Metals II

Anne Mertens

LIÈGE université

M.M.S
Metallic Materials Science

Outline

- Introduction
  - Summary of previous lecture
  - Controlling the structure of a material
- Driving force for structural change
- Kinetics I: diffusive transformation
- Kinetics II: nucleation
- Kinetics III: displacive transformation

Introduction

Summary of previous lecture

Summary of Lecture I

- Aim: select the best material for a given application
- Many ≠ criteria must be taken into account
  - – Physical properties (density, conductivity...)
  - – Mechanical properties (yield stress, fatigue...)
  - – Corrosion resistance
  - – Bio-compatibility
  - – Processability, formability
  - – Cost
  - – ...

Summary of Lecture I

- Aim: select the best material for a given application
- Many ≠ criteria must be taken into account

⇒ Need for a methodology

⇒ Need for database of materials properties

Data for metals

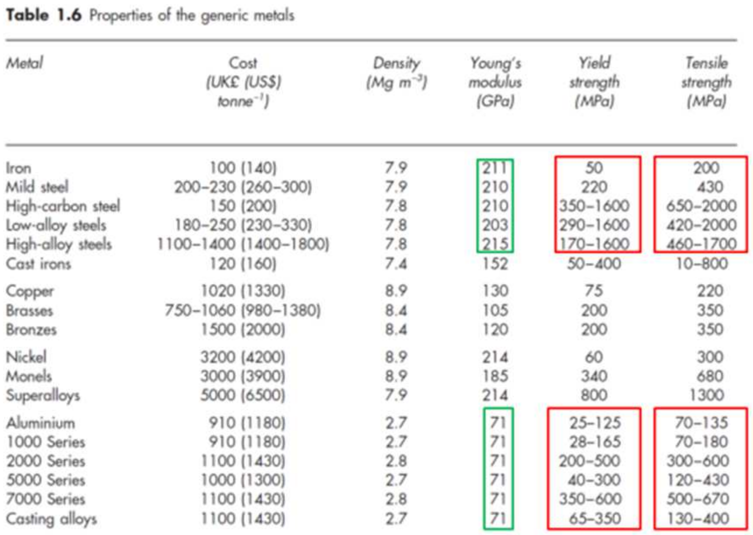


Table 1.6 Properties of the generic metals

Metal	*Cost (UK£ (US$) tonne^{-1})*	*Density (Mg m^{-3})*	*Young's modulus (GPa)*	*Yield strength (MPa)*	*Tensile strength (MPa)*
Iron	100 (140)	7.9	211	50	200
Mild steel	200–230 (260–300)	7.9	210	220	430
High-carbon steel	150 (200)	7.8	210	350–1600	650–2000
Low-alloy steels	180–250 (230–330)	7.8	203	290–1600	420–2000
High-alloy steels	1100–1400 (1400–1800)	7.8	215	170–1600	460–1700
Cast irons	120 (160)	7.4	152	50–400	10–800
Copper	1020 (1330)	8.9	130	75	220
Brasses	750–1060 (980–1380)	8.4	105	200	350
Bronzes	1500 (2000)	8.4	120	200	350
Nickel	3200 (4200)	8.9	214	60	300
Monels	3000 (3900)	8.9	185	340	680
Superalloys	5000 (6500)	7.9	214	800	1300
Aluminium	910 (1180)	2.7	71	25–125	70–135
1000 Series	910 (1180)	2.7	71	28–165	70–180
2000 Series	1100 (1430)	2.8	71	200–500	300–600
5000 Series	1000 (1300)	2.7	71	40–300	120–430
7000 Series	1100 (1430)	2.8	71	350–600	500–670
Casting alloys	1100 (1430)	2.7	71	65–350	130–400

[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

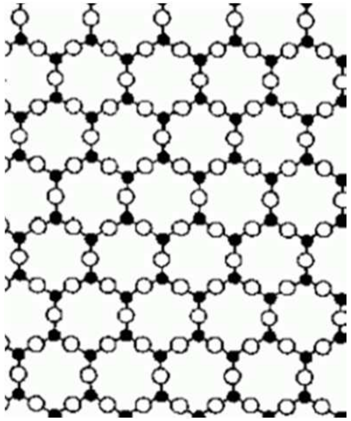
Structure-insensitive

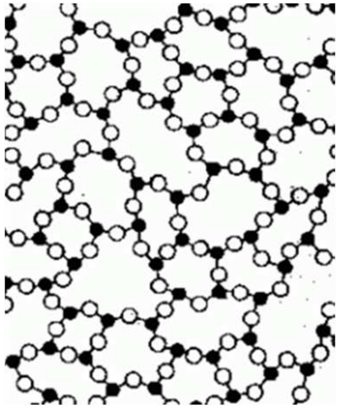
vs

structure-dependent

Summary of Lecture I

- Materials with desired properties
- Some properties of metals are **structure**-dependent
  - Crystalline vs amorphous structure



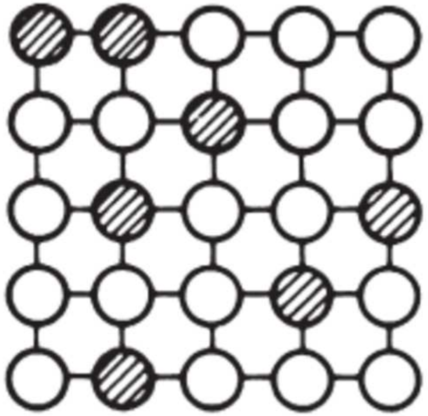


[http://www.majordifferences.com/2013/02/difference-between-crystalline-and.html#.Wb42e9E69PY]

Summary of Lecture I

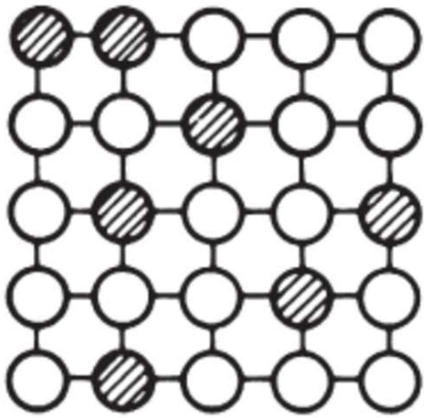
- Materials selection to fulfill desired properties
- Some properties of metals are **structure**-dependent
  - Phase = region of material with homogeneous properties (uniform physical and chemical properties)
  - Example 1: liquid water + ice = 2 different phases
  - Example 2: Cu fully dissolved in Al = 1 phase

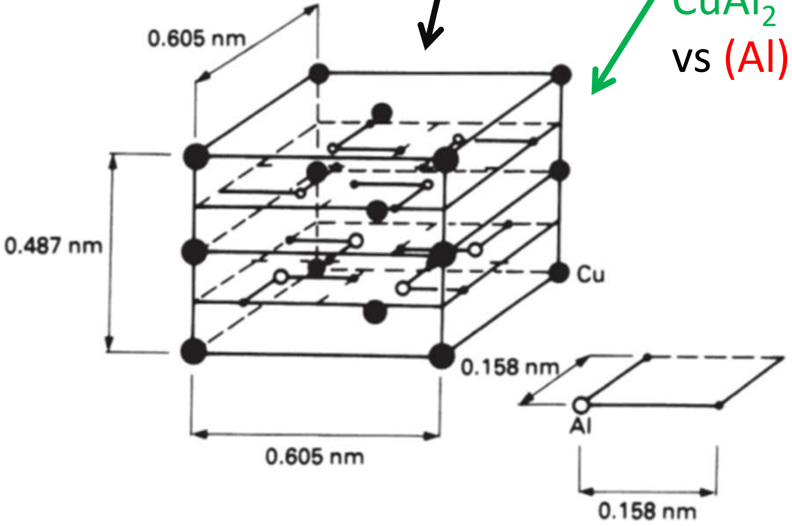
Solid solution



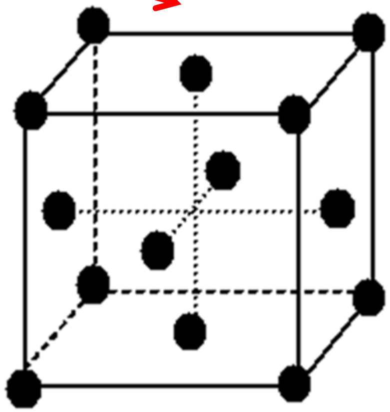
Summary of Lecture I

- Materials selection to fulfill desired properties
- Some properties of metals are **structure**-dependent
  - Phase = region of material with homogeneous properties
    Phases: solid solution, intermetallic compounds...





$CuAl_2$ in Al-Cu alloys
vs (Al) solid solution

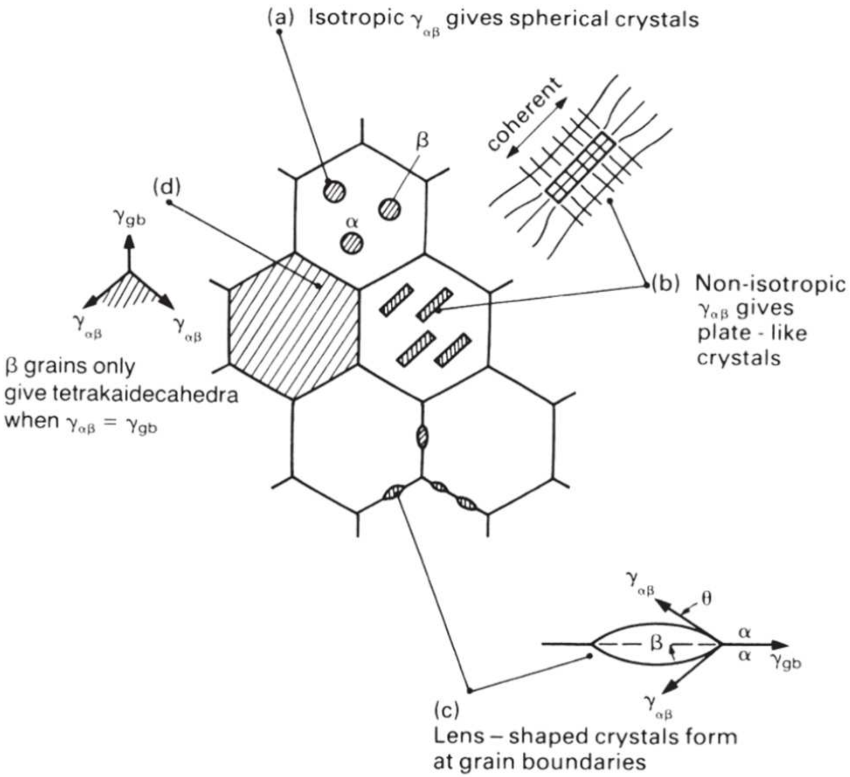


[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

[http://deuns.chez.com/sciences/cristallo/cristallo2.html]

Summary of Lecture I

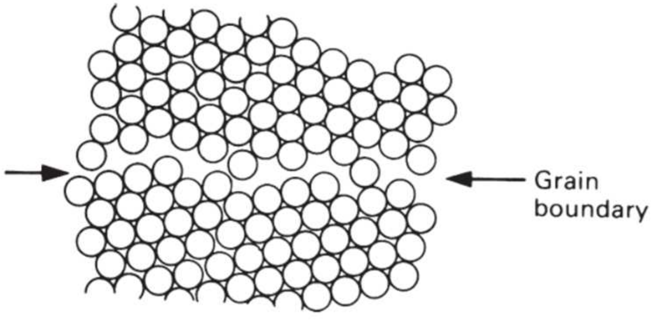
- Materials selection to fulfill desired properties
- Some properties of metals are **structure**-sensitive
  - – Metals are often polycristalline material
  - – Individual crystal = grain
  - $\Rightarrow$ **Grain size and shape**

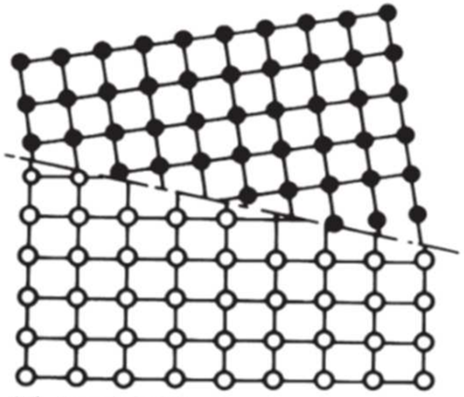


[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Summary of Lecture I

- Materials selection to fulfill desired properties
- Some properties of metals are **structure**-sensitive
  - Grain size and shape
  - **Grain and interphase boundaries**





(d) Incoherent

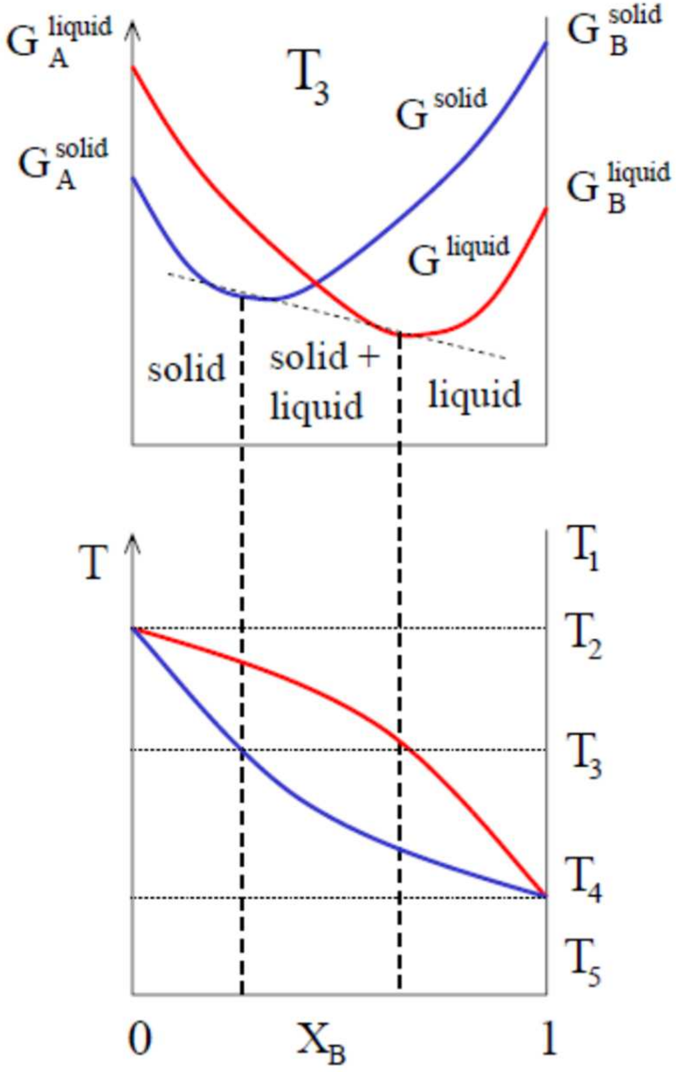
[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Summary of Lecture I

- Materials selection to fulfill desired properties
- Some properties of metals are **structure**-sensitive
  - Crystalline vs amorphous structure
  - Phases (solid solution, intermetallic compounds...)
  - Grain size and shapegrain and interphase boundaries
- How can we control the structure?
  - **Equilibrium** (or stable) structure:
    by playing with the **chemical composition**

Summary of Lecture I

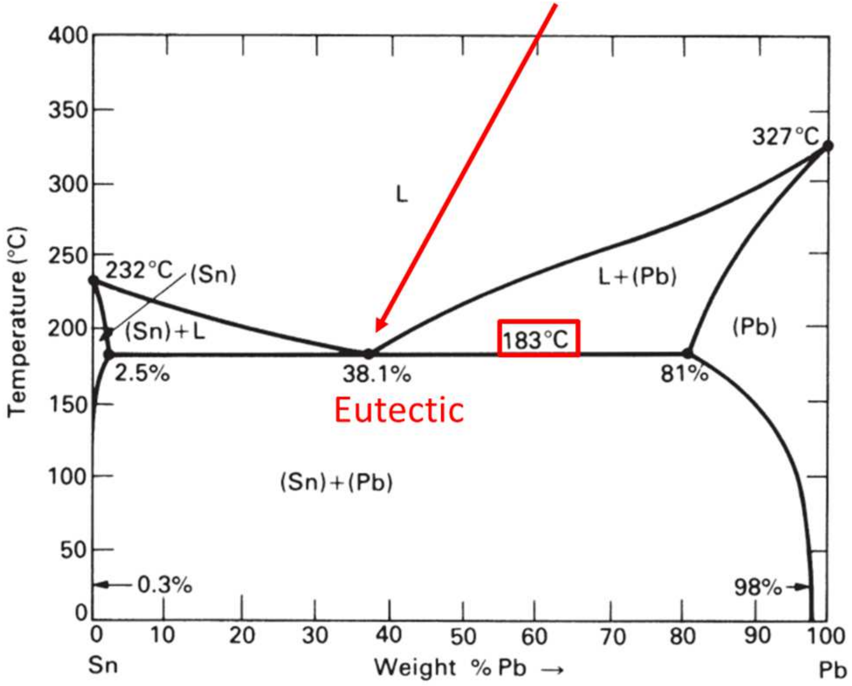
- How can we control the structure?
  - **Equilibrium** structure: A system is in equilibrium when its energy is minimized Equilibrium = G minimum with G: enthalpy
  - **Phase diagram**



L. Zhigilei, Phase diagrams and Kinetics, University of Virginia]

Summary of Lecture I

- How can we control the structure?
  - **Equilibrium** structure:
    by playing with the **chemical composition**
    e.g.: use the Pb-Sn phase diagram to select a solder material with low melting temperature



[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

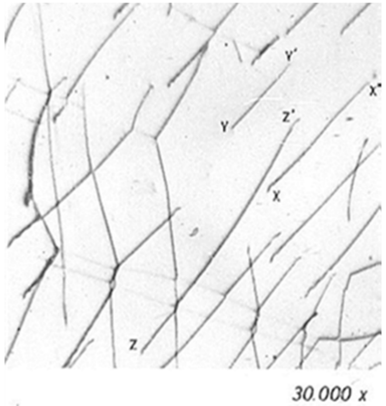
Introduction

How can we control the structure of
a metallic material?
⇒ Playing with structural change

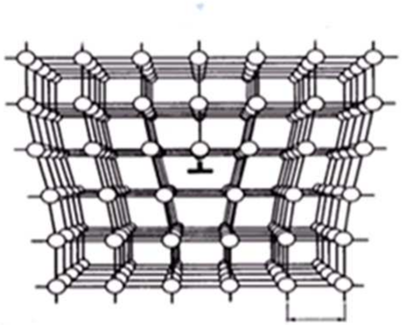
Playing with structural change

- Example 1: plastic deformation

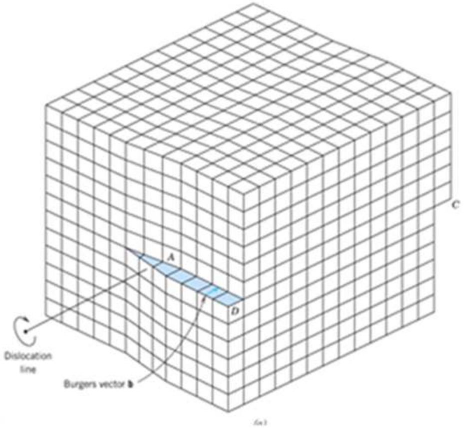
  Creation and propagation of crystalline defects



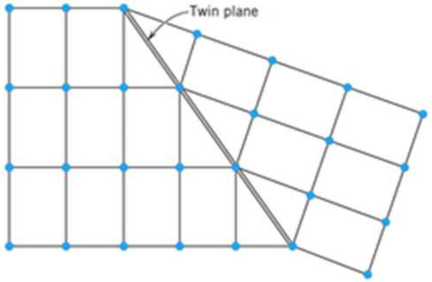
Dislocations (TEM)



Edge dislocation



Screw dislocation



Twin

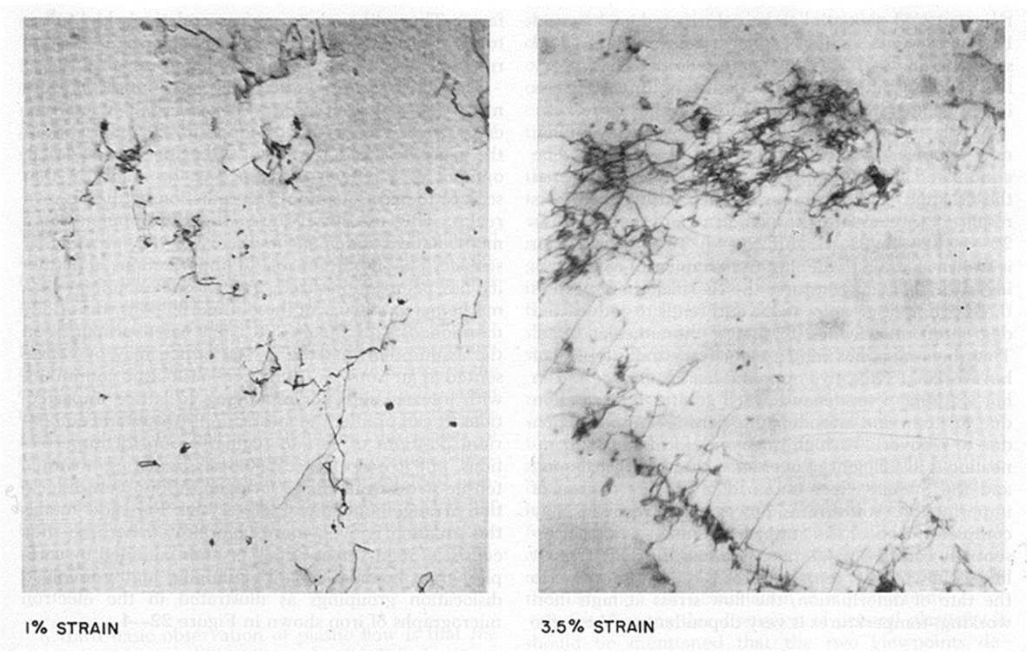
Plastic deformation occurs by dislocations glide

[J. Lecomte-Beckers, Phys0904 "Physique des Matériaux"]

Playing with structural change

- Example 1: plastic deformation

  Creation and propagation of crystalline defects



1% STRAIN

3.5% STRAIN

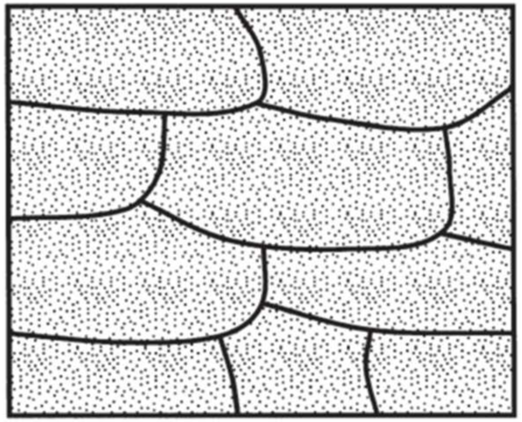
Dislocations density $\uparrow$
$\Rightarrow$ Entanglement
$\Rightarrow$ Dislocations glide
more difficult
$\Rightarrow$ Strength $\uparrow$
$\Rightarrow$ **Work hardening**

[J. Lecomte-Beckers, Phys0904 "Physique des Matériaux"]

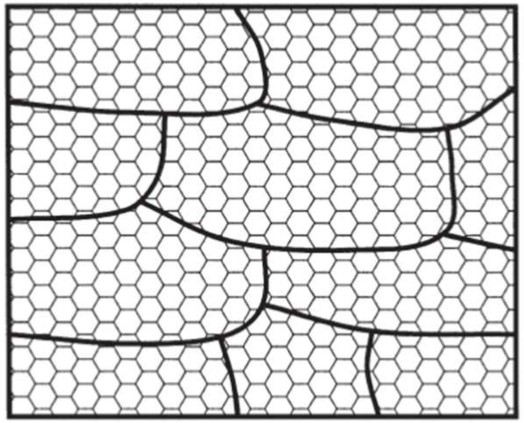
Playing with structural change

- Example 1: plastic deformation

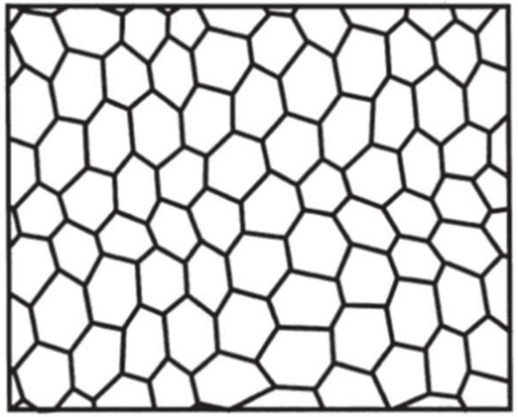
  Recovery and recrystallisation



Deformed structure



Recovery = organisation of crystalline defects



Recrystallization = formation of new grains

Grain size has a strong influence on properties!

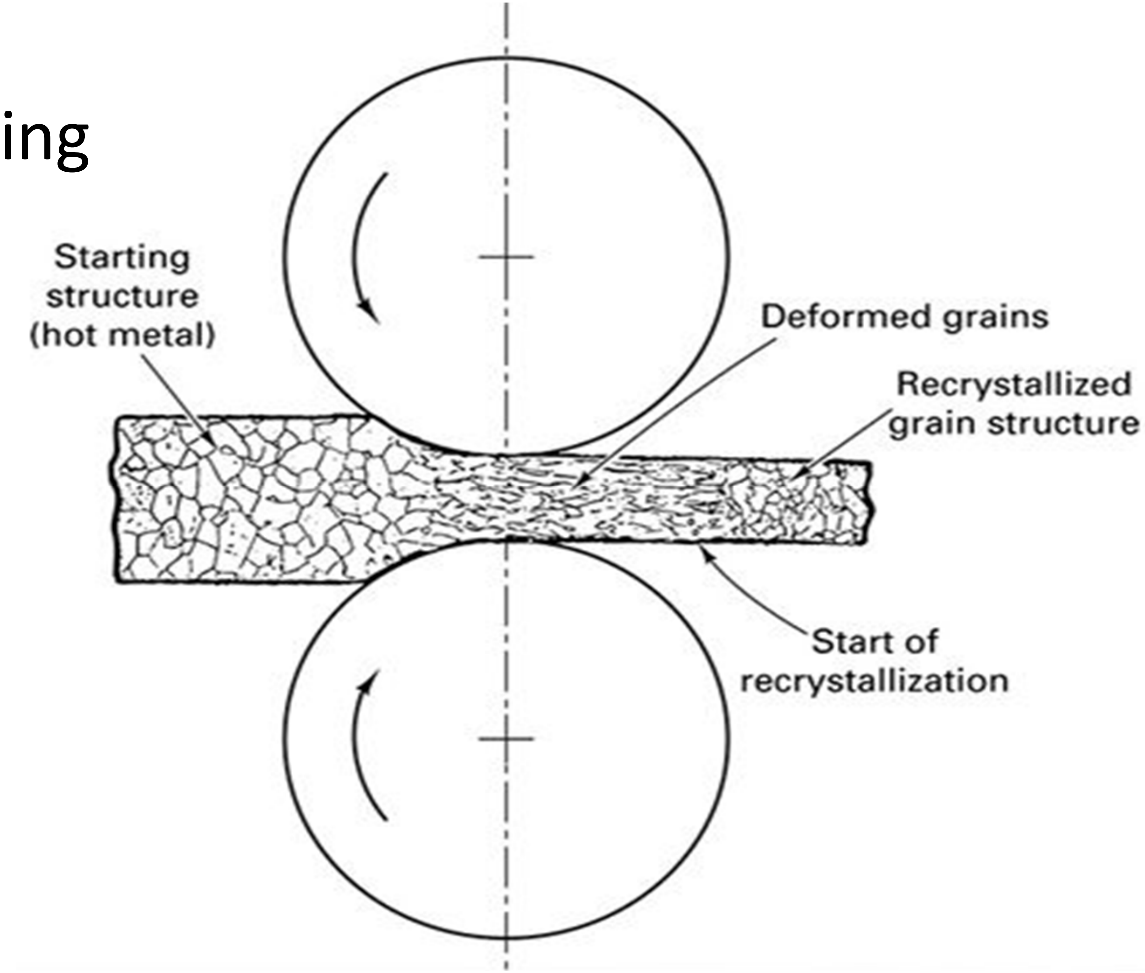
≠ structures ⇒ ≠ properties

[J. Lecomte-Beckers, Phys0904 "Physique des Matériaux"]

Playing with structural change

- Example 1: plastic deformation

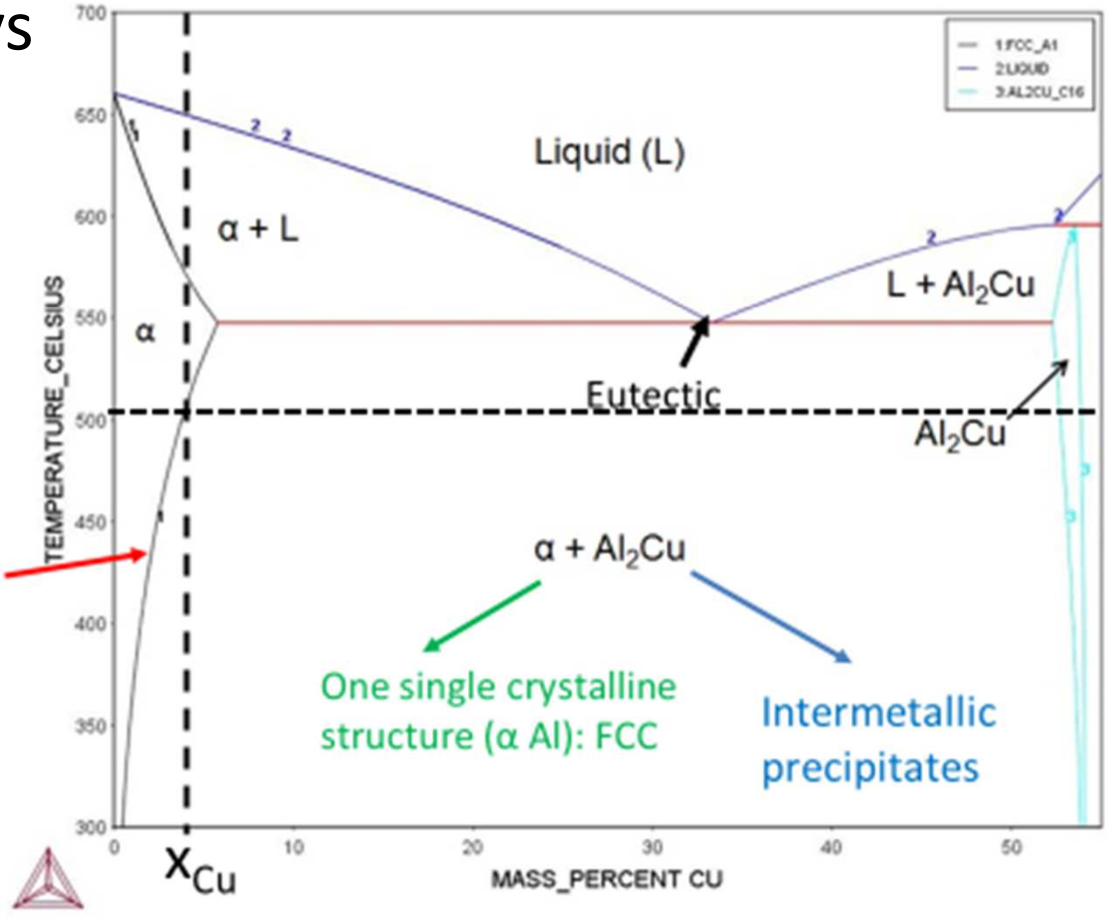
  Practically: hot rolling



Playing with structural change

- Example 2: Intermetallic compounds

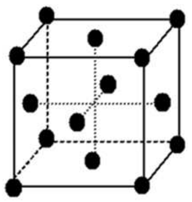
Al-Cu alloys



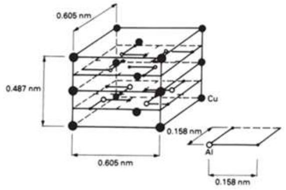
Miscibility gap - Solubility of Cu in Al decreases with T

One single crystalline structure (α Al): FCC

Intermetallic precipitates



FCC Al



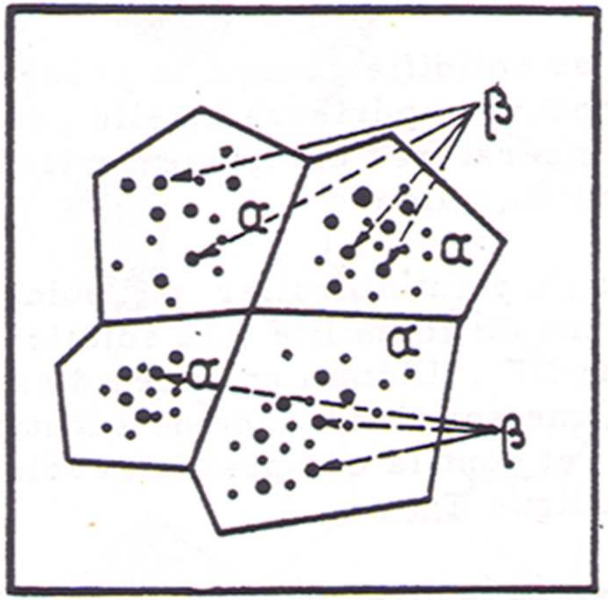
Al_2Cu

Playing with structural change

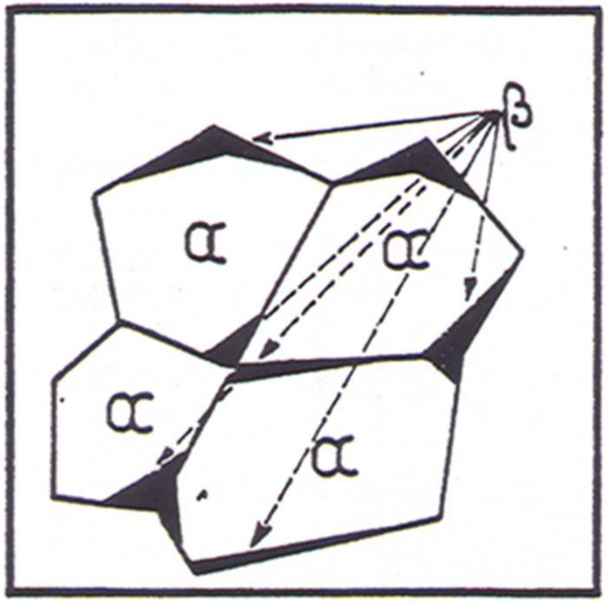
- Example 2: Intermetallic compounds

  Al-Cu alloys

  Finely distributed intermetallics give more efficient strengthening than coarse precipitates



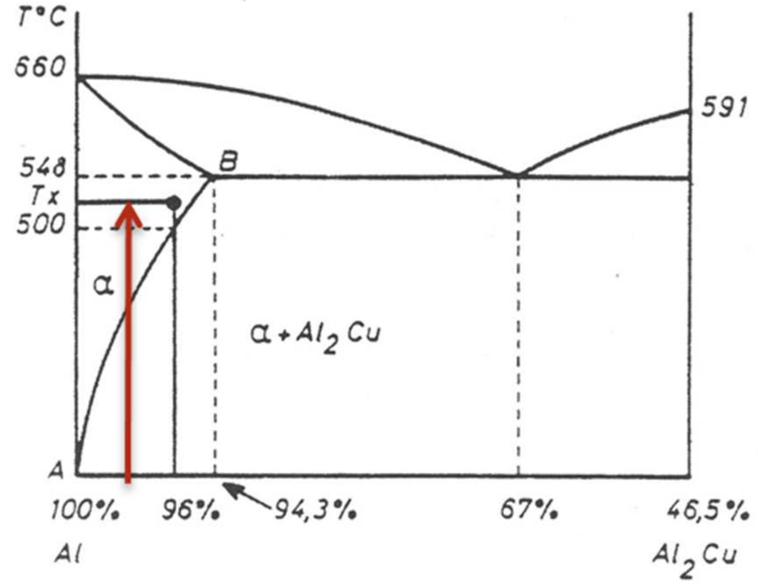
stronger than



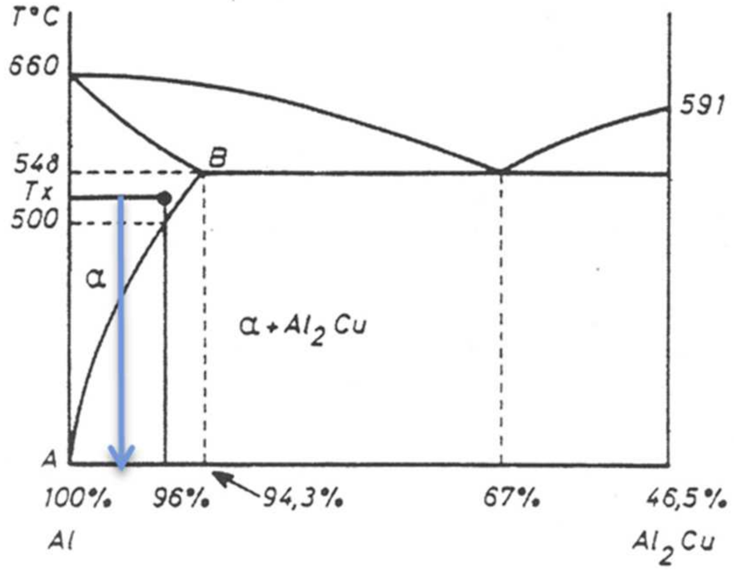
Playing with structural change

- Example 2: Intermetallic compounds

Heat treatment to control the formation of Al_2Cu and obtain optimized properties



1. Solution treatment

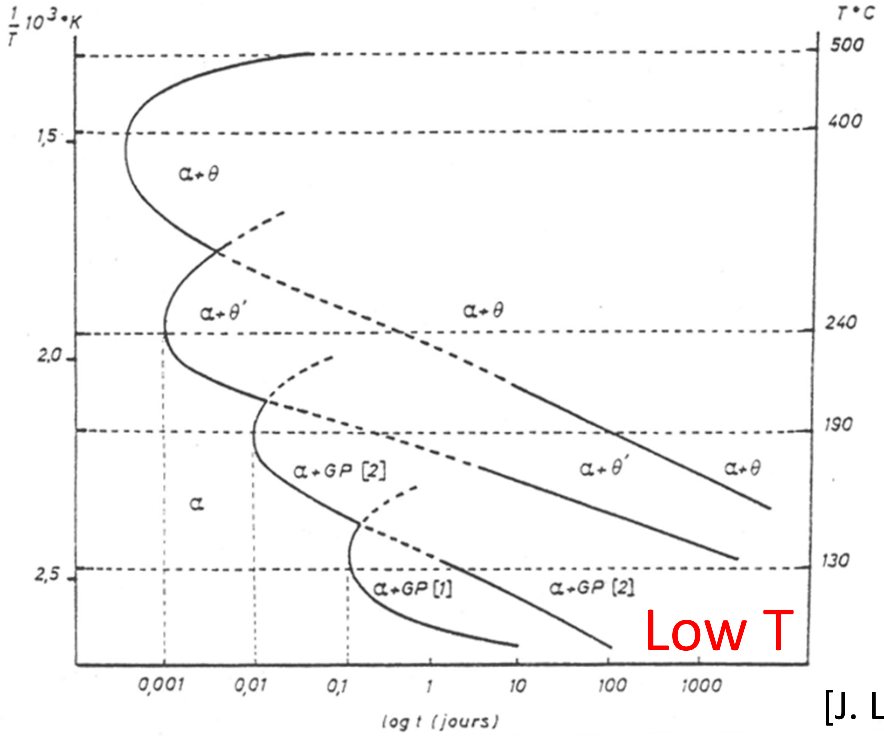


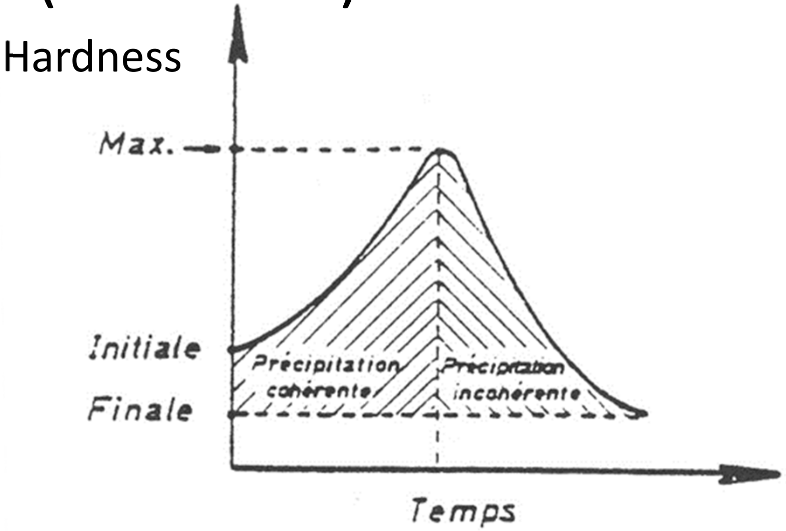
2. Quench (to keep Cu in solid solution)

Playing with structural change

- Example 2: Intermetallic compounds

Heat treatment to control the formation of Al_2Cu and obtain optimized properties (Hardness)





Low T

⇒ Small coherent precipitates

[J. Lecomte-Beckers, Phys0904 "Physique des Matériaux"]

3. Ageing (formation of intermetallic Al_2Cu precipitates)

Outline

- Introduction
- Driving force for structural change
  - General principles
  - Applications to phase transformations
- Kinetics I: diffusive transformation
- Kinetics II: nucleation
- Kinetics III: displacive transformation

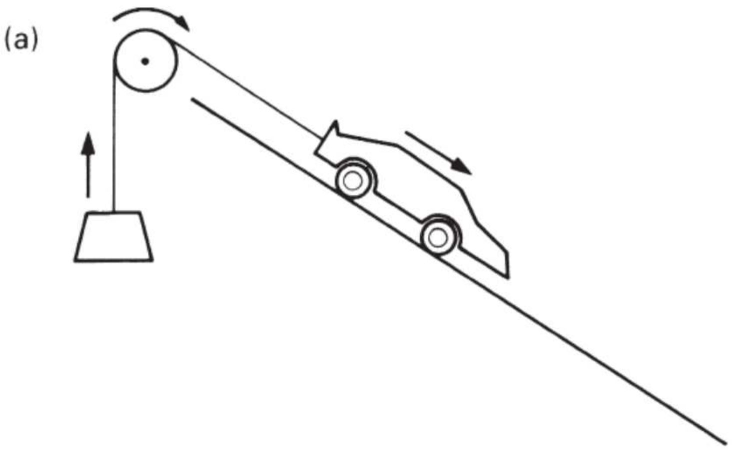
Driving force for structural change

When is it possible to change the structure of metallic materials?

Conditions for change

- Structural change is **possible** when there is a **driving force** for change
- Driving force = energy available for change or to do work

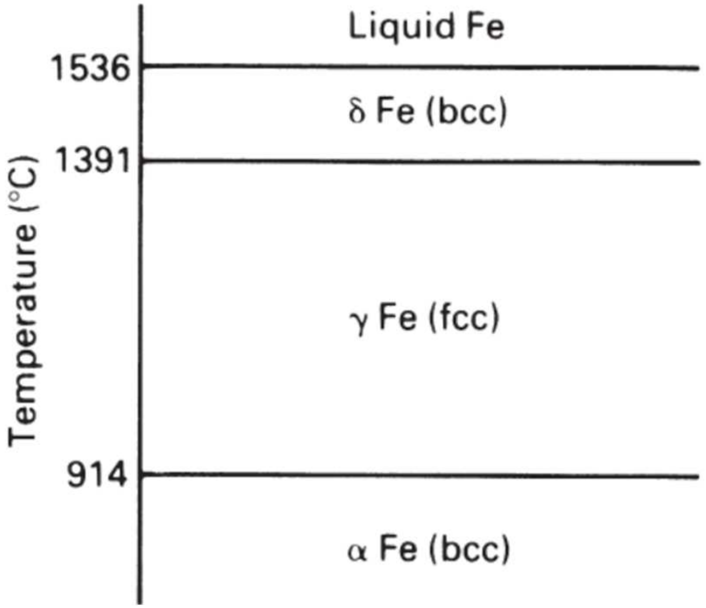
  E.g.: Potential energy for a car moving downhill

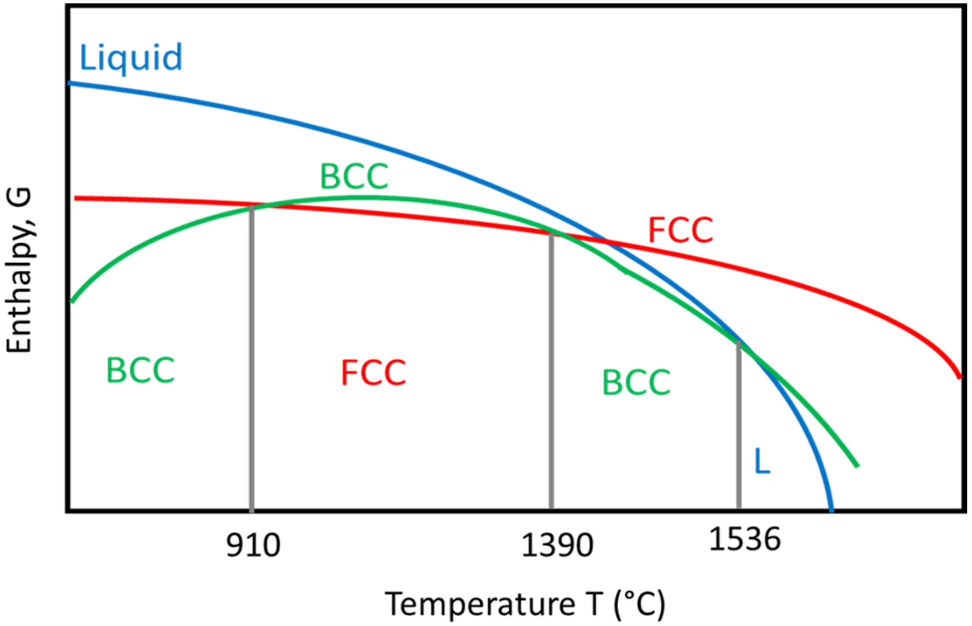


[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Conditions for change

- Structural change is **possible** when there is a **driving force** for change
- Driving force = minimizing the free enthalpy for the allotropic transformations of pure Fe



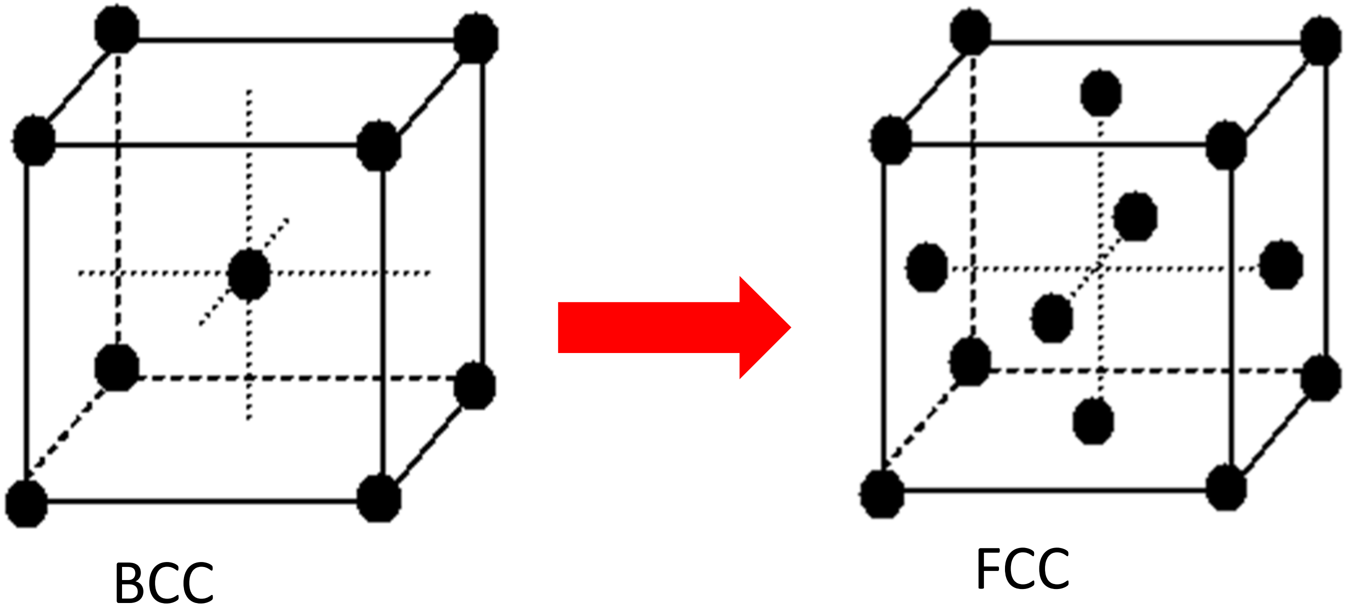


[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Conditions for change

- To change from BCC to FCC structures, atoms need to move

⇒ Diffusion, rate = f(T)



[http://deuns.chez.com/sciences/cristallo/cristallo2.html]

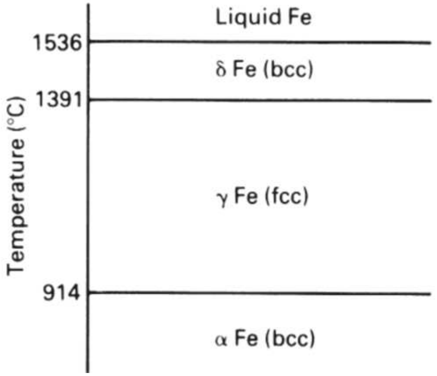
Conditions for change

- Structural change is **possible** when there is a **driving force** for change
- Even if there is a driving force, change may not occur at a measurable pace/speed

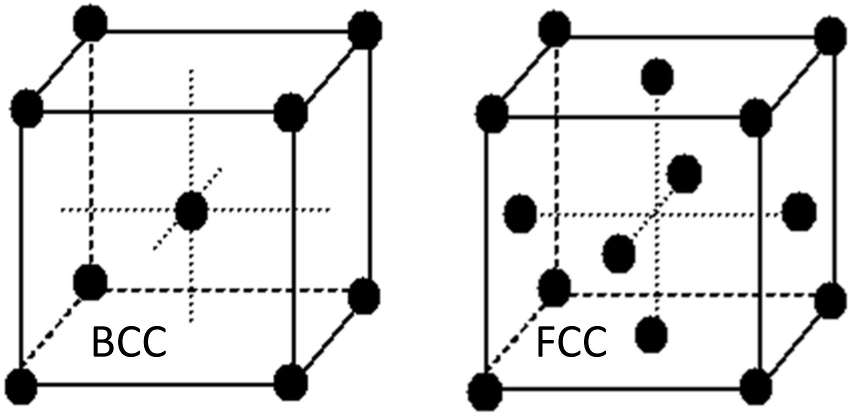
⇒ Route or mechanism for transformation?

⇒ **Kinetics!**

Atomic diffusion, rate = f(T)



[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

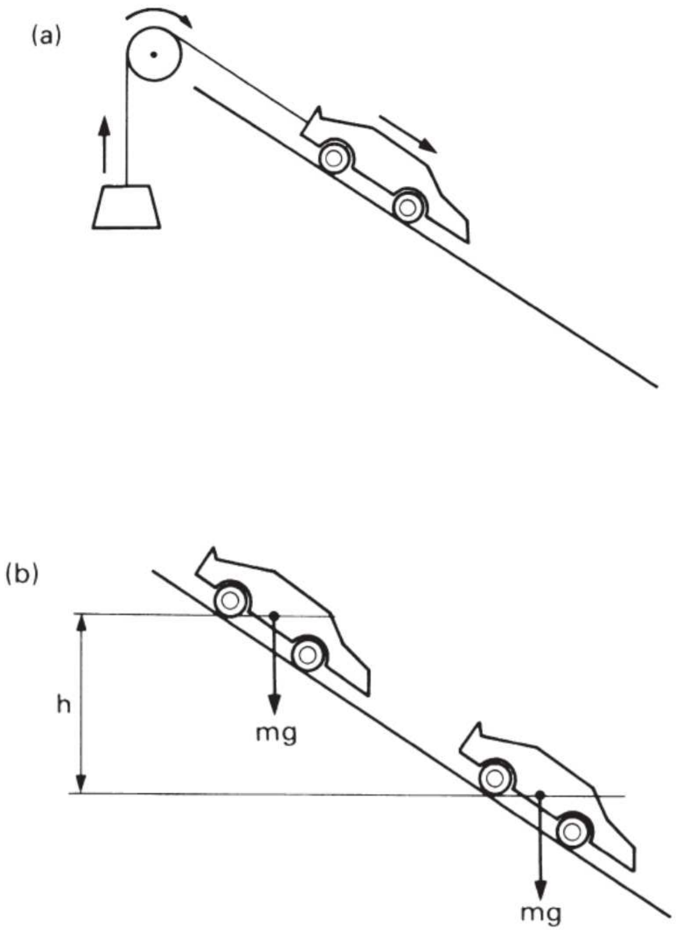


[http://deuns.chez.com/sciences/cristallo/cristallo2.html]

Driving force

For a car moving downhill

$$\underbrace{W_f}_{\text{Free work}} = \underbrace{mgh}_{\text{Potential energy}}$$



[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Driving force

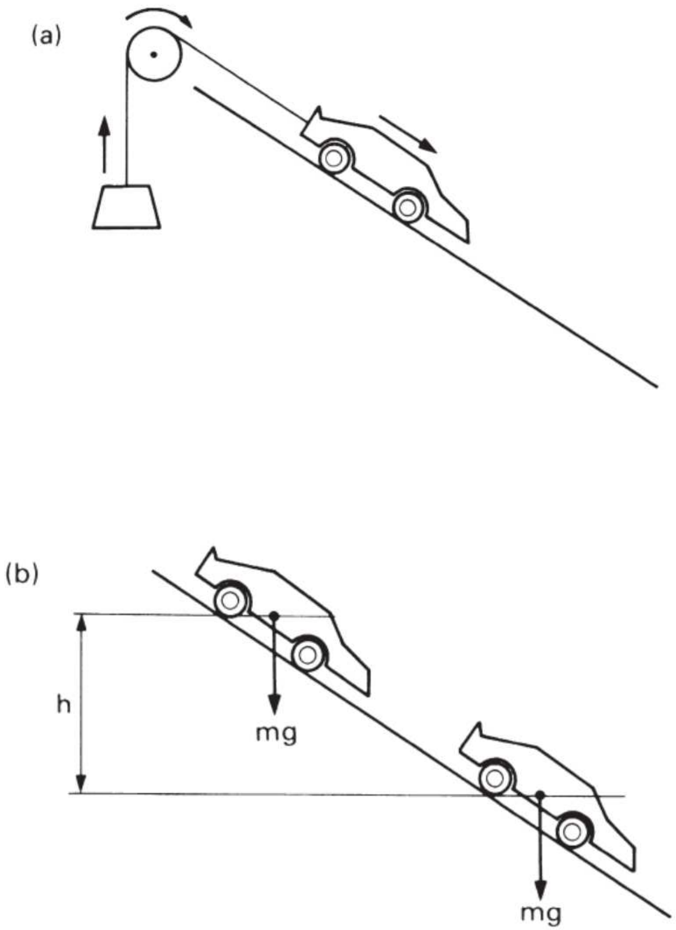
For a car moving downhill

$$W_f \quad \boxed{\leq} \quad mgh$$

Free work

Potential energy

Part of the energy available will be lost (friction in wheel bearings, air resistance...)



[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Driving force

For a car moving downhill with an initial velocity v

$$W_f \quad \leq \quad mgh + 1/2\, mv^2$$

Free work

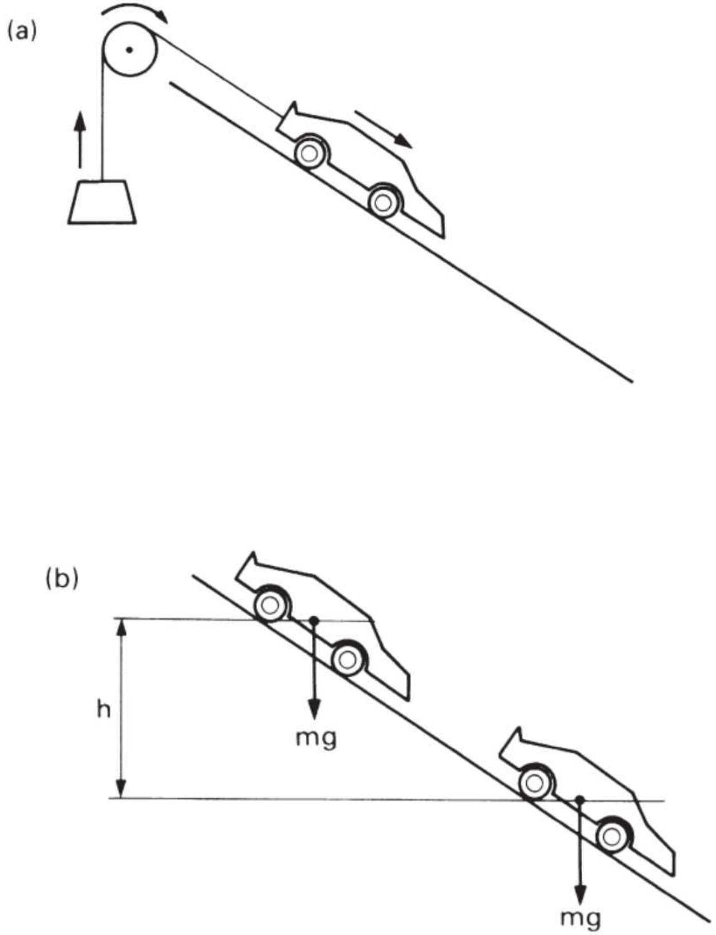
Potential energy

Kinetic energy

External energy

-ΔN

Directed (non-random) movement



[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Driving force

Generally:

$$W_f \leq -\Delta N - \Delta U$$

Free work

External energy

Internal energy

- intrinsic to the material
- chemical energy, thermal energy stored in atomic vibrations, elastic strain energy...

Driving force

Generally:

$$W_f \leq Q - \Delta N - \Delta U$$

Free work

Heat can be turned into work, e.g. steam boiler

External energy

Internal energy

Driving force

Generally:

$$W = Q - \Delta N - \Delta U$$

Total work

External energy

Internal energy

Heat can be turned into work, e.g. steam boiler

Any energy lost in one way must re-appear somewhere else

1st law of thermodynamics = conservation of energy

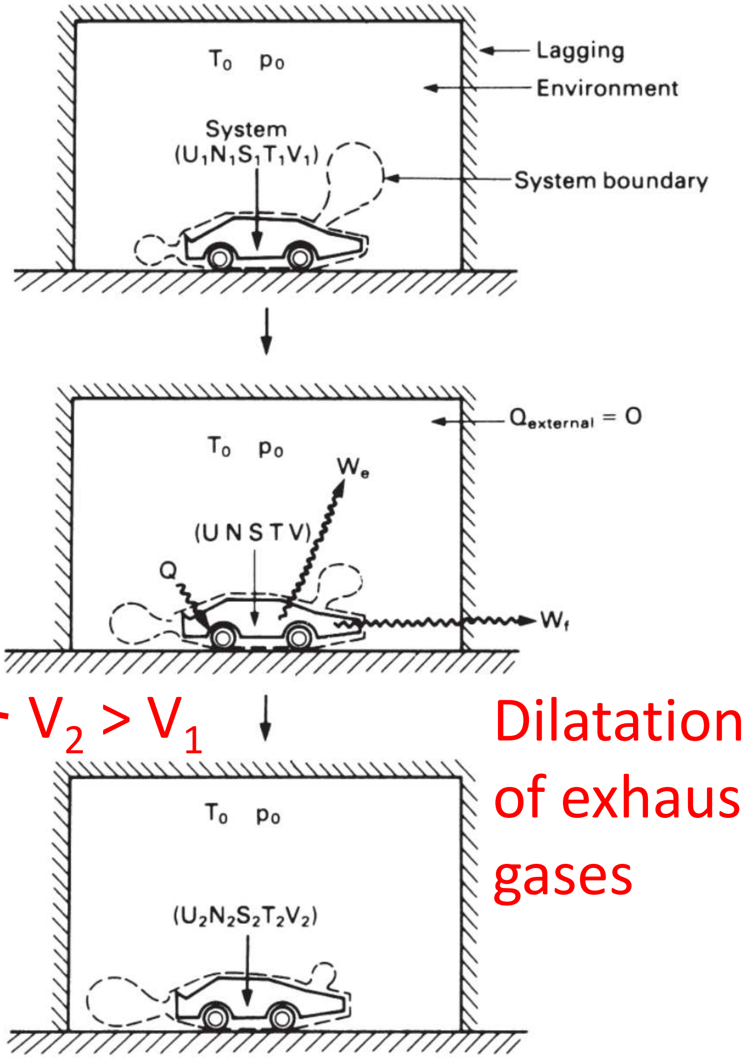
Driving force

$T_0, p_0 = cst$

What about W_f (free work)?

$$W = Q - \Delta N - \Delta U$$

$$W = Q - (U_2 - U_1) - (N_2 - N_1)$$



$$W_e = p_0 (V_2 - V_1)$$

$V_2 > V_1$

Dilatation of exhaust gases

$$W_f = W - W_e$$

[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Driving force

What about W_f (free work)? T_0, p_0 = cst

$$W = Q - \Delta N - \Delta U$$

$$W = Q - (U_2 - U_1) - (N_2 - N_1)$$

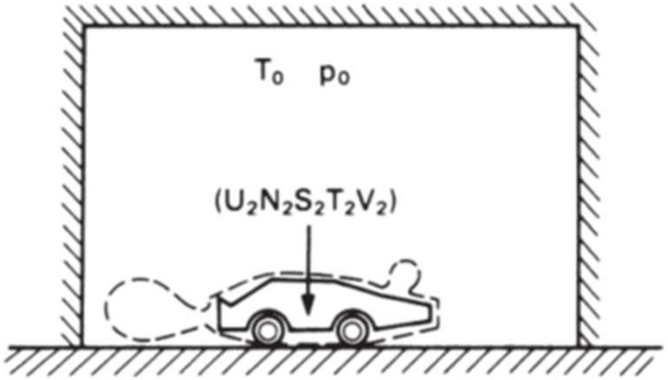
$$W_e = p_0\,(V_2 - V_1)$$

$$W_f = W - W_e$$

$$\boldsymbol{W_f = Q - (U_2 - U_1) - p_0\,(V_2 - V_1) - (N_2 - N_1)}$$

Reversibility ?

Reversible change: **2nd law of thermodynamics**



$dS = dQ/T$ with **S: entropy**

$$S_2 - S_1 = \int_Q \frac{dQ(T)}{T}$$

But we don't know dQ(T) !?

$(S_2 - S_1)_{car} = - (S_2 - S_1)_{environment}$ → T_0 cst !

$(S_2 - S_1)_{car} = - (S_2 - S_1)_{environment} = Q/T_0$

Driving force for reversible change

$\Delta S = Q/T_0$

Then

$W_f = Q - (U_2 - U_1) - p_0\,(V_2 - V_1) - (N_2 - N_1)$

can be rewritten as

$W_f = -\,\Delta U - p_0\Delta V + T_0\Delta S - \Delta N$

$\Rightarrow$ *How much free work is available for driving a* ***reversible*** *change*

Driving force for reversible change

$W_f = - \Delta U - p_0 \Delta V + T_0 \Delta S - \Delta N$

One can also write:

$A = U + pV - TS$ *where A: availability*

$H = U + pV$ *where H: enthalpy*

$G = H - TS$ *where G: free enthalpy*

Stability and metastability

Reminder of Lecture I

Intuitively:

A system is in equilibrium when it exhibits **no further tendency to change with time**

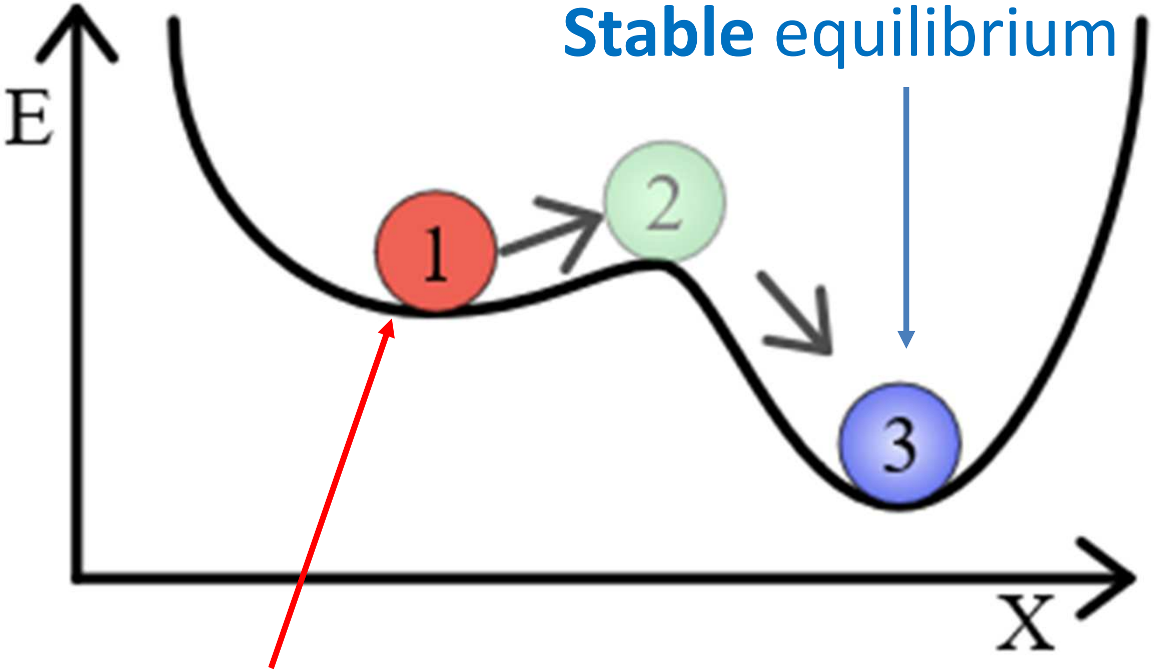
Thermodynamics:

A system is in equilibrium when its energy is minimized

Equilibrium = **G minimum** with G: free enthalpy

Stability and metastability

Equilibrium = **G minimum**

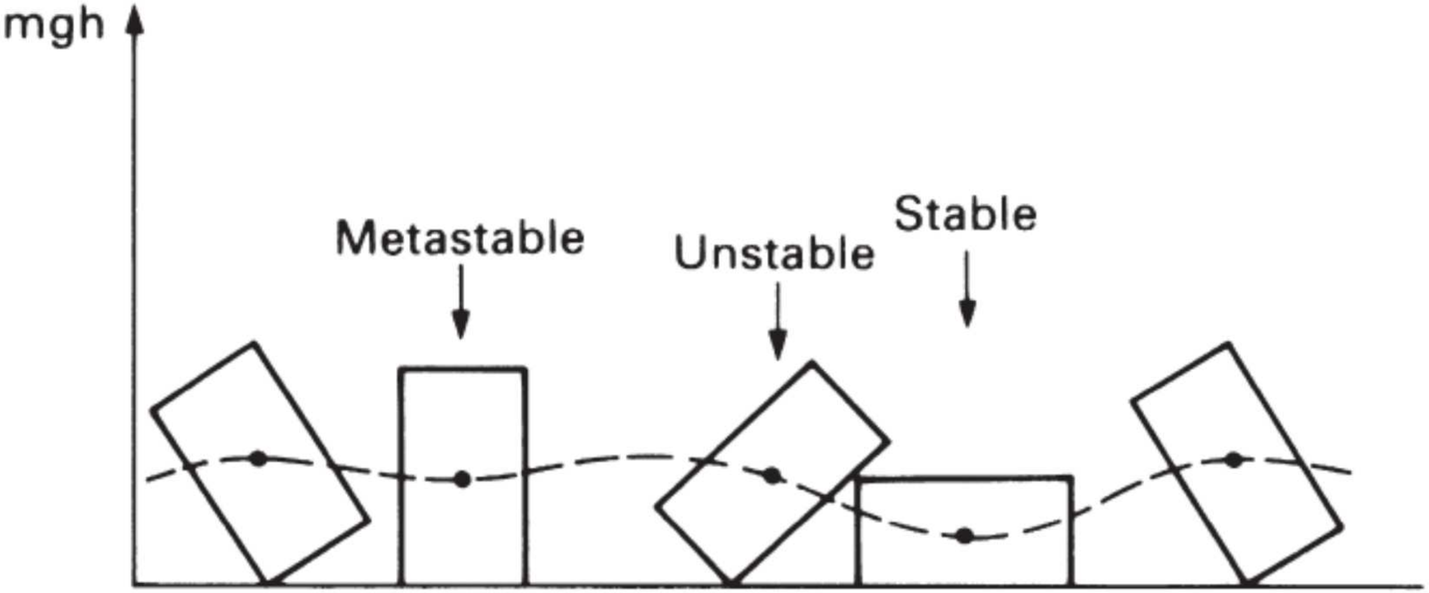


Absolute minimum
Stable equilibrium

Relative minimum
Metastable equilibrium

Stability and metastability

In the simple case where the energy of the system is expressed as **potential energy**



[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Outline

- Introduction
- Driving force for structural change
  When is it possible to change the structure of metallic materials?
  - General principles
  - Applications to phase transformations
- Kinetics I: diffusive transformation
- Kinetics II: nucleation
- Kinetics III: displacive transformation

Driving force for solidification

Water solidifies into ice (T, p cst)

- If p = 1 atm, **T_m = 273 K**
- Mixture of water and ice is in equilibrium

$$\Delta G = 0 = (U + pV - T_m S)_{ice} = (U + pV - T_m S)_{water}$$
$$= (H - T_m S)_{ice} = (H - T_m S)_{water}$$

$\Rightarrow \Delta H = T_m \Delta S$ with ΔH: **"latent heat of solidification"**

[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Driving force for solidification

Water solidifies into ice (T, p cst)

- If p = 1 atm, **T = 272 K (just below T_m)**
- Water has a tendency to freeze

$W_f = -[(H-TS)_{ice} - (H-TS)_{water}] > 0$

$W_f = - \Delta H + T\Delta S$

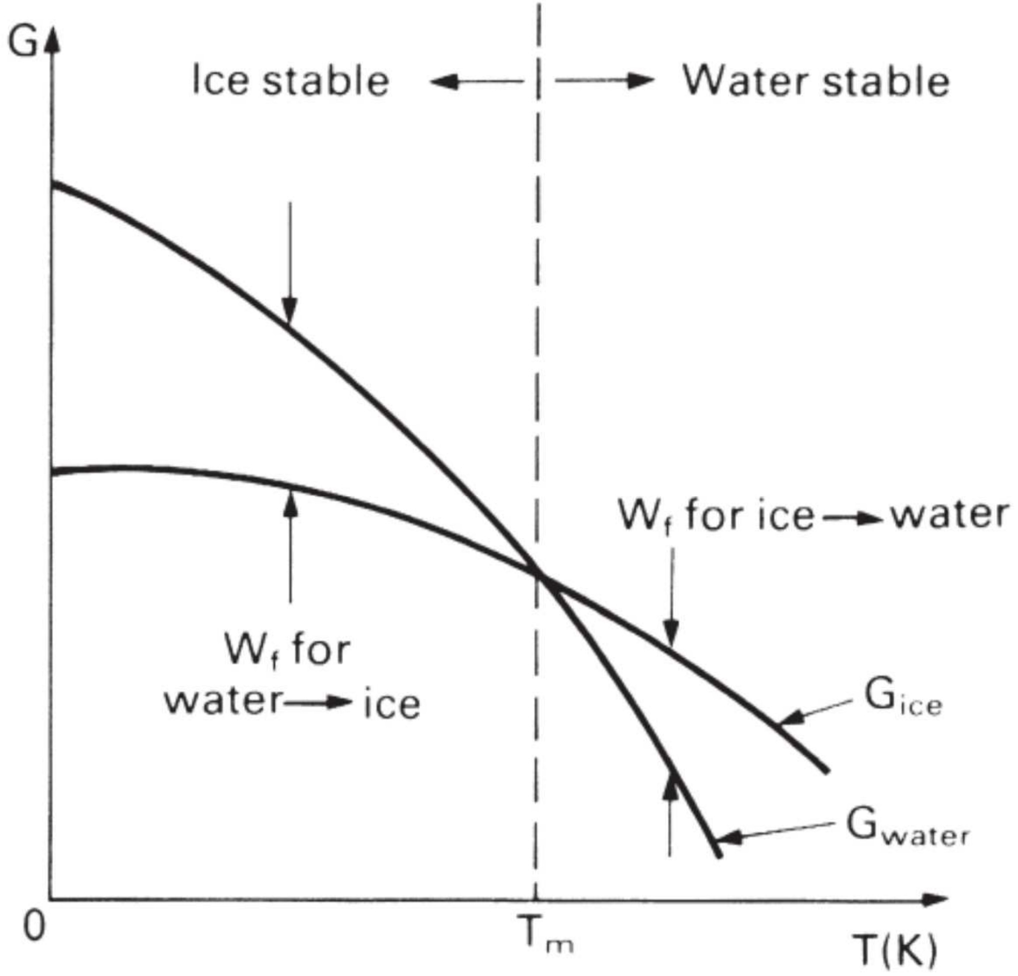
Assuming that ΔH and ΔS do not change much with T

$W_f(T) = - \Delta H + T(\Delta H/T_m)$

From calorimetry experiments, $\Delta H = - 334\ \mathrm{kJ\ kg^{-1}}$

$W_f = 1{,}22\ \mathrm{kJ\ kg^{-1}}$

Driving force for solidification

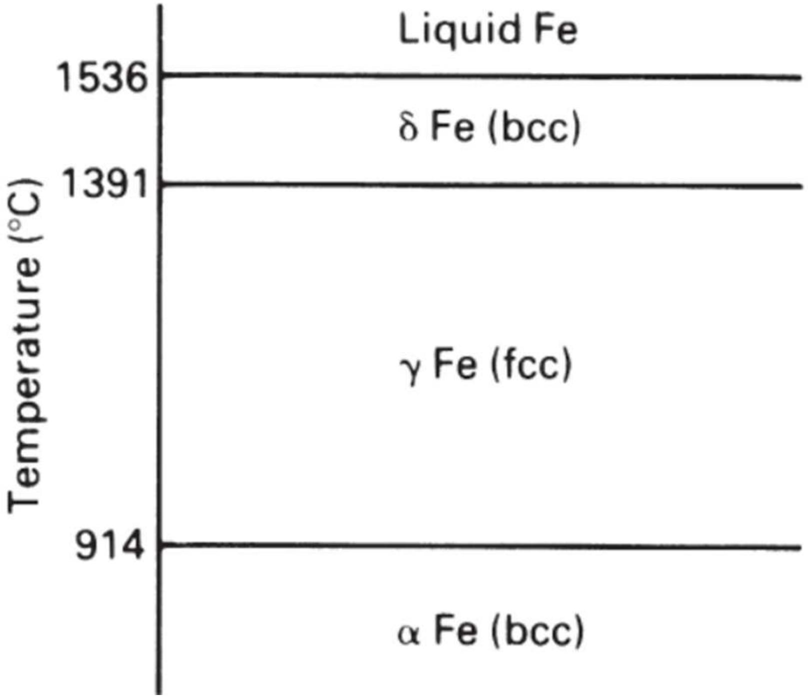


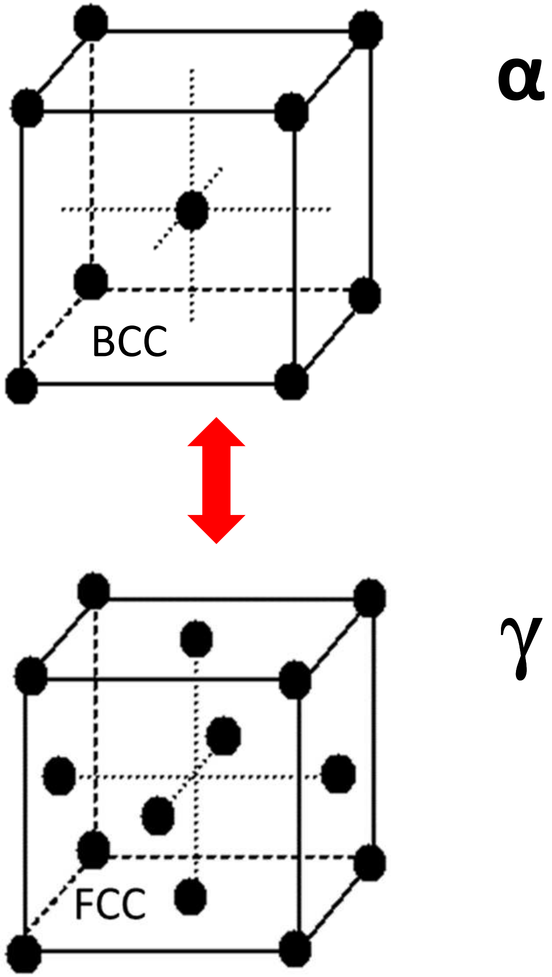
[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Driving force for solid-state phase transformation

Same approach for

- the α - γ transition in Fe



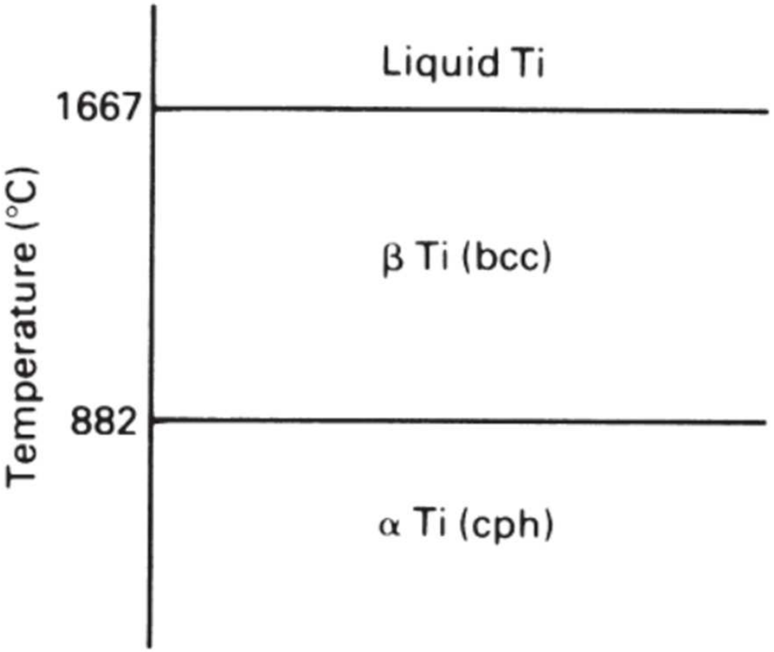


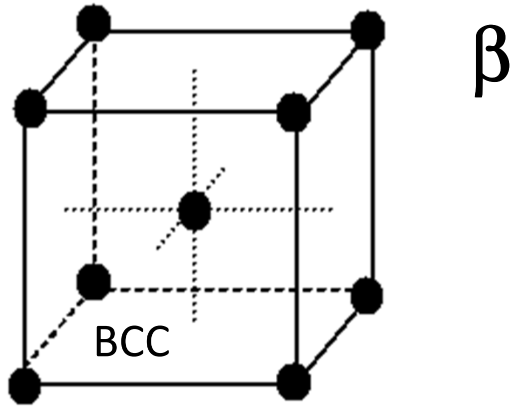
[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

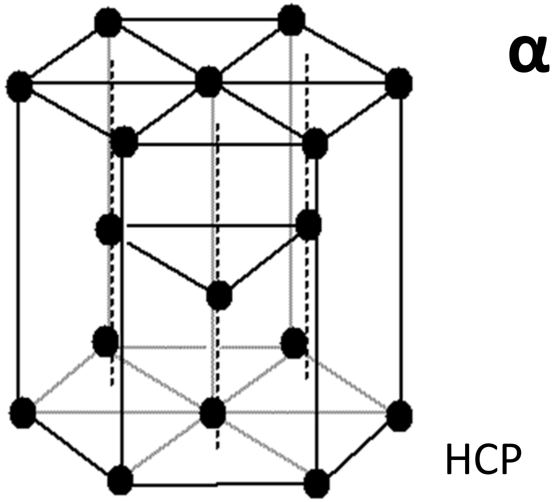
Driving force for solid-state phase transformation

Same approach for

- the α - β transition in Ti







[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Driving force for solid-state phase transformation

Same approach for

- the α - γ transition in Fe
- the α - β transition in Ti

$$W_f(T) = -\frac{\Delta H}{T_e}(T_e - T)$$

with T_e the temperature at which the 2 solid phases are in equilibrium

Driving force for solid-state phase transformation

$$W_f(T) = -\frac{\Delta H}{T_e}(T_e - T)$$

with T_e = 1155 K and ΔH = - 3,48 J mol^{-1}
for the α - β transition in Ti

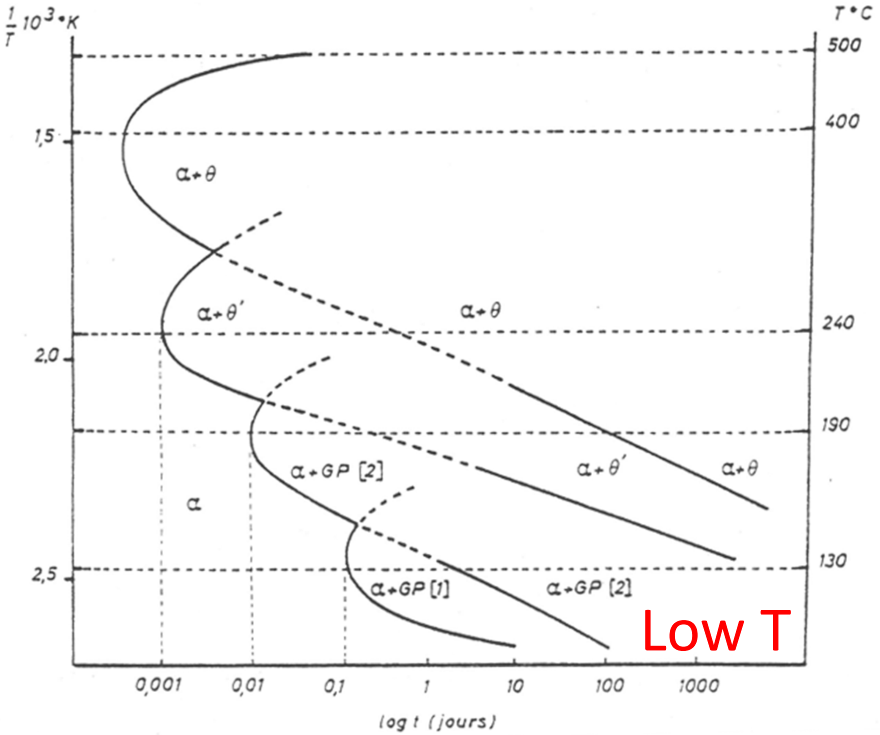
⇒ W_f = 3,0 J mol^{-1} for a T departure from T_e of 1 K

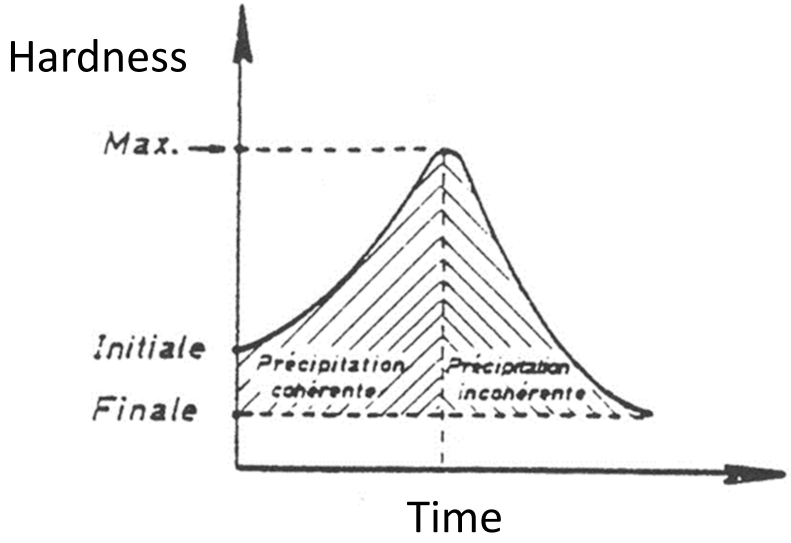
⇒ W_f for solid-state transformation are ~ 1/3 of W_f for solidification

Precipitate coarsening

Heat treatment to control the formation of Al_2Cu and obtain optimized properties (Hardness)

→ Why do we need to control the heat treatment?





⇒ Small coherent precipitates

[J. Lecomte-Beckers, Phys0904 "Physique des Matériaux"]

Precipitate coarsening

Driving force = Reducing the area of interface between the precipitates and the matrix

Assuming γ: energy of interface per unit area

For a precipitate with radius r,
the interfacial energy is: $4\pi r^2 \gamma$

Precipitate coarsening

Driving force = Reducing the area of interface between the precipitates and the matrix

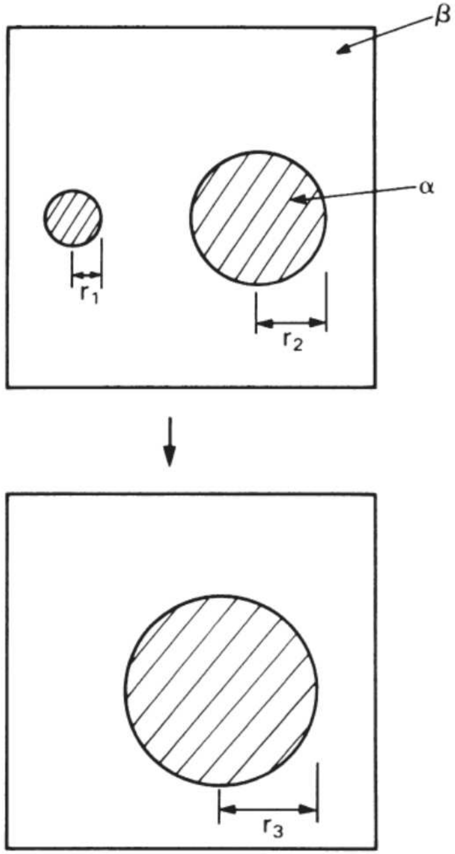
$$\Delta A = 4\pi r_3^2\gamma\ - 4\pi r_1^2\gamma\ - 4\pi r_2^2\gamma$$

Conservation of volume:

$$\frac{4}{3}\pi r_3^3 = \frac{4}{3}\pi r_1^3 + \frac{4}{3}\pi r_2^3$$

$$\Rightarrow$$

$$\Delta A = 4\pi\gamma[(r_1^3 + r_2^3)^{\frac{2}{3}} - (r_1^2 + r_2^2)]$$



[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Precipitate coarsening

$$\Delta A = 4\pi\gamma[(r_1^3 + r_2^3)^{\frac{2}{3}} - (r_1^2 + r_2^2)]$$

When $r_1 = r_2/2$

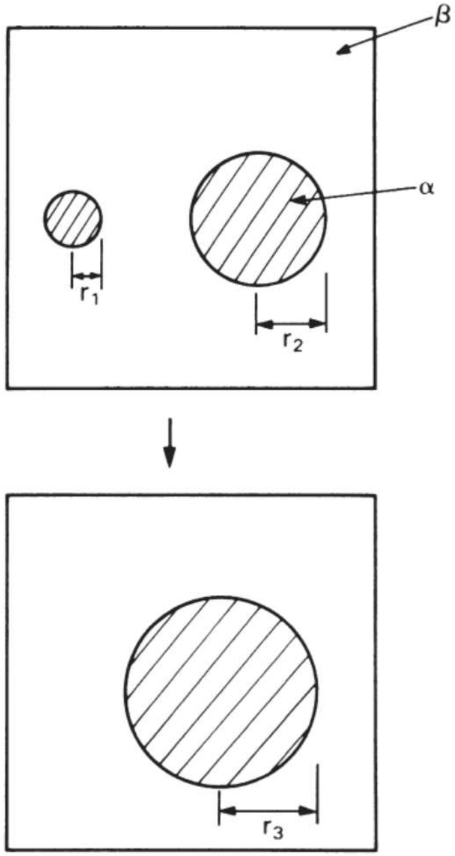
$$\Rightarrow \Delta A = -4\pi\gamma(-0{,}17 r_2^2)$$

For incoherent precipitates,

$\gamma = 0{,}5\ \mathrm{J\ m^{-2}}$

If $r_2 = 10^{-7}$ m

$\mathbf{W_f = 7\ J\ mol^{-1}}$



[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

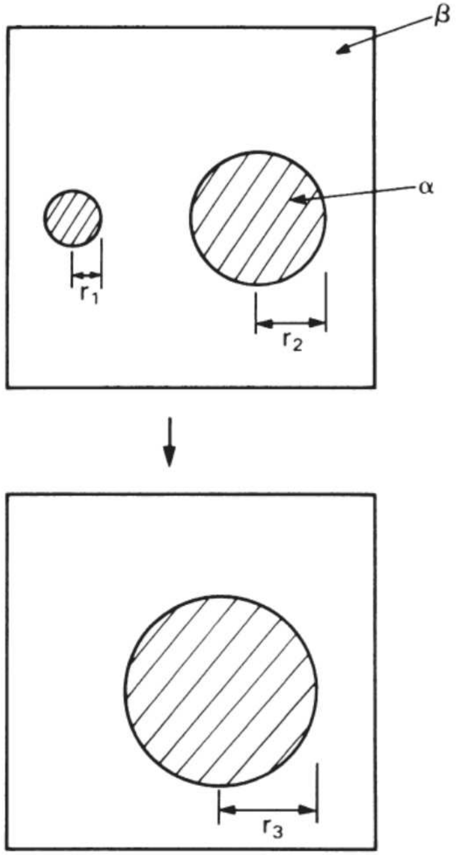
Precipitate coarsening

For incoherent precipitates,

$\gamma = 0{,}5$ J m^{-2}, and if $r_2 = 10^{-7}$ m

$W_f = 7$ J mol^{-1}

It is a challenge to avoid coarsening!



[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

One first possible way:

For coherent precipitates,

$\gamma = 0{,}05$ J m^{-2}

$W_f = 0{,}7$ J mol^{-1}

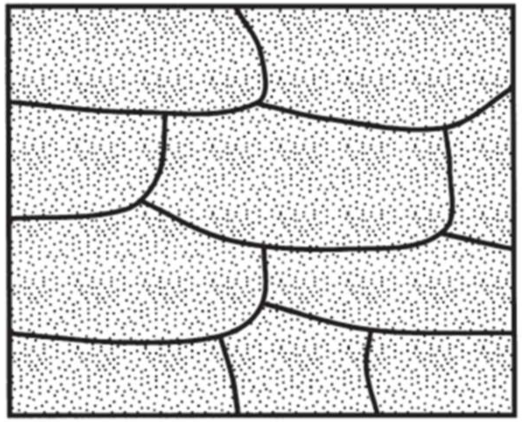
$\Rightarrow$ Select alloying elements for coherent precipitation

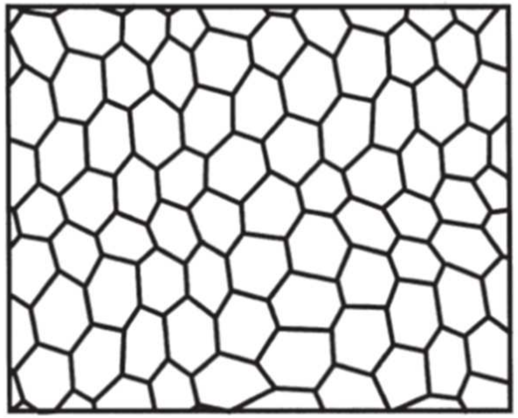
Other solid state changes

- Grain growth:
  Grain boundary energy per unit area
  $\gamma = 0{,}5 \text{ J m}^{-2}$

- Recrystallisation:
  Strain energy per unit volume ~15 J mol^{-1}

Deformed structure





Recrystallised new strain-free grains

Orders of magnitude

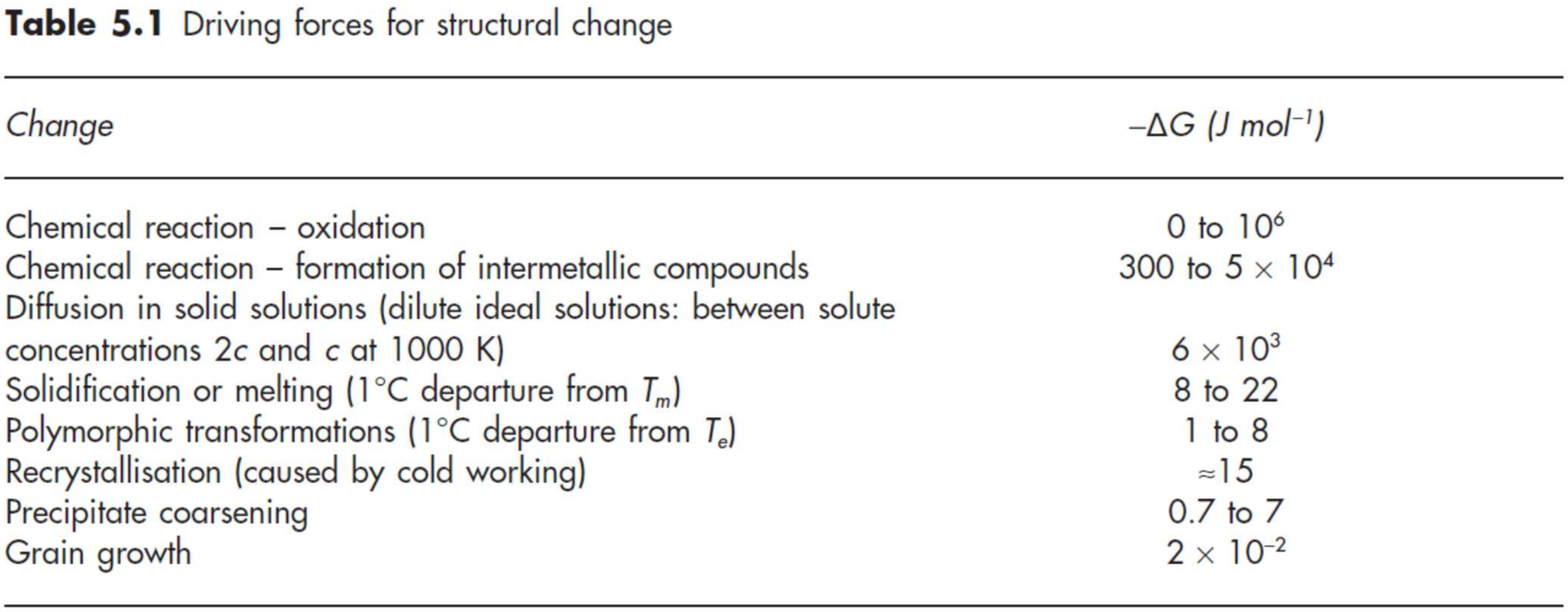


Table 5.1 Driving forces for structural change

Change	*$-\Delta G$ (J mol^{-1})*
Chemical reaction – oxidation	0 to 10^6
Chemical reaction – formation of intermetallic compounds	300 to 5×10^4
Diffusion in solid solutions (dilute ideal solutions: between solute concentrations 2*c* and *c* at 1000 K)	6×10^3
Solidification or melting (1°C departure from T_m)	8 to 22
Polymorphic transformations (1°C departure from T_e)	1 to 8
Recrystallisation (caused by cold working)	≈15
Precipitate coarsening	0.7 to 7
Grain growth	2×10^{-2}

Outline

- Introduction
- Driving force for structural change
- Kinetics I: diffusive transformation
- Kinetics II: nucleation
- Kinetics III: displacive transformation

Kinetics of structural change:

1 - diffusive transformations

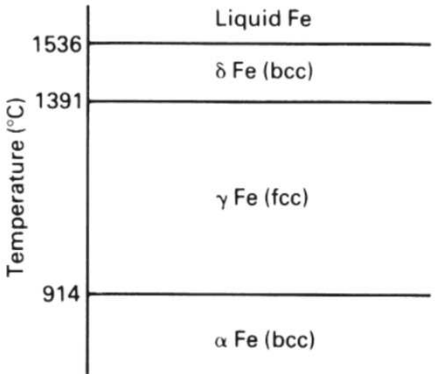
Speed of change?

- Structural change is possible when there is a driving force for change
- Even if there is a driving force, change may not occur at a measurable **pace/speed**

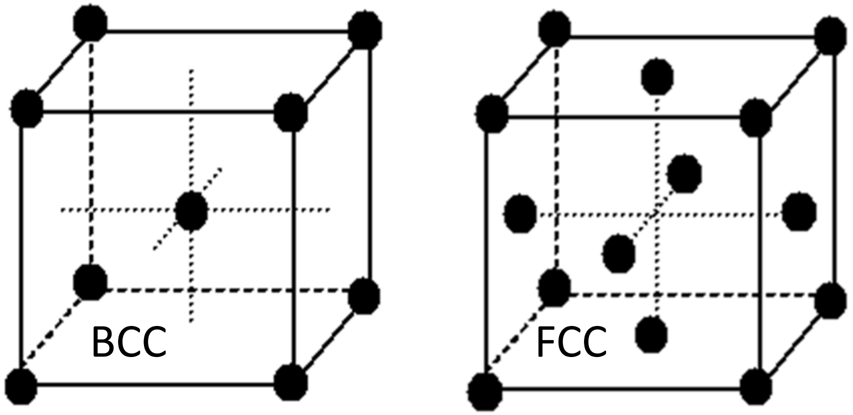
⇒ Route or **mechanism** for transformation?

⇒ **Kinetics!**

Atomic diffusion, rate = f(T)



[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]



[http://deuns.chez.com/sciences/cristallo/cristallo2.html]

Kinetics of solidification

Reminder: driving force for solidification

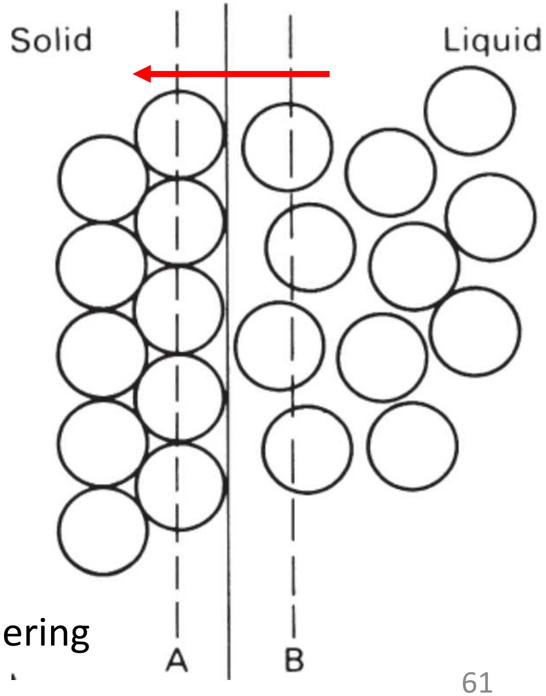
$$W_f = -\Delta G$$

$$\Delta G \cong \frac{\Delta H}{T_m}(T_m - T) \text{ for small } (T_m - T)$$

Speed ?

Kinetics of solidification:

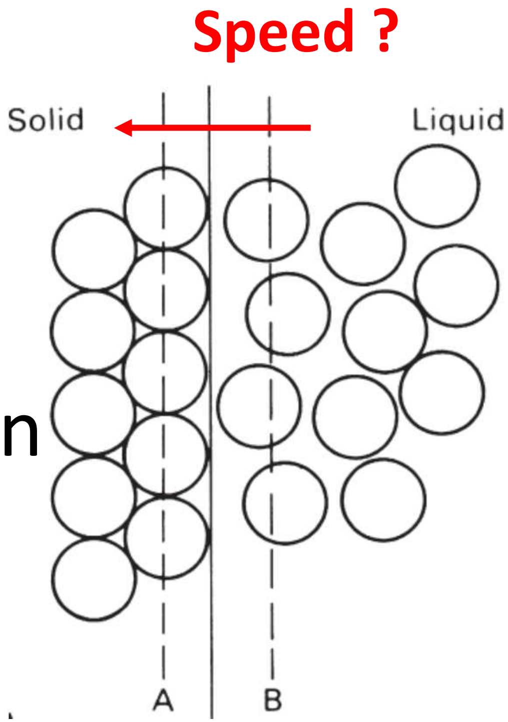
How fast do atoms diffuse due to that driving force?



[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Kinetics of solidification

Kinetics of solidification:
How fast do atoms diffuse ?



Atoms vibrate due to thermal agitation

A given atom has a probability *p* to possess an energy higher than $q=3kT_m$

$$p = e^{-q/kT_m}$$

[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Kinetics of solidification

Based on probabilisitic considerations, the solidification rate is given by:

$$v \approx \frac{d}{6h} e^{-q/_{kT}} \frac{\Delta H (T_m - T)}{T_m}$$

with

d: molecular/atomic diameter

h: Planck's constant

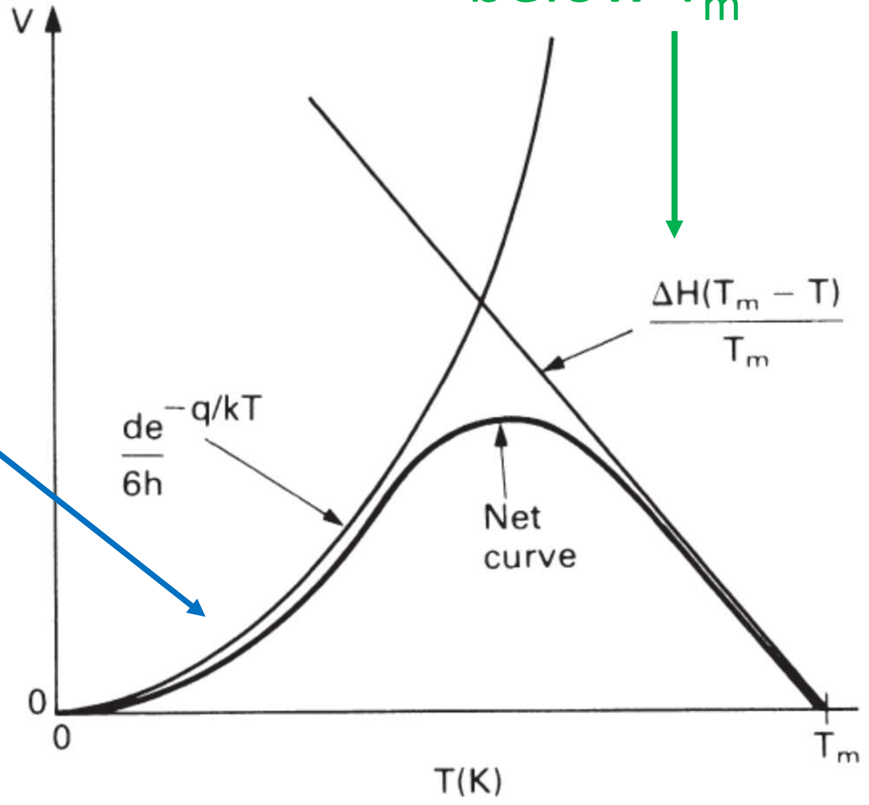
Kinetics of solidification

Solidification rate:

$$v \approx \frac{d}{6h} e^{-q/kT} \frac{\Delta H (T_m - T)}{T_m}$$

1st, solidification rate increases below T_m

2nd, solidification rate decreases when T decreases further



[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Kinetics of solid-state phase change

Driving force:

$$\Delta G \cong \frac{\Delta H}{T_e}(T_e - T)$$

Transformation rate:

$$v \approx \frac{d}{6h} e^{-q/_{kT}} \frac{\Delta H(T_e - T)}{T_e}$$

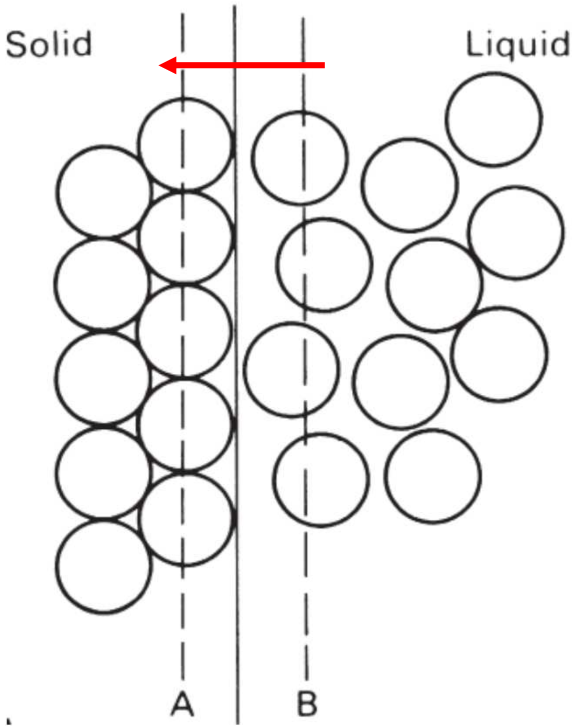
for a diffusive transformation

Kinetics of diffusive transformation

Movement of atoms between 2 phases

$\Rightarrow$ The **2 phases are already present**

$\Rightarrow$ There are **pre-existing nuclei** of the "new" phase



[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Outline

- Introduction
- Driving force for structural change
- Kinetics I: diffusive transformation
- Kinetics II: nucleation
- Kinetics III: displacive transformation

Kinetics of structural change:

2 - nucleation

Kinetics of diffusive transformation

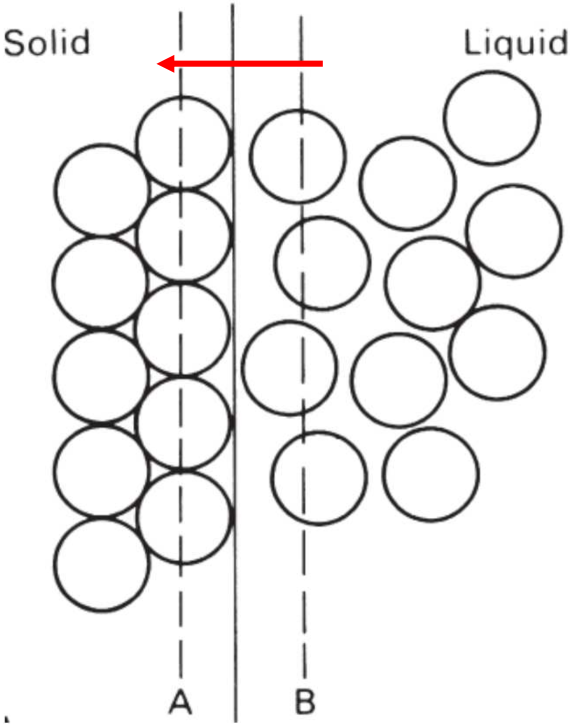
Movement of atoms between 2 phases

$\Rightarrow$ The **2 phases are already present**

$\Rightarrow$ Nuclei of the "new" phase

$\Rightarrow$ 2 possible mechanisms for nucleation:

1. Homogeneous
2. Heterogeneous



[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Homogeneous nucleation

In a liquid, thermal agitation may bring together a small group of atoms to form a tiny crystal

1. If $T>T_m$, this tiny crystal will disappear
2. If $T<T_m$, this tiny crystal may remain stable and grow

$\Rightarrow$ What is the probability of finding a stable nucleus at $T< T_m$?

Homogeneous nucleation

What is the probability of finding a stable nucleus at $T < T_m$?

- Driving force: $\Delta G \cong \frac{\Delta H}{T_m}(T_m - T)$, accounting for the volume of the nucleus with radius r:

$$\frac{4}{3}\pi r^3 \frac{\Delta H}{T_m}(T_m - T)$$

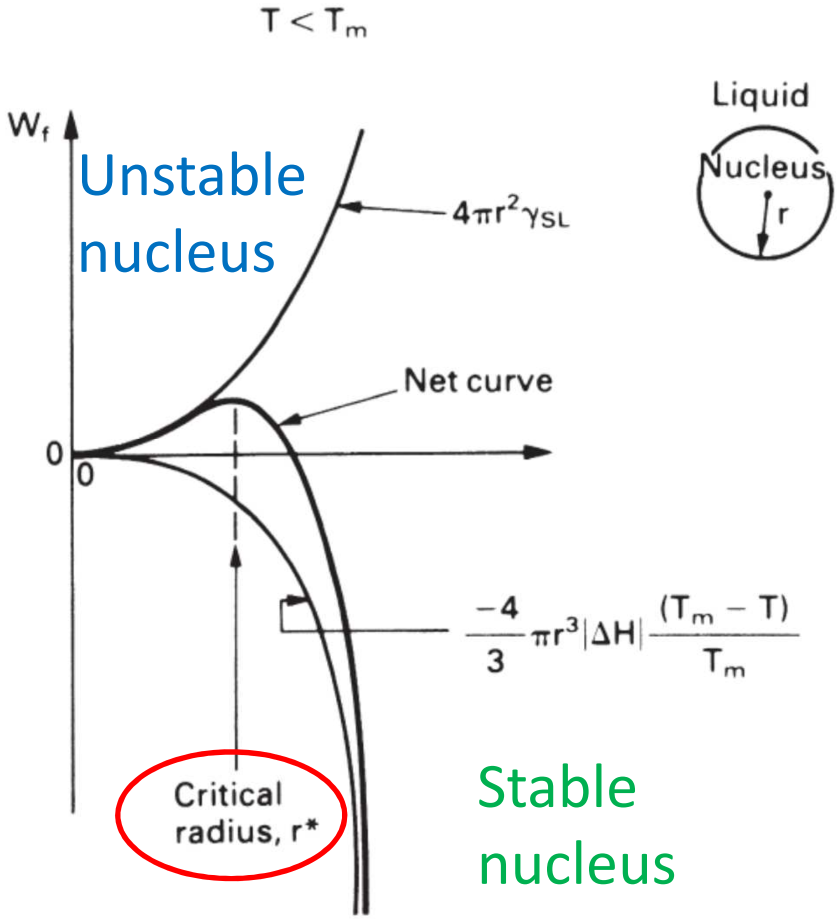
- Work to create the solid-liquid interface:

$$4\pi r^2 \boxed{\gamma_{sl}} \longrightarrow \text{Interfacial energy}$$

Homogeneous nucleation

Work of nucleation

$$\mathrm{W_f} = 4\pi r^2 \gamma_{sl} - \frac{4}{3}\pi r^3 \frac{\Delta H}{T_m}(T_m - T)$$



Unstable nucleus

Stable nucleus

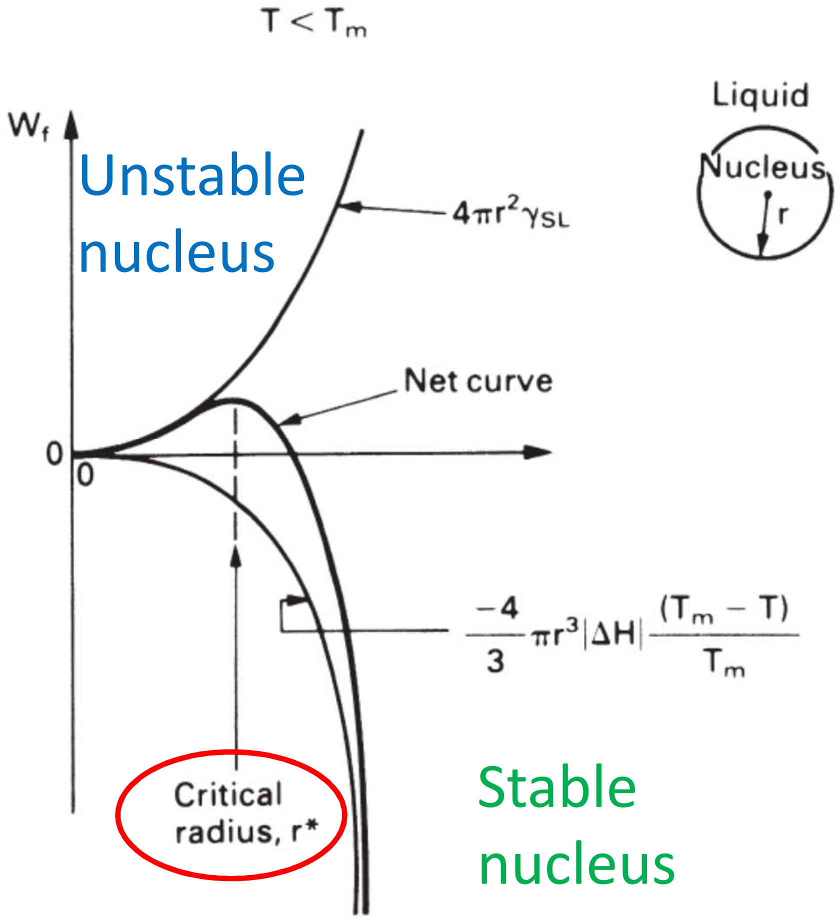
[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Homogeneous nucleation

Critical radius:

$$\frac{dW_f}{dr} = 0$$

$$r^* = \frac{2\gamma_{sl} T_m}{|\Delta H|(T_m - T)}$$



[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Homogeneous nucleation

Critical radius: $r^* = \frac{2\gamma_{sl}T_m}{|\Delta H|(T_m - T)}$

Formation of a nucleus that is big enough is not likely!

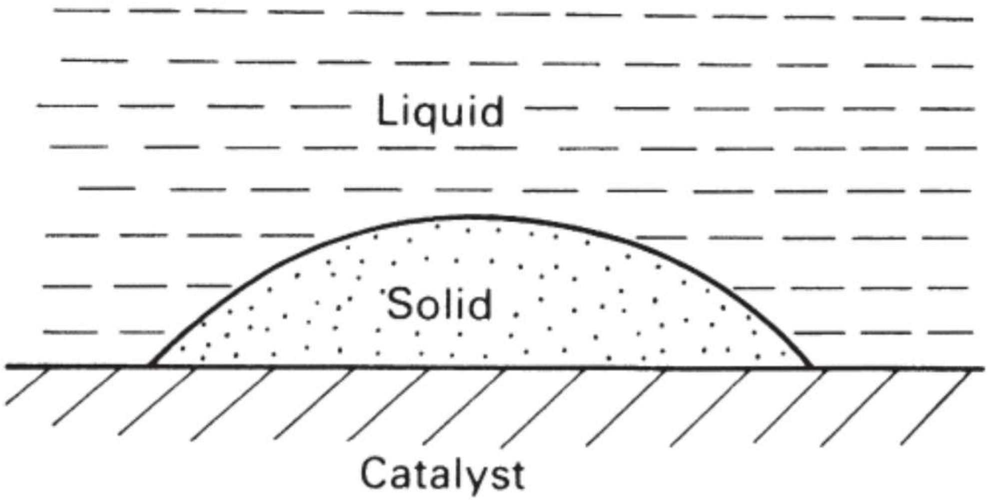
For homogeneous nucleation to happen,
$(T_m - T) \approx 100$ K i.e. huge undercooling!

$\Rightarrow$ Heterogeneous nucleation much more frequent!

Heterogeneous nucleation

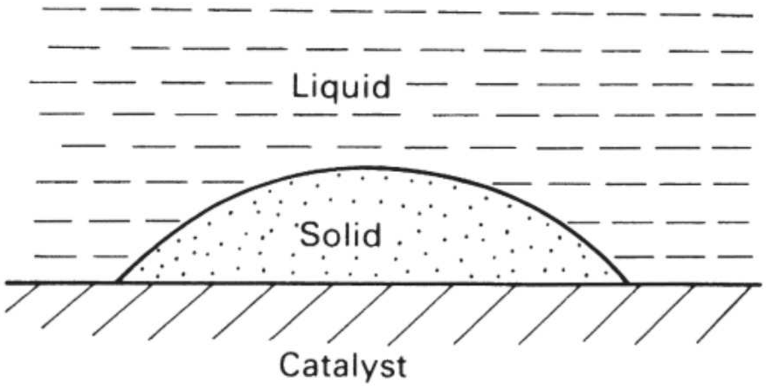
"Dirt" particles act as solid catalysts for nucleation

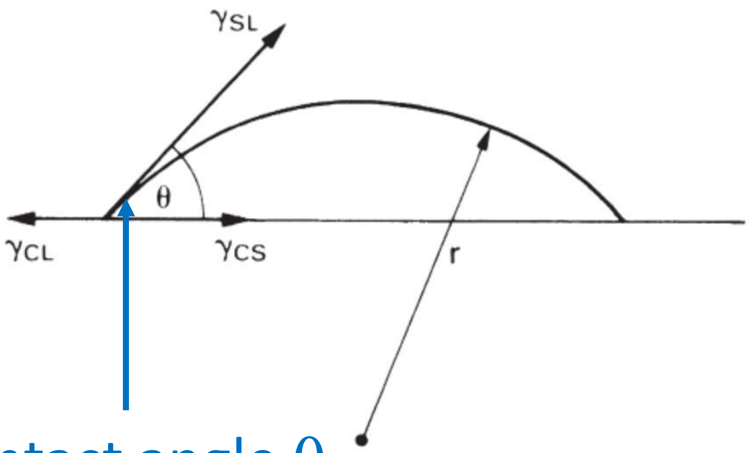
Pre-existing particle helps stabilise solid nuclei



[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Heterogeneous nucleation





Critical radius

$$r^* = \frac{2\gamma_{sl}T_m}{|\Delta H|(T_m - T)}$$

is the same as for homogeneous nucleation

But the volume of the critical nucleus is ≠!

Nucleus = spherical cap

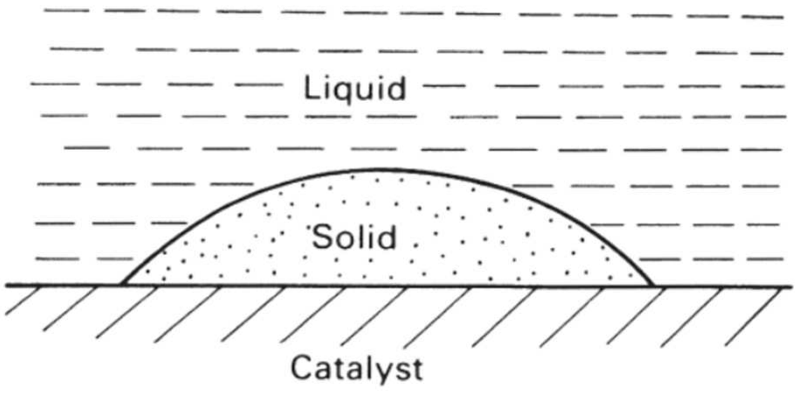
[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

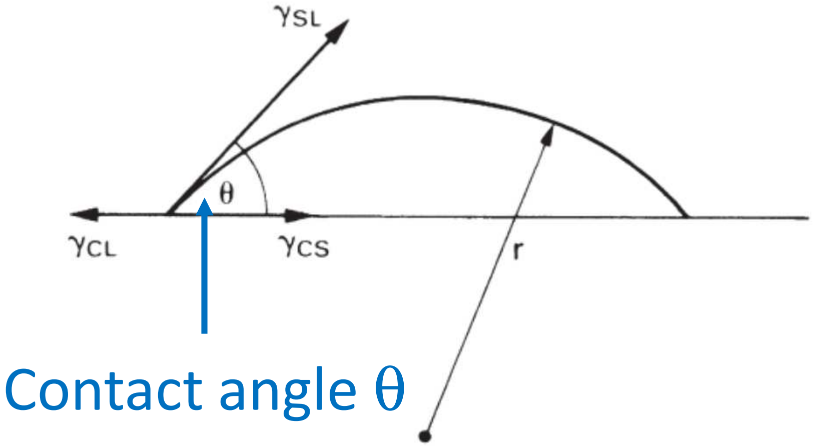
Heterogeneous nucleation

Volume of critical nucleus:

$$V^*_{het} \;=\; \frac{2}{3}\pi(r^*_{het})^3\left\{1-\frac{3}{2}\cos\theta+\frac{1}{2}cos^3\theta\right\}$$

While $V^*_{hom} = \frac{4}{3}\pi(r^*_{hom})^3$





Contact angle θ

[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Heterogeneous nucleation

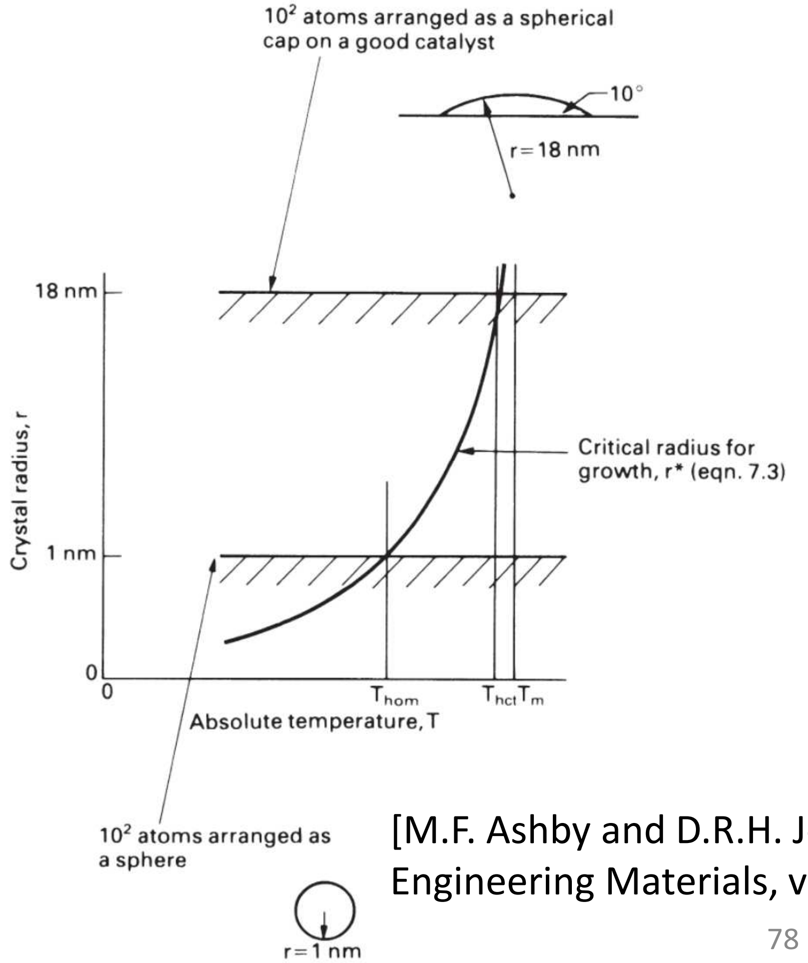
Take a nucleus formed by 10^2 atoms and $\theta = 10°$

V^*_{het} and V^*_{hom}

$\Rightarrow r^*_{het}$ and r^*_{hom}?

$$r^*_{het} = 18{,}1 r^*_{hom}$$

$\Rightarrow$ Heterogeneous nuclei are always bigger!



[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Heterogeneous nucleation

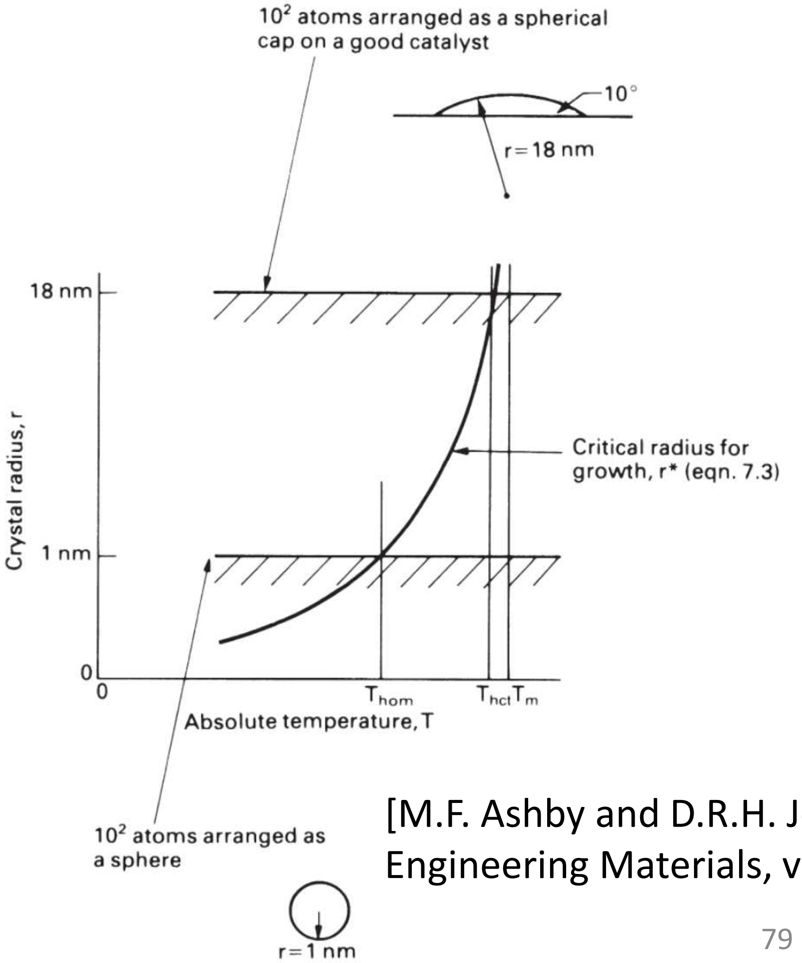
Take a nucleus formed by 10^2 atoms and $\theta = 10°$

$$r^*_{het} = 18{,}1 r^*_{hom}$$

$\Rightarrow$ Undercooling:

$$T_m - T_{het} = \frac{T_m - T_{hom}}{18{,}1}$$

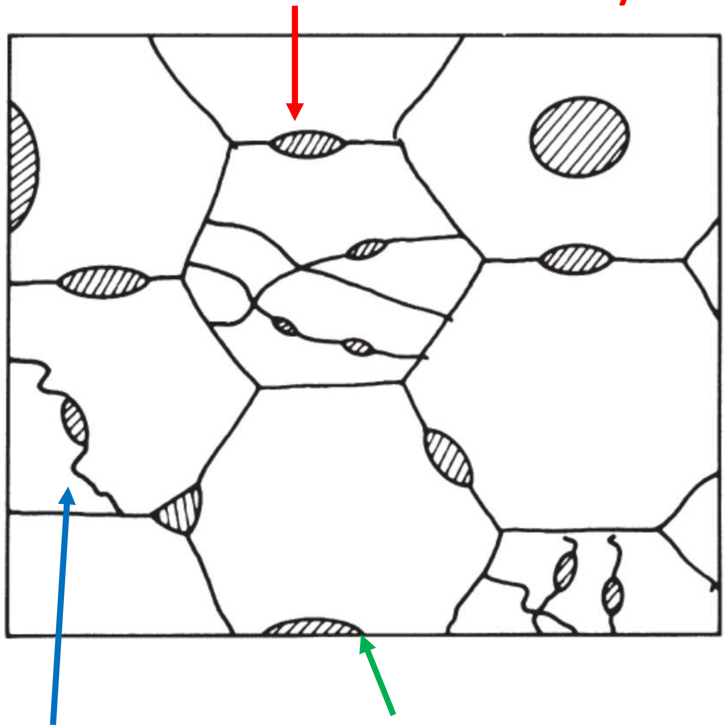
$$\approx 5K$$



[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Nucleation in solids

- Heterogeneous nucleation on crystalline defects

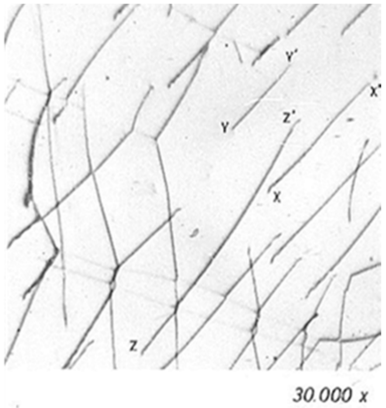


Grain boudary

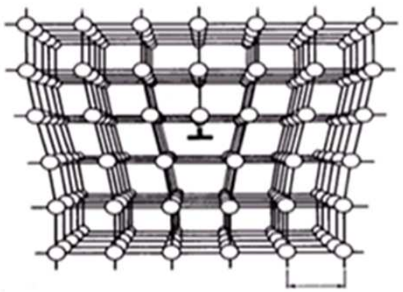
Dislocations

Free surface

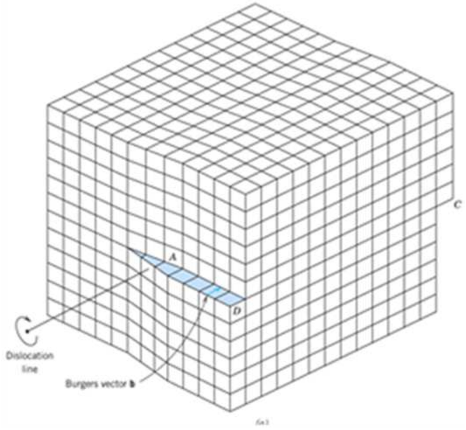
[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]



Dislocations (TEM)



Edge dislocation



Screw dislocation

[J. Lecomte-Beckers, Phys0904 "Physique des Matériaux"]

Outline

- Introduction
- Driving force for structural change
- Kinetics I: diffusive transformation
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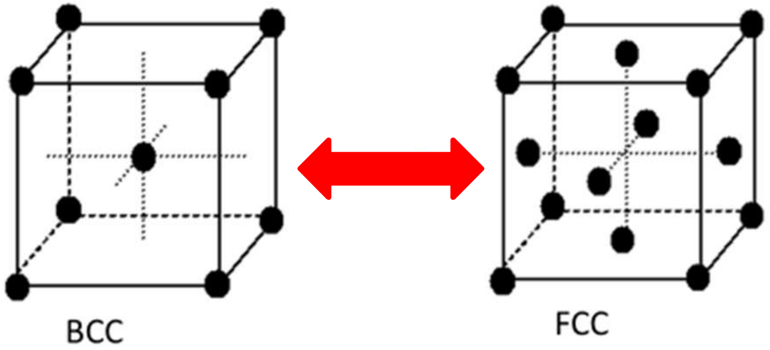
- Kinetics III: displacive transformation

Kinetics of structural change:

3 - displacive transformations

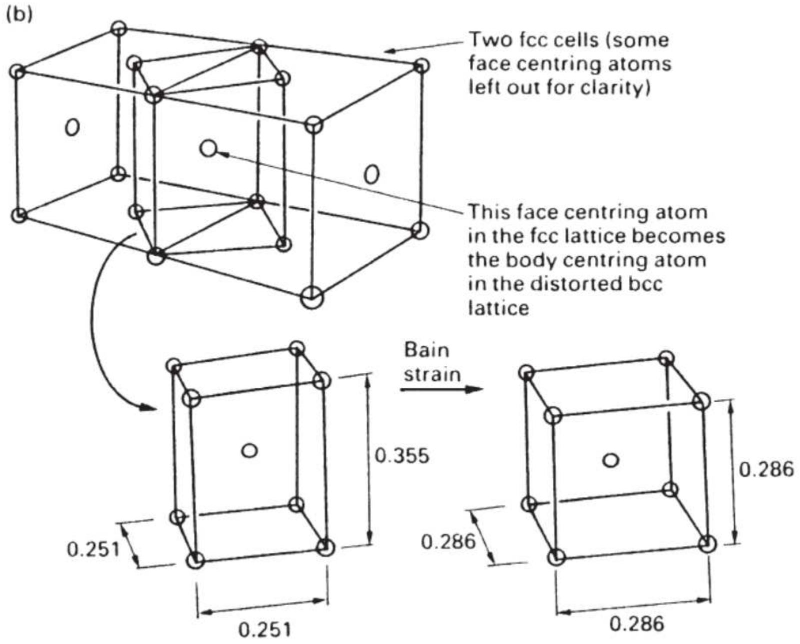
Reminder "Physics of Materials"

Phase transformations in steel may occur by **≠ mechanisms**



[http://deuns.chez.com/sciences/cristallo/cristallo2.html]

Diffusion



[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Coordinated shuffling of atoms ← **Displacement**

Transformations in C steels

[M.F. Ashby and D.R.H. Jones,
Engineering Materials, vol. 2]

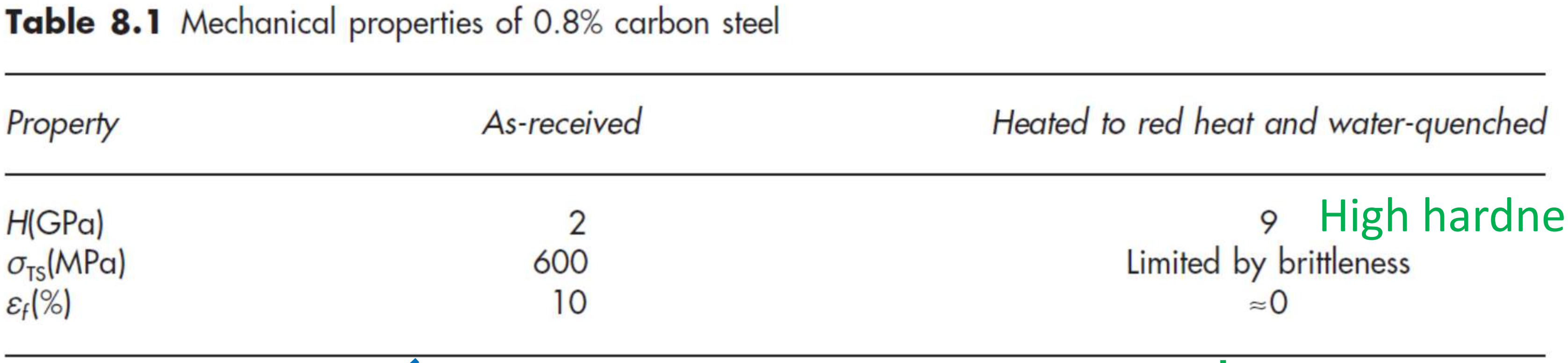
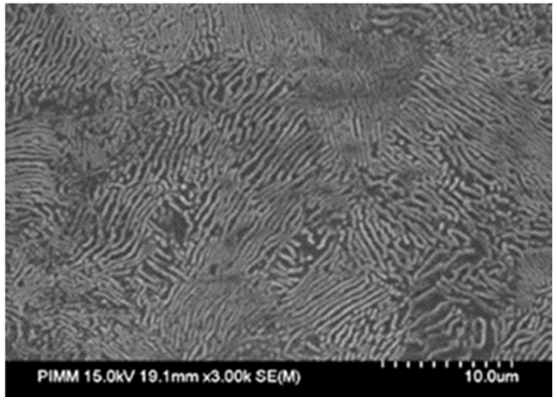


Table 8.1 Mechanical properties of 0.8% carbon steel

Property	*As-received*	*Heated to red heat and water-quenched*
H(GPa)	2	9
σ_{TS}(MPa)	600	Limited by brittleness
ε_f(%)	10	≈ 0

High hardness

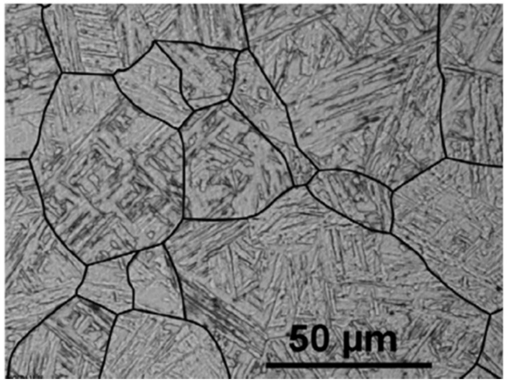
Diffusion
⇒ Pearlite



[Baczmanski et al., MSF, 2014]

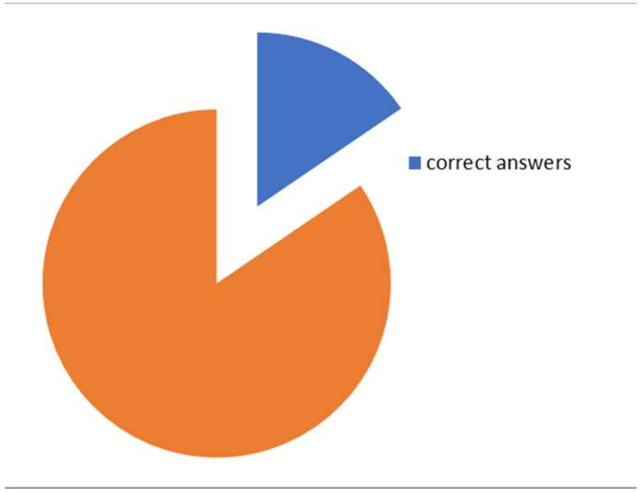
Same chemical composition,
but different structures
⇒ **Different mechanical properties**

Displacement
⇒ **Martensite**



[Christien et al., Mater. Char., 2013]

Martensite



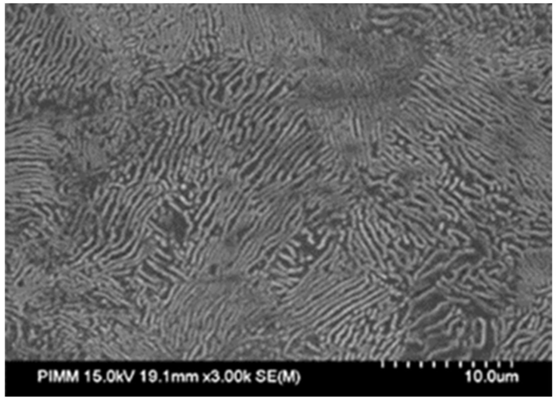
- *What is martensite in steel?*

$\Rightarrow$ ***18% of correct answers in last week test!***

- Martensite = metastable phase that forms after **fast cooling** (quench) of C steel
- It forms by a **displacive** mechanism.
- It is very **hard** and **brittle**.

Transformations in C steels

Diffusion $\Rightarrow$ Pearlite

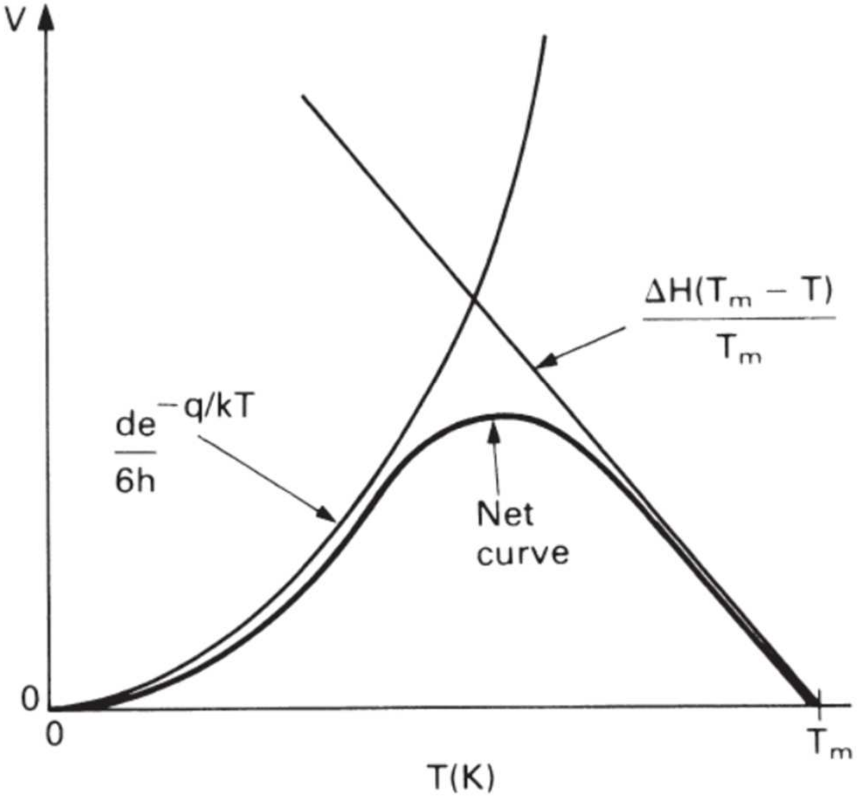


[Baczmanski et al., MSF, 2014]

Diffusion is thermally activated!
Interface velocity varies with T

What is the overall rate of transformation (transformed volume per second)?

Interface velocity



[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Transformation in C steels

Diffusive transformation: Overall rate of transformation

- We know the interface velocity
- We need to know the area of interface
  - area of interface = f(number of nuclei)
  - Fewer nuclei means smaller interfacial area and a smaller transformaiton rate

$\Rightarrow$ Overall rate $\propto$ number of nuclei * interface velocity

Transformation in C steels

Overall rate ∝ number of nuclei * interface velocity

↓

(varies with T)

Does it vary with T?

For heterogeneous nucleation on grain boundaries:

$r^* = \frac{2\gamma_{\alpha\beta}T_e}{|\Delta H|(T_e - T)}$: critical radius ↓ when T ↓

However, when T ↓, thermal energy and agitation ↓ , and so does the probability of forming a nucleus

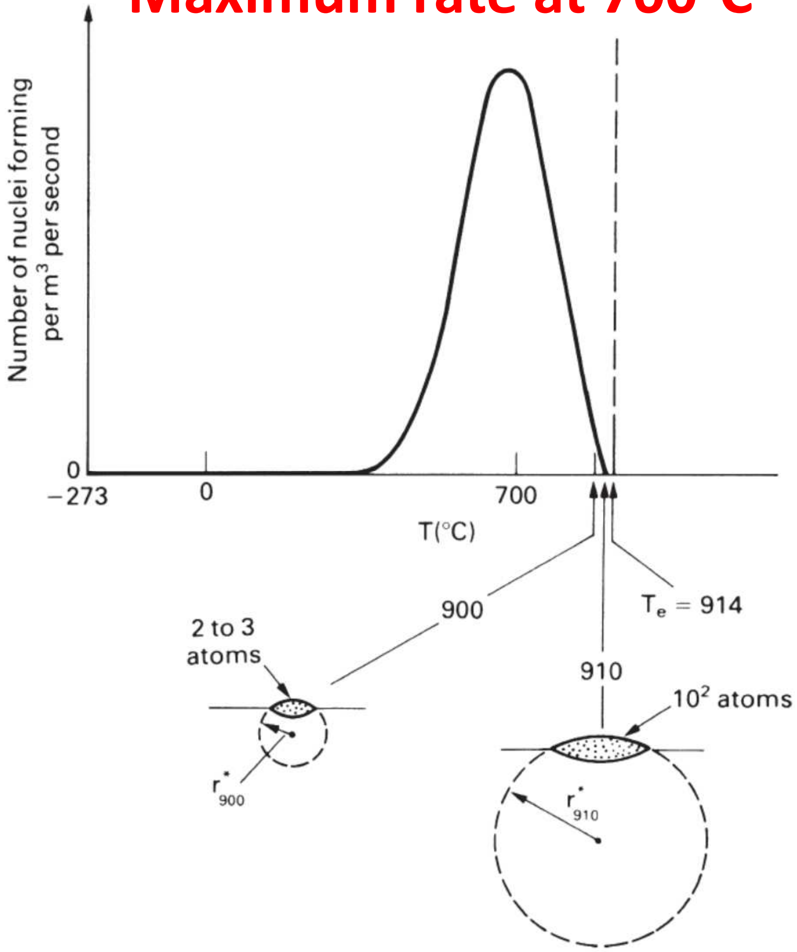
Transformation in C steels

Number of nuclei

- Critical radius ↓ when T ↓
- Thermal energy and agitation ↓

⇒ Probability of forming a nucleus ↓

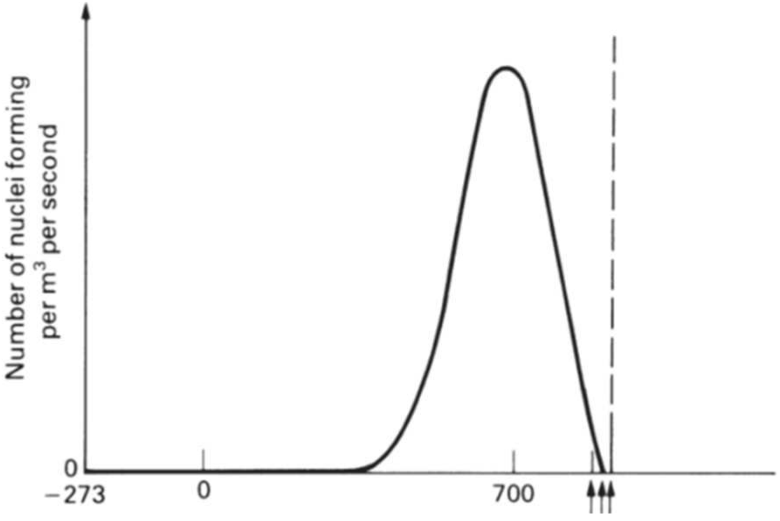
Maximum rate at 700°C

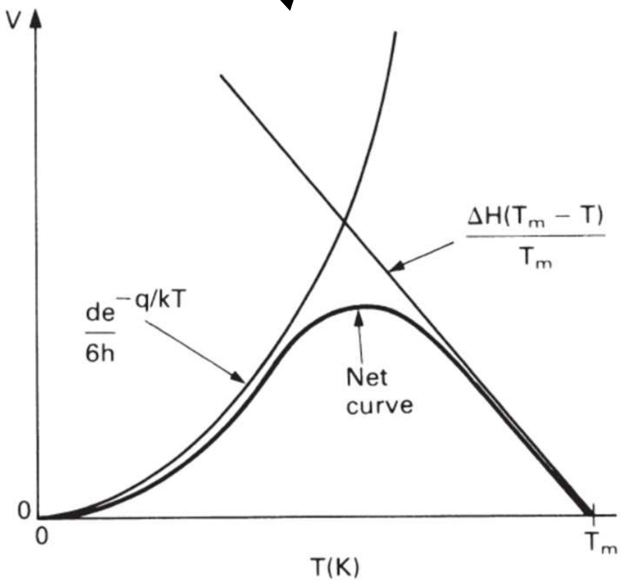


[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Transformation in C steels

Overall rate ∝ number of nuclei * interface velocity

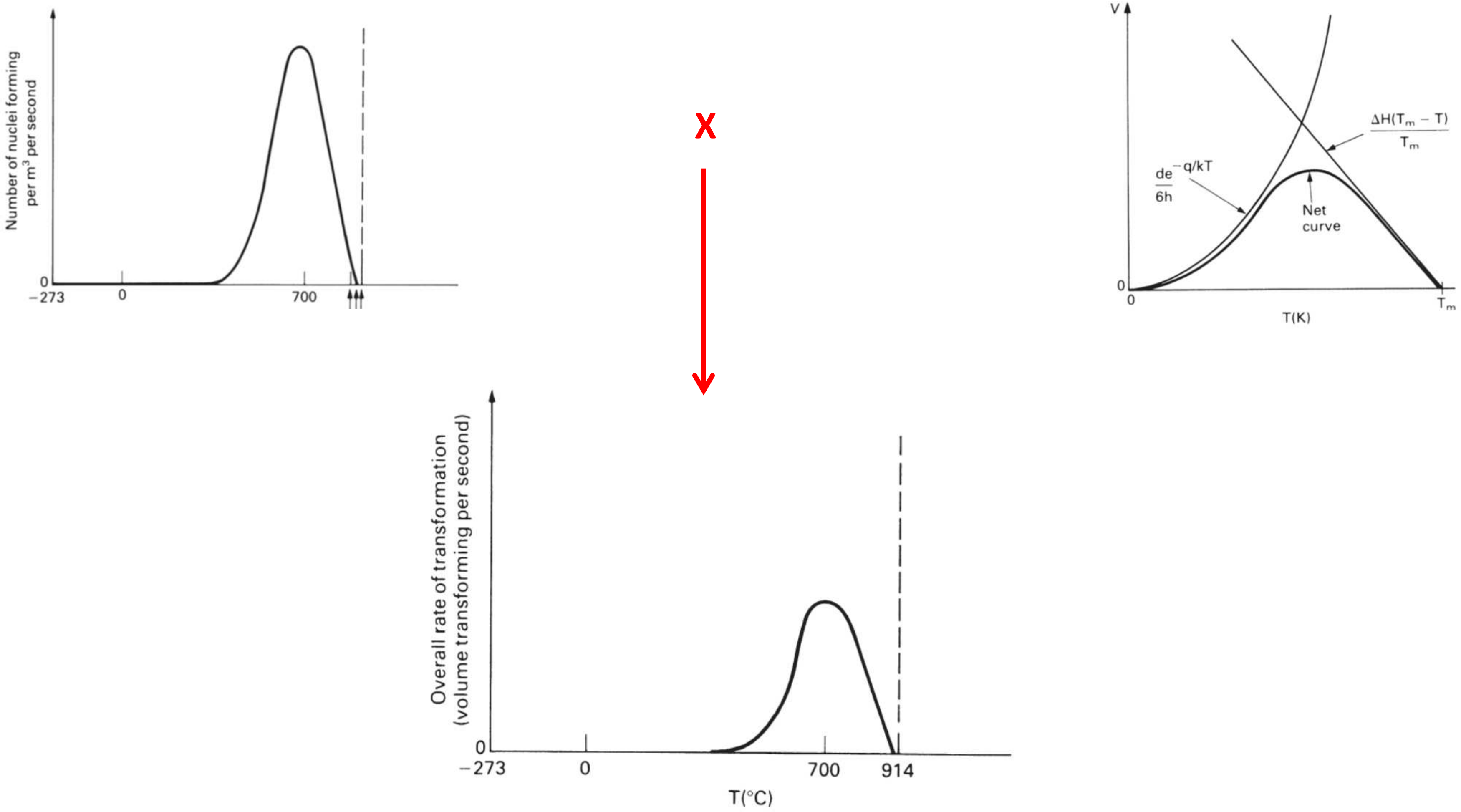




[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Transformation in C steels

Overall rate $\propto$ number of nuclei * interface velocity

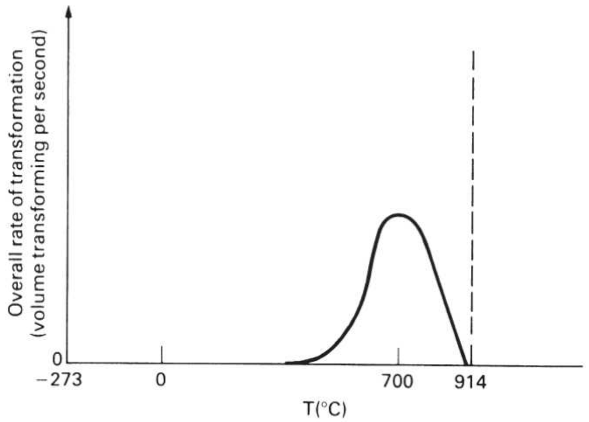


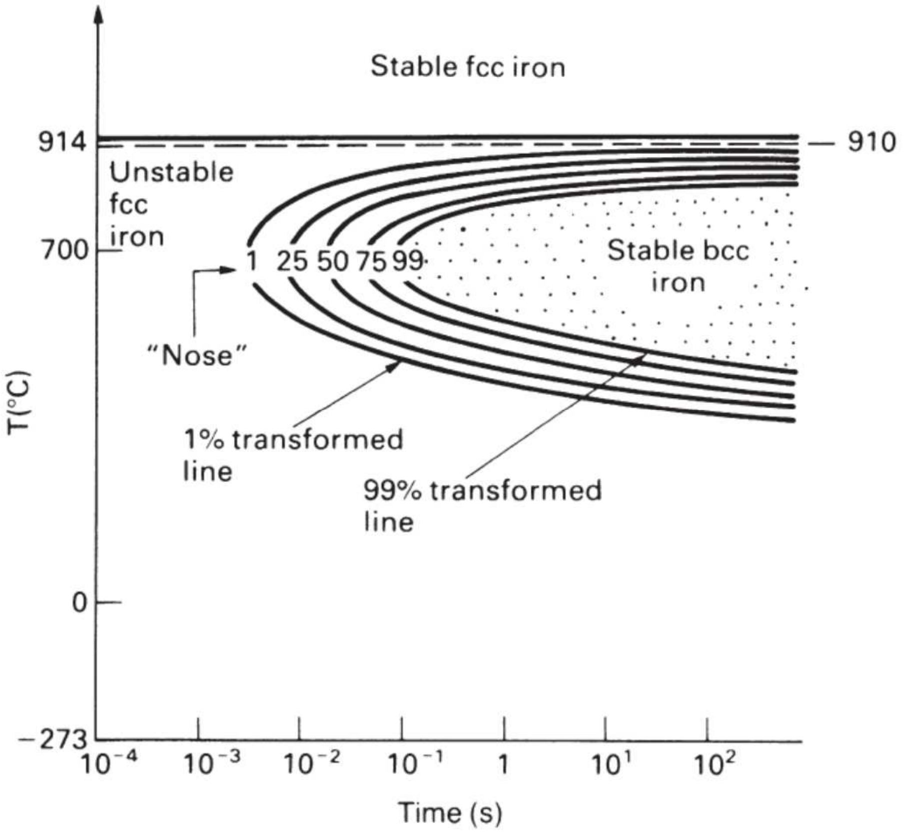
[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Transformation in C steels

Overall rate ∝ number of nuclei * interface velocity

TTT Diagram





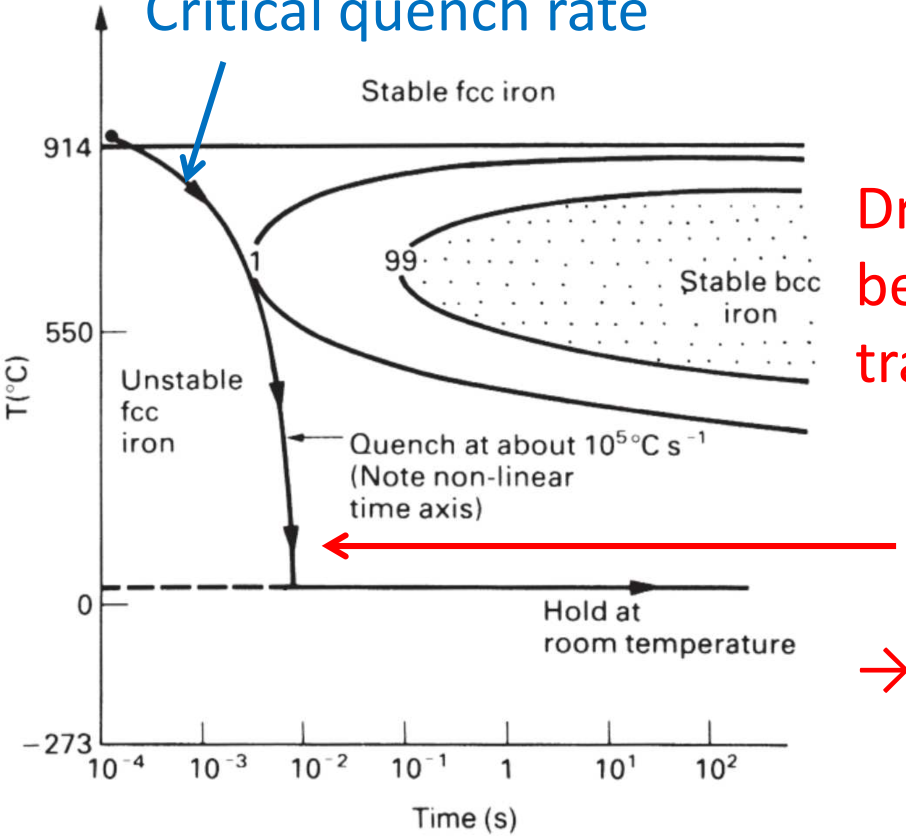
Practically, overall kinetics for diffusive transformations are described by "C-curves".

(See course "Physics of Materials")

[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Transformation in C steels

For a displacive transformation to occur, diffusive transformation should not take place!



Critical quench rate

Driving force for transformation becomes so high that the transformation occurs

- without diffusion
- by coordinated shuffling of atoms at speed ~ sound

→ Athermal transformation

(See course "Physics of Materials")

[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Transformation in C steels

Displacive vs diffusive transformations

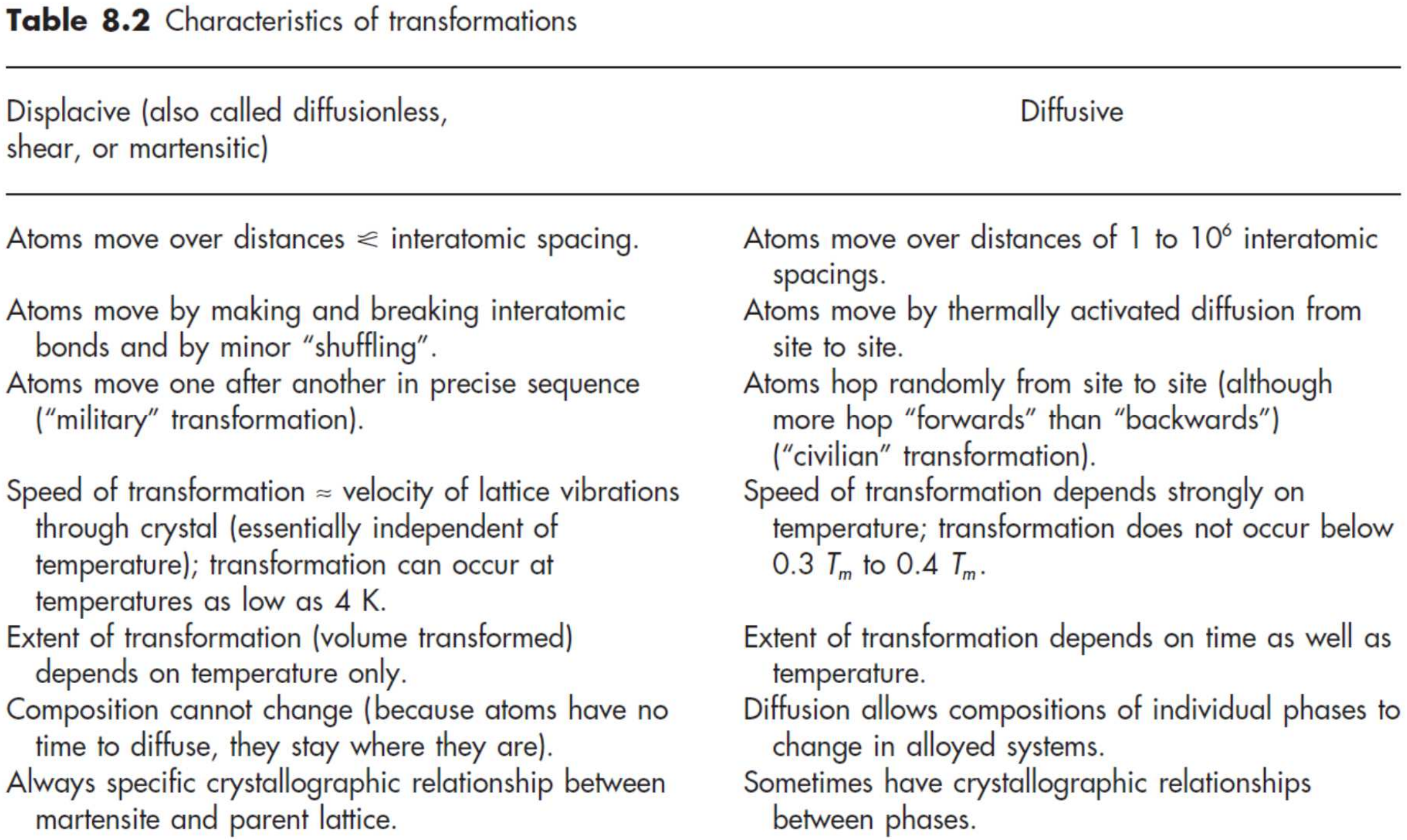
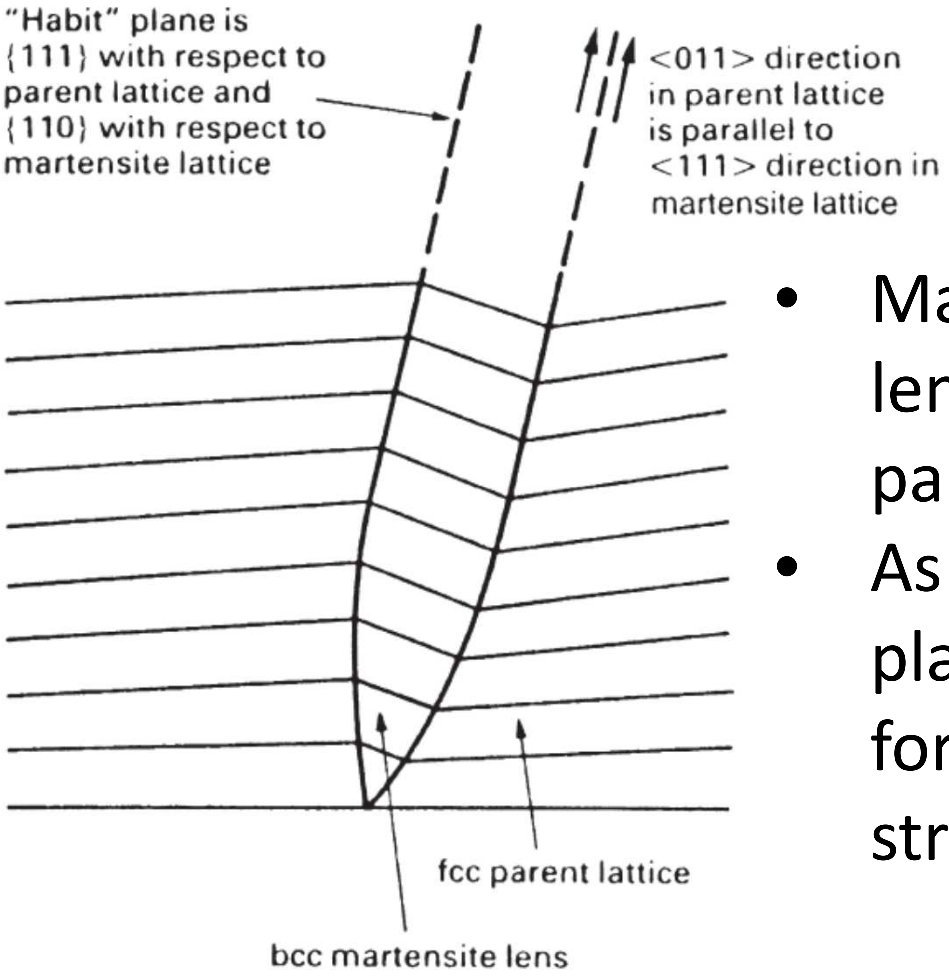


Table 8.2 Characteristics of transformations

Displacive (also called diffusionless, shear, or martensitic)	Diffusive
Atoms move over distances $\lessapprox$ interatomic spacing.	Atoms move over distances of 1 to 10^6 interatomic spacings.
Atoms move by making and breaking interatomic bonds and by minor "shuffling".	Atoms move by thermally activated diffusion from site to site.
Atoms move one after another in precise sequence ("military" transformation).	Atoms hop randomly from site to site (although more hop "forwards" than "backwards") ("civilian" transformation).
Speed of transformation ≈ velocity of lattice vibrations through crystal (essentially independent of temperature); transformation can occur at temperatures as low as 4 K.	Speed of transformation depends strongly on temperature; transformation does not occur below 0.3 T_m to 0.4 T_m.
Extent of transformation (volume transformed) depends on temperature only.	Extent of transformation depends on time as well as temperature.
Composition cannot change (because atoms have no time to diffuse, they stay where they are).	Diffusion allows compositions of individual phases to change in alloyed systems.
Always specific crystallographic relationship between martensite and parent lattice.	Sometimes have crystallographic relationships between phases.

[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Martensitic transformation in C steels

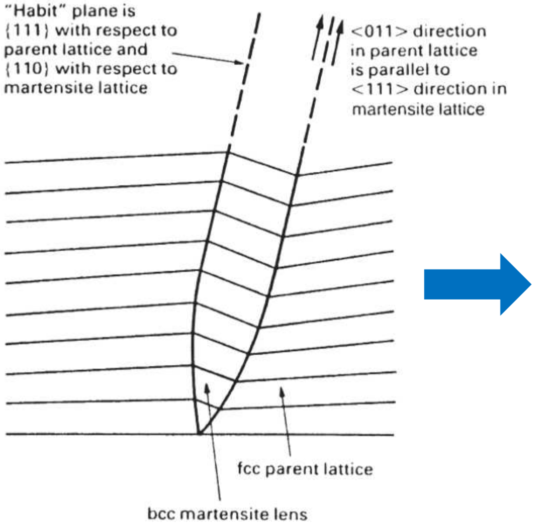


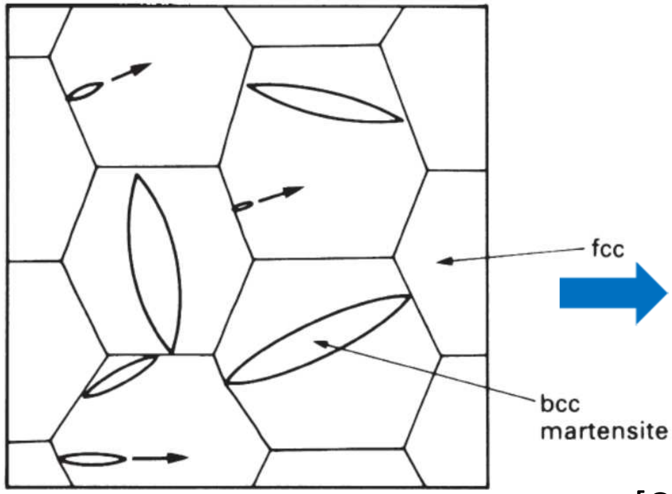
- Martensite forms as lenses coherent with the parent FCC lattice
- As the lenses grow, lattice planes distort: driving force is consumed as strain energy

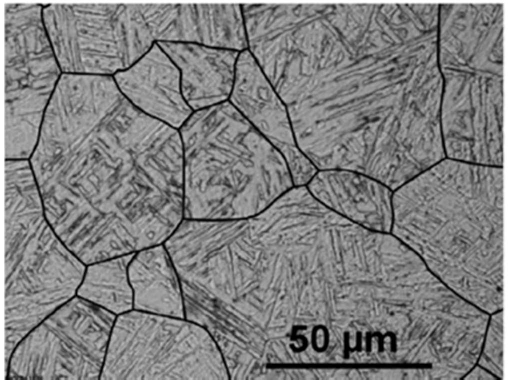
[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Martensitic transformation in C steels

Typical morphology in laths or needles







[Christien et al., Mater. Char., 2013]

[M.F. Ashby and D.R.H. Jones, Engineering Materials, vol. 2]

Summary

Materials selection: desired properties

⇒ Materials properties may be

- structure independent (E, c_p...)
- structure dependent (σ_y, fatigue resistance...)

⇒ Controlling/changing the structure

- Is change possible? → Driving force
- Is change measurable? → Kinetics → Mechanisms
  - Diffusion
  - Displacement
  - Nucleation

Assume the pre-existence then growth of nuclei of the new phase