EPMA Powder Metallurgy Summer School

27 June – 1 July 2016 - Valencia, Spain

Introduction to Materials Science

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Some of the figures used in this presentation were taken from
R.E. Reed-Hill, Physical Metallurgy Principles
2° edition, PWS-KENT Publishing Company, Boston

Why Materials Science ?

The PM process transforms a raw material into a final product thorugh a sequence of operations based on various chemical and structural transformations of the processed metal.

The suxcess of the process depends on the ability to properly manage these transformations, which are studied and explained by Materials Science (and Physical Chemistry).

Materials Science studies the **relationships between the structure/microstructure of a material and its properties**, which influence its behavior when subject to thermal loading, mechanical loading, electrical and magnetic fields, etc.

Physical Chemistry investigates the reactions between a material and any environment in contact with, both in solid and liquid state

Thermodynamics and kinetics

Thermodynamics
Defines the driving force of a transformation and, in general, of all phenomena occurring in materials. The reference is the equilibrium state, defined by a minimum of the Gibbs free-energy **G**. The driving force is the excess of Gibbs free-energy with respect to the equlibrium one, since all the materials tend spontaneously towards the equilibrium.

Kinetics
Defines the rate of a transformation and, in general, of all phenomena occurring in materials. It depends on several parameters but mostly on temperature.

Thermodynamics says if a given transformation may occur or not; kinetics says how fast transformation will occur

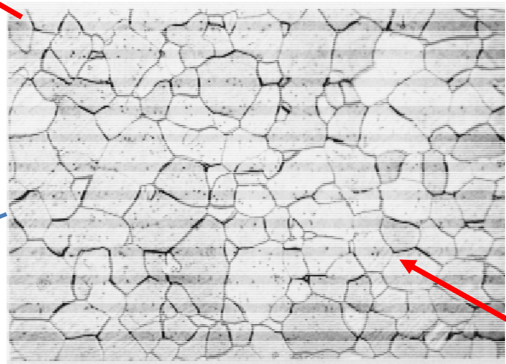
Transformations in PM

The conventional PM process		Transformations occurring in the processed metal
Powder production		
- in solid state	---->	Reaction with the atmosphere
- from a liquid phase	---->	Melting and solidification
Shaping		
- compaction	---->	Elastic and plastic deformation
Sintering		
- free sintering	---->	Structural transformations activated by temperature
	---->	Reaction with the atmosphere
Secondary operations		
- sizing	---->	Plastic deformation
- re-compaction	---->	Plastic deformation
- heat treatments	---->	Structural transformations activated by temperature
- others		
Alternative processes		
Pressure assisted sintering	---->	Deformation at high temperature / Structural transformations activated by temperature
Additive manufacturing	---->	Melting and solidification / Structural transfromations activated by temperaure

The structure of metals

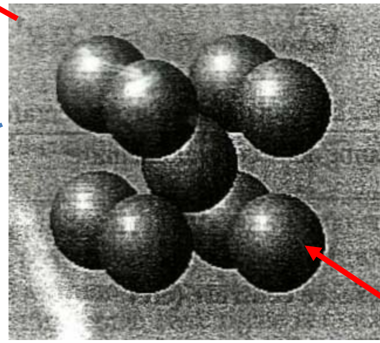
Iron parts for magnetic applications

Micrometric range
Optical microscope; SEM/microanalysis

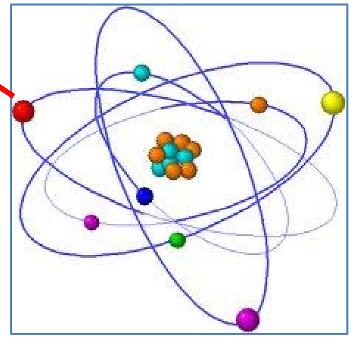


The **microstructure**: the policrystalline aggregate. Grains (crystals) and grain boundary

Nanometric range
X-Ray Diffraction



The **structure**: the unit cell
Atoms are organized according to a defined geometrical order



The **structure of atom**
Nucleus and electrons

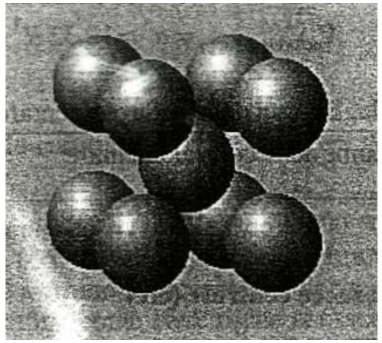
The formation of the structure of metals

The liquid metal

Solidification with:

- geometrical disorder → amorphous metal
- geometrical order → crystalline metal

The structure

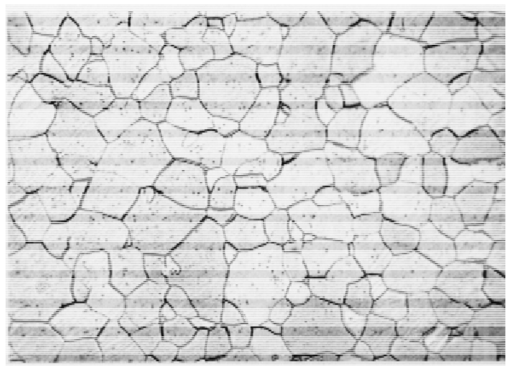


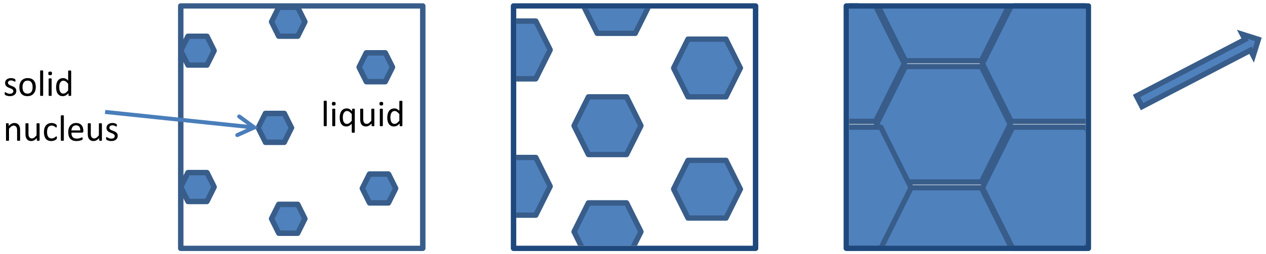
Solidification of a crystalline metal

Nucleation and growth of:

- one single crystal → single crystal
- a population of crystals → policrystalline aggregate

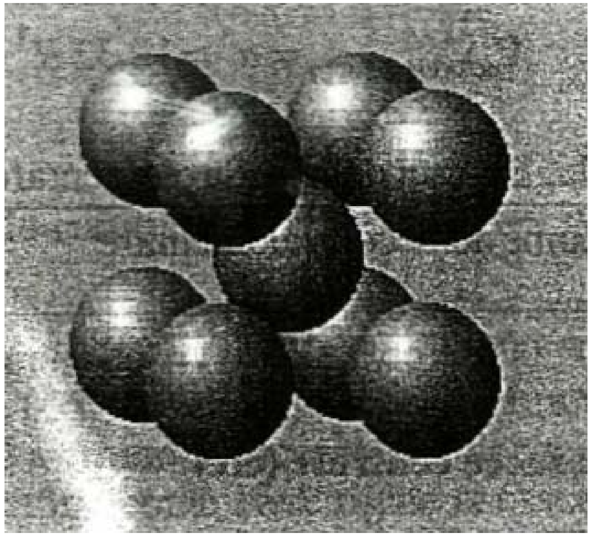
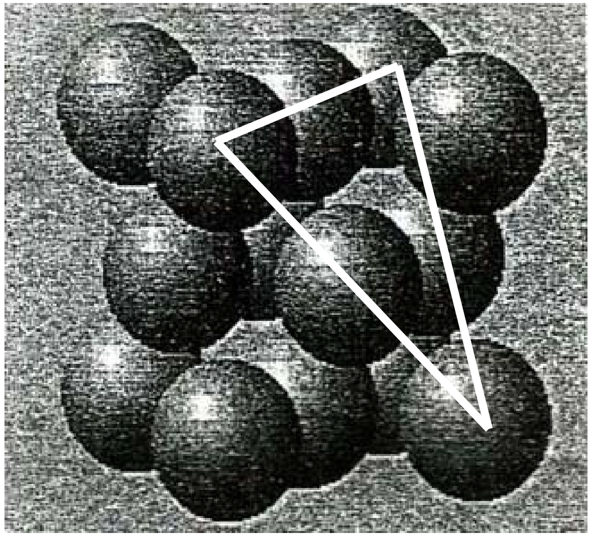
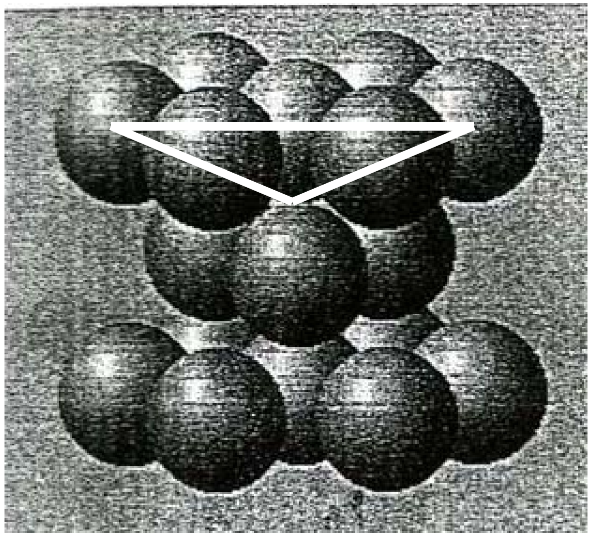
The microstructure





The same mechanism occurs during solid state transformations, included recrystallization

The structure of metals: the unit cell of crystalline metals

The body-centered cubic structure **bcc**	The face-centered cubic structure **fcc**	The hexagonal closed packed structure **hcp**
		
Examples: iron	copper-aluminum	titanium

The fcc and hcp metals are tendencially more ductile than the bcc ones

The crystal structure of metals: defects

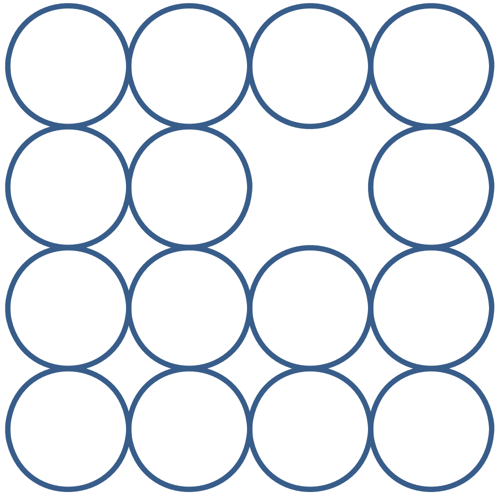
Any imperfection in the regular packing of atoms

Vacancies
Interstitial atoms
Substitutional atoms

Dislocations

Stacking faults
Twins / twin boundaries

Grain boundary



The crystal structure of metals: defects

Any imperfection in the regular packing of atoms

Vacancies

Interstitial atoms (carbon and nitrogen in iron)

Substitutional atoms

Dislocations

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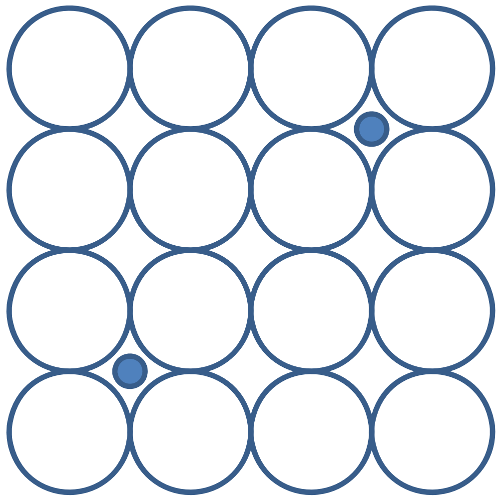
Grain boundary



The crystal structure of metals: defects

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Substitutional atoms (Cr, Ni, Mo,… in iron)

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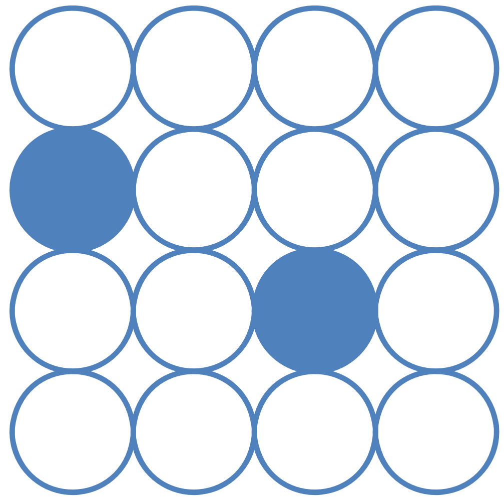

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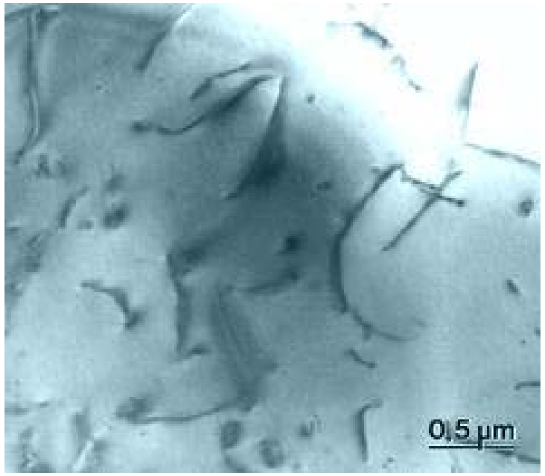

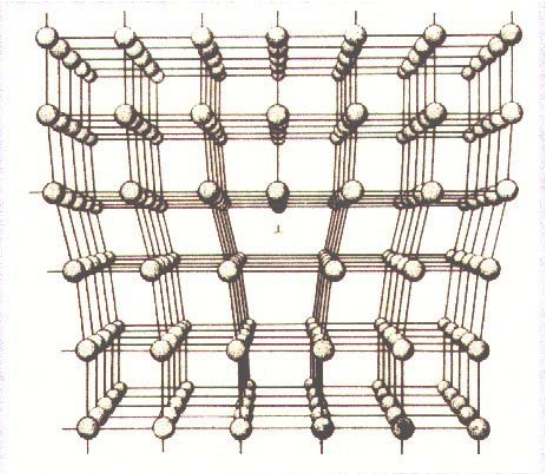

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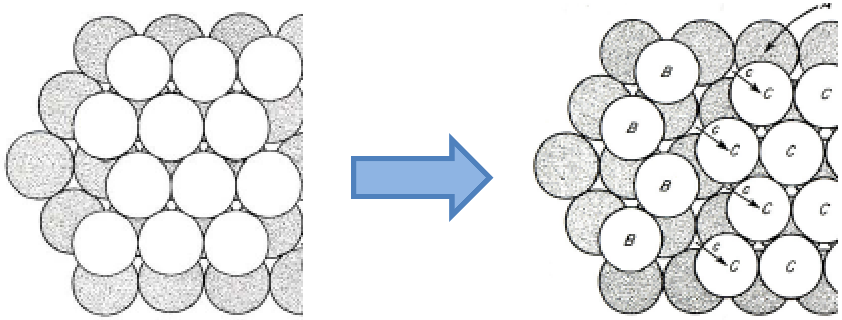

Dislocations

Stacking faults
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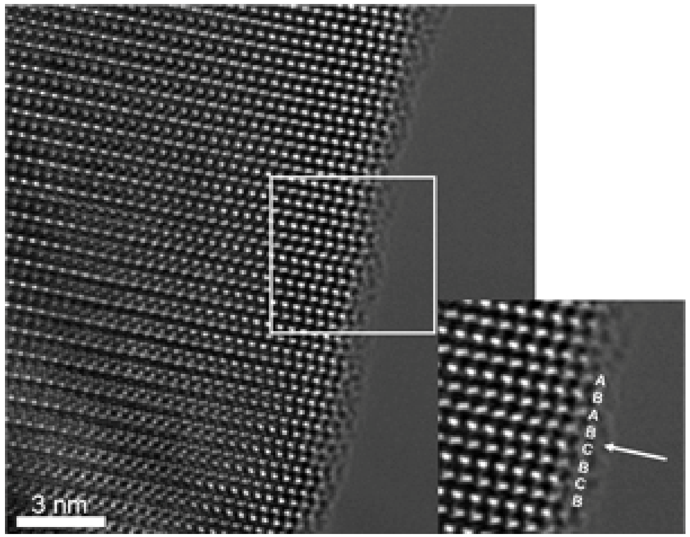

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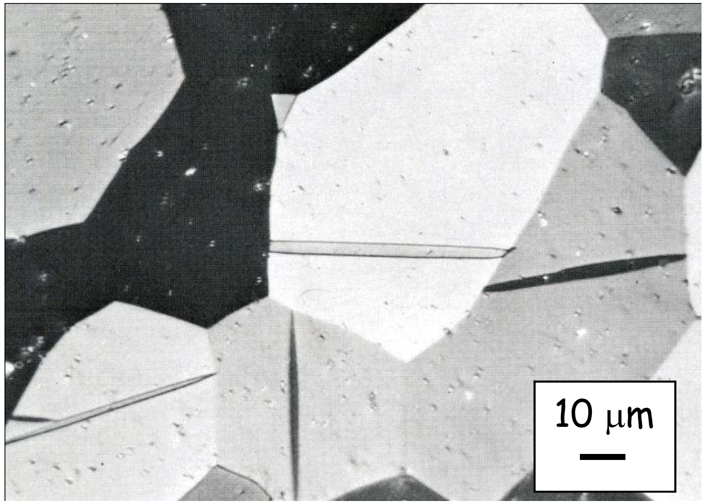

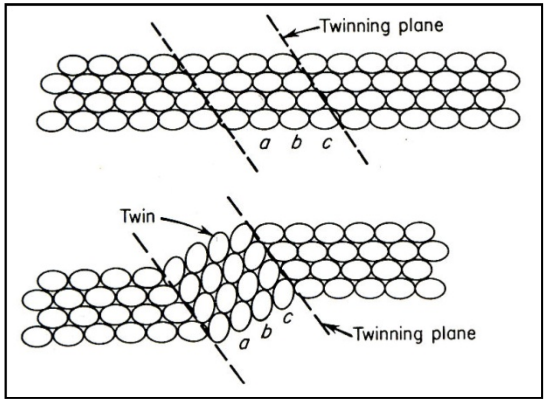

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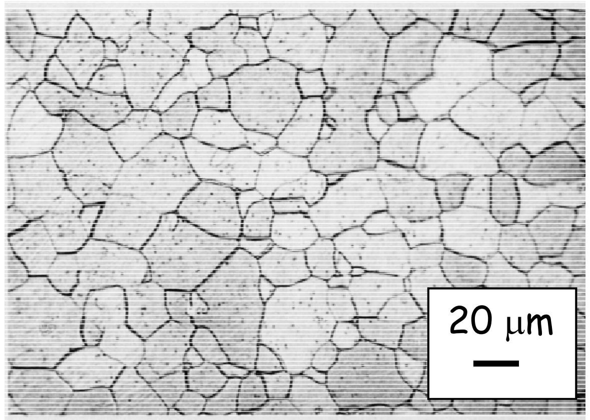

Vacancies
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Dislocations

Stacking faults
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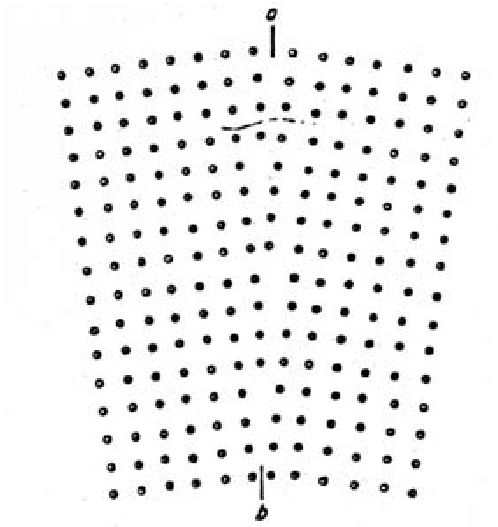

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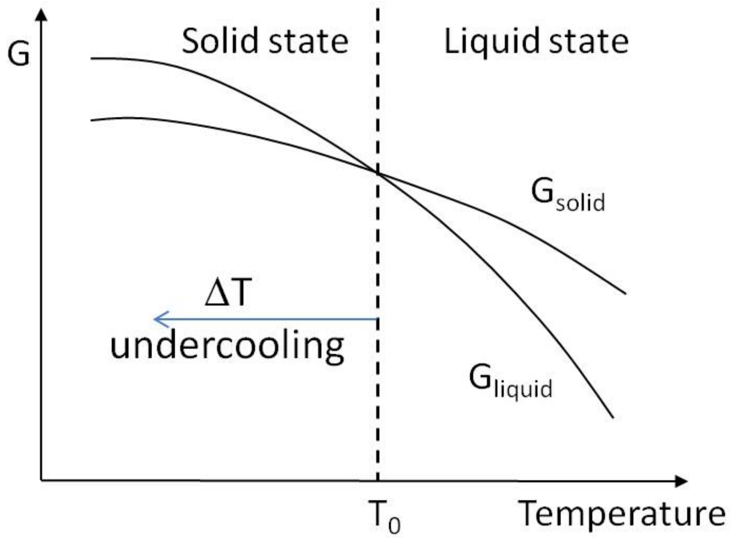
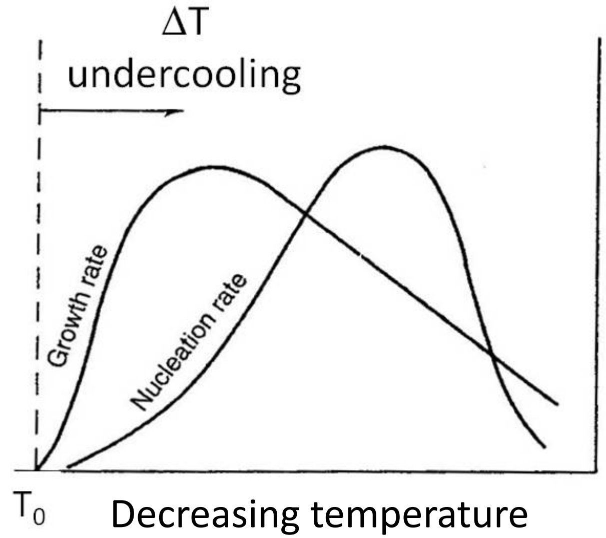
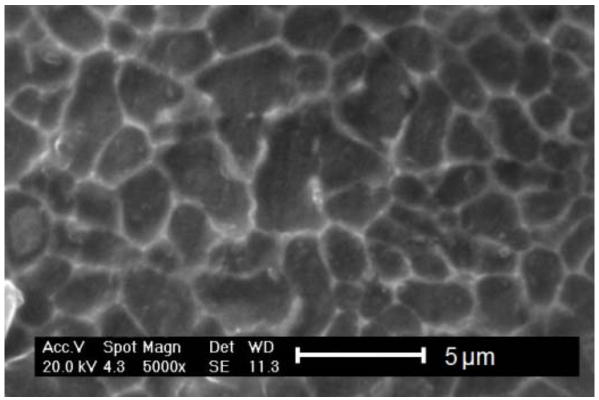
Solidification: the liquid-solid transformation





Nucleation and growth of a population of crystals. At temperature below T_0

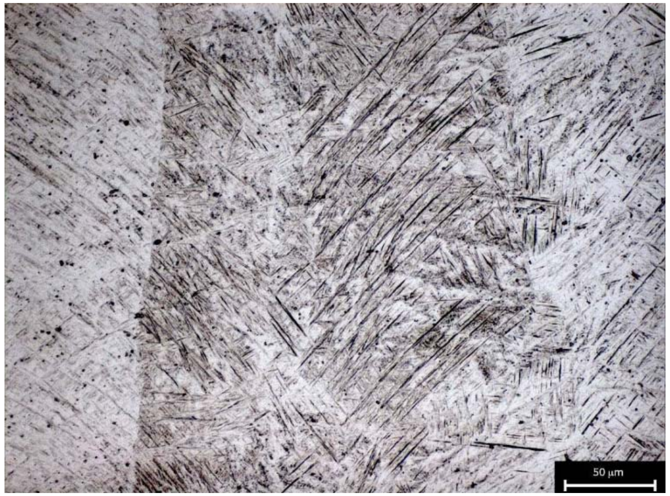
The higher the undercooling, the higher the nucleation rate, the smaller the size of the solid crystals



Metallic powders produced by atomization of a liquid have a very fine microstructure

Solidification: the liquid-solid transformation

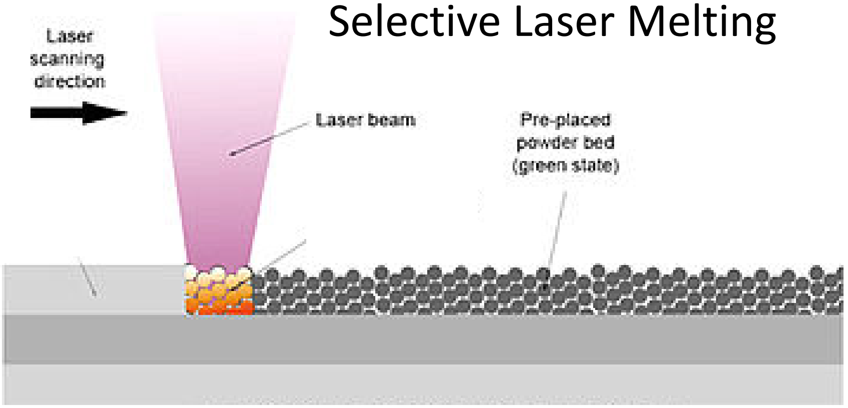
In additive manufacturing processes, as Selective Laser Melting, undercooling is very high and the microstructure results very fine …….

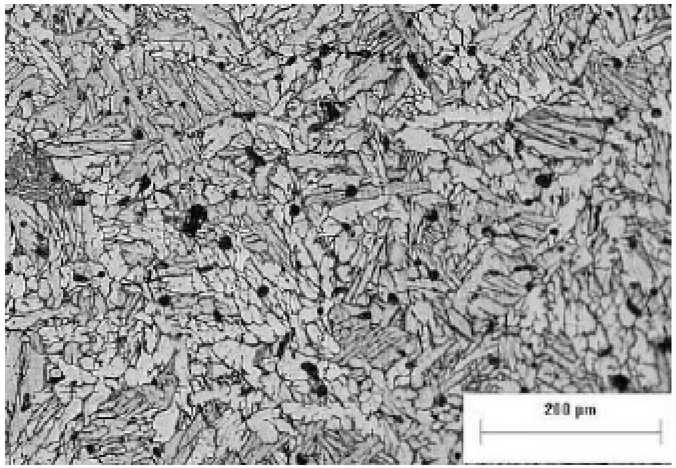


As-built microstructure of Ti6Al4V alloy, very brittle and unacceptable

…… much finer than after conventional sintering

Selective Laser Melting





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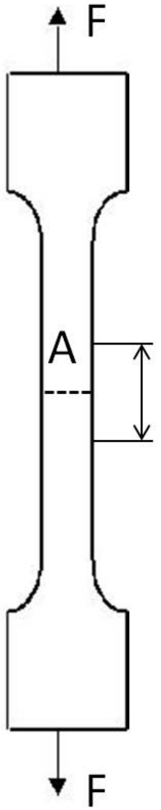
Elastic and plastic deformation of metals

The tensile test



F = force (N)

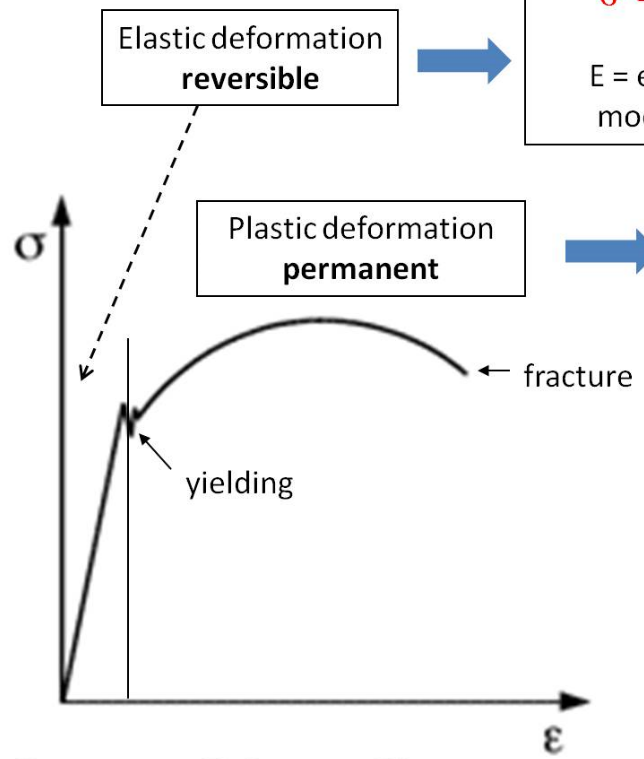
A = cross section (mm^2)

l_0 = length of a segment (mm)

σ = F/A = stress (MPa)

$\varepsilon = (l-l_o)/l_0 = \Delta l/l_0$ = strain (%)

The tensile stress-strain curve



$\sigma = E\,\varepsilon$

E = elastic modulus

$\varepsilon_t = \ln(\varepsilon+1)$

$\sigma_t = \sigma\,(\varepsilon+1)$

$\sigma_t = k\,\varepsilon_t^{\,n}$

σ_t = true stress

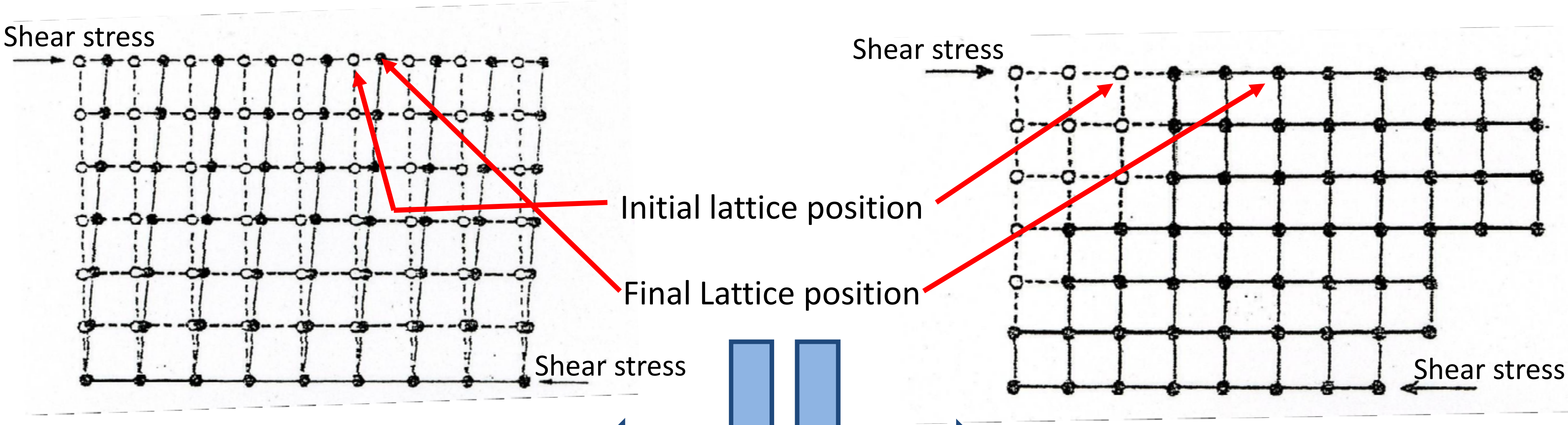
ε_t = true strain

n = strain hardening coefficient

Elastic and plastic deformation of metals

Elastic deformation

Plastic deformation



non equilibrium position

reversible deformation

equilibrium position

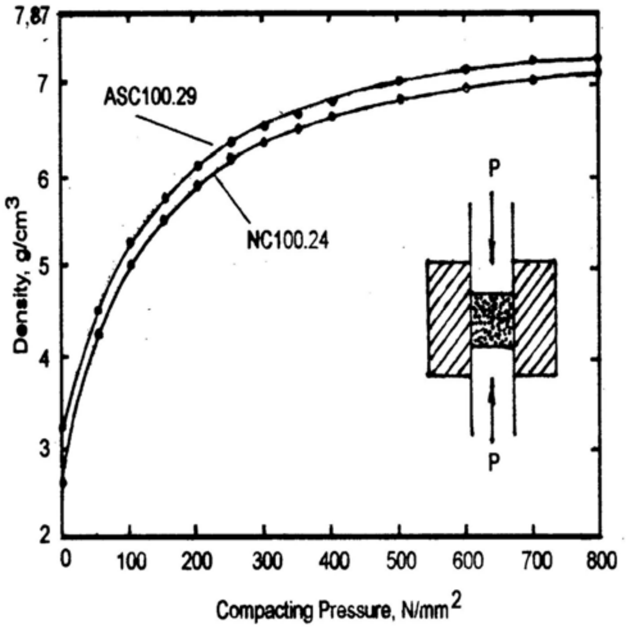
permanent deformation

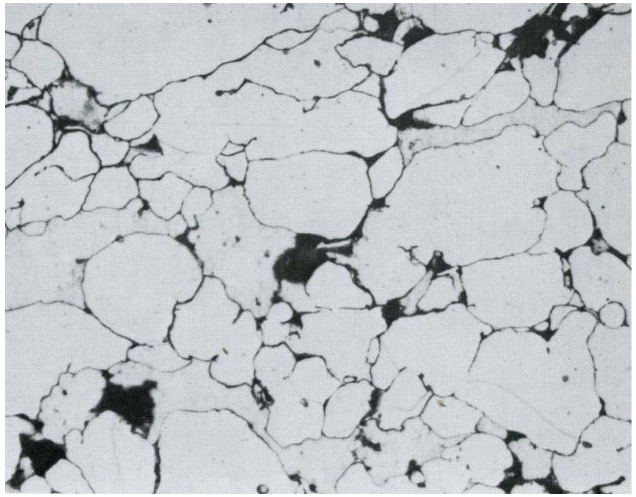
Elastic and plastic deformation of metals

During compaction, powder are deformed plastically (by a compressive stress).

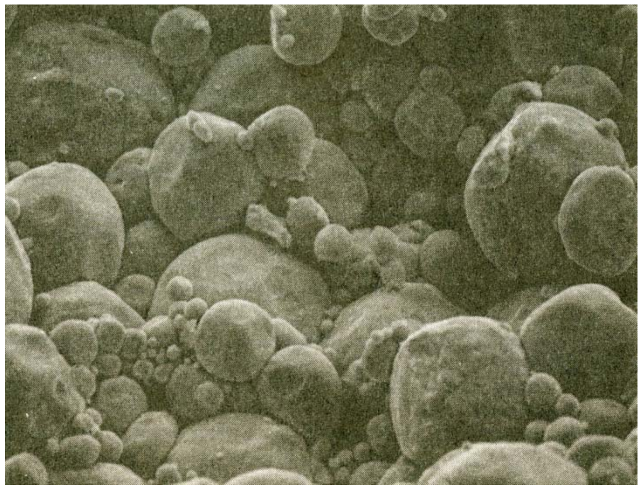
Elastic deformation does not provide any densification and strength.

The compaction curve of two iron powders





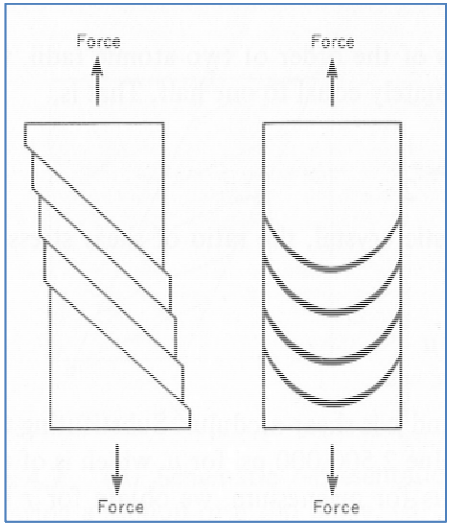
Microstructure and ....

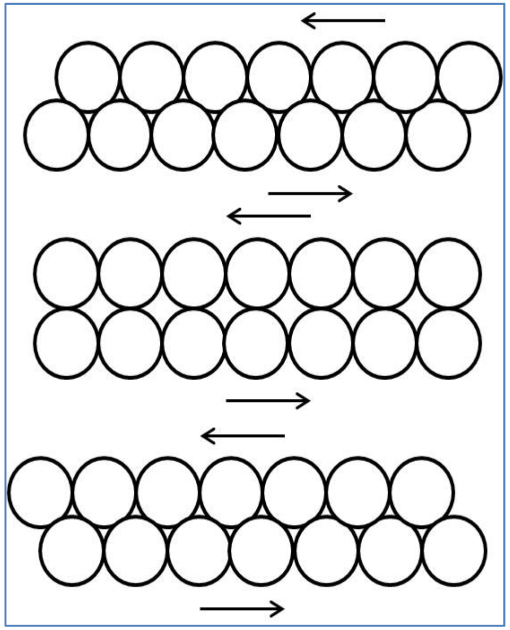


..... fracture surface of a green part

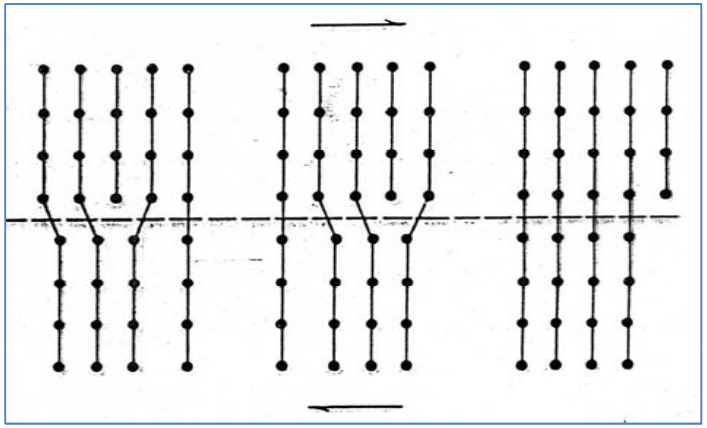
Plastic deformation of metals

Plastic deformation occurs by slip of the lattice planes caused by a shear stress





Slip of the lattice planes occurs by the movement (gliding) of dislocations



Plastic deformation of metals

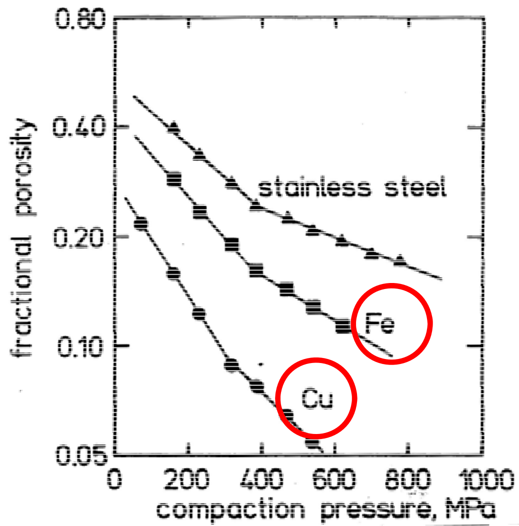
The shear stress to promote slip (Nabarro Peierls shear stress) ……..

$$\tau_{NP} = \frac{2G}{(1-\nu)} e^{-[2\pi a/(1-\nu)b]}$$

…….. depends on:

- distance between planes (a) and atoms (b)
- temperature (through G)
- impurities

It depends on the crystal structure; it is tendencially smaller in fcc crystals, and for this reason metals with fcc structure are more ductile than the other ones, and their powders have a better compressibility



It increases with the content of impurities, and for this reason the cemical quality of the powders influences compressibility

It decreases on increasing temperature, and for this reason plastic deformation is enhanced on increasing temperature (warm/hot compaction)

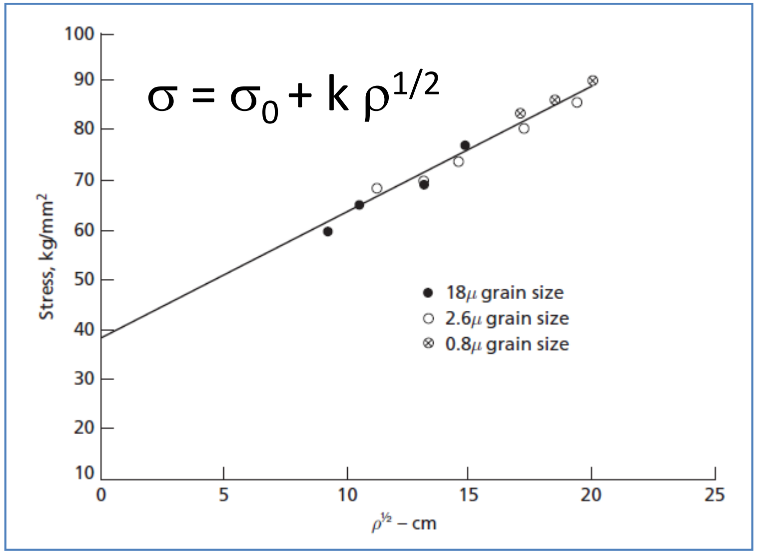
Plastic deformation of metals

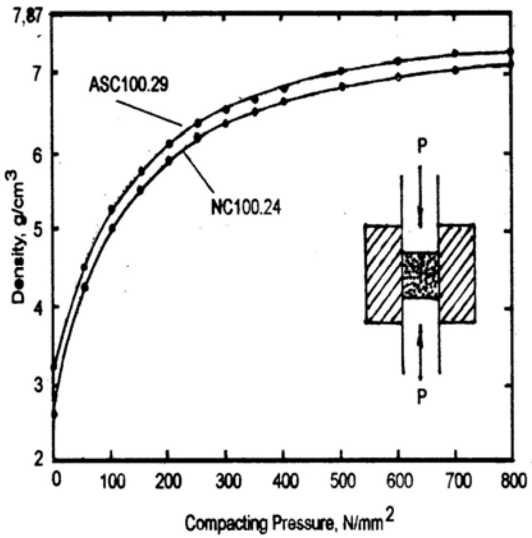
The resistance to plastic deformation of a metal depends on:

1. **The density of dislocation in the crystal (strain hardening)**
2. The grain size (grain refining)
3. The content of alloying elements (solution hardening)
4. The presence of precipitates (precipitation hardening)

Dislocation density ρ increases during plastic deformation, and this increases the stress required to move dislocations.

For this reason the compaction curve decreases its slope continuously and the full density cannot be attained





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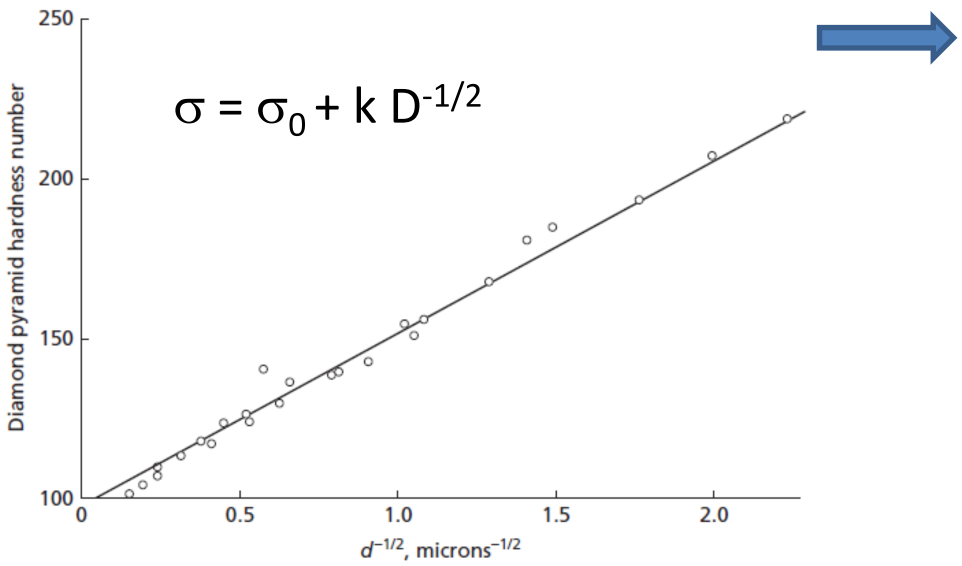
The stress to promote plastic deformation increases when grain size (D) decreases



For this reason, grain growth which may occur on sintering, has to be prevented to preserve mechanical strength of the sintered parts

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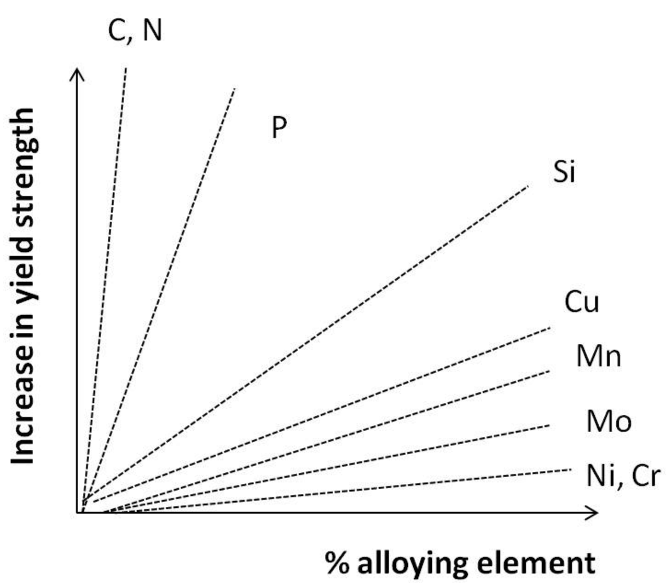
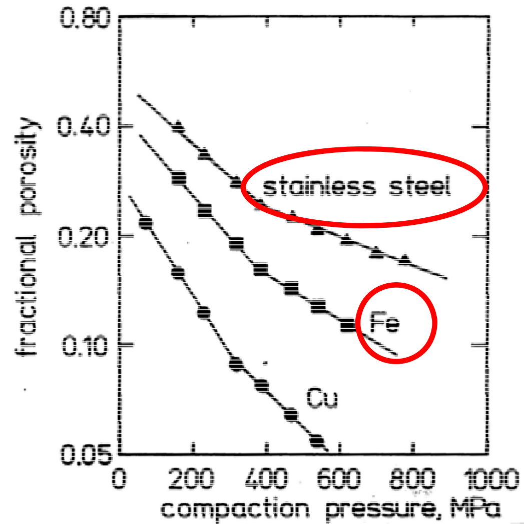
The stress to move dislocations increases in presence of alloying elements



This is the reason why alloys are have less compressibility than pure metals and compressibility decreases with the content of alloying elements



Plastic deformation of metals

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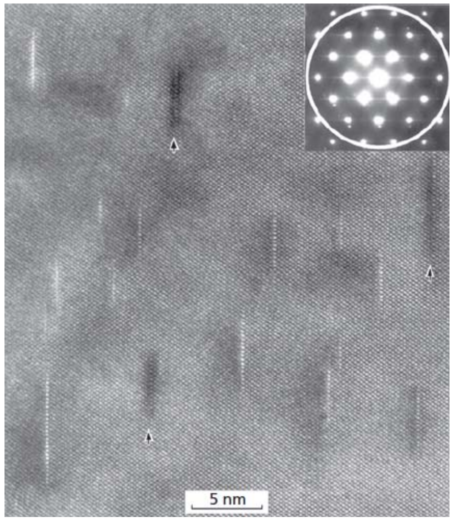
3. The content of alloying elements (solution hardening)
4. **The presence of precipitates (precipitation hardening)**

The stress to move dislocations increases in presence of precipitates, in particular if they are sumbicrometric



This mechanism is used in some technological alloys, the most important example are aluminum alloys.
The effect is obtained by means of a specific heat treatment:
Precipitation-hardening

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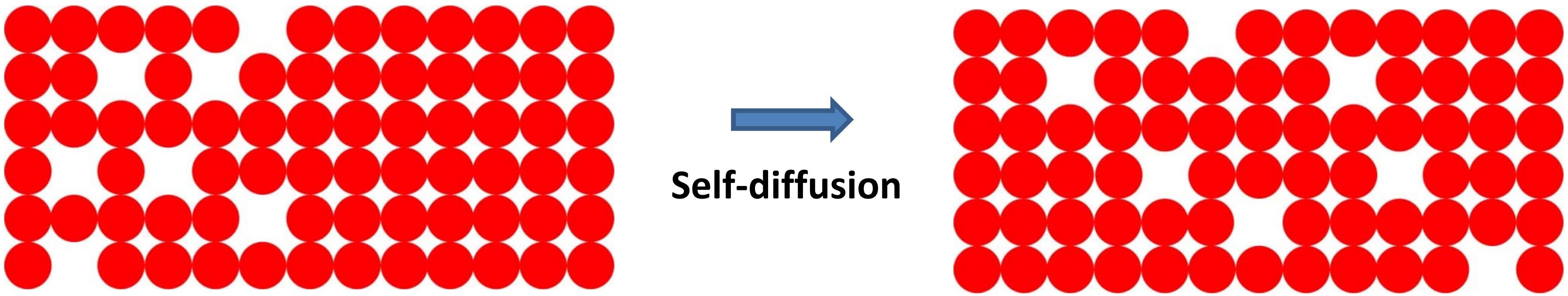
Structural transformations activated by temperature: Diffusion

Diffusion is a mass transport phenomenon involving single atoms, which tends to eliminate concentration gradients in metals.

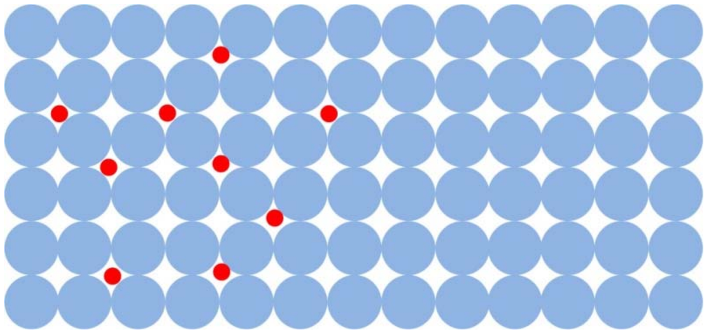
It is activated by temperature in presence of :
- Vacancies concentration gradients (self-diffusion)
- Impurities/alloying elements concentration gradients (interstial/substitutional diffusion)

Vacancies concentration gradients **Homogeneous distribution of vacancies**



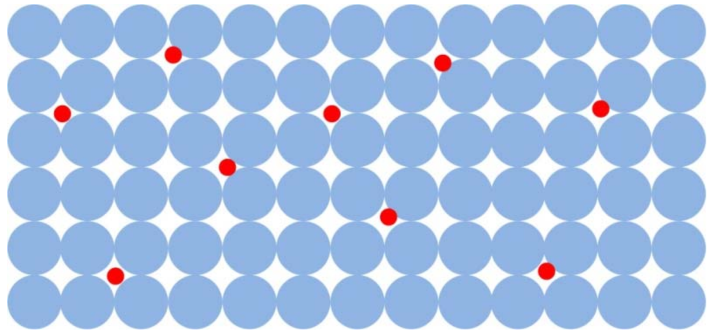
Structural transformations activated by temperature: Diffusion

Interstitial concentration gradients

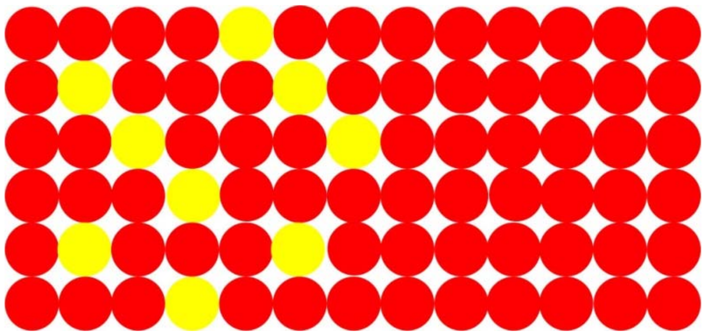


Interstitial diffusion

Homogeneous distribution of interstitials

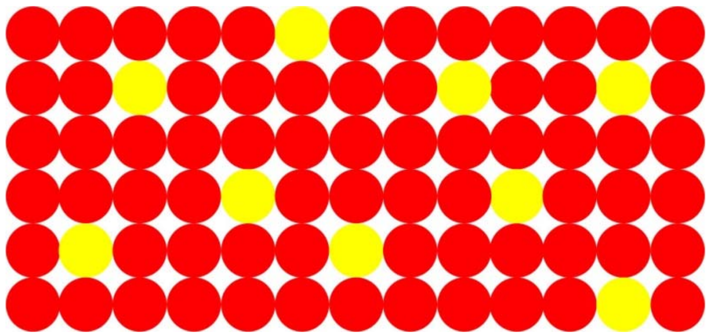


Substitutional concentration gradients

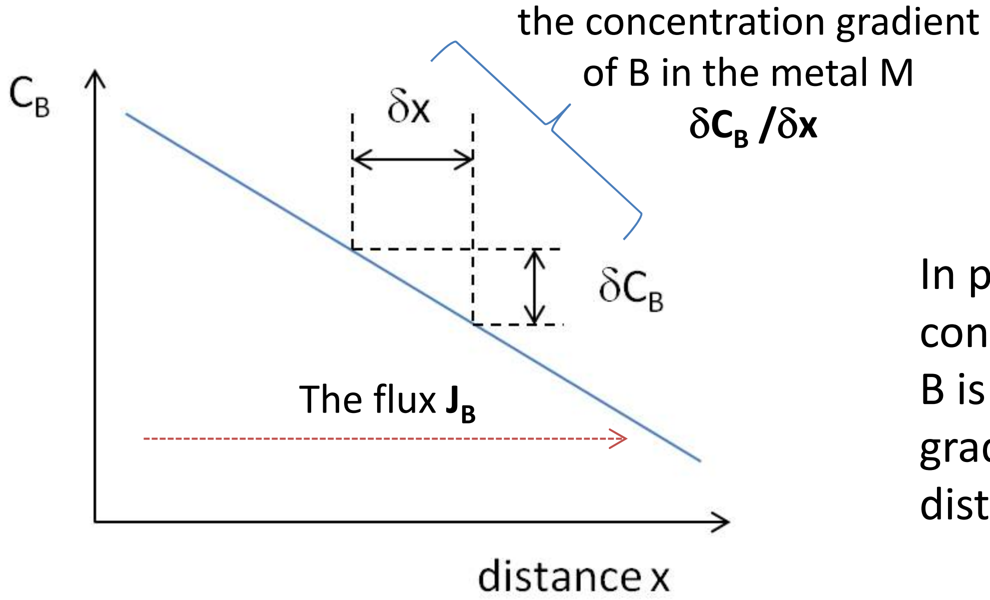


Substitutional diffusion

Homogeneous distribution of substitutionals



Structural transformations activated by temperature: Diffusion



In presence of a (vacancies/atoms) concentration gradient $\delta C_B / \delta x$, a flux J_B of B is activated which tends to eliminate the gradient leading to a homogeneous distribution of vacancies/atoms

$$J_B = -D_B \, \delta C_B / \delta x$$

D_B = diffusion coefficient of B in the metal M

B = vacancies → self-diffusion
B = other atoms → diffusion of B in M

} depend on temperature

$$D = D_0 \, e^{(-Q/RT)}$$

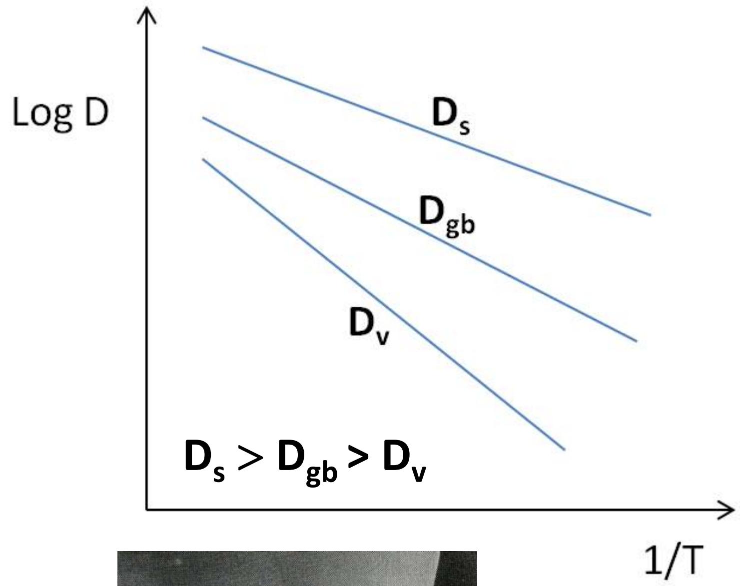
Structural transformations activated by temperature: Diffusion

Different diffusion paths

Surface diffusion $\mathbf{D_s = D_{s,0}\, e^{(-Qs/RT)}}$

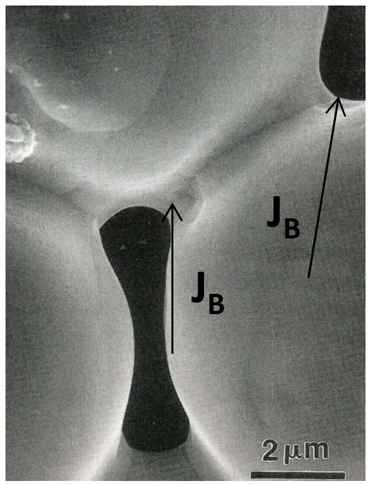
Grain boundary diffusion $\mathbf{D_{gb} = D_{gb,0}\, e^{(-Qgb/RT)}}$

Volume (lattice) diffusion $\mathbf{D_v = D_{v,0}\, e^{(-Qv/RT)}}$



The main sintering mechanism is diffusion due to a vacancies concentration gradient between the neck and the bulk of the particles (**self-diffusion**)

In alloys produced by blends of elemental powders, **diffusion of alloying elements** is activated and **contributes to sintering**



Structural transformations activated by temperature: Grain growth

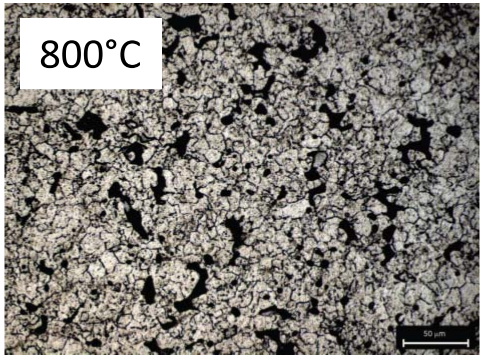
Grain growth is a temperature activated phenomenon which leads to a progressive increase in the mean grain size.

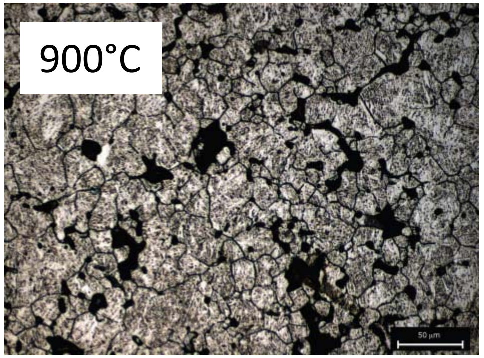
It occurs during sintering and heat treatments.

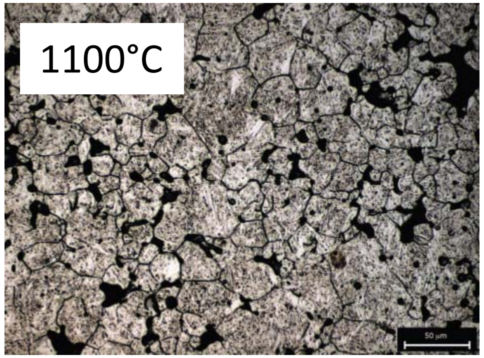
The **driving force** of grain growth is the Gibbs free energy ΔG associated to the grain boundary surface ΔS

$\Delta G = \gamma_{gb} \, \Delta S$

which can be decreased only if the grain boundary surface decreases



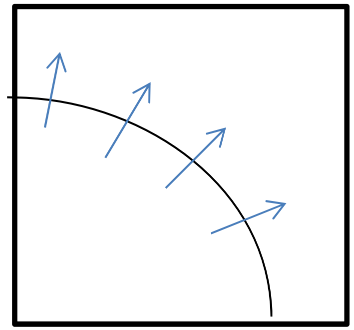




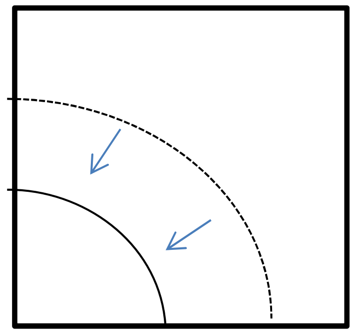
Structural transformations activated by temperature: Grain growth

The **mechanism** of grain growth is **diffusion** coupled to **grain boundary migration**

Diffusion

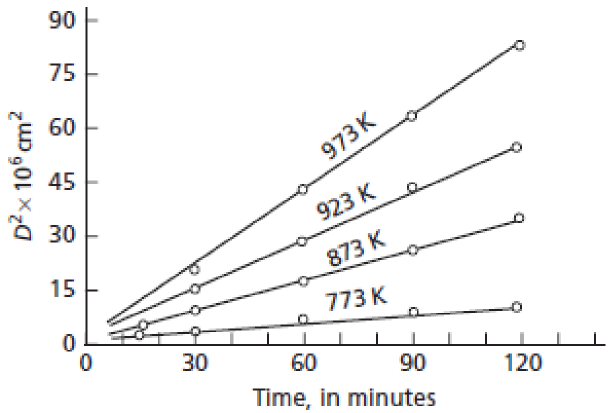


Grain boundary migration



The **grain growth kinetics**

$$D^2 - D_0^2 = K_0\, e^{(-Q/RT)}\, t$$

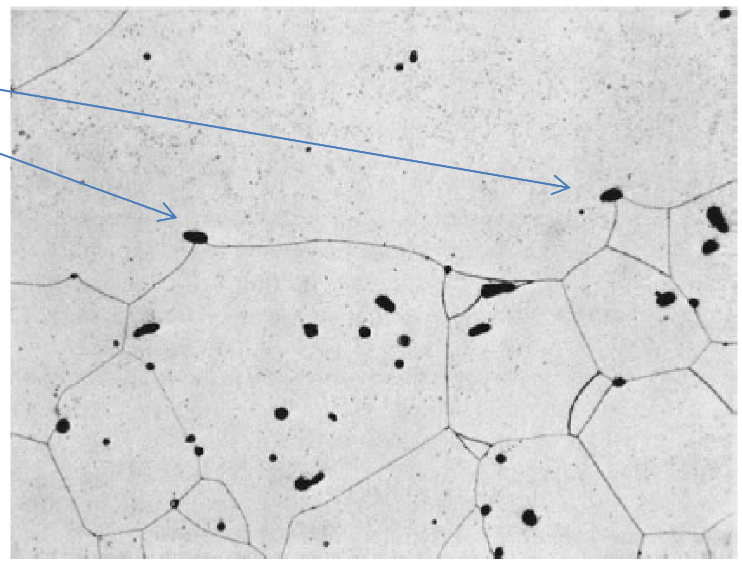


Structural transformations activated by temperature: Grain growth

Grain growth causes a decrease of mechanical properties of materials, therefore it should be either avoided or, at least, minimized.

Grain growth is slown down and sometimes inhibited by the presence of particles of second phases on the grain boundary

The same effect is provided by pores in sintering



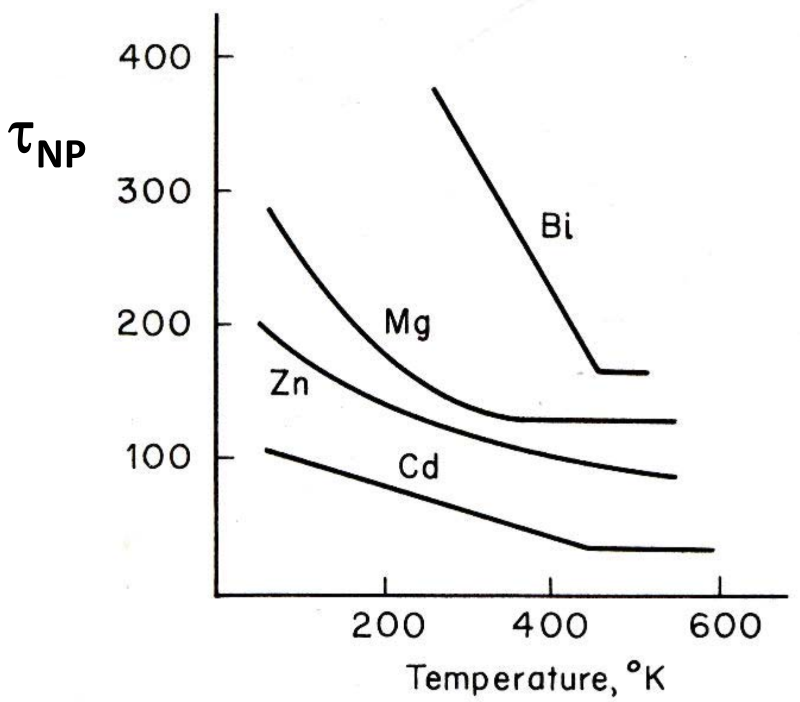
Transformations in PM

The conventional PM process		Transformations occurring in the processed metal
Powder production		
- in solid state	------>	Reaction with the atmosphere
- from a liquid phase	------>	Melting and solidification
Shaping		
- compaction	------>	Elastic and plastic deformation
Sintering		
- free sintering	------>	Structural transformations activated by temperature
	------>	Reaction with the atmosphere
Secondary operations		
- sizing	------>	Plastic deformation
- re-compaction	------>	Plastic deformation
- heat treatments	------>	Structural transformations activated by temperature
- others		
Alternative processes		
Pressure assisted sintering	------>	**Deformation at high temperature / Structural transformations activated by temperature**
Additive manufacturing	------>	Melting and solidification / Structural transfromations activated by temperaure

Plastic deformation at high temperature

At high temperature plastic deformation of metals is enhanced since:

1. **The stress to move dislocations decreases with temperature**
2. The strain hardening is eliminated by recovery and mainly by recrystallization, which decrease the density of dislocations



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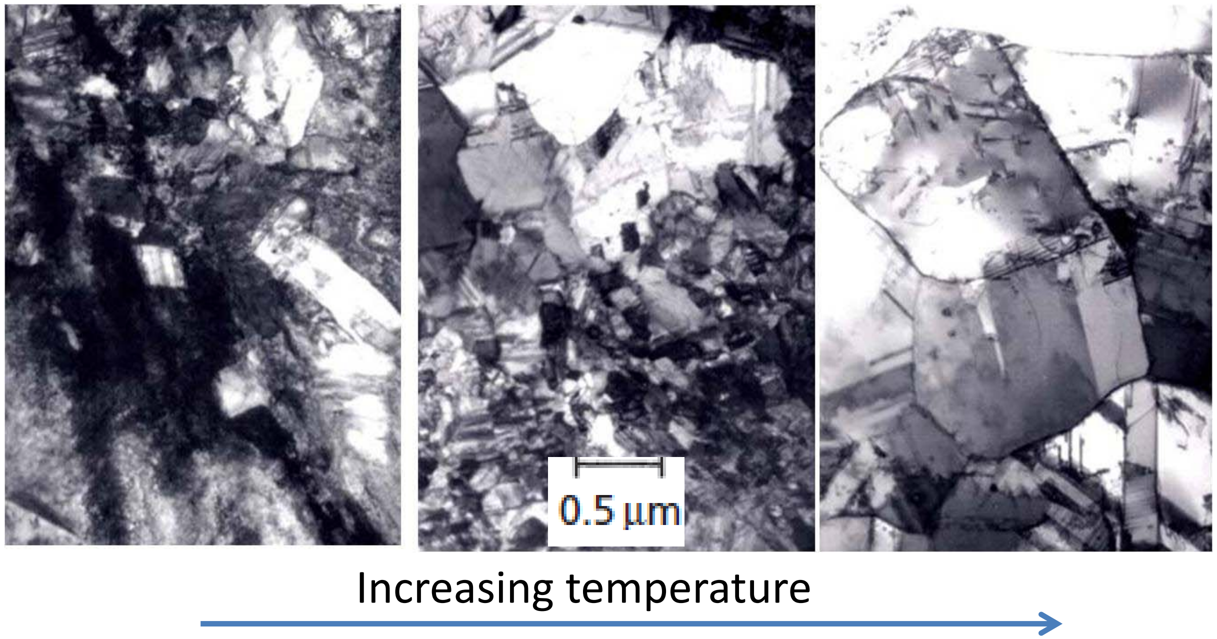
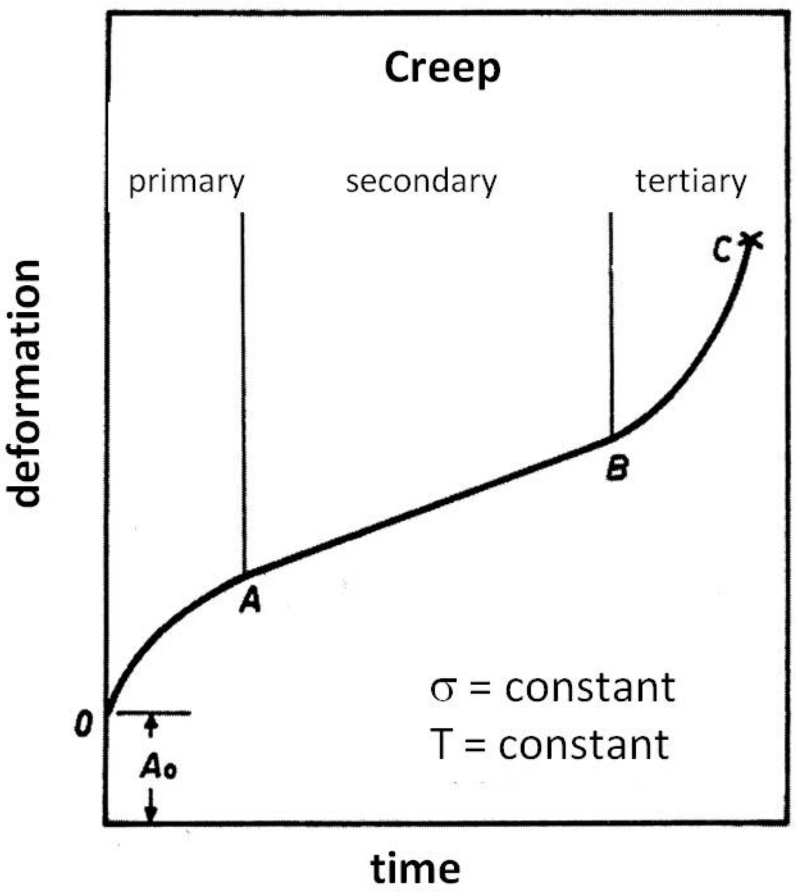


Dislocation density decreases – resistance to plastic deformation decreases

Plastic deformation at high temperature

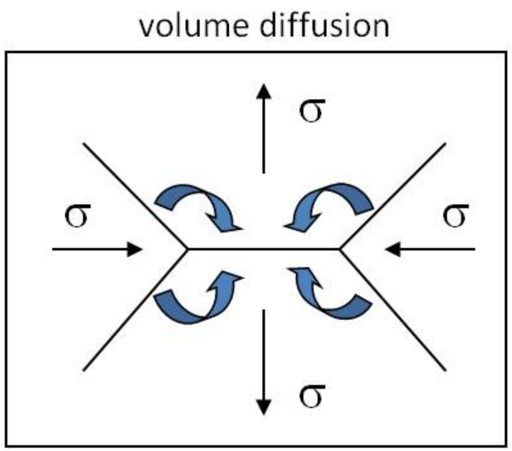
At high temperature plastic deformation of metals is enhanced since:

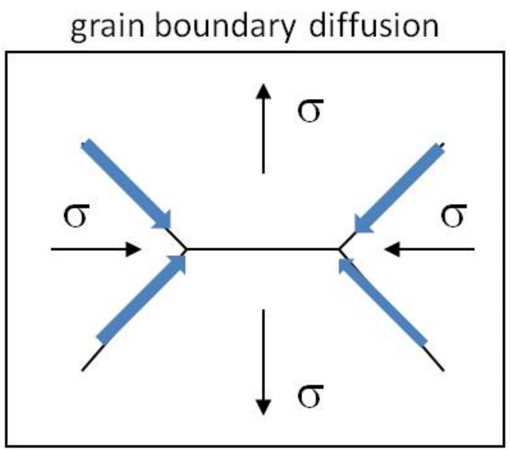
3. A new deformation mechanism is activated: creep



Creep:
time depending permanent deformation occurring at high temperaure under a constant load, due to:

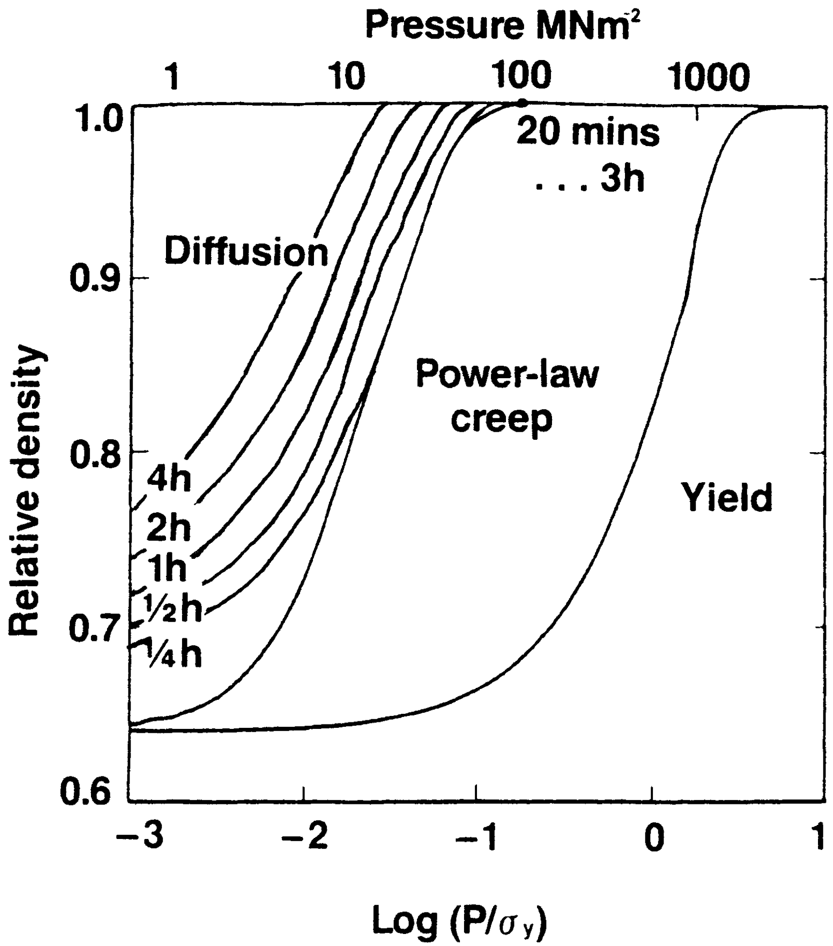
1. volume diffusion (Nabarro-Herring)
2. grain boundary diffusion Coble)
3. dislocation motion by climbing (power law)





Deformation = densification

Densification during pressure-assisted sintering techniques is the result of the combination/sequence of deformation at high temperature and diffusion



Transformations in PM

The conventional PM process	Transformations occurring in the processed metal
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Sintering	
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	Reaction with the atmosphere
Secondary operations	
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- heat treatments	Structural transformations activated by temperature
- others	
Alternative processes	
Pressure assisted sintering	Deformation at high temperature / Structural transformations activated by temperature
Additive manufacturing	Melting and solidification / **Structural transfromations activated by temperaure**

Structural transformations activated by temperature: Phase transformations. The case of steel

Some of the metals have different “allotropic” forms in solid state.
Iron, for instance, is:
- bcc up to 912°C (α iron)
- fcc from 911°C up to 1394°C (γ iron)
- bcc from 1392°C up to the melting temperature (1536°C) (δ iron)

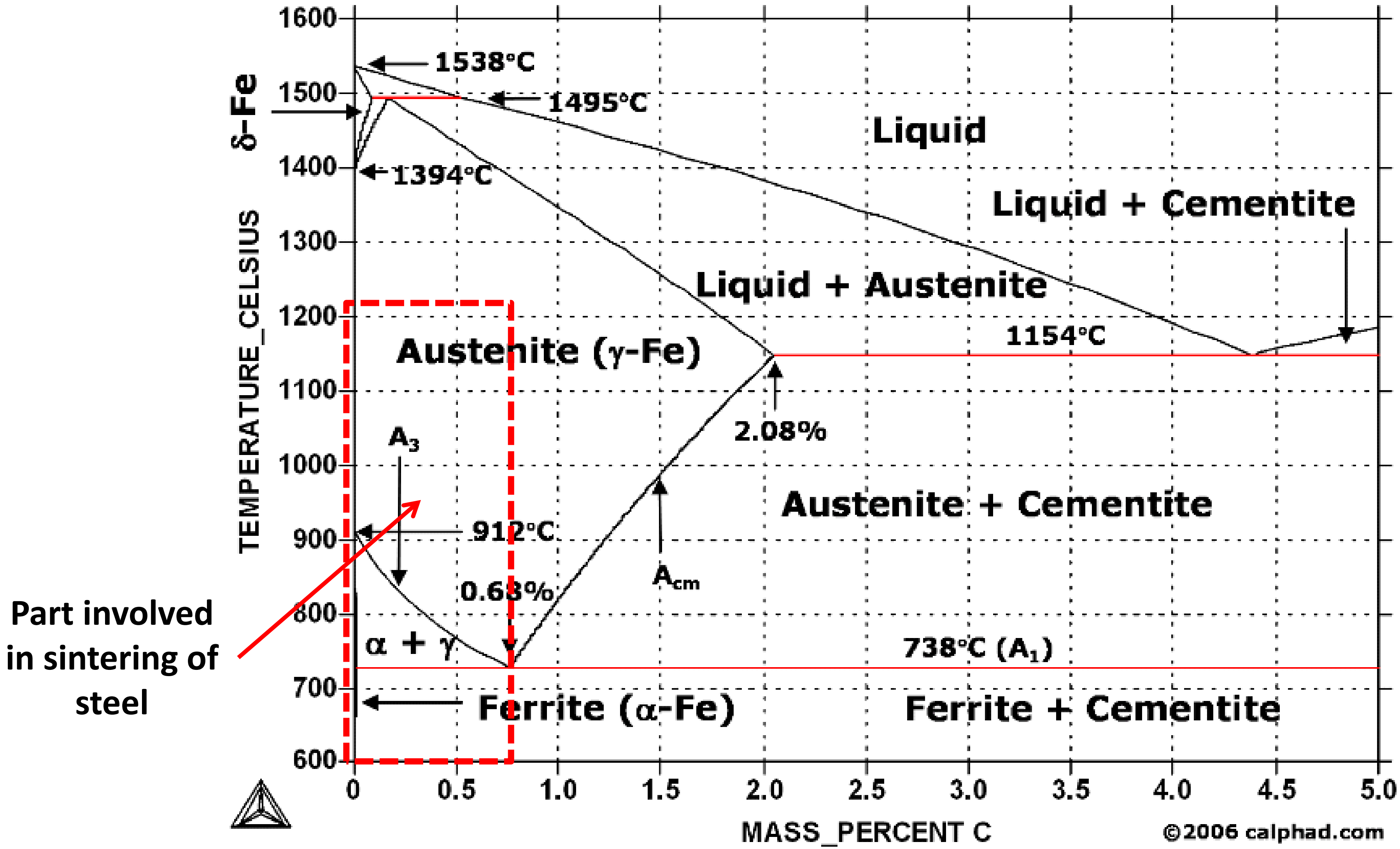
These transformations occur on heating and cooling (solid state transformations)

Carbon is added to iron to produce steel. The solubility of carbon in iron is strongly dependent on the allotropic form: much higher in the fcc (austenite) than in the two bcc ones (α and δ ferrite). Above the solubility limit, carbon forms cementite Fe_3C.

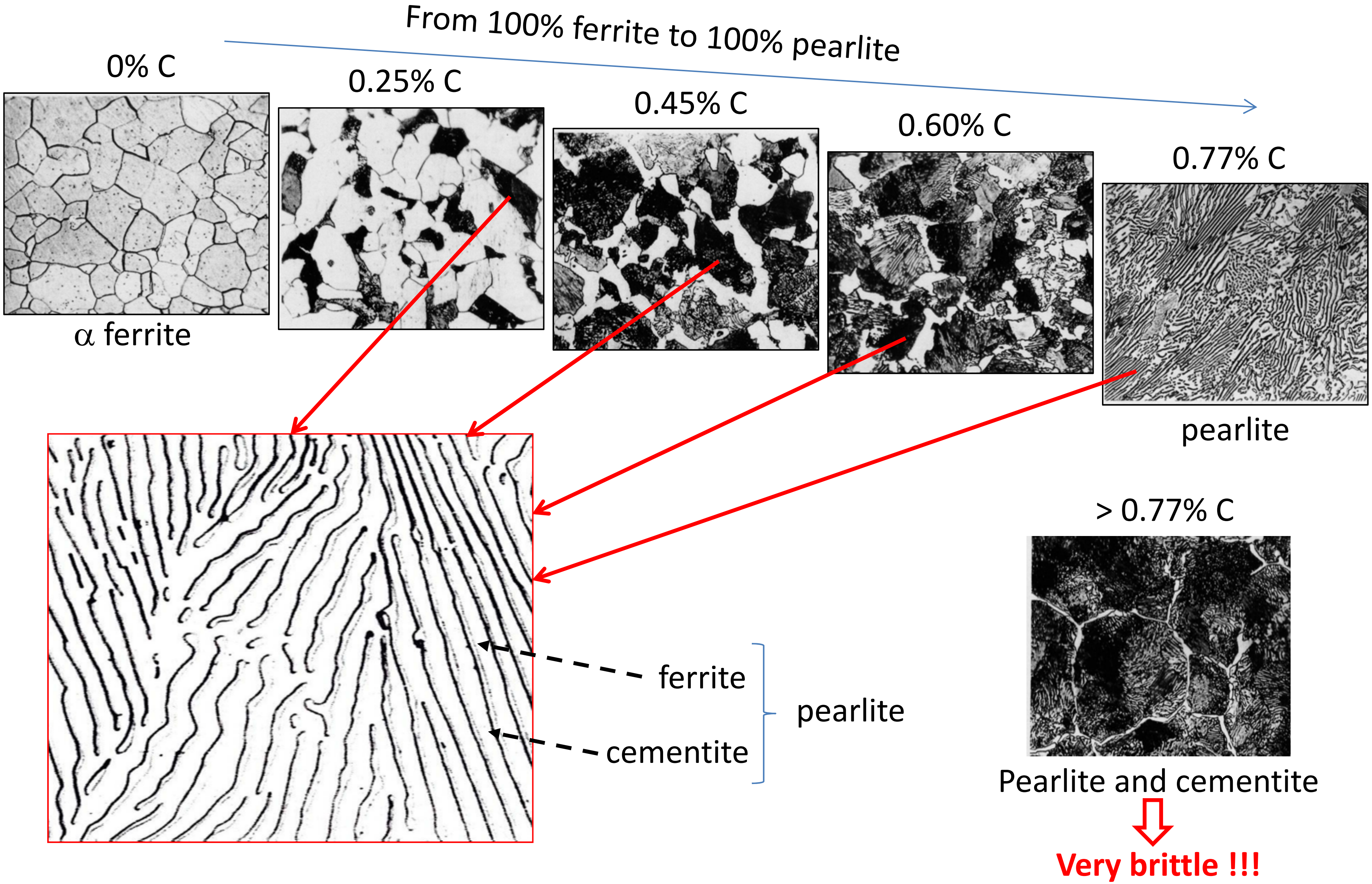
Moerover, the presence of carbon:
- affects the temperatures at which the solid state transformations occur
- promotes the formation of “non equilibrium” constituents on cooling of austenite

All these phenomena are described by the Fe-C phase diagram and by the CCT curves of austenite

The Iron-carbon phase diagram



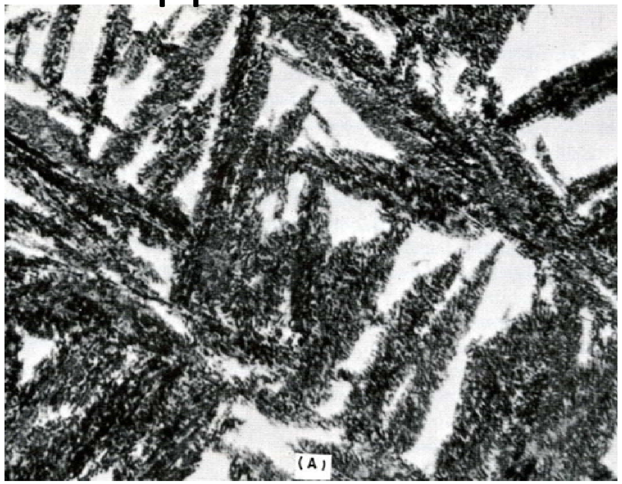
The microstructure of steel: slow cooling



The microstructure of steel: increasing cooling rate

Increasing cooling rate

Upper bainite



Lower bainite

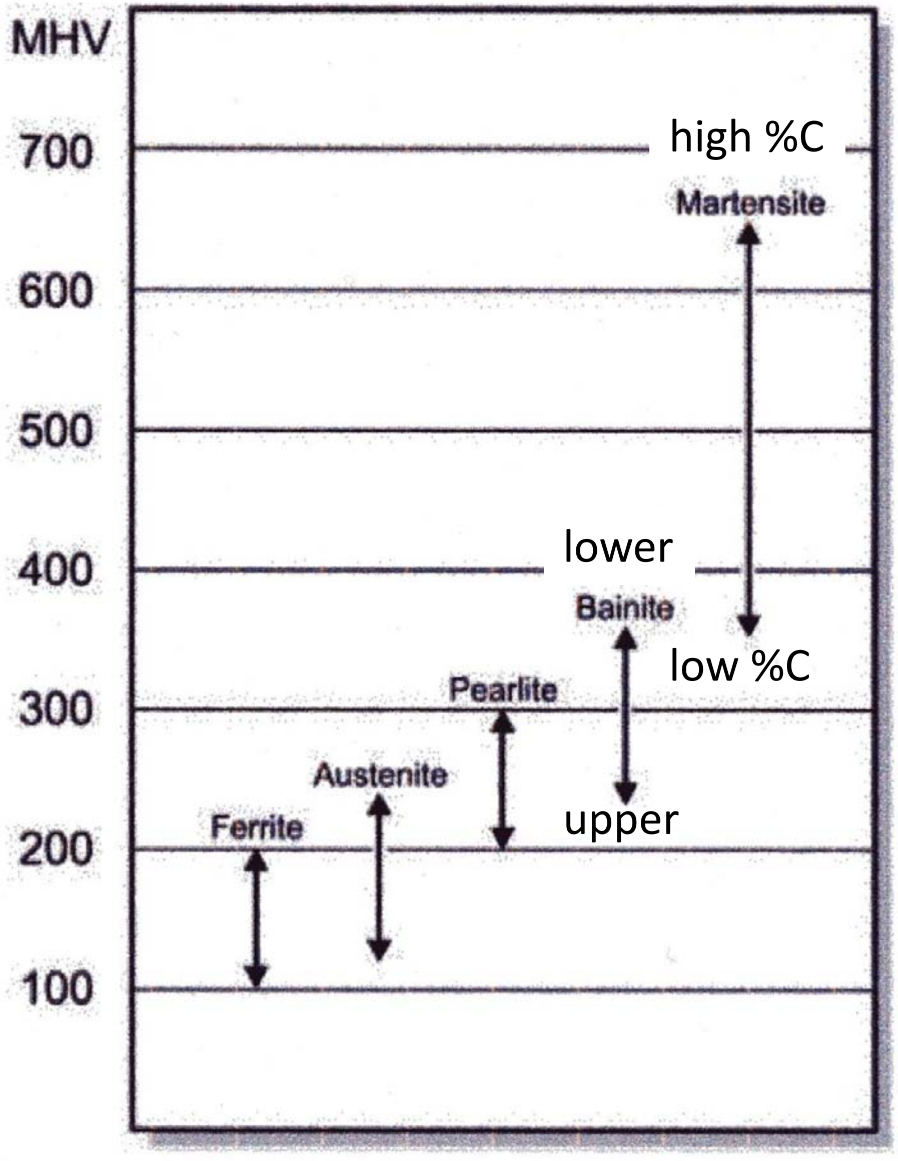
Martensite

The properties of the microstructural constituents: hardness

On increasing hardness
- both yield strength and fatigue strength tendencially increase ,
- ductility decreases (brittleness increases),

- but:

1. Lower bainite is harder and less brittle than upper bainite
2. **Martensite is definitely too brittle**, therefore it cannot be used in practical applications; **a tempering treatment is mandatory to reduce its brittleness (tempered martensite)**

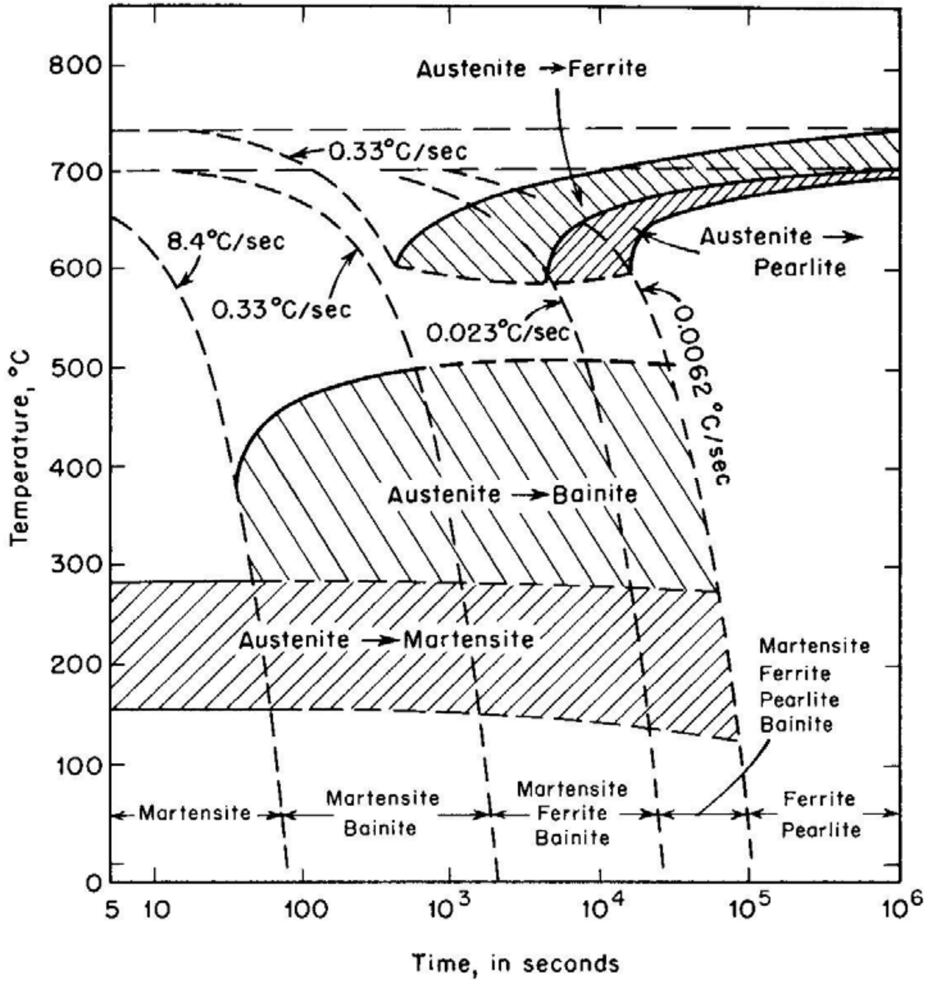


The CCT diagrams

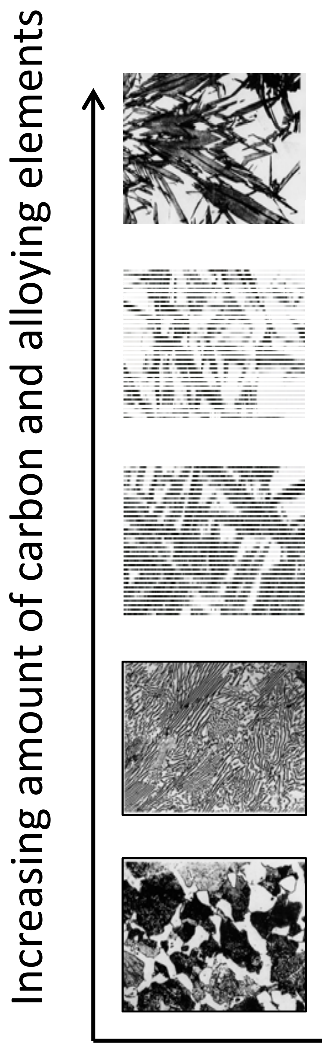
They describe the trasformations of austenite on continuous cooling, as that occurring in heat treatments and in sintering

Since the trasformations of austenite on continuous cooling depend on:
- carbon content
- alloying elements
- austenite grain size

each steel has its own CCT diagram, which depends on the temperature from which cooling starts



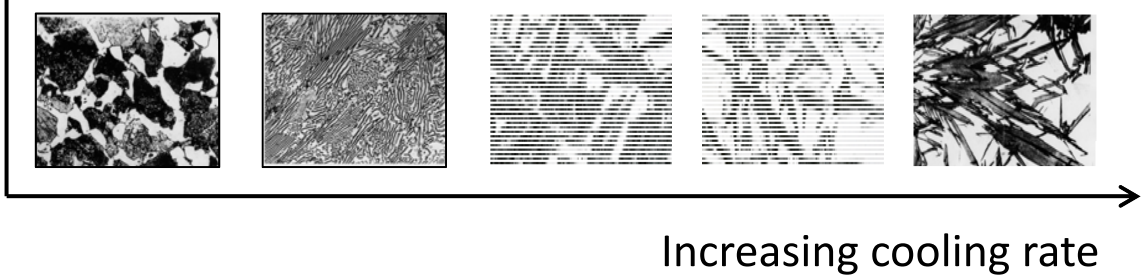
The transformations of austenite



In principle, on increasing the content of carbon and of the alloying elments and the heating rate, the product of the austenite transformation changes from ferrite/pearlite to pearlite, upper bainite, lower bainite and finally to martensite

The increase in austenite grain size favors the formation of martensite.

To obtain martensite, the cooling rate must be higher than a **critical cooling rate** which depends on the composition of the steel. The lower this critical cooling rate, the higher the steel **hardenability**



Thank you for your kind attention and……

……. have a nice School

alberto