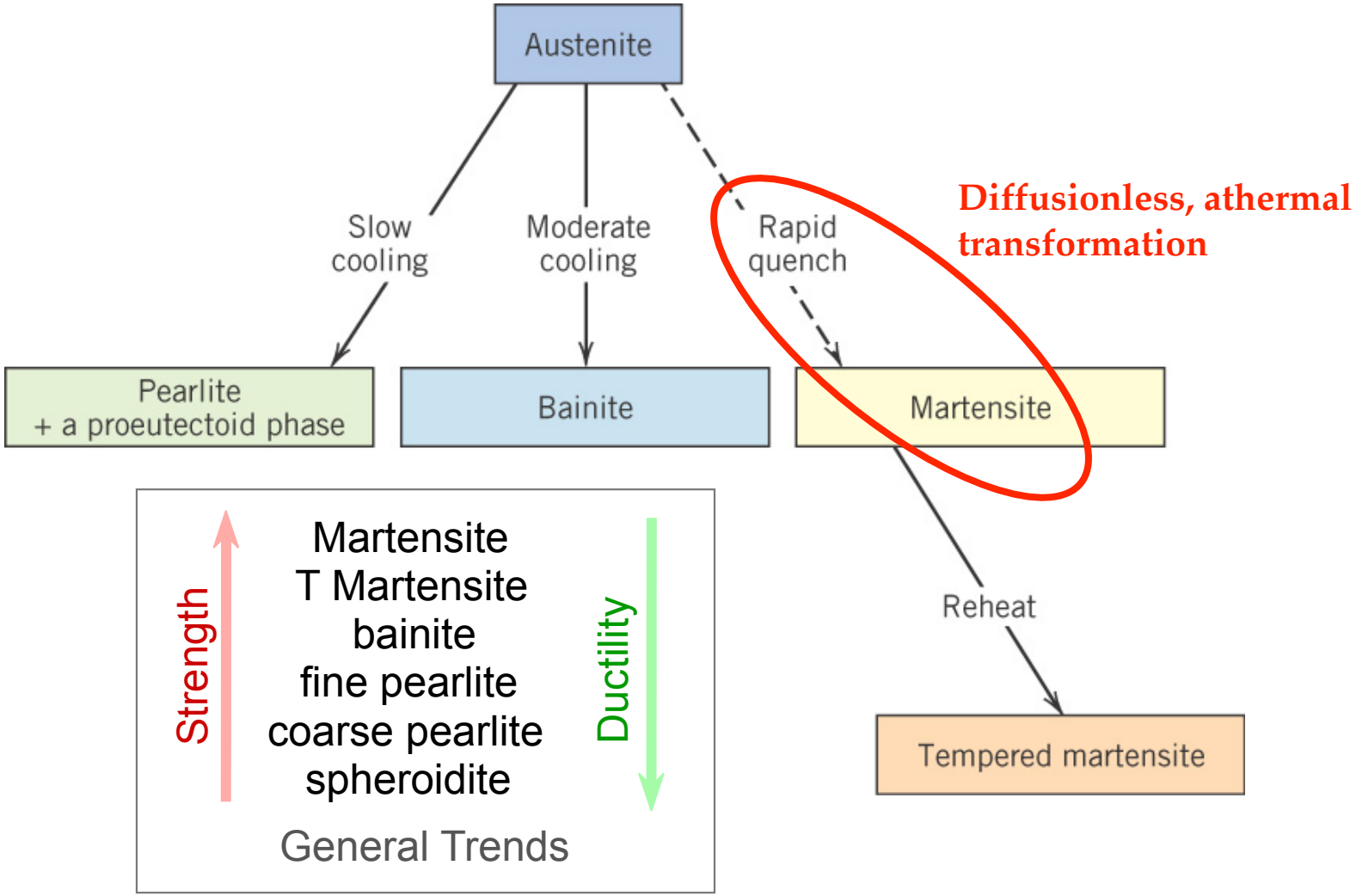
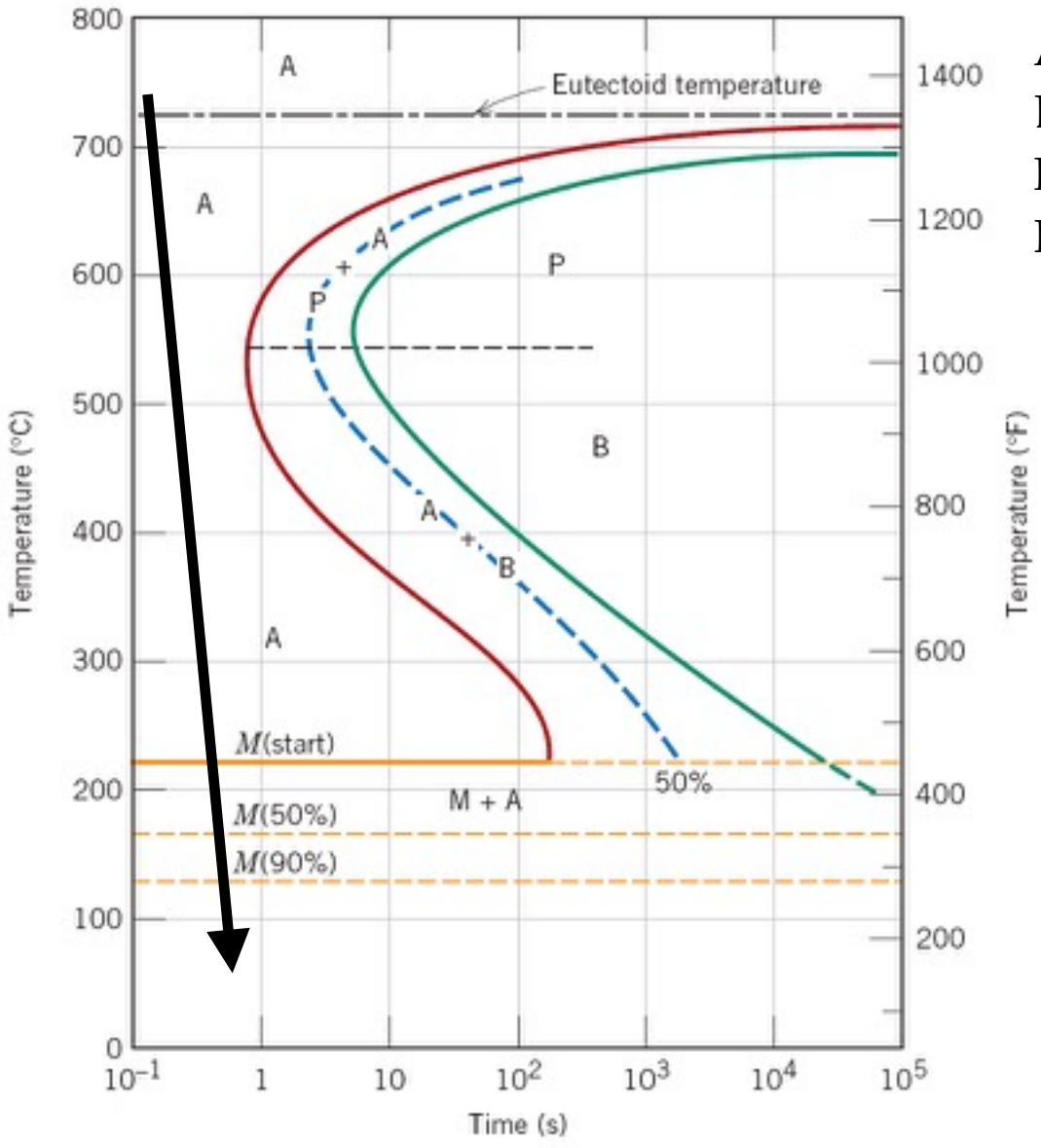
- applying an external stress

Transformations from austenite



Solid lines are diffusional transformations, dashed is diffusionless martensitic transformation

Time-Temperature-Transformation (TTT) diagram



A: Austenite
B: Bainite
P: Pearlite
M: Martensite

- Transformation starts only after cooling to M_S (martensite start temperature)
- The fraction transformed increases with the undercooling below M_S.
- Horizontal lines indicate that the martensitic transformation is independent of time; it is a function only of the temperature to which the alloy is quenched.

Martensitic transformations

- Involves heating to the austenizing temperature and cooling fast enough to avoid the formation of ferrite, pearlite or bainite, to obtain pure martensite.
- By rapid cooling (quenching) of austenite at such a high rate, the carbon atoms do not have time to diffuse out of the crystal structure in large enough quantities.
- Austenite (fcc) transforms to a highly strained bct form that is supersaturated with carbon.
- The resulting shear deformations produce large numbers of dislocations, which is a primary strengthening mechanism of steels.
- Austenite that does not transform to martensite is called retained austenite.

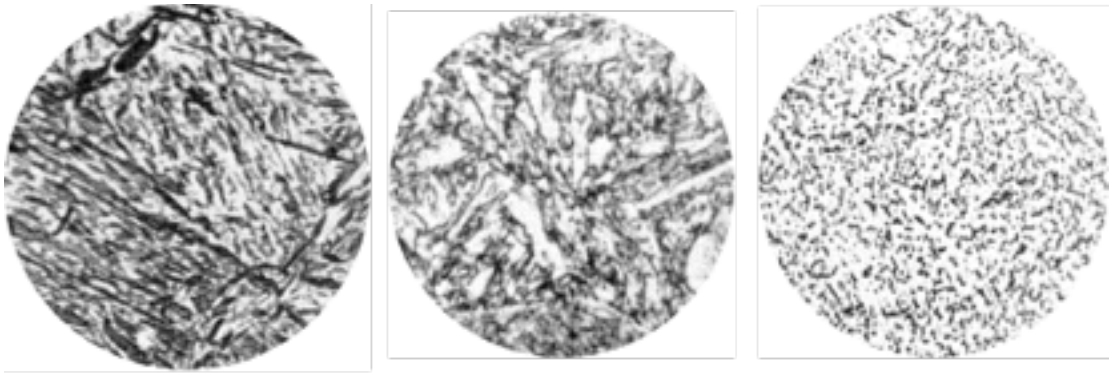
Martensitic steels

Quenching is the most common method to harden a steel.

Martensite is very hard and brittle and cannot be used directly after quenching for any application.

Normally tempered after quenching to improve ductility. This is called tempered martensite.

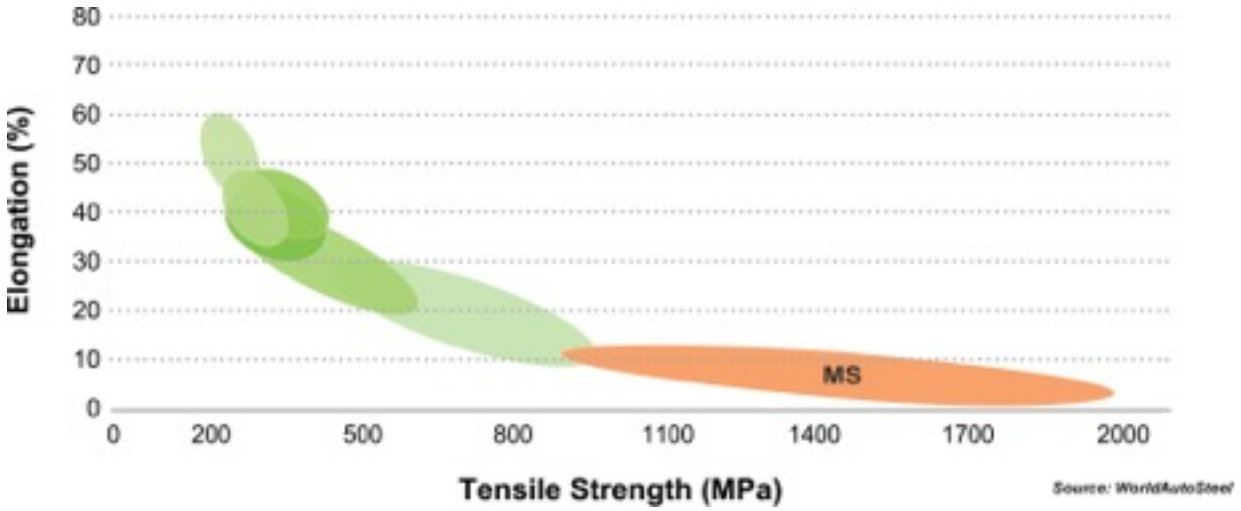
Post-quench treatment (tempering):
- reduces martensite brittleness
- reduces residual stresses caused by quenching



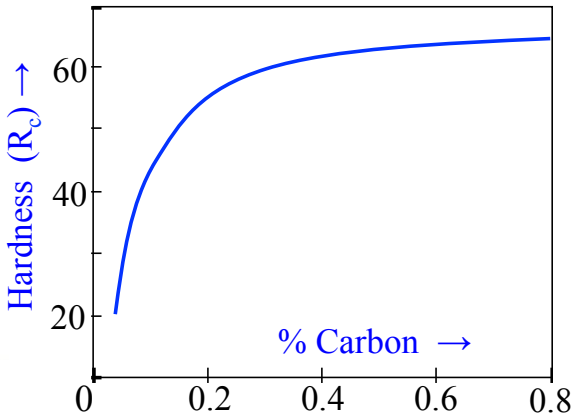
Martensite | Tempered martensite | Heavily tempered

Martensitic steels

- Consist of a martensite matrix containing small amounts of ferrite and/or bainite.
- Martensite hardness depends on the carbon content.
- If the intended application requires a high level of hardness (e.g. knives), only stress relief annealing will be performed.



Martensite hardness as a function of carbon content



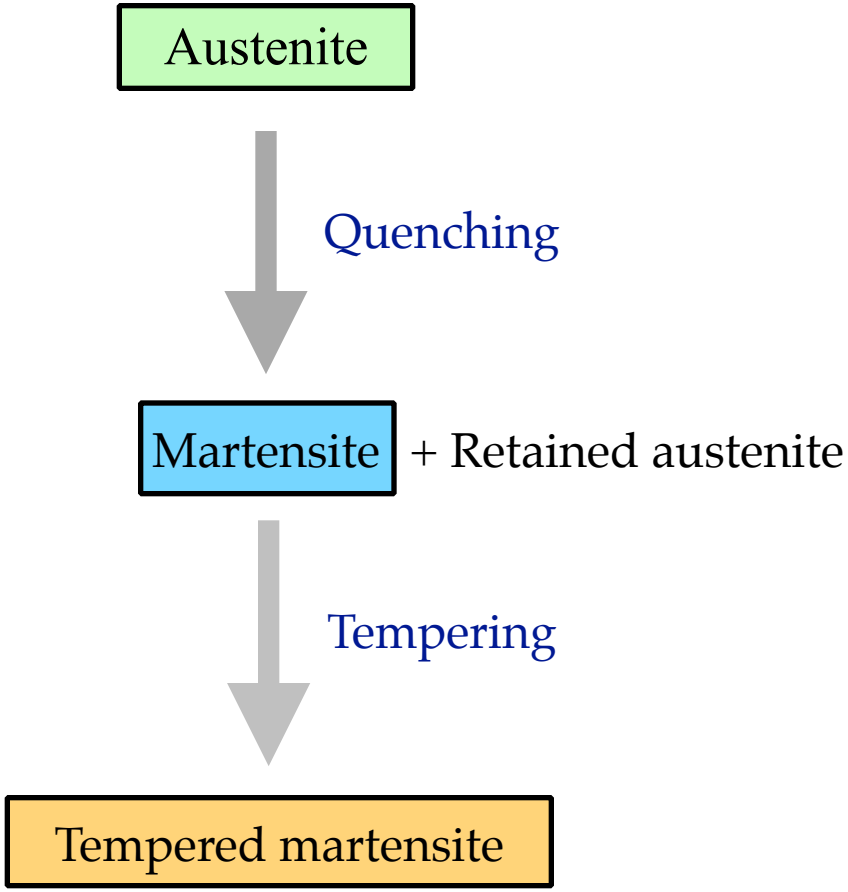
Martensitic steels

Martensitic steels are used where hardness, strength, and wear resistance are required.

Typical applications for martensitic steels:

- cutting utensils
- sport knives
- surgical and dental instruments
- fasteners, springs and ball bearings
- press plates
- power hand tools
- steam and gas turbines

Martensitic steels

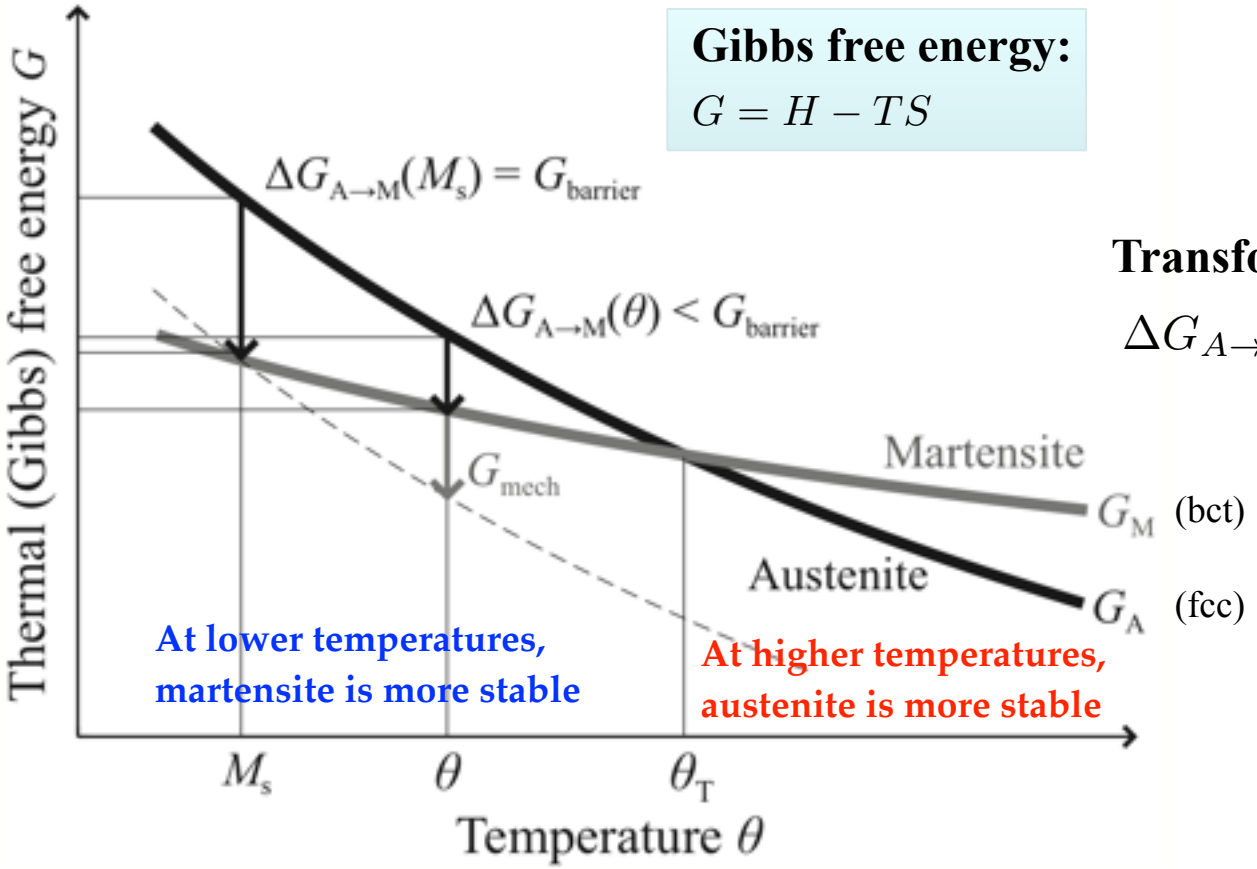


Martensitic transformations

Martensitic transformations can be induced by:

- changing the temperature (quenching)
- applying an external stress

Martensitic transformations



Gibbs free energy:

$G = H - TS$

Transformation condition:

$$\Delta G_{A\to M}(\theta) + G_{\text{mech}} \geq G_{\text{barrier}}$$

- Transformation starts at M_S, where the difference in thermal energy $\Delta G_{A\to M}(\theta)$ is sufficient to overcome the transformation energy barrier.

- At temperatures higher than M_S, transformation may occur with the assistance of an applied stress, such that G_{mech} is sufficient to overcome the transformation barrier.

Martensitic transformations

When a volume of material (V) transforms three energies have to be considered:

(i) change in G (assume we are working at constant T & P),

(ii) increase in γ (interface free energy),

(iii) increase in strain energy.

$$\Delta G = V\Delta G_{\mathrm{v}} + A\gamma + V\Delta G_{\mathrm{s}}$$

ΔG_{v} Gibbs free energy per unit volume

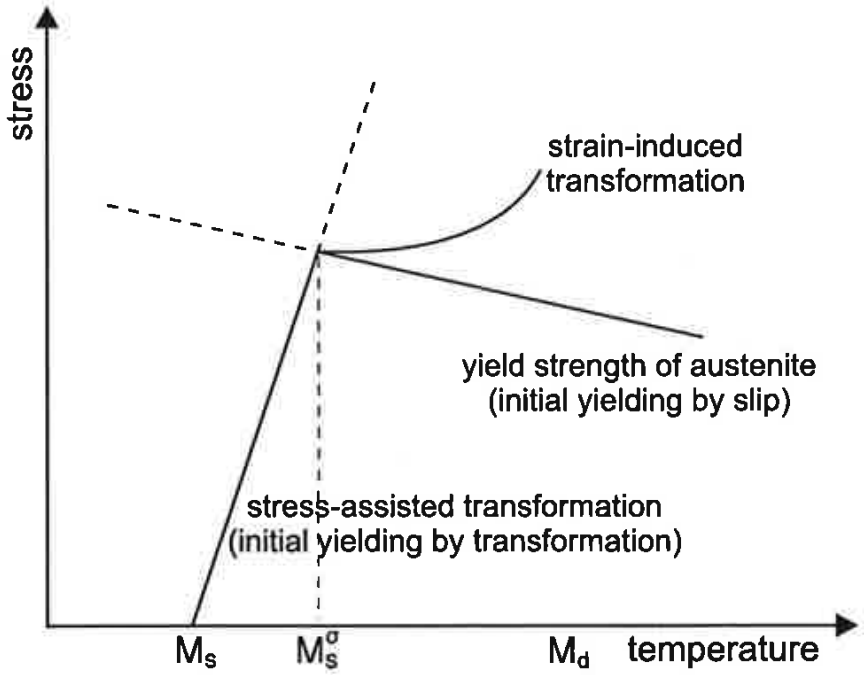
ΔG_{s} strain energy per unit volume

Parameter	Fe–22Mn–3Al–3Si	Fe–25Mn–3Al–3Si	Fe–28Mn–3Al–3Si	Fe–16Mn	Fe–18Mn	Fe–20Mn	Fe–22Mn
γ_{exp} (mJ m^{-2})[a]	15 ± 3	21 ± 3	38.8 ± 5	26 ± 3.1	22 ± 2.6	18 ± 2.2	15 ± 1.8
μ (GPa)[b]	72	72	72	69	69	69	69
ν[b]	0.24	0.24	0.24	0.23	0.23	0.23	0.23
e_{11}[c]	−0.0032	−0.0041	−0.0058	−0.0029	−0.0029	−0.0025	−0.0033
e_{22}[c]	−0.0032	−0.0041	−0.0058	−0.0029	−0.0029	−0.0025	−0.0033
e_{33}[c]	−0.0051	−0.0061	−0.0067	−0.0145	−0.0144	−0.0146	−0.0153
VS[c]	−0.011	−0.014	−0.018	−0.020	−0.020	−0.019	−0.022
E_{dil} (J mol^{-1})[d]	24.1	38.3	61.1	69.2	69.4	65.1	81.7
E_{sh} (J mol^{-1})[d]	0.6	0.7	0.2	21.8	21.4	24.0	23.3
$2\rho E_{str}$ (mJ m^{-2})[d]	1.4 ± 0.9	2.3 ± 1.4	3.6 ± 2.2	5.4 ± 0.5	5.4 ± 0.5	5.3 ± 0.5	6.2 ± 0.5
T^{fcc}_{Neel} (K)[e]	267	282	298	310	332	352	370
T^{hcp}_{Neel} (K)[e]	123	137	153	94	106	118	129
$2\rho\Delta G^{fcc\rightarrow hcp}_{Chem}$ (mJ m^{-2})[f]	−6.7	−0.2	9.1	−48.4	−43.9	−38.8	−33.3
$2\rho\Delta G^{fcc\rightarrow hcp}_{Mag}$ (mJ m^{-2})[f]	1.5	2.0	2.6	3.9	6.0	8.3	10.7
$\sigma^{\gamma/\varepsilon}$ (mJ m^{-2})[g]	9.3 ± 1.6	8.6 ± 1.7	11.8 ± 2.7	32.5 ± 1.6	27.3 ± 1.3	21.6 ± 1.1	15.7 ± 0.9

D.T. Pierce, J.A. Jiménez, J. Bentley, D. Raabe, C. Oskay, J.E. Wittig
Acta Materialia, 2014, 68:238-253

Martensitic transformations

- Martensite can be induced to form by stress or strain at temperatures above M_S.
- The higher the temperature above M_S, the greater is the magnitude of the stress required.
- In the case of stress assisted martensite, the martensite start temperature at a given stress level σ is termed M_S^σ



Stress-assisted: by application of stress below the yield limit

Strain-induced: by plastic deformation of the material

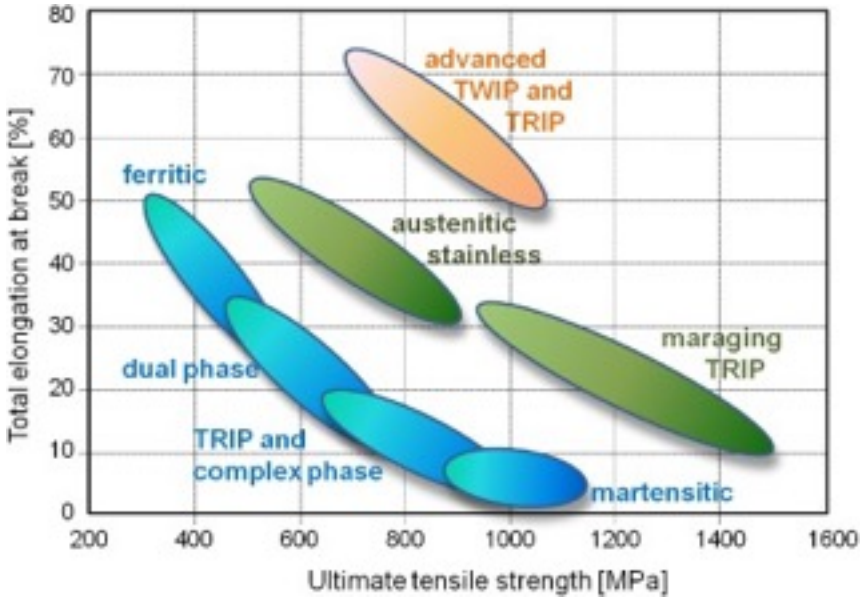
TRIP steel

- **TRIP** stands for **TR**ansformation-**I**nduced **P**lasticity

- TRIP steels are a new generation of advanced high strength steels (AHSS).

- TRIP steels can enhance their mechanical properties during "in-service" by means of martensite formation under applied stress.

- The TRIP effect increases the strength and ductility, due to the dislocations generated by the plastic deformation during martensitic transformation.



Typical composition of TRIP steels (in wt %)

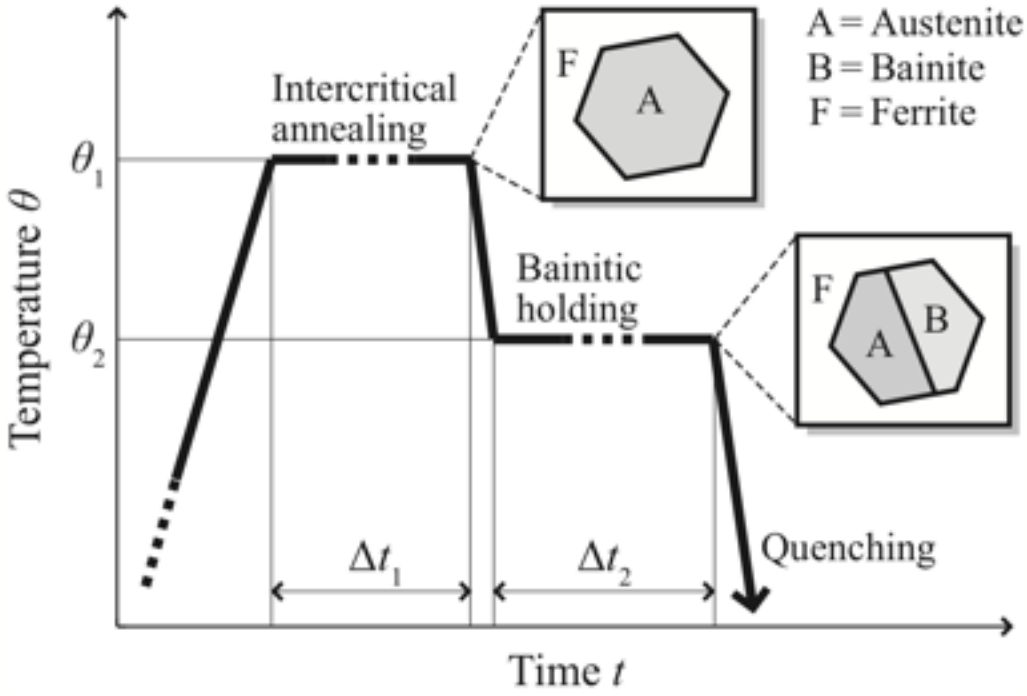
Steel No.	C	Mn	Si	Al	P	Fe
2	0.18	1.56	0.02	1.73	0.017	Balance
4	0.18	1.65	0.45	1.01	0.015	Balance
5	0.21	1.41	1.07	0.32	0.017	Balance
10	0.19	1.47	0.87	0.33	0.024	Balance
11	0.19	1.47	0.22	0.94	0.024	Balance

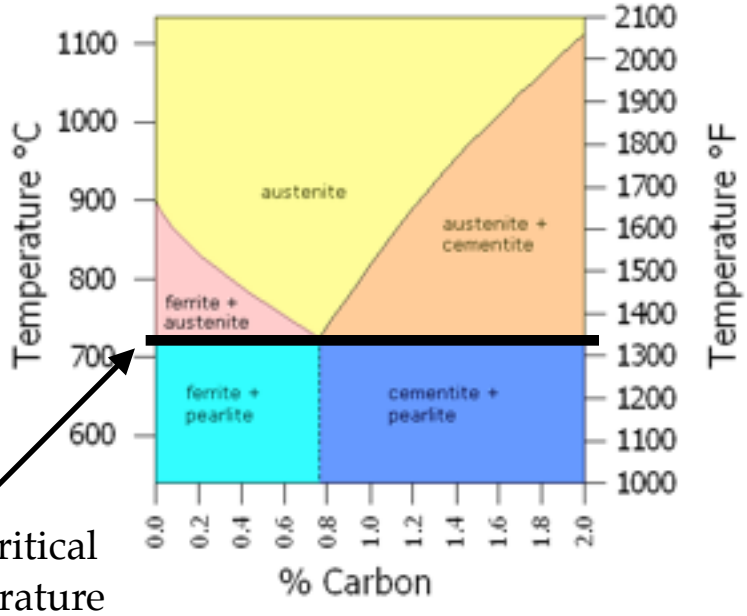
Lin Li, B.C.De Cooman, P. Wollants,Y. He,X. Zhou
J. Mater. Sci. Technol., 2004, 20(2):135-138

How are TRIP steels produced?

Two step heat treatment:

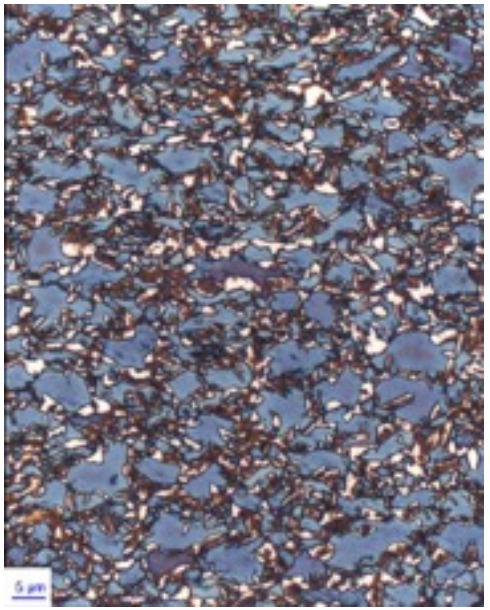
1. Heating to the intercritical temperature
2. Isothermal hold at an intermediate temperature, which produces some bainite

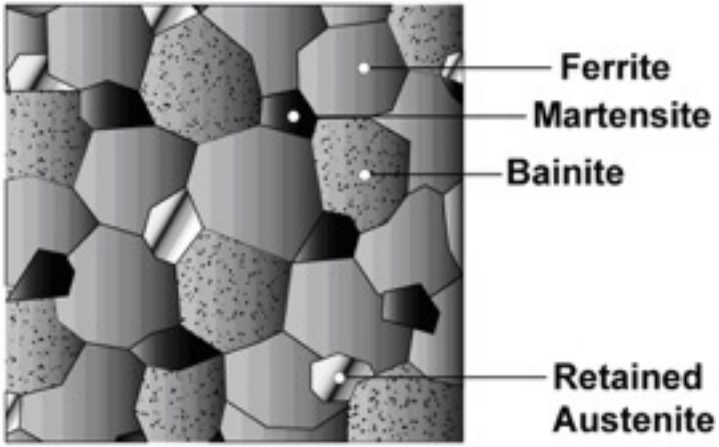


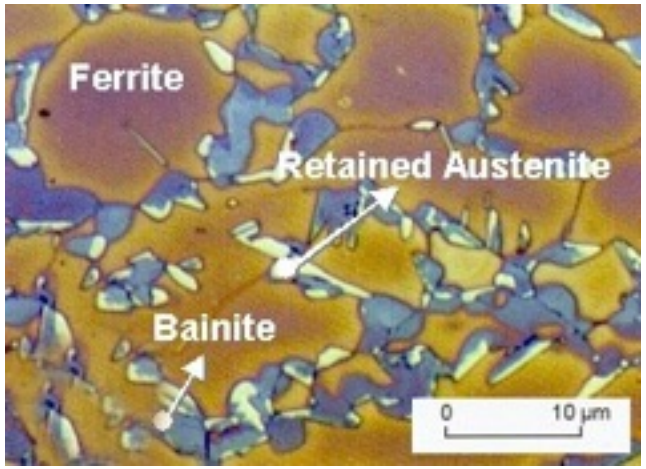


TRIP steel microstructure

- Microstructure of TRIP steels: islands of retained austenite and bainite dispersed in a soft ferritic matrix.
- Minimum of 5% to 15% of retained austenite.
- Hard phases such as martensite and bainite are present in varying amounts.





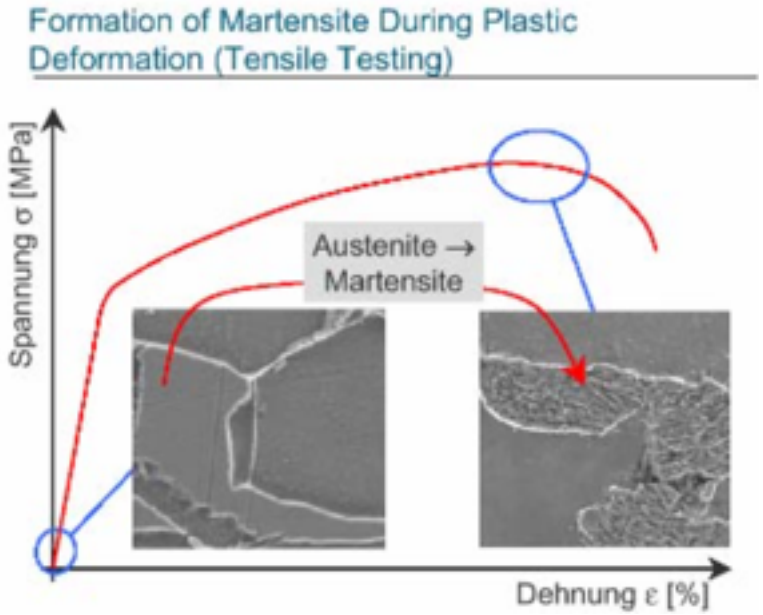


TRIP steel

During deformation, the hard secondary phases in the soft ferrite matrix creates a high work hardening rate.

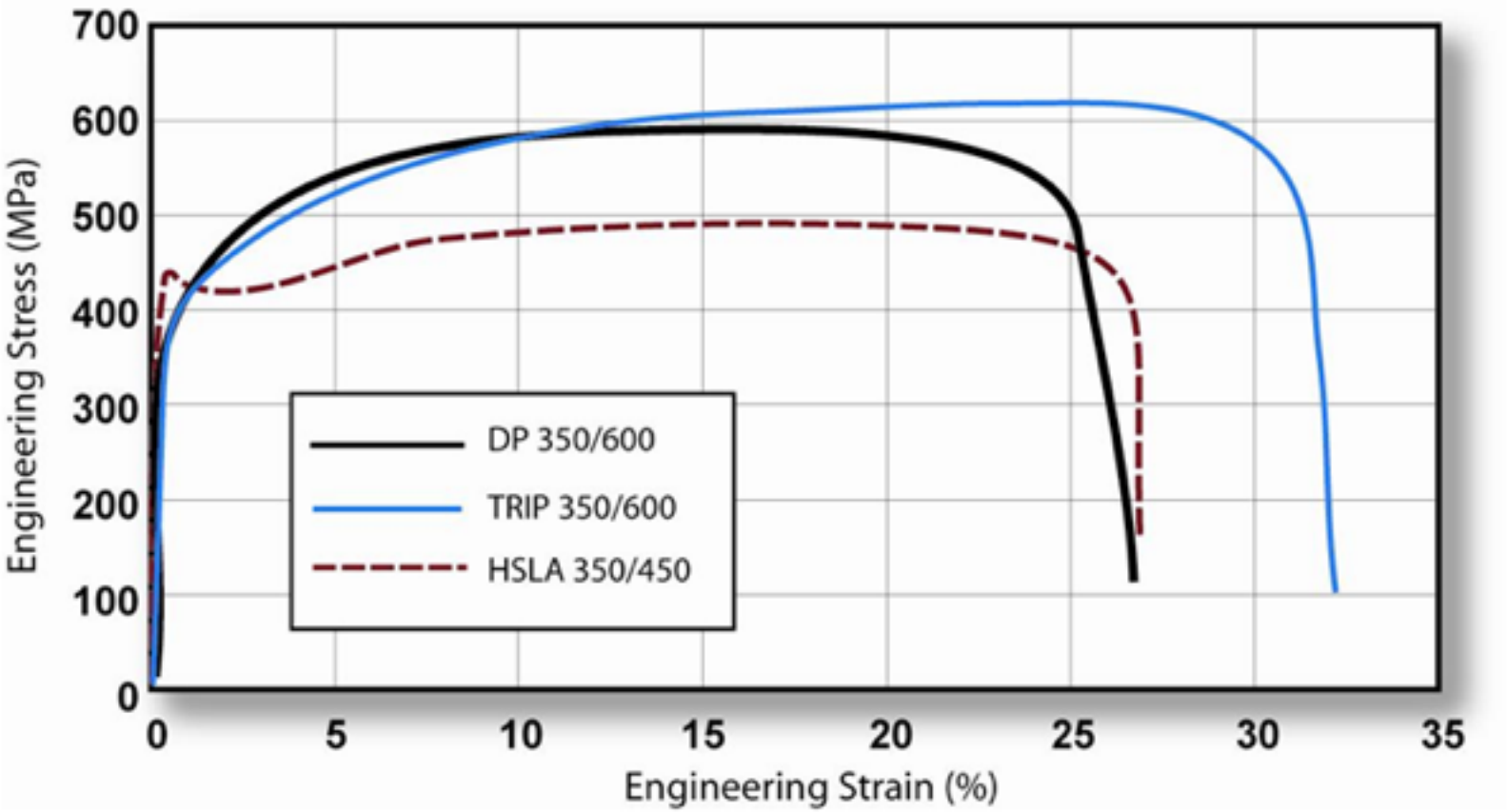
Retained austenite progressively transforms to martensite with increasing strain (TRIP effect) and increases the work hardening rate at higher strain levels.

The TRIP effect results in:
- high strength
- high ductility
- high energy absorption capacity



TRIP steels are particularly suitable for parts designed to absorb energy in an impact.

TRIP steel

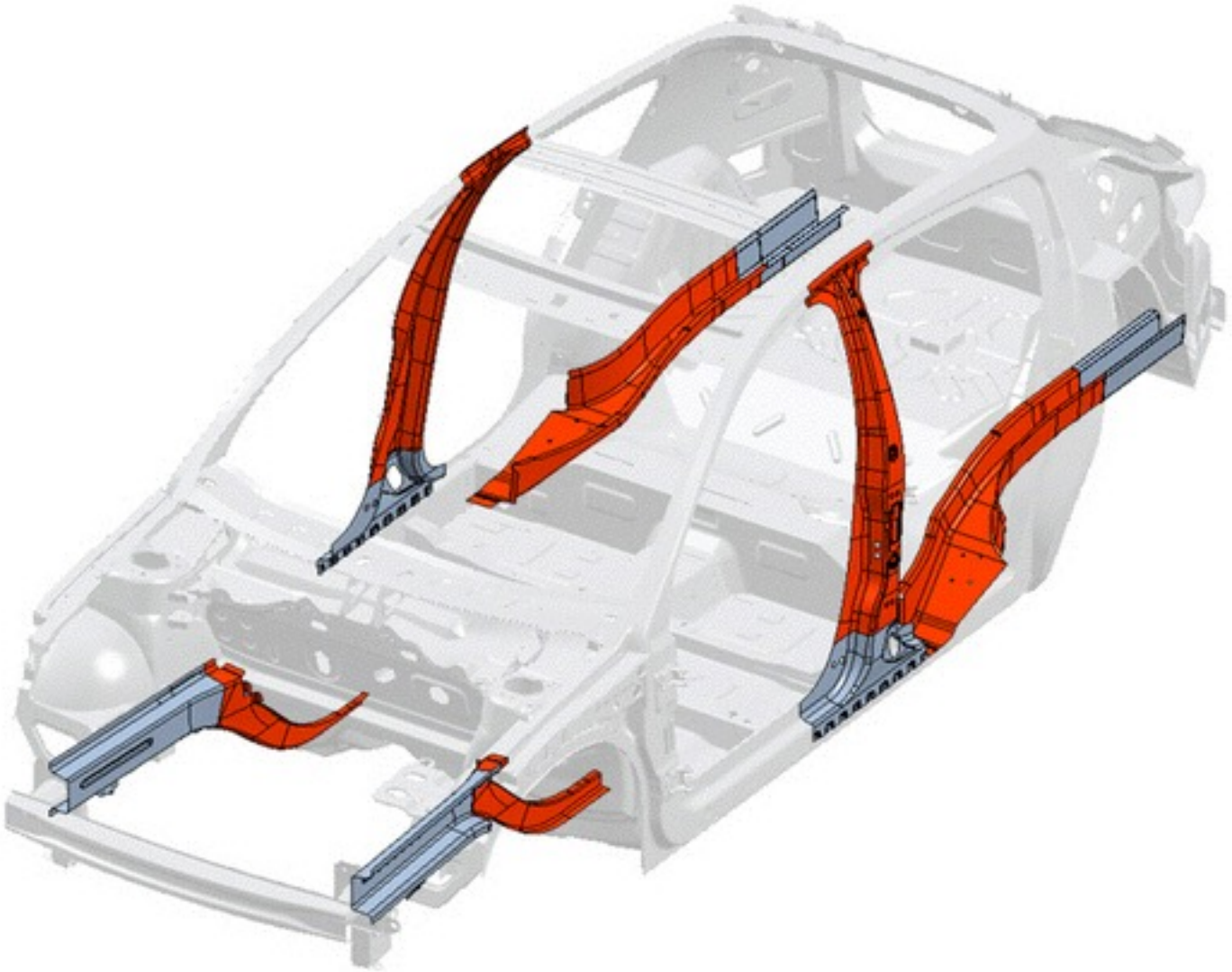

Engineering Stress (MPa)
700
600
500
400
300
200
100
0
0
5
10
15
20
25
30
35
Engineering Strain (%)
DP 350/600
TRIP 350/600
HSLA 350/450

TRIP steel applications

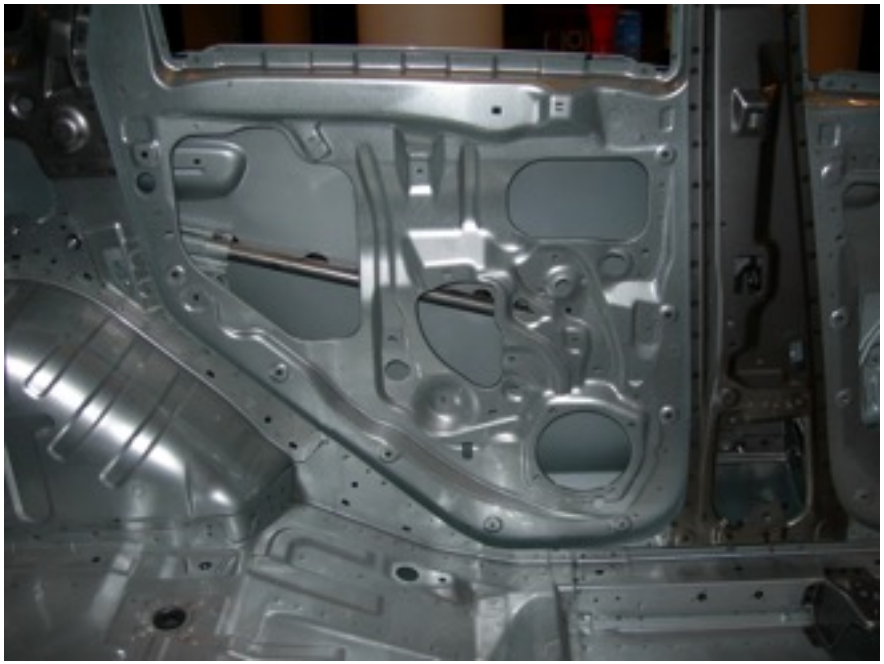
TRIP steels are used in automotive structural and safety parts such as:

- cross members
- longitudinal beams
- B-pillar reinforcements
- bumper reinforcements
- sills

TRIP steel applications



TRIP steel applications

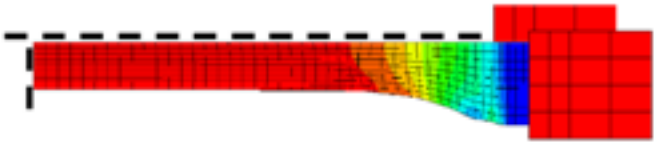


Crash-reinforcement bar in the door panel

Crash-reinforcement bar in the door panel and B-pillar

http://www.msm.cam.ac.uk/phase-trans/2005/TRIP.steels.html

Summary

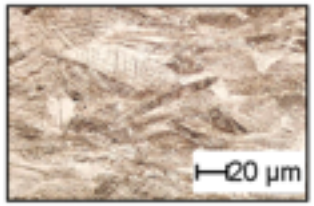


strain

% C	% Si	% Mn	% Cr	% Mo	% Ni
0,02	0,51	0,70	17,55	0,42	8,75

alloy

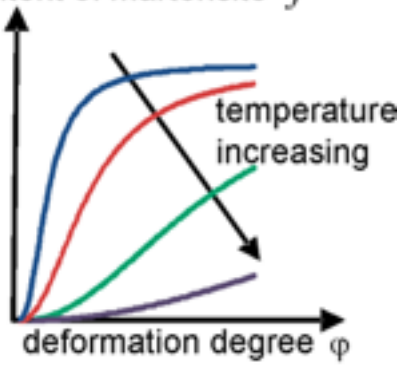
content of martensite



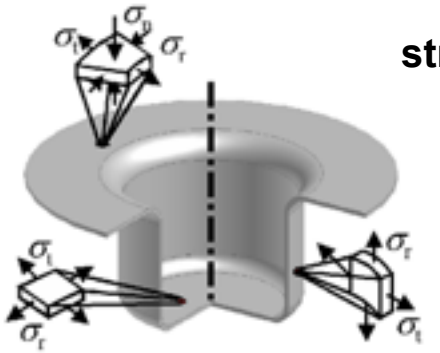
martensite evolution

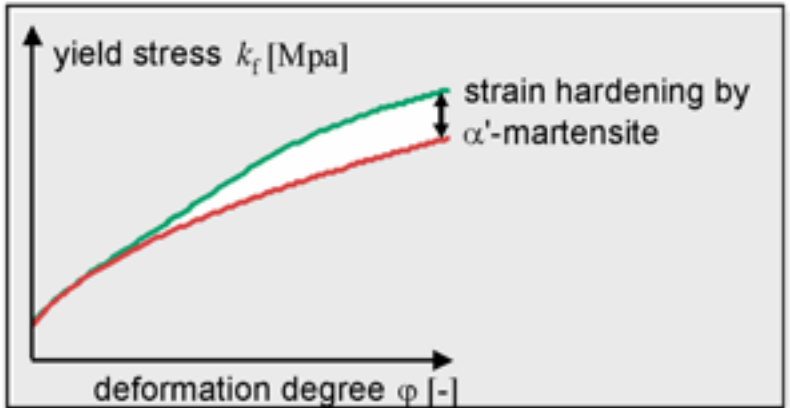
temperature

content of martensite $f^{\alpha'}$

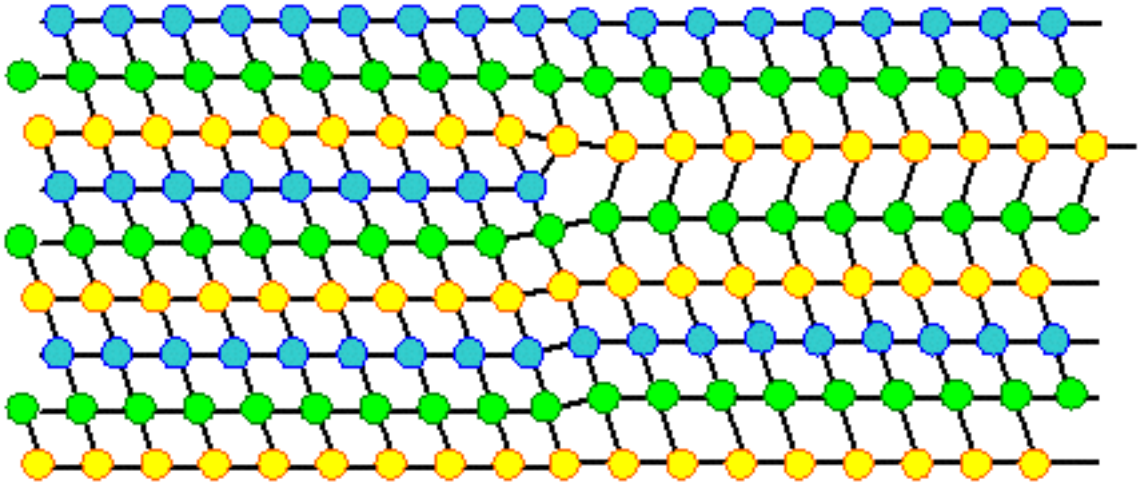


stress state

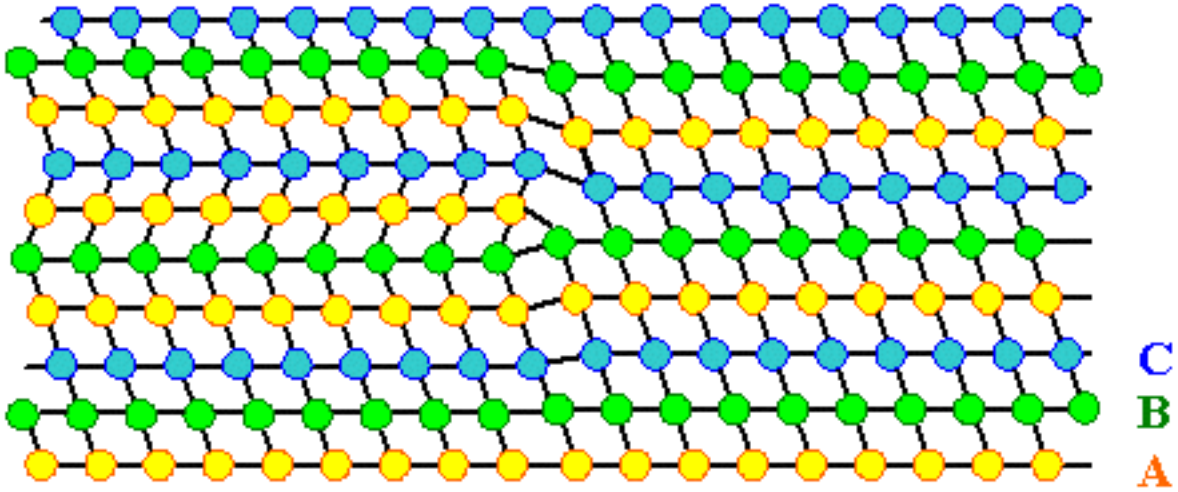




Thank you for you attention
and have a nice weekend!



Intrinsic stacking fault



Extrinsic stacking fault

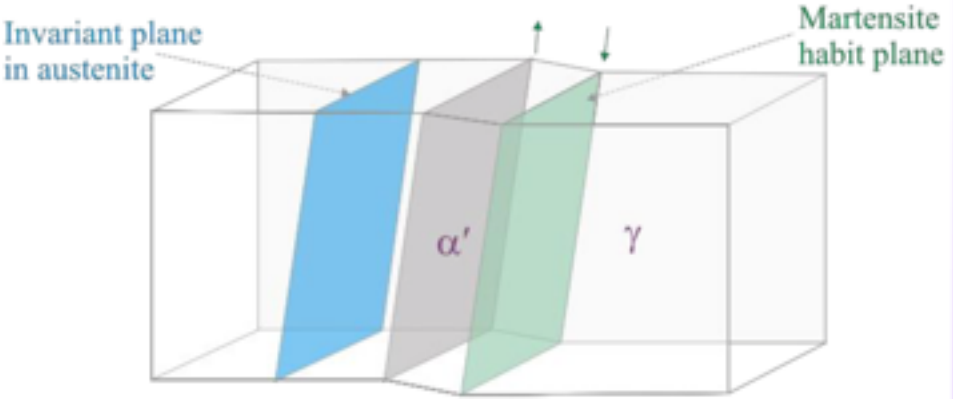
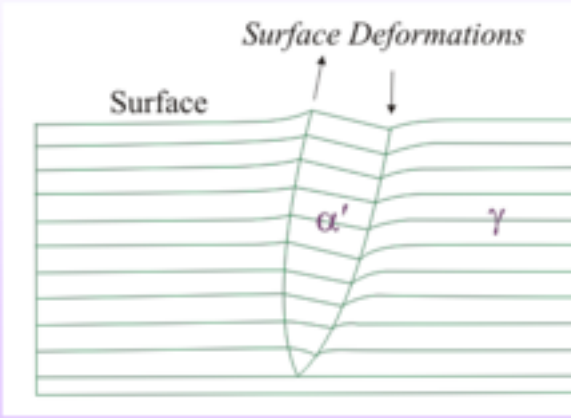
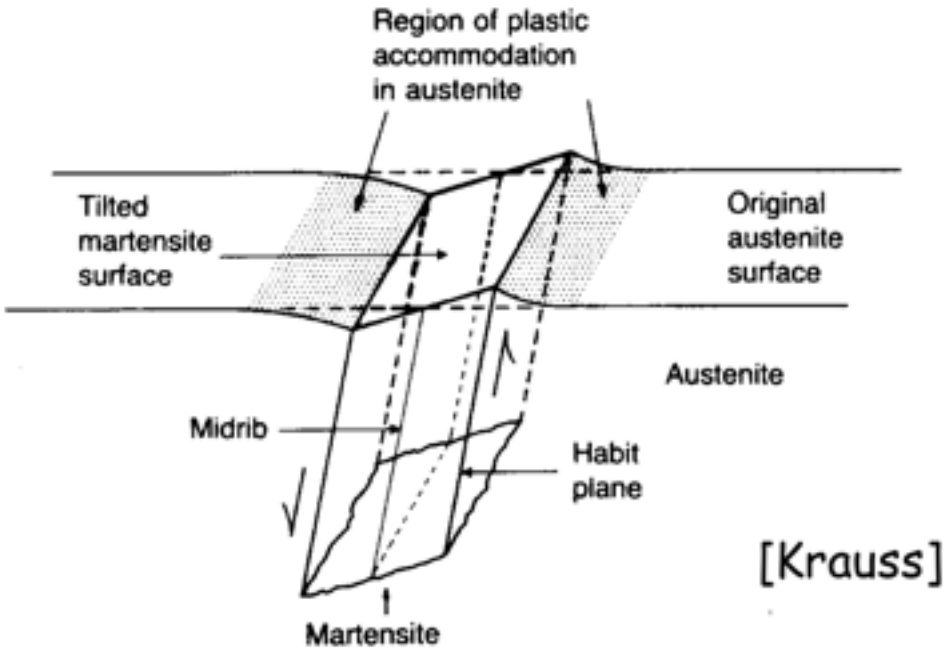


Illustration of the coherence of the martensitic plate with the surrounding austenite



Surface deformations caused by the Mar



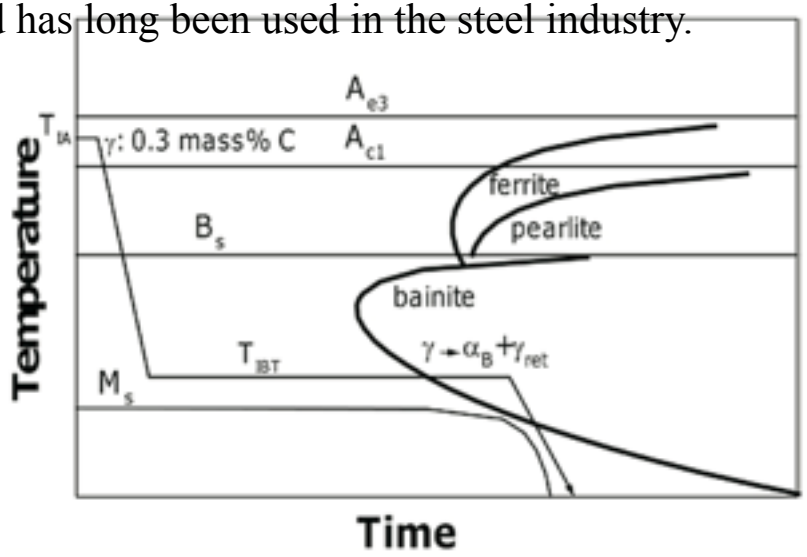
[Krauss]

Why study martensitic transformations?

They occur in many different materials such as:

- ceramics
- polymer systems
- steels are the classical example (and a rare case of a mechanically hard martensite)
- shape memory alloys

The Middle Age Knights used to heat their swords in fire and quench them in cold water; after that, the swords became much harder. This method has long been used in the steel industry.

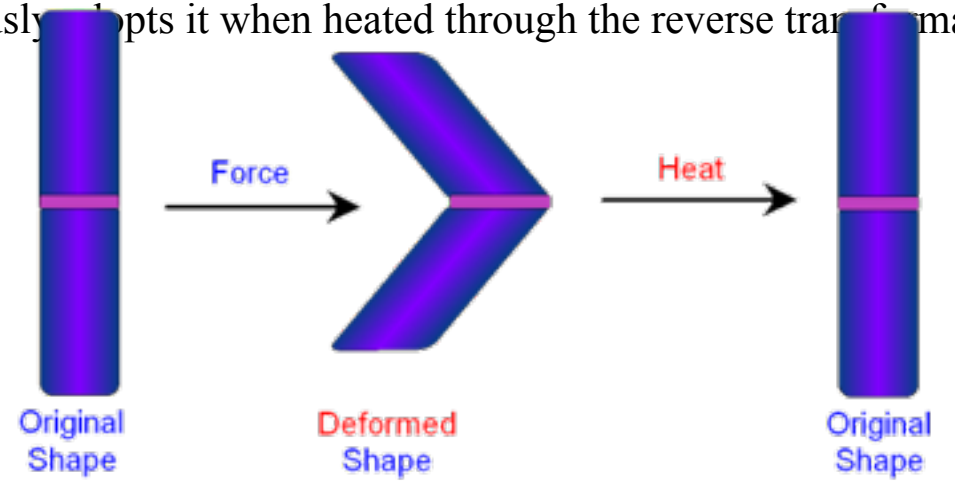


Shape memory effect

In carbon steels, stress-assisted martensite transformation are irreversible, transformation from martensite to austenite can only be realized by re-heating.

Shape memory alloys: stress-assisted transformations are crystallographic reversible.

Au-Cd, In-Tl, Ni-Ti, some Cu-based alloys and other systems. Due to TMTs and especially reverse transformation, alloys exhibit unusual thermomechanical behaviours and shape memory capabilities. For that reason they are referred to as shape memory alloys (SMA) If a SMA initially in the parent phase condition is cooled to the martensite phase, nothing occurs macroscopically, but if an external load is applied, the piece is deformed in an apparent plastic way (the deformed shape remains after the load is released). In fact, the deformation takes place not by the movement of dislocations, but by a reorientation of the martensite variants towards those favored by the external load. If the piece is heated up till the reverse transformation takes place, the parent phase crystal structure and shape is spontaneously restored. It seems that the material "remembers" its original shape and spontaneously adopts it when heated through the reverse transformation. This is the shape memory effect.



Types of phase transformations

Martensitic transformation in steels can be classified as:

athermal, i.e. rapid transformation during quenching,

isothermal, i.e. slower transformation while holding the steel at a constant temperature,

stress-assisted, i.e. by application of stress below the yield limit of the steel, and

strain-induced, i.e. by plastic deformation of the steel.