LECTURE NOTES

MME 201

INTRODUCTION TO PHYSICAL METALLURGY

B.TECH 3rd SEMESTER

MME 201

INTRODUCTION TO PHYSICAL METALLURGY

Course Coordinators

Avala Lava Kumar
Department of Metallurgical & Materials Engineering (MME)
Veer Surendra Sai University of Technology (VSSUT), Burla-768018
E-mail : lavakumar.vssut@gmail.com Phone: (+91) (7077110110)

Suneeti Purohit
Department of MME, VSSUT, Burla – 768018
E-mail : suneeti.purohit@gmail.com
Phone : (+91) 8339037187

Gautam Behera
Department of MME, VSSUT, Burla – 768018
E-mail : gautamiitkgpian@gmail.com
Phone : (+91) 8339037187

INTRODUCTION TO PHYSICAL METALLURGY

The course aims to provide a general introduction to the field of Physical Metallurgy. The course covers crystal structures, solidification, equilibrium phase diagrams, transformation diagrams, diffusion, liquid to solid transformations, ferrous and non-ferrous materials, cold work, recovery and Recrystallization.

Course Overview

The module provides a systematic overview of the major principles of physical metallurgy. Students successfully completing the module will have a critical awareness of how these principles relate to current issues in exploiting structural alloys in engineering applications.

Learning Outcomes

Upon successful completion of the module, students should be able to ►Show a systematic understanding of the role that crystal structures play in material properties. ►Evaluate critically the relevance of phase diagrams, isothermal transformation diagrams and continuous cooling transformation diagrams to understanding real alloys and their microstructure.► Display a critical awareness of the relevance of key areas, e.g. diffusion, defects, transformation type, to current problems in designing, processing and exploiting real alloys. ►Show a systematic understanding of the complex interplay between microstructure, processing and engineering properties in metallic materials.

MME 201 : INTRODUCTION TO PHYSICAL METALLURGY

CONTENTS

INTRODUCTION TO PHYSICAL METALLURGY

References

- ❑ Introduction to Physical Metallurgy (*This is the major reference for this course*)

  Sidney H. Avner

  McGraw Hill Education (India) Private Limited

- ❑ Materials Science & Engineering E-book (A *learners guide*) (*This is the major reference for this Notes, we directly taken these slides with slight modifications*)

  Anandh Subramaniam & Kantesh Balani (IITK)

  MHRD, Govt. of India through NMEICT

- ❑ Materials Science and Engineering (5th Edition)
  V. Raghavan
  Prentice-Hall of India Pvt. Ltd., 2004.

- ❑ Callister's Materials Science and Engienering
  William D Callister (Adapted by R. Balasubramaniam)
  Wiley Inida (P) Ltd., 2007.

- ❑ The Science and Engineering of Materials
  Donald. R. Askeland & Pradeep Phulé
  Cengage Learning, 2006.

- ❑ Materials Science & Engineering (NPTEL Course)

  Ranjit Bauri (IITM)

Introduction

Avala Lava Kumar *: Suneeti Purohit : Gautam Behera

Department of Metallurgical & Materials Engineering (MME)

Veer Surendra Sai University of Technology (VSSUT), Burla -768018

**E-mail : lavakumar.vssut@gmail.com*

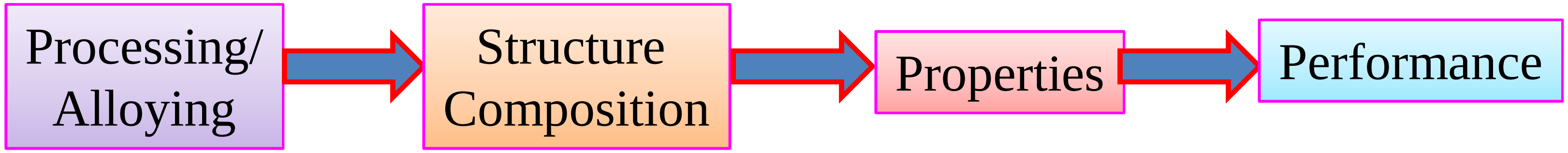
Introduction

What is physical metallurgy?

- Evolution of structures in solid as it from liquid
- Effect of alloy elements/ impurities on the transformation processes
- Effect of processing techniques on evolution of structure
- Structure property relation.

Objectives

- At some point of time or the other an engineering problem involves issues related to material selection. Understanding the behavior of materials, particularly structure-property correlation, will help selecting suitable materials for a particular application.
- To provide a basic understanding of the underlying principles that determines the evolution the evolution of structures in metals and alloys during their processing and its relation with their properties & performance in service.



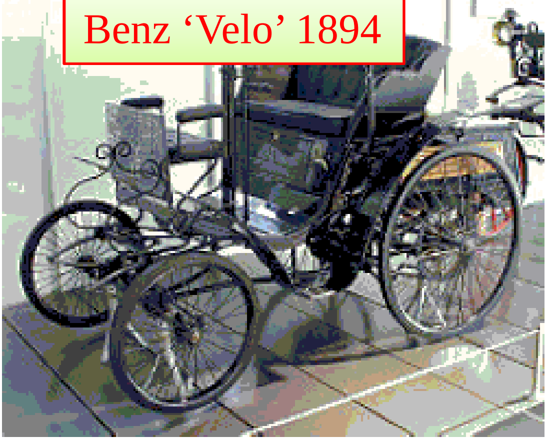
The Impact of Materials on progress

Revolution in Transportation

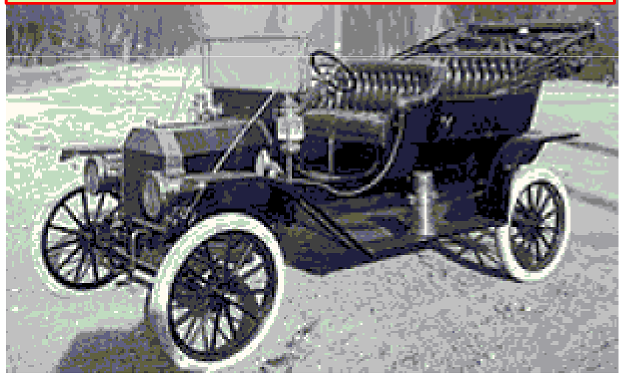
- By 1890 we had Copper, Bronze, Iron, Steel , Aluminum and Rubber in addition to Wood. This paved the way for series of inventions leading to a paradigm shift in the road transport from horse carriages to motorized vehicles.
- *Ford Motors – The first assembly line for mass production of commercial vehicles*

Road Transport before

Benz ‘Velo’ 1894



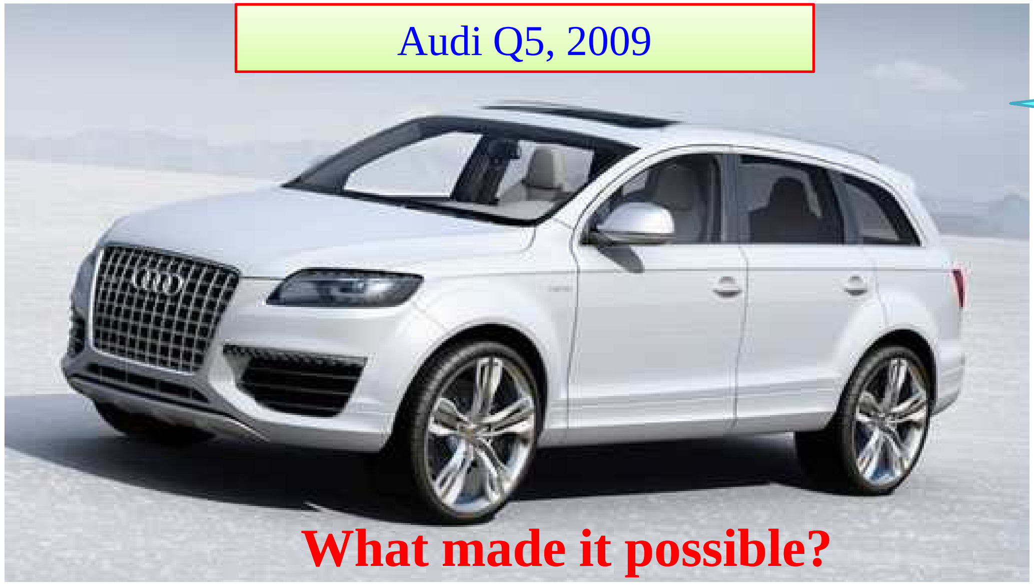
Ford T Model, 1910 The first affordable automobile.



Ford Capri Model, 1962

Advent of new materials like Mg, polymers and technologies and innovations. – T to Capri

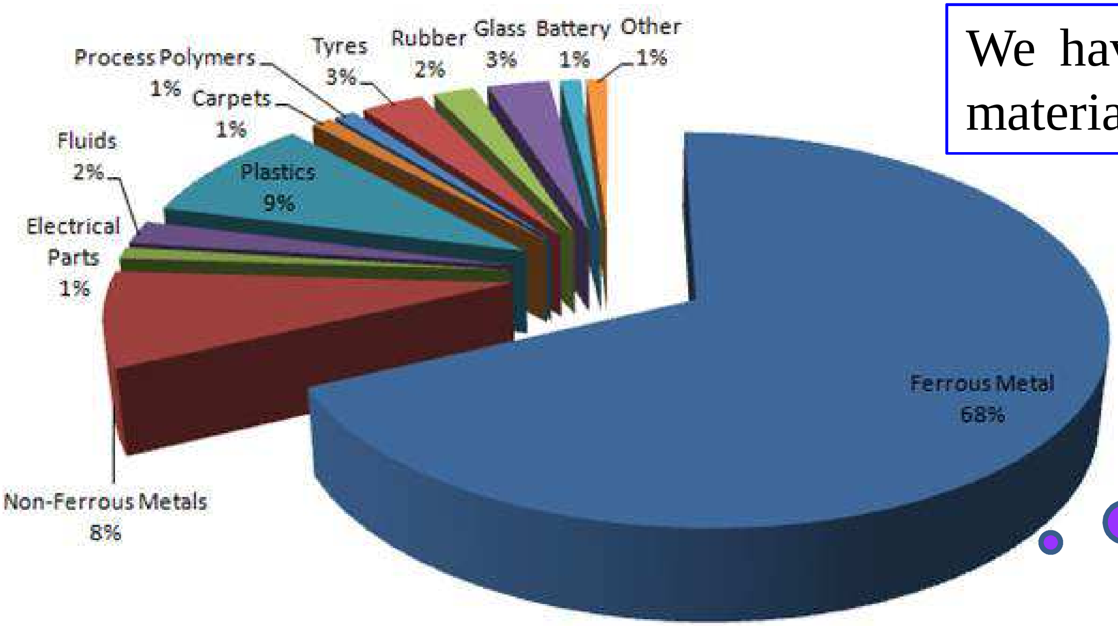
The Impact of Materials on progress



Audi Q5, 2009

What made it possible?

From there to today's advanced modern cars



We have come of ages, developed new materials and technologies based on them

The application of these advanced materials has led to the modern day cars

The Impact of Materials on progress

Powerful Engines

- From Cast iron blocks to more compact, lighter and powerful engine blocks – Material development has made it all possible

.

- Engine components are traditionally made from ferrous alloys. Emphasis on weight reduction for higher fuel efficiency has increased usage of aluminum for cylinder blocks, cylinder heads, and other engine components. Some engine covers and intake manifolds are made of magnesium. Titanium is also used in high-speed engines connecting rods to reduce reciprocating mass.

Interior

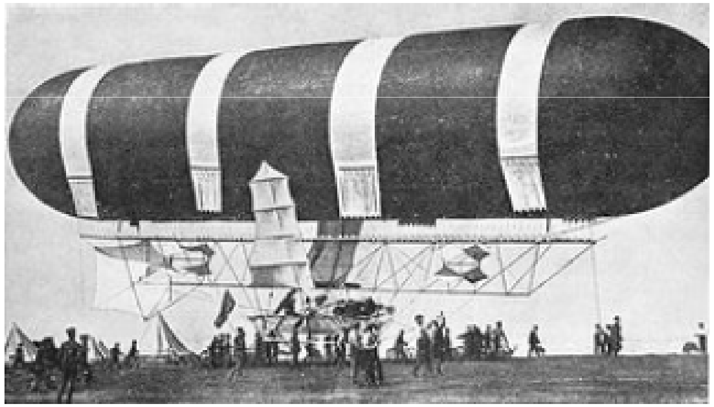
Availability of materials like synthetic rubber, variety of polymers, foams has provided new dimension and aesthetic look to automotive interiors

The Impact of Materials on progress

Invention of Aero plane - 1902

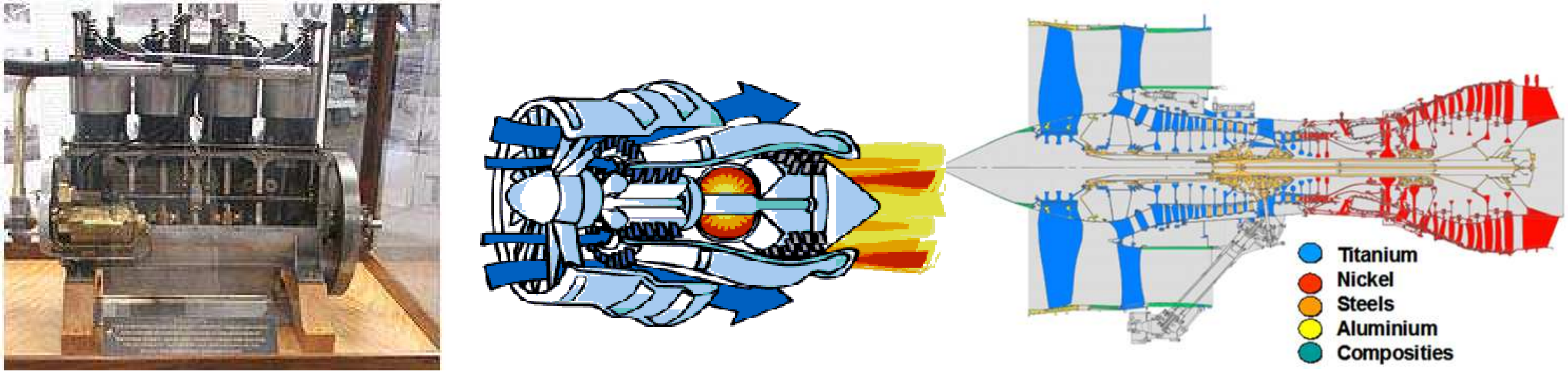
From Wright Brothers' invention

Through this to ……………

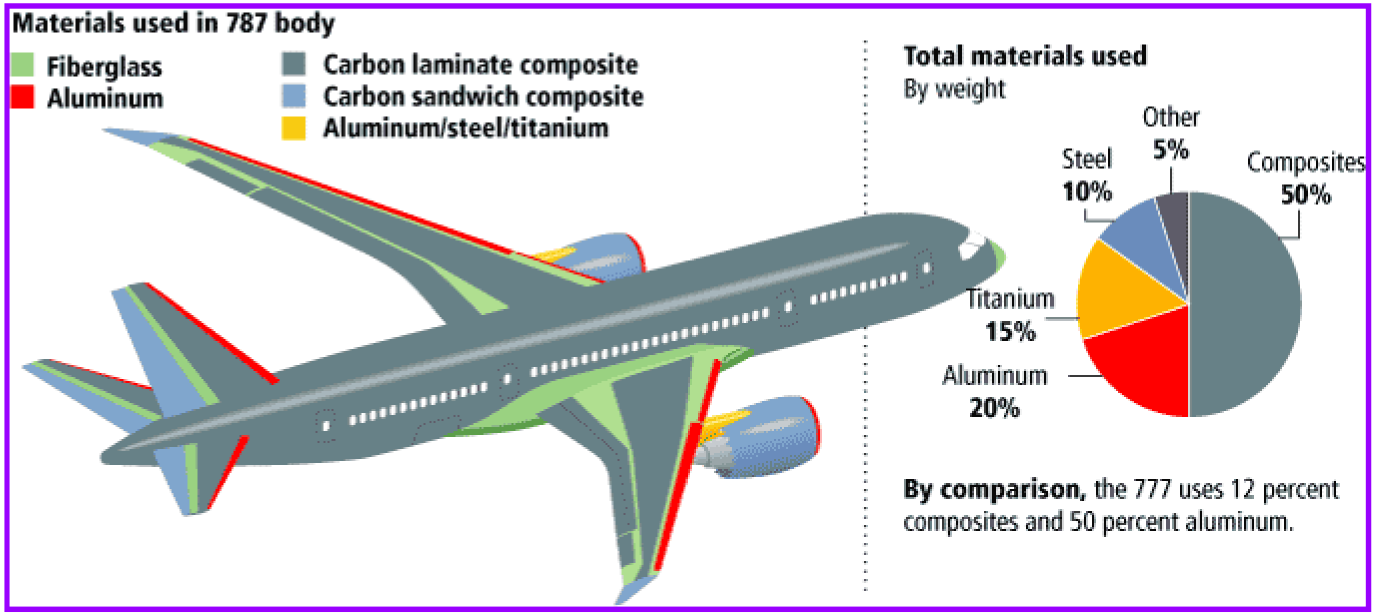


….. Modern Aviation

The Impact of Materials on progress



From the first engine used by Wright brothers to Powerful modern jet engines

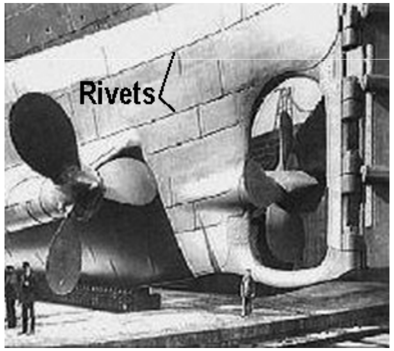


By comparison, the 777 uses 12 percent composites and 50 percent aluminum.

Aircraft body structure

The Impact of Materials on progress

Waterways – Transport and Safety RMS Titanic, a classic example…..!



Steel quality – Poor: High S and P and low Mn:S ratio, compared to high quality modern grade steels

The composition of steels from the titanic, a lock gate and ASTM A36

	C	Mn	P	S	Si	Cu	O	N	MnS
Titanic	0.21	0.47	0.045	0.069	0.017	0.024	0.013	0.0035	6.8:1
Lock Gate	0.25	0.52	0.01	0.03	0.02	-	0.018	0.0035	17.3:1
ASTM A36	0.20	0.55	0.012	0.037	0.007	0.01	0.079	0.0032	14.9:1

The Impact of Materials on progress

Modern cruise : As luxurious as Titanic – Better safety due to use of advanced materials like fiber reinforced composites (FRP) combined with advanced navigation system.

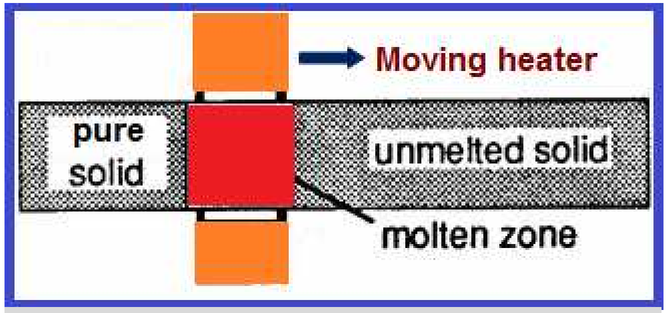
The Impact of Materials on progress

The Electronics Revolution

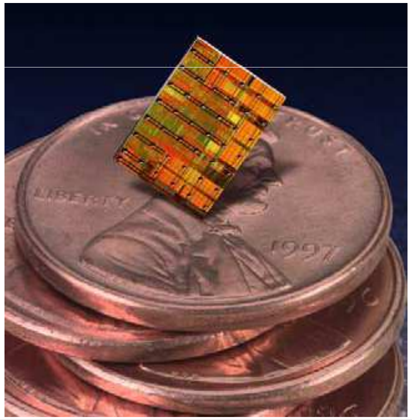
Silicon – the heart of every electronic component

1940 - Harvard MarkI Electro-mechanical computer – 5 tons, 8 x 51 feet and 500 miles of wire

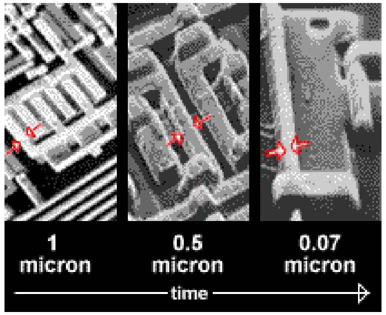
1959 – IBM Computer, 33 feet long



Invention high purity Si through zone refining



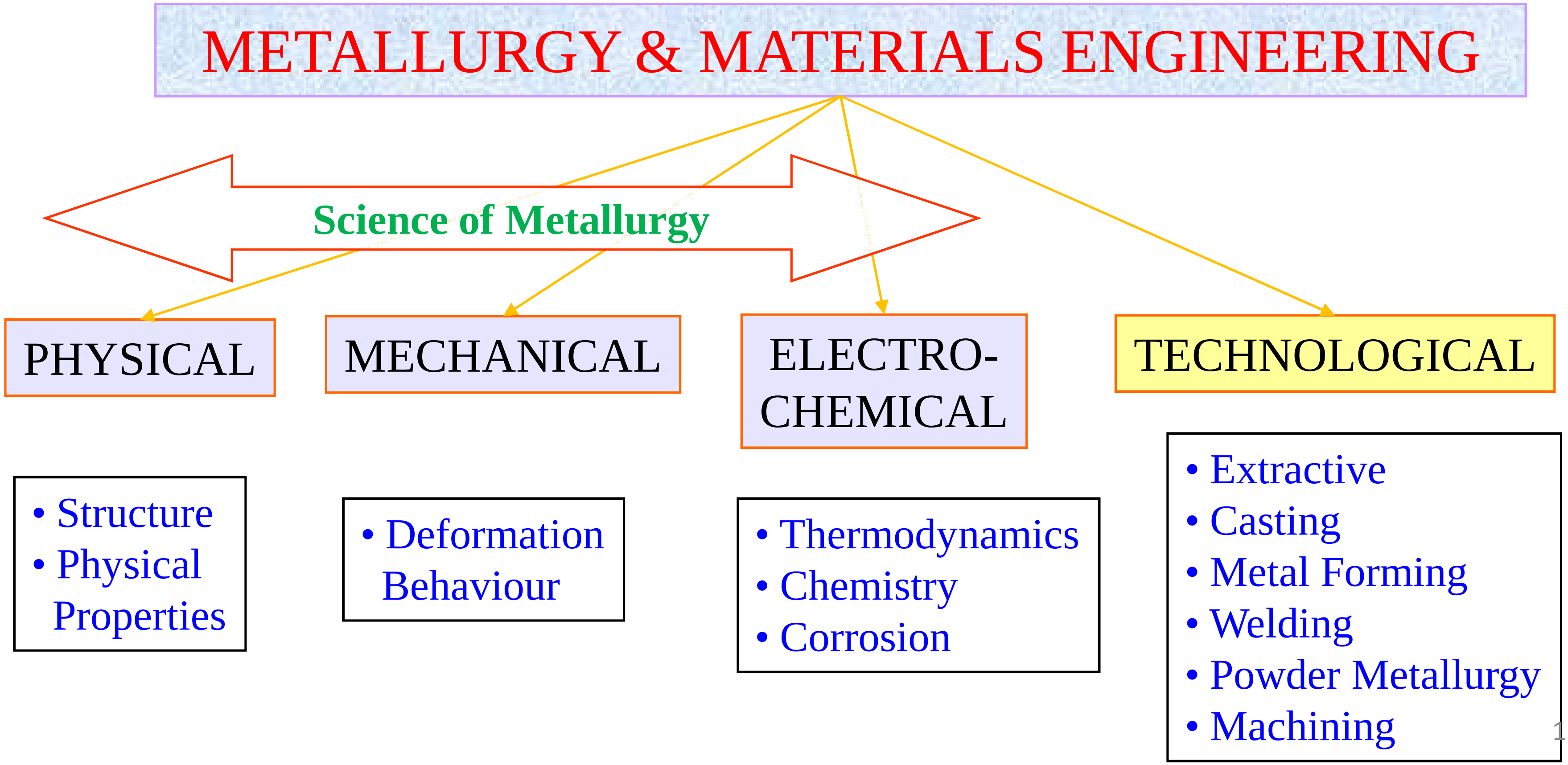
Integrated circuit (IC) or Silicon chip



Smaller and smaller microchips have brought the whole world on our palm top

A General Classification

- The broad scientific and technological segments of Metallurgy & Materials Science are shown in the diagram below.
- To gain a comprehensive understanding of Metallurgy, all these aspects have to be studied.



METALLURGY & MATERIALS ENGINEERING

Science of Metallurgy

PHYSICAL
- Structure
- Physical Properties

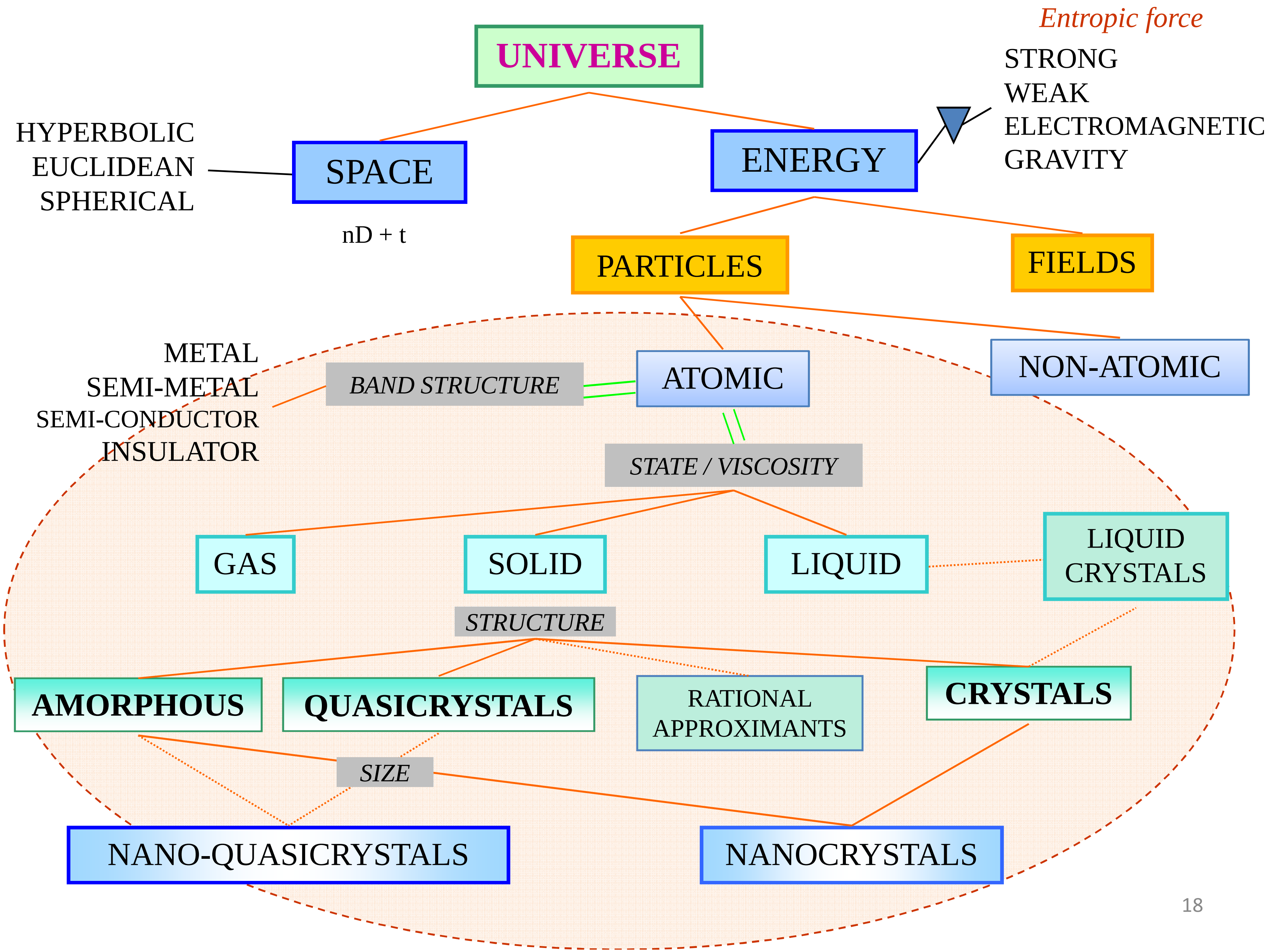
MECHANICAL
- Deformation Behaviour

ELECTRO-CHEMICAL
- Thermodynamics
- Chemistry
- Corrosion

TECHNOLOGICAL
- Extractive
- Casting
- Metal Forming
- Welding
- Powder Metallurgy
- Machining

A Broad Overview

- ☐ We shall start with a broad overview of .. well...almost everything! *(the next slide)*
- ☐ The typical domain of materials science is enclosed in the ellipse. *(next slide)*
- ☐ Traditionally materials were developed keeping in view a certain set of properties and were used for making components and structures.
- ☐ With the advancement of materials science, materials are expected to perform the role of an 'intelligent' structure or a mechanism.
  A good example of this would be applications of shape memory alloys:
  - ● they can be used to make deployable antennas (STRUCTURE) or
  - ● actuators (MECHANISM).
- ☐ Though it will not be practical to explain all aspects of the diagram (presented in the next slide) in this elementary course, the overall perspective should be kept at the back of one's mind while comprehending the subject.
- ☐ A point to be noted is that one way of classification does not clash with another. E.g. from a *state* perspective we could have a liquid which is a metal from the *band structure perspective*. Or we could have a metal *(band structure viewpoint)* which is amorphous *(structural viewpoint)*.



Entropic force

UNIVERSE

HYPERBOLIC
EUCLIDEAN
SPHERICAL

SPACE

nD + t

ENERGY

STRONG
WEAK
ELECTROMAGNETIC
GRAVITY

PARTICLES

FIELDS

METAL
SEMI-METAL
SEMI-CONDUCTOR
INSULATOR

BAND STRUCTURE

ATOMIC

NON-ATOMIC

STATE / VISCOSITY

GAS

SOLID

LIQUID

LIQUID CRYSTALS

STRUCTURE

AMORPHOUS

QUASICRYSTALS

RATIONAL APPROXIMANTS

CRYSTALS

SIZE

NANO-QUASICRYSTALS

NANOCRYSTALS

A Broad Overview

- ❑ Based on state (phase) a given material can be Gas, Liquid or Solid
  (based on the thermodynamic variables: P, T,…).
  Intermediate/coexistent states are also possible (i.e clear demarcations can get blurred).
  (Kinetic variables can also affect how a material behaves: e.g. at high strain rates some materials may behave as solids and as a liquid at low strain rates)
- ❑ Based on structure (arrangement of atoms/molecules/ions) materials can be Crystalline, Quasicrystalline or Amorphous.
  Intermediate states (say between crystalline and amorphous; i.e. partly crystalline) are also possible. *Polymers are often only partly crystalline.*
- ▪ Liquid Crystals (‘in some sense’) are between Liquids and Crystals.
- ❑ Based on Band Structure we can classify materials into Metals, Semi-metals, Semiconductors and Insulators.
- ▪ Based on the size of the entity in question we can Nanocrystals, Nanoquasicrystals etc.

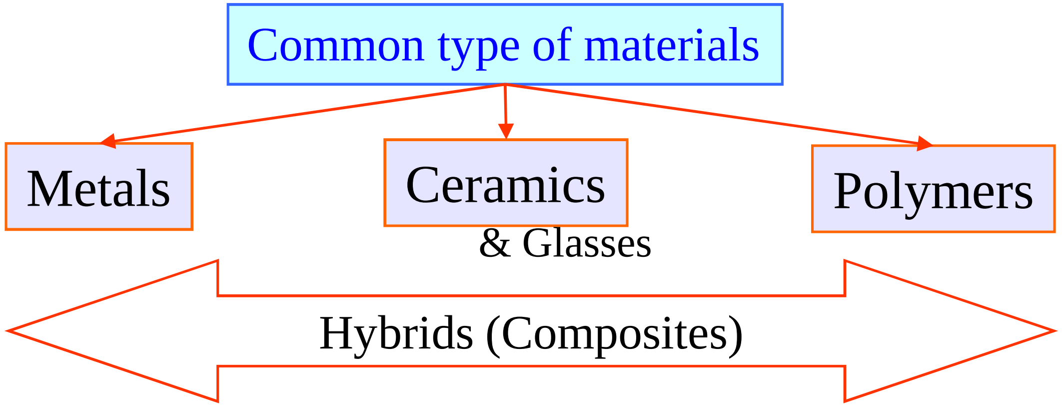
Strange?
A polycrystalline vessel for drinking fluids is sometimes referred to as GLASS!
And, a faceted glass object is sometimes referred to as a crystal!

Faceted glass objects are sometimes called crystals!

A Common Perspective

- Let us consider the common types of *Engineering Materials*.
- These are Metals, Ceramics, Polymers and various types of composites of these.
- A composite is a combination of two or more materials which gives a certain benefit to at least one property → A comprehensive classification is given in the next slide. The term Hybrid is a superset of composites.
- The type of atomic entities (ion, molecule etc.) differ from one class to another, which in turn gives each class a *broad 'flavour'* of properties.
  - Like metals are usually ductile and ceramics are usually hard & brittle
  - Polymers have a poor tolerance to heat, while ceramics can withstand high temperatures
  - Metals are opaque (in bulk), while silicate glasses are transparent/translucent
  - Metals are usually good conductors of heat and electricity, while ceramics are poor in this aspect.
  - If you heat semi-conductors their electrical conductivity will increase, while for metals it will decrease
  - Ceramics are more resistant to harsh environments as compared to Metals
- Biomaterials are a special class of materials which are compatible with the body of an organism ('biocompatible'). Certain metals, ceramics, polymers etc. can be used as biomaterials.

Bonding and structure are key factors in determining the properties of materials



Common type of materials

Metals

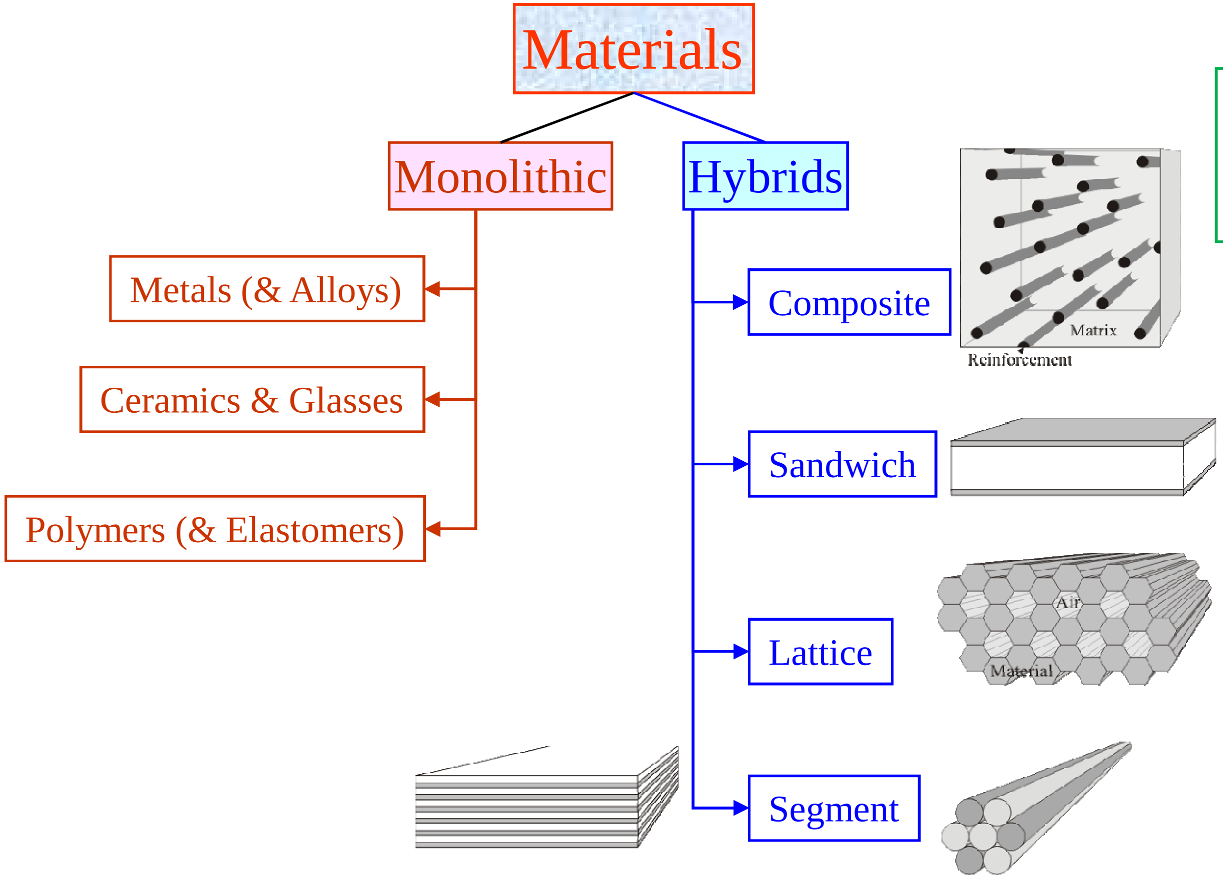
Ceramics & Glasses

Polymers

Hybrids (Composites)

Diamond is poor electrical conductor but a good thermal conductor!! (phonons are responsible for this)

Classification of materials



Materials

Monolithic

- Metals (& Alloys)
- Ceramics & Glasses
- Polymers (& Elastomers)

Hybrids

- Composite
- Sandwich
- Lattice
- Segment

Composites: have two (or more) solid components; usually one is a matrix and other is a reinforcement

Sandwich structures: have a material on the surface (one or more sides) of a core material

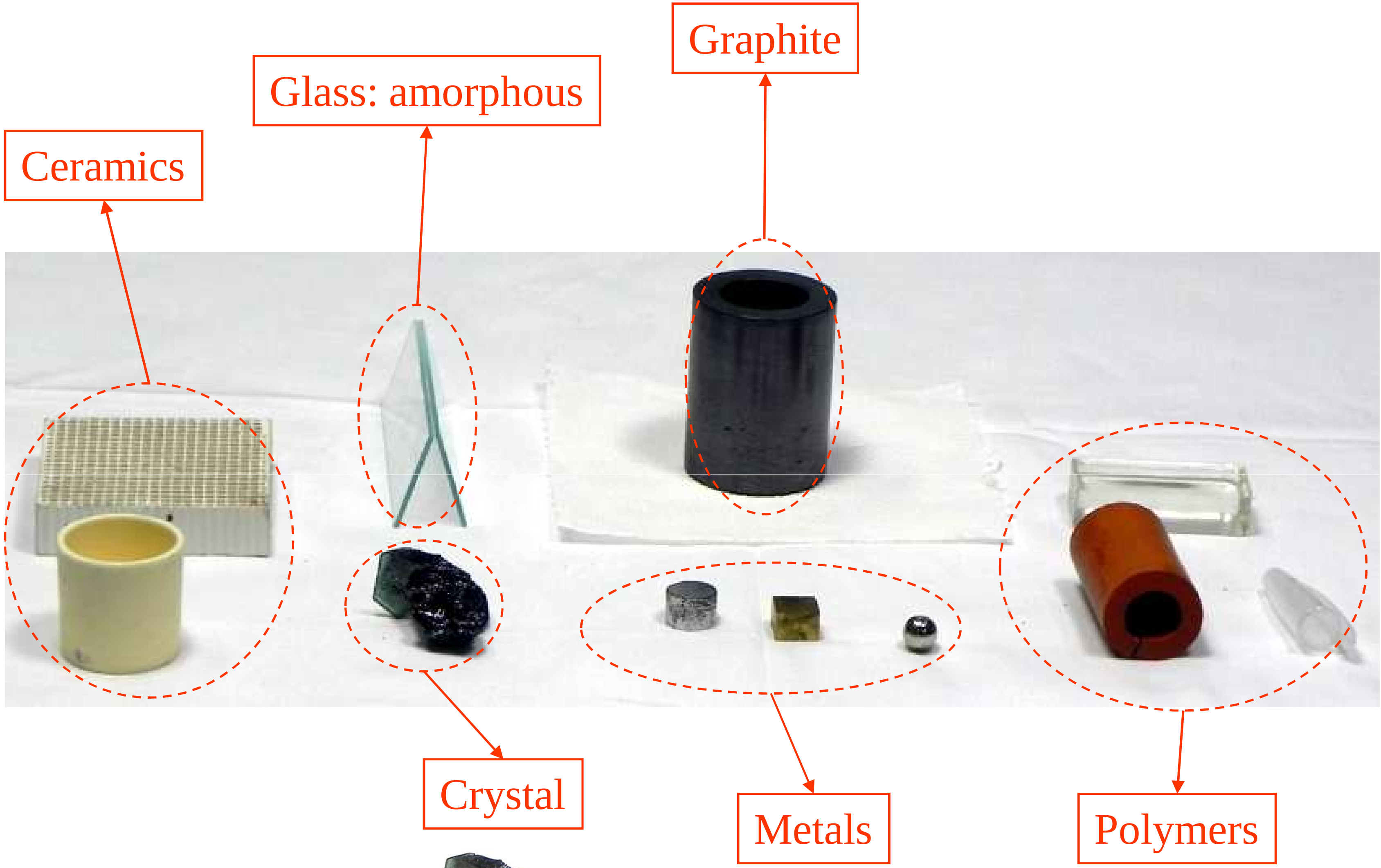
Lattice* Structures: typically a combination of material and space (e.g. metallic or ceramic forms, aerogels etc.).

Segmented Structures: are divided in 1D, 2D or 3D (may consist of one or more materials).

Hybrids are designed to improve certain properties of monolithic materials

*Note: this use of the word 'lattice' should not be confused with the use of the word in connection with crystallography.

common materials : with various ‘viewpoints’

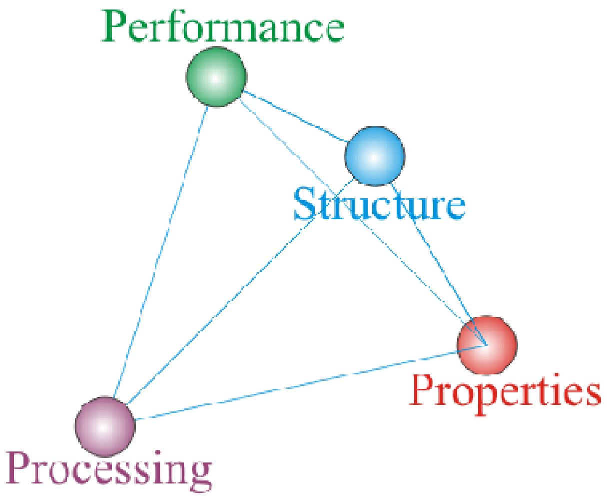


Classes of property

Economic	Price and Availability, Recyclability
General Physical	Density
Mechanical	Modulus, Yield and Tensile strength, Hardness, Fracture strength, Fatigue strength, Creep strength, Damping
Thermal	Thermal conductivity, Specific Heat
Electric & Magnetic	Resistivity, Dielectric constant, Magnetic permeability
Environmental interactions	Oxidation, corrosion and wear
Production	Ease of manufacturer, joining, finishing
Aesthetic (Appearance)	Colour, Texture, Feel.

The Materials Tetrahedron

- ❑ A materials scientist has to consider four ‘intertwined’ concepts, which are schematically shown as the ‘Materials Tetrahedron’.
- ❑ ▪ When a certain performance is expected from a component (and hence the material constituting the same), the ‘expectation’ is put forth as a set of properties.
  - ▪ The material is synthesized and further made into a component by a set of processing methods (casting, forming, welding, powder metallurgy etc.).
  - ▪ The structure (at various lengthscales) is determined by this processing.
  - ▪ The structure in turn determines the properties, which will dictate the performance of the component.
- ❑ Hence each of these aspects is dependent on the others.

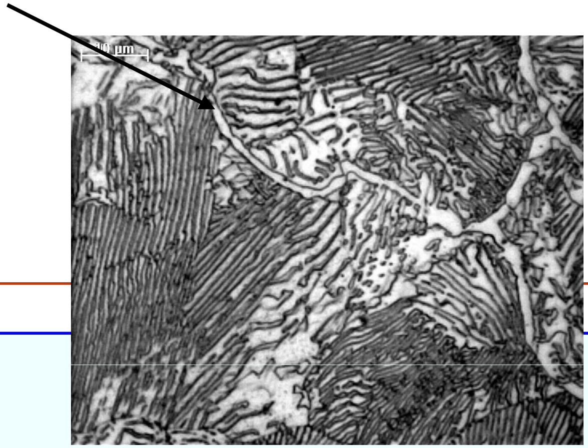


The Materials Tetrahedron

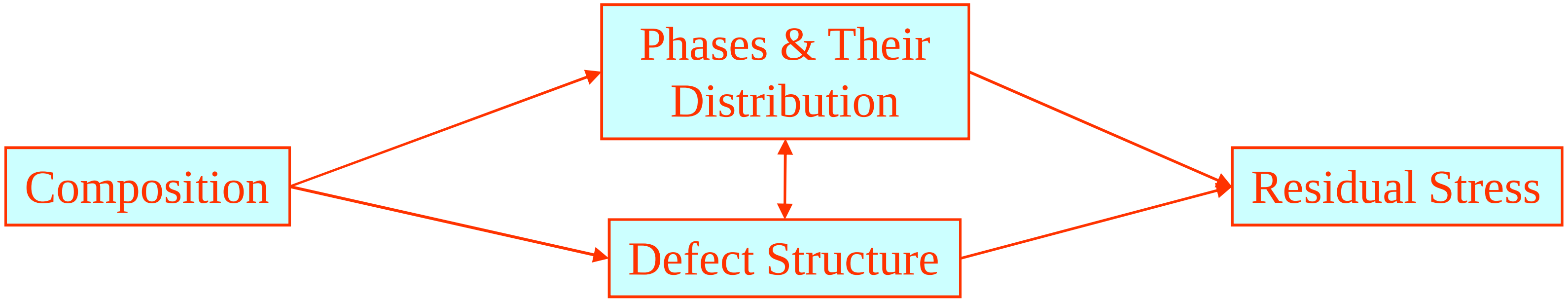
The broad goal of Metallurgy & Materials Engineering is to understand and ‘Engineer’ this Tetrahedron

❑ What determines the properties of materials?

- ➢ Cannot just be the composition!
  - ➔ Few 10s of ppm of Oxygen in Cu can degrade its conductivity
- ➢ Cannot just be the amount of phases present!
  - ➔ A small amount of cementite along grain boundaries can cause the material to have poor impact toughness
- ➢ Cannot just be the distribution of phases!
  - ➔ Dislocations can severely weaken a crystal
- ➢ Cannot just be the defect structure in the phases present!
  - ➔ The presence of surface compressive stress toughens glass

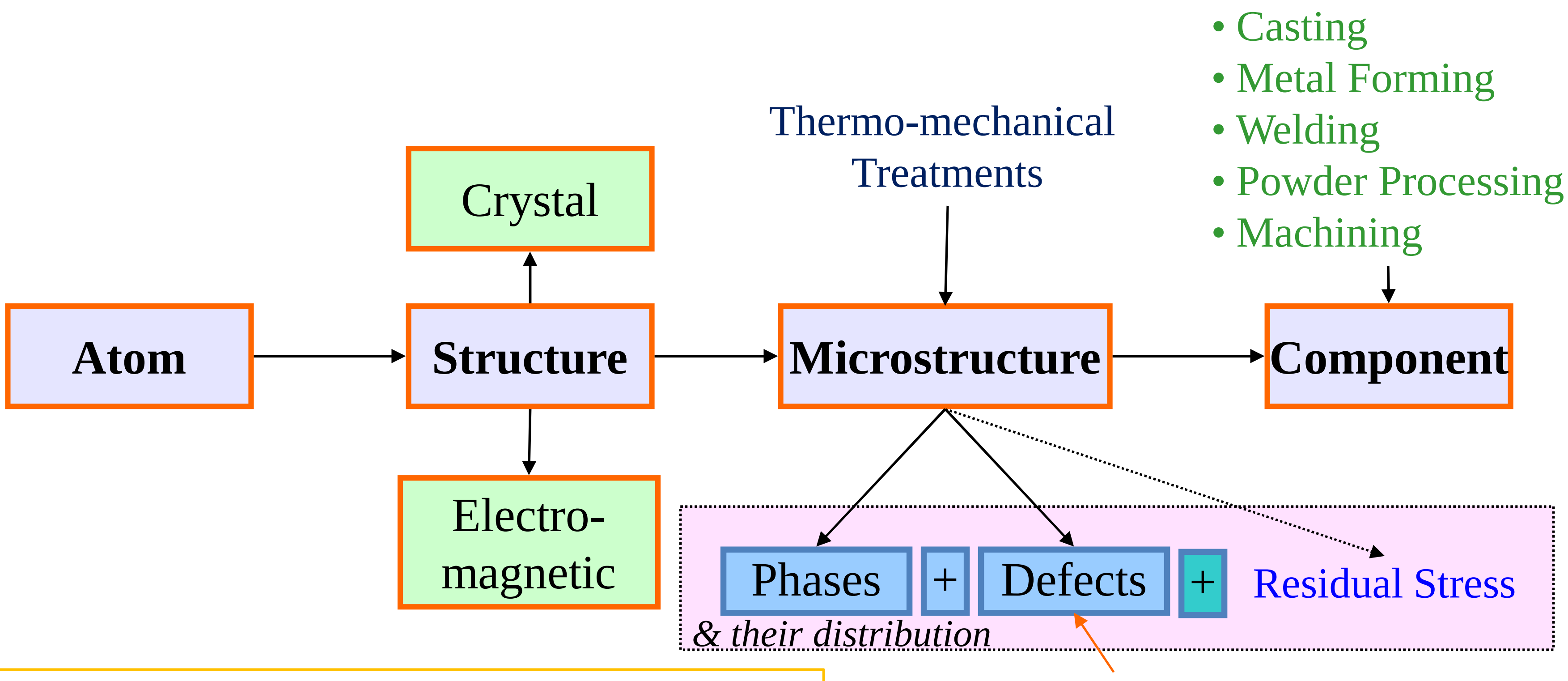


- ❑ The following factors put together determines the properties of a material:
  - ➢ Composition
  - ➢ Phases present and their distribution
  - ➢ Defect Structure *(in the phases and between the phases)*
  - ➢ Residual stress *(can have multiple origins and one may have to travel across lengthscales)*
- ❑ These factors do NOT act independent of one another *(there is an interdependency)*



Hence, one has to *traverse across lengthscales* and look at various aspects to understand the properties of materials

Length scales in metallurgy



Thermo-mechanical Treatments

- Casting
- Metal Forming
- Welding
- Powder Processing
- Machining

Crystal

Atom → **Structure** → **Microstructure** → **Component**

Electro-magnetic

Phases + Defects + Residual Stress

& their distribution

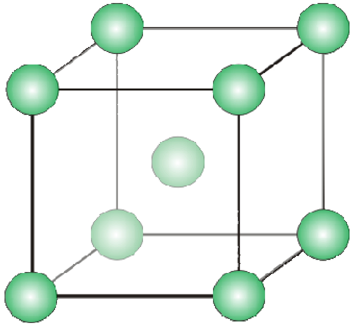
- ❑ Structure could imply two types of structure:
  - ➢ Crystal structure
  - ➢ Electromagnetic structure
  - ▪ *Fundamentally these aspects are two sides of the same coin*
- ❑ Microstructure can be defined as: (Phases + Defect Structure + Residual Stress) *and their distributions*
- ❑ Microstructure can be 'tailored' by thermo-mechanical treatments

- Vacancies
- Dislocations
- Twins
- Stacking Faults
- Grain Boundaries
- Voids
- Cracks

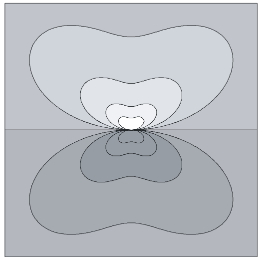
Processing determines shape and microstructure of a component

Length scales in metallurgy

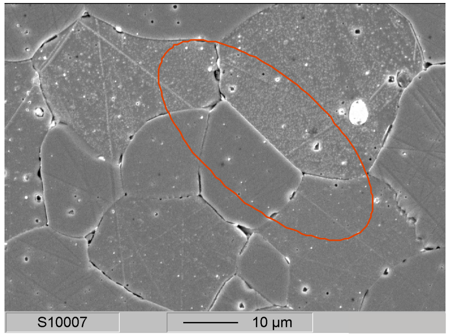
Let us start with a cursory look at the lengthscales involved in Materials Science



Angstroms

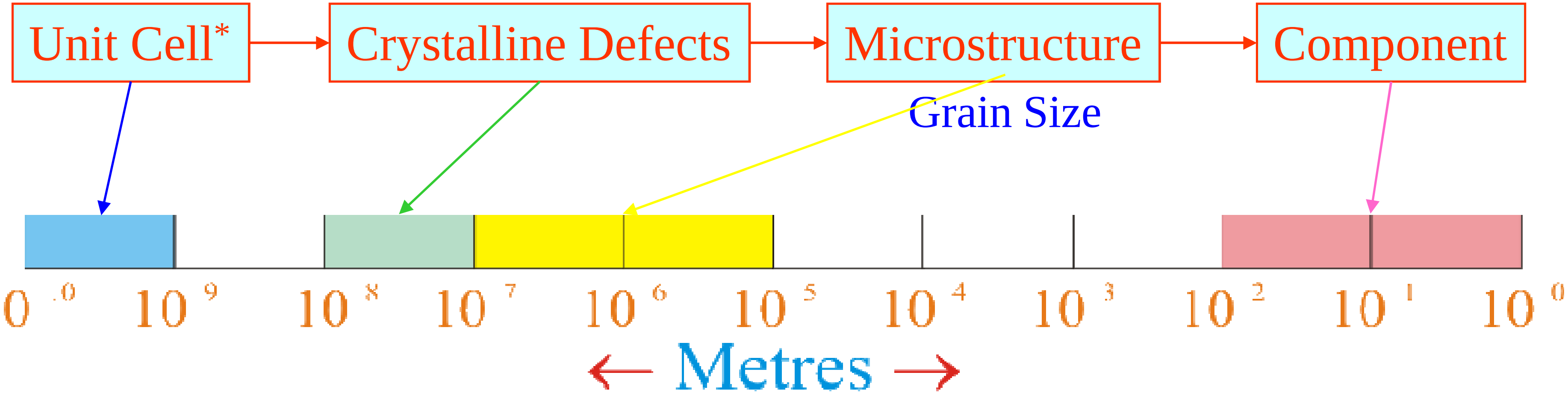


Dislocation Stress fields → Nanometers



Microns

Centimeters



Unit Cell* → Crystalline Defects → Microstructure → Component

Grain Size

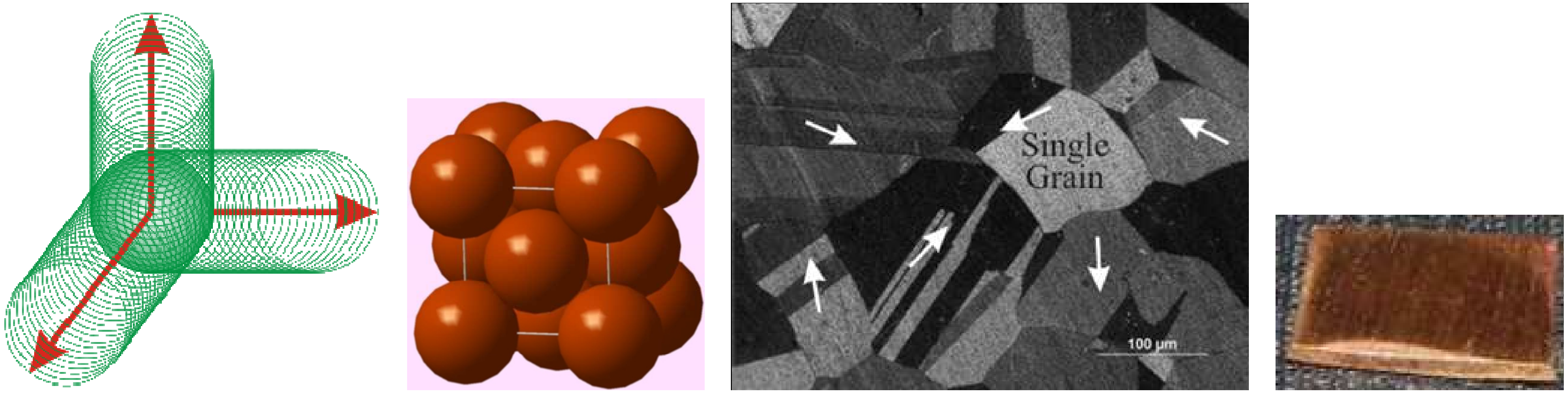
← Metres →

*Simple Unit Cells

Change of properties across lengthscales: polycrystalline copper (CCP structure)

Atomic level (Å) → Unit Cell level (few Å-nm)→ Grain level (nm-μm) → Material level (cm)

- At the atomic level there is order only in the average sense (at $T > 0K$) as the atoms are constantly vibrating about the mean lattice position. Hence, in a strict sense the perfect order is missing (a). The unit cell level is the level where the atomic arrangement becomes evident (crystal structure develops) and concepts like Burgers vector emerge, b. It is at this level that averaging with respect to probabilistic occupation of lattice positions in disordered alloys is made (say Ni_{50}-Al_{50} alloy is defined by a 50-50 probability of Ni or Al occupying a lattice position). At the grain level (c, which is a single crystal), there is nearly perfect order (as the scale of atomic vibrations are too small compared to grain scale); except for the presence of defects like vacancies, dislocations etc. At this scale the material is also anisotropic (e.g. with respect to the elastic stiffness, which is represented by three independent numbers: E_{11}, E_{12} & E_{44}). It is to be noted that the Cu crystal may be isotropic with respect to other properties. At the material level (d), assuming that the grains are randomly oriented, there is an averaging of the elastic modulii and the material becomes isotropic. At this scale, the crystalline order which was developed at the grain level (c) is destroyed at the grain boundaries and there is no long range order across the sample. When the material is rolled or extruded, it will develop a *texture* (preferred directional properties), which arises due to partial reorientation of the grains. That is, we have recovered some of the inherent anisotropy at the grain scale. As we can see, concepts often get 'inverted' as we go from one lengthscale to another.



(a) Thermal vibration (b) Unit cell of Cu (c)Grain Structure (d) Sample of Cu

Traversing four lengthscales in a Cu polycrystal: schematic of the changing order and properties. a) instantaneous snapshot of a vibrating atom, b) crystalline order (unit cell), c), grain level (single crystal- anisotropy) , d) the material level (isotropy due to randomly oriented grains).

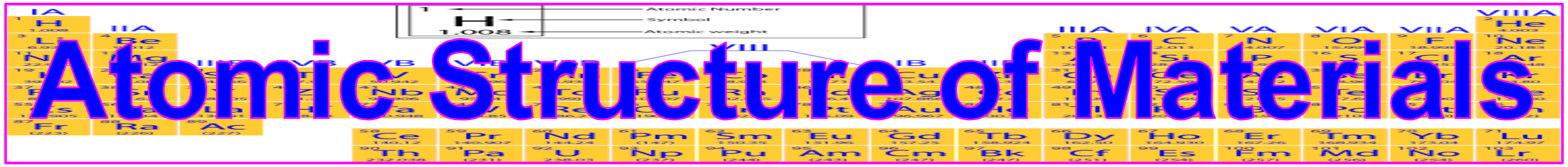
Summary

- ☐ Properties of a material are determined by two important characteristics:
  - ➢ Atomic structure
  - ➢ Electromagnetic structure – the bonding character

(Bonding in some sense is the simplified description of valence electron density distributions)

- ☐ There are microstructure 'sensitive' properties (often called structure sensitive properties) and microstructure insensitive properties *(note the word is sensitive and not dependent).*
- ☐ ➢ Microstructure 'sensitive' properties → Yield stress, hardness, Magnetic coercivity…
  - ➢ Microstructure insensitive properties → Density, Elastic modulus…
- ☐ Hence, one has to keep in focus:
  - ➢ Atomic structure
  - ➢ Electromagnetic structure/Bonding
  - ➢ Microstructure

  to understand the properties.



Atomic Structure of Materials

Avala Lava Kumar *: Suneeti Purohit : Gautam Behera

Department of Metallurgical & Materials Engineering (MME)

Veer Surendra Sai University of Technology (VSSUT), Burla -768018

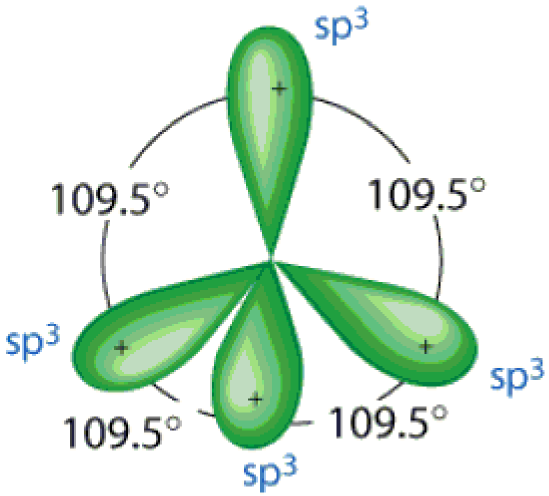
**E-mail : lavakumar.vssut@gmail.com*

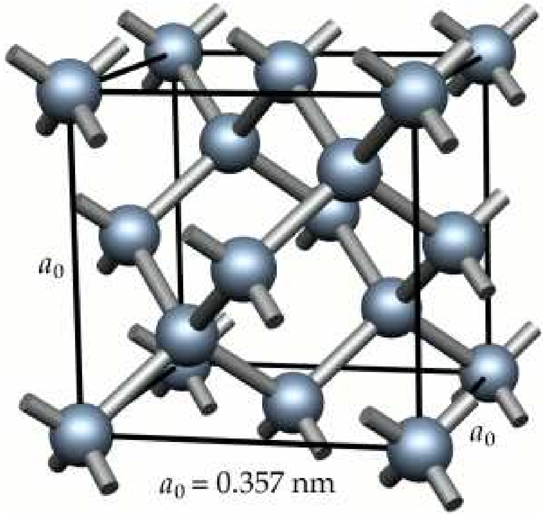
Introduction

- *In order to understand the structure of materials and its correlation to property, we have to start form the basic element of matter – The Atom*
- An atom consists of a nucleus composed of protons and neutrons and electrons which encircle the nucleus.
- Protons and electrons have same and opposite charge of 1.6 x10^{-19} C.
- Atomic number (Z) = Number protons = number of electrons
- Atomic mass (A) = proton mass + neutron mass
- Isotopes are the same element having different atomic masses. Number of protons in isotopes remains same while number of neutrons varies.
- Atomic mass unit (amu) = 1/12 mass of Carbon 12 (^{12}C)
- 1 mol of substance contains 6.023 x 10^{23} (Avogadro’s number) atoms or molecules.
- Atomic weight = 1 amu/atom (or molecule) = 1 g/mol = Wt. of 6.023 x 10^{23} atoms or molecules.
    - For example, atomic weight of copper is 63.54 amu/atom or 63.54 g/mole

Role of atomic structure in materials

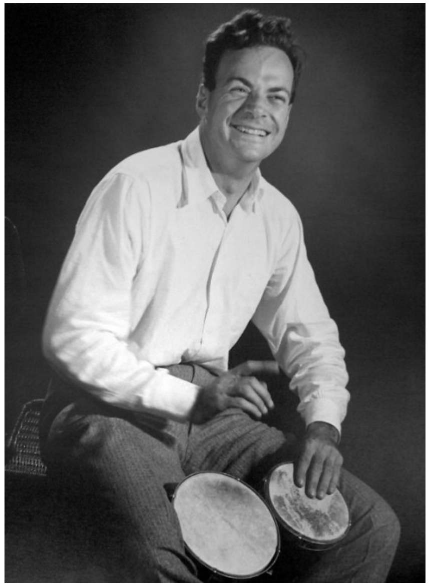
- As we know, common to all materials is that they are composed of **atoms**.
- The properties (whether mechanical, electrical, chemical etc) of all solid materials are dependent upon the relative positions of the atoms in the solid (in other words the atomic structure of the material) and their mutual interaction i.e. the nature of the bonding (whether e.g. covalent, ionic, metallic, van der Waals).
- There are examples of where the atom-atom interactions is strongly reflected in the atomic structure. An example is diamond. Here the carbon-carbon interactions lead to a very directional covalent bond called a sp^3 bond which has tetrahedral symmetry – this leads to an open structure as shown below.





Role of atomic structure in materials

- ☐ Of course carbon can also take the form of graphite. Here the carbon atoms are arranged in a rather different structure and graphite has very different properties to diamond!
- ☐ In other solid systems (for example many of the metallic elements) the atomic structure is dictated by how well we can 'pack' the atoms into 3D space – 'packing efficiency' – this leads to dense close-packed structures as we will also discuss in *crystal structure* chapter.
- ☐ So it is vital that to understand the properties of material, and to improve those properties for example by adding or removing atoms, we need to know the material's atomic structure.

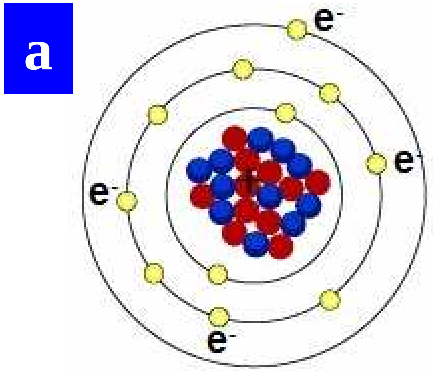


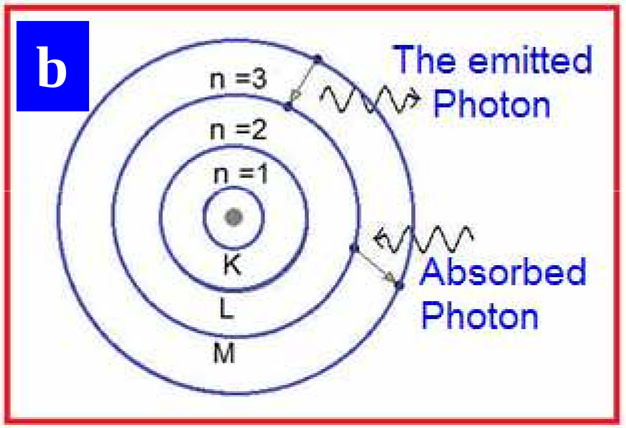
As Richard Feynman said….!

> ***"It would be very easy to make an analysis of any complicated chemical substance; all one would have to do would be to look at it and see where the atoms are…"***

Atomic structure : The Bohr model

- ❑ Electrons revolve around a positively charged nucleus in discrete orbits (K, L, M or n=1, 2, 3 respectively) with specific levels of energy.
- ❑ Electrons positions are fixed as such, however, an electron can jump to higher or lower energy level by absorption or emission of energy respectively.





Limitations of the Bohr Model

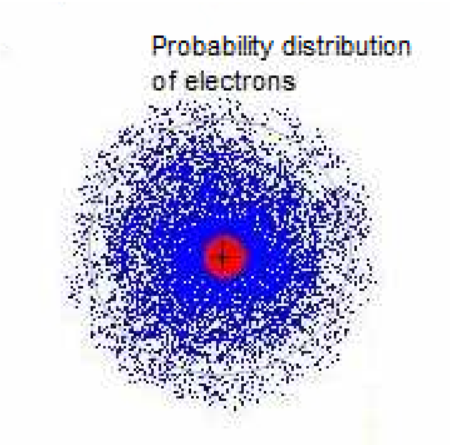
- ❑ Although the Bohr's model was the first and best model available at the time of its discovery, it had certain limitations and could not explain many phenomena involving electrons

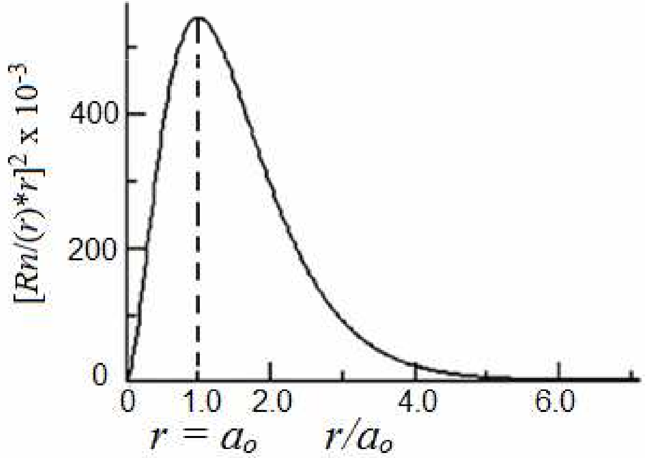
Heisenberg's uncertainty principle:

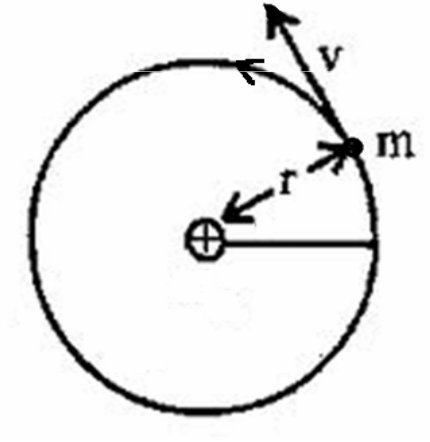
The position and momentum of an electron can not be determined simultaneously. This also disapproves the hypothesis in the Bohr model that electrons revolve around certain circular orbits

Wave-Mechanical Model

- The wave-mechanical or wave-particle model was proposed to address the limitations in the Bohr model.
- The basic premise of this model is the wave-particle duality of electrons i.e. electrons are considered to have both wave-like and particle-like characteristics.
- The position of an electron is defined as the probability of finding it at different locations in an electron cloud around the nucleus i.e. position of an electron is described by a probability distribution instead of discrete orbits.







Probability distribution vs. distance from nucleus

Probability of finding an electron is maximum at the Bohr radius

The Bohr radius, r = $\dfrac{4\pi\varepsilon_0\hbar^2}{me^2}$

Quantum Numbers

- ☐ Four parameters or numbers called Quantum numbers are needed to describe the distribution and position of electrons in an atom.
- ☐ The first three of them (n, ℓ, m_ℓ) describe the size, shape, and spatial orientation of the probability density distribution of electrons

Principal quantum number, ***n***

- ☐ It describes electron shells as shown in the Bohr model. Values of ***n*** can be 1, 2, 3, 4….. Corresponding to electron shells K, L, M, N……. The value of ***n*** also determines the size or distance of the shells from the nucleus.
- ☐ Number of electrons in a shell = $2n^2$ for example; number of electrons in K shell ($n=1$) = 2×1^2 = 2, and L shell ($n=2$) = 2×2^2 = 8 and so on.

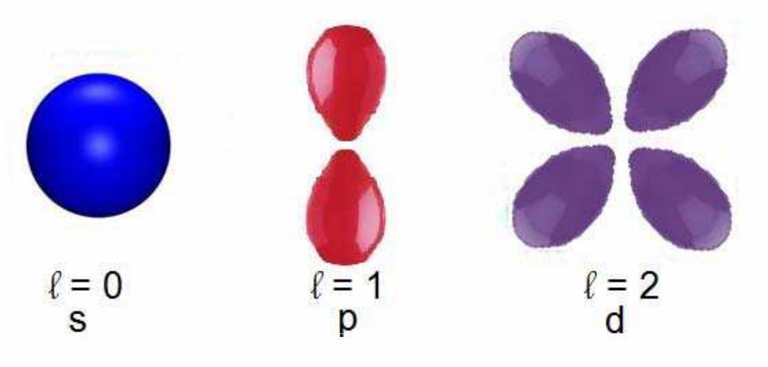
Azimuthal or Angular quantum number, $\boldsymbol{\ell}$

- ☐ It signifies subshell or electron orbital – s, p, d, f and so on. I can take values of from 0 to n-1. K shell, n = 1, one 's' orbital. L, n=2, two orbitals, s, p. M, n=3, three orbitals s, p, d. for N, n=4, four orbital's s, p, d, f and so on.

Quantum Numbers

Azimuthal or Angular quantum number, ℓ

- The value of ℓ decides the shape of the orbital as shown in the figure below. ‘s’ orbital (ℓ =0) – spherical, p (ℓ =1)- polar or dumbbell shaped, d(ℓ =2) – double-dumbbell shaped.



Magnetic quantum number, m_ℓ

- Orbital's are associated with energy states. Magnetic quantum number determines the number of energy states in each orbital.
- This number depends on the value of ℓ . m_ℓ can take values from $-\ell$ to $+\ell$ e.g. $\ell = 1$ (p orbital) m_ℓ = -1, 0, +1 (three states). Only one state for the s orbital (ℓ = 0), as m_ℓ can take only one value (0). In general no. of states = $2\ell+1$

Orbital	S	p	d	f
No. of states	1	3	5	7

Quantum Numbers

Spin quantum number, m_s

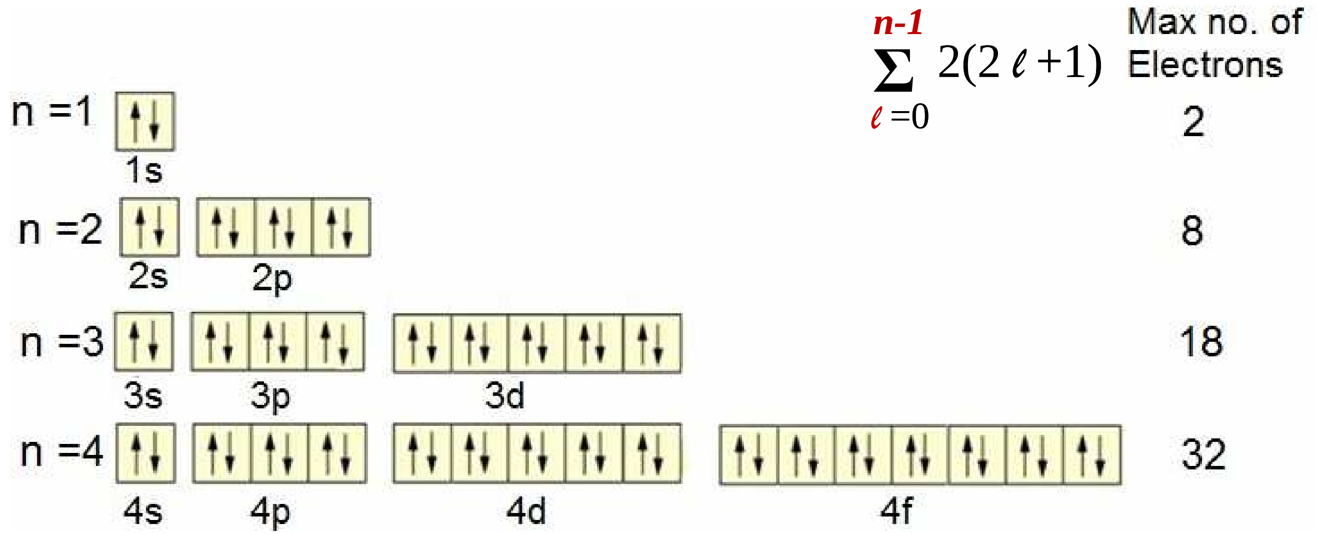
- Each electron is associated with a spin moment. The fourth quantum number, ms is related to this spin moment of electrons. It can have only two values, + ½ and – ½.

Pauli’s exclusion principle

- It states that not more than two electrons having opposite spin can occupy the same energy state.
- Based on this principle, number of electrons in different orbital's (s, p, d ….) can be obtained. For example, ‘s’ orbital has only one energy state, so it can accommodate only two electrons having opposite spins.

Electron Configuration

The quantum mechanic principles as discussed before allow determination of electron configuration i.e. the manner in which electron states are occupied in a given atom.Σ



$$\sum_{\ell=0}^{n-1} 2(2\ell+1)$$

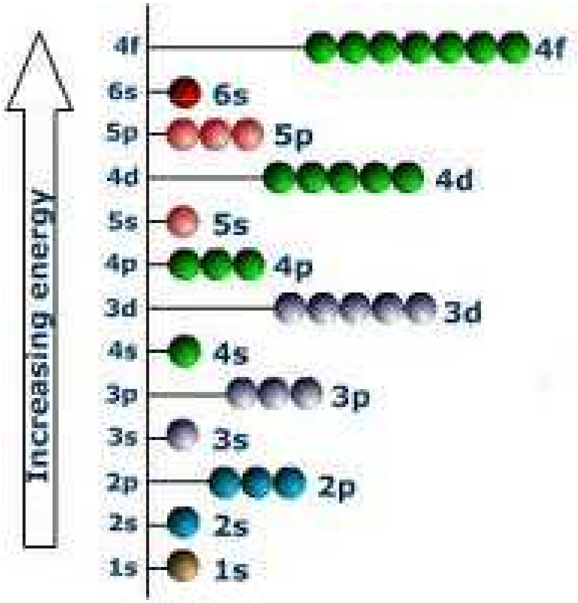
Electron configuration based on quantum numbers. Total number of electrons in a shell is $2n^2$ or $\sum_{\ell=0}^{n-1} 2(2\ell+1)$

The manner or sequence of filling of electron orbital's is decided a by a set of two principles / rules:

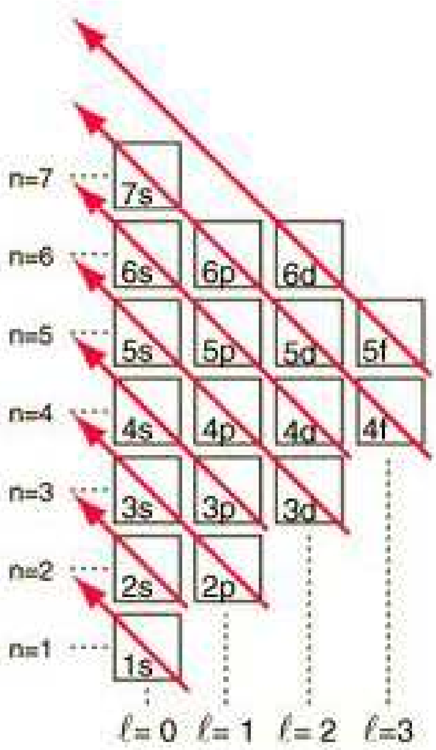
- ❑ Aufbau principle
- ❑ Madelung's rule

Electron Configuration

- Aufbau principle (German meaning is *building up*) : it states that lower energy states will be filled up first.
- Madelung's rule : Orbitals fill in the order of increasing ($n+\ell$). 4s ($n+\ell = 4+0 = 4$) will be filled before 3d ($n+\ell = 3+2 = 5$) and 5s ($n+\ell = 5+0 = 5$)
- For orbital with same values of ($n+\ell$), the one with lower 'n' will be filled first. 3d will be filled before 4p.



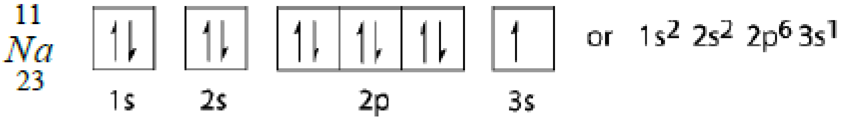
Aufbau principle



Madelung rule

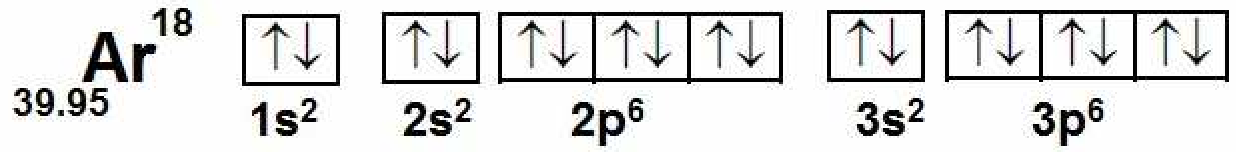
Electron Configuration

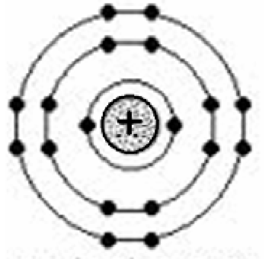
- Based on the foregoing discussion, it is now possible to find the electron configuration for a given atom.
- For example, sodium Na^{11}_{23} has 11 electrons – the configuration is shown in the first figure. The second picture shows the Bohr configuration.



Valence electrons

- The electrons in the outer most shell are known as valence electrons. Na has one valence electron (the 3s electron). These electrons are responsible for chemical reaction and atomic bonding.
- Look at the electron configuration of inert gases (He, Ne, Ar, Kr, Xe) in the previous table. Their valence electron cell is completely filled unlike any other element.



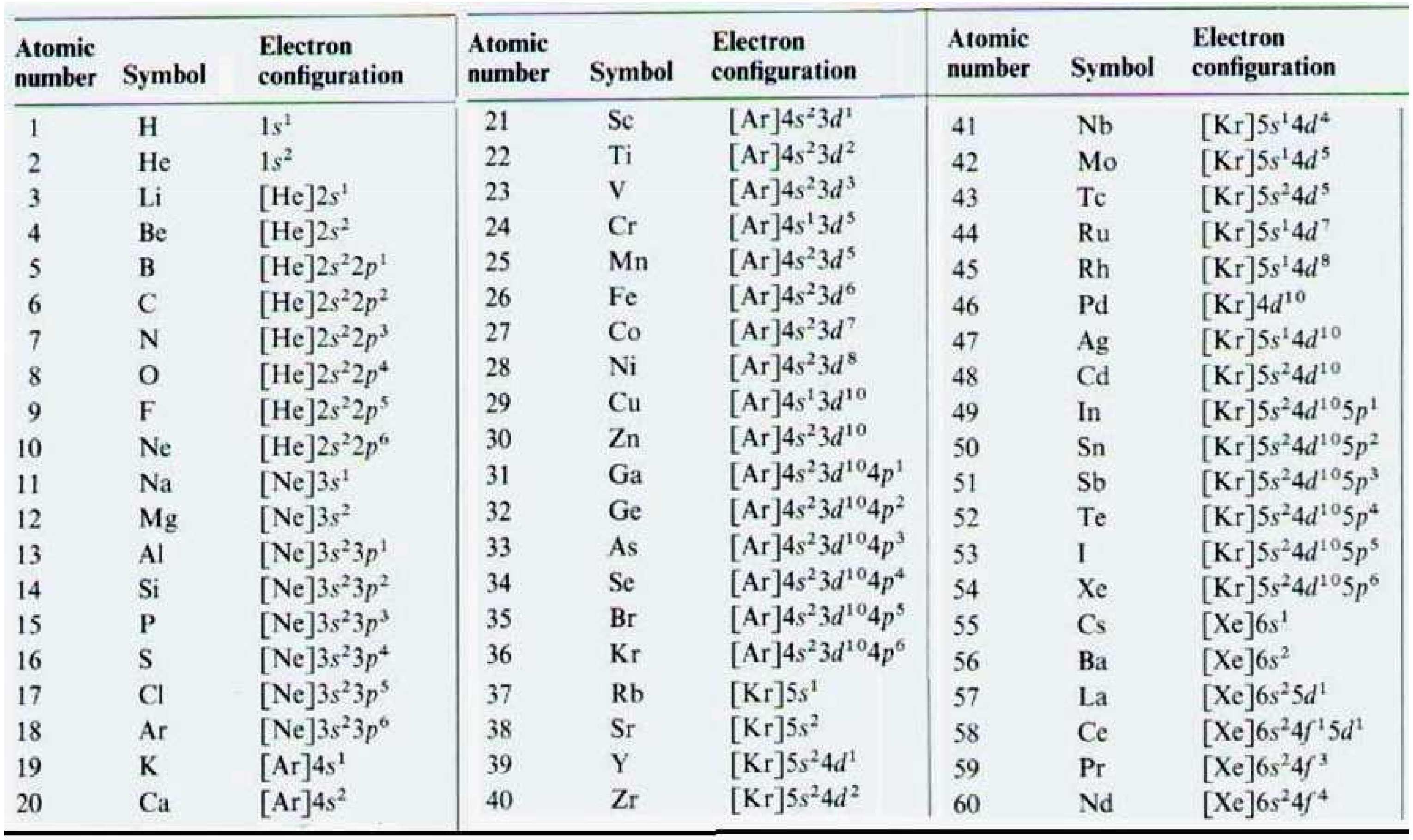


Ar (18) 2,8,8

Electron Configuration

- ❑ Note that the configuration of higher atomic number elements can be expressed by the previous inert element configuration.
- ❑ It is the tendency of every element to attain the lowest energy stable configuration that forms the basis of chemical reactions and atomic bonding.

Electron Configuration of Elements

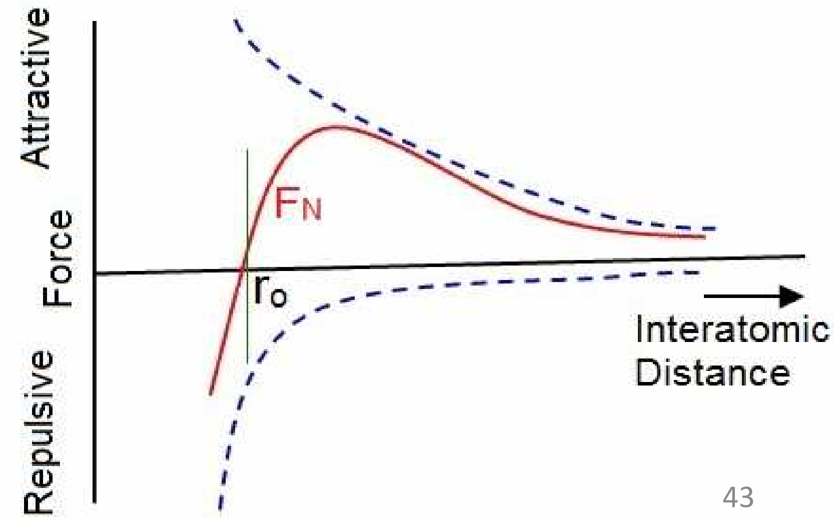


Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration
1	H	$1s^1$	21	Sc	[Ar]$4s^23d^1$	41	Nb	[Kr]$5s^14d^4$
2	He	$1s^2$	22	Ti	[Ar]$4s^23d^2$	42	Mo	[Kr]$5s^14d^5$
3	Li	[He]$2s^1$	23	V	[Ar]$4s^23d^3$	43	Tc	[Kr]$5s^24d^5$
4	Be	[He]$2s^2$	24	Cr	[Ar]$4s^13d^5$	44	Ru	[Kr]$5s^14d^7$
5	B	[He]$2s^22p^1$	25	Mn	[Ar]$4s^23d^5$	45	Rh	[Kr]$5s^14d^8$
6	C	[He]$2s^22p^2$	26	Fe	[Ar]$4s^23d^6$	46	Pd	[Kr]$4d^{10}$
7	N	[He]$2s^22p^3$	27	Co	[Ar]$4s^23d^7$	47	Ag	[Kr]$5s^14d^{10}$
8	O	[He]$2s^22p^4$	28	Ni	[Ar]$4s^23d^8$	48	Cd	[Kr]$5s^24d^{10}$
9	F	[He]$2s^22p^5$	29	Cu	[Ar]$4s^13d^{10}$	49	In	[Kr]$5s^24d^{10}5p^1$
10	Ne	[He]$2s^22p^6$	30	Zn	[Ar]$4s^23d^{10}$	50	Sn	[Kr]$5s^24d^{10}5p^2$
11	Na	[Ne]$3s^1$	31	Ga	[Ar]$4s^23d^{10}4p^1$	51	Sb	[Kr]$5s^24d^{10}5p^3$
12	Mg	[Ne]$3s^2$	32	Ge	[Ar]$4s^23d^{10}4p^2$	52	Te	[Kr]$5s^24d^{10}5p^4$
13	Al	[Ne]$3s^23p^1$	33	As	[Ar]$4s^23d^{10}4p^3$	53	I	[Kr]$5s^24d^{10}5p^5$
14	Si	[Ne]$3s^23p^2$	34	Se	[Ar]$4s^23d^{10}4p^4$	54	Xe	[Kr]$5s^24d^{10}5p^6$
15	P	[Ne]$3s^23p^3$	35	Br	[Ar]$4s^23d^{10}4p^5$	55	Cs	[Xe]$6s^1$
16	S	[Ne]$3s^23p^4$	36	Kr	[Ar]$4s^23d^{10}4p^6$	56	Ba	[Xe]$6s^2$
17	Cl	[Ne]$3s^23p^5$	37	Rb	[Kr]$5s^1$	57	La	[Xe]$6s^25d^1$
18	Ar	[Ne]$3s^23p^6$	38	Sr	[Kr]$5s^2$	58	Ce	[Xe]$6s^24f^15d^1$
19	K	[Ar]$4s^1$	39	Y	[Kr]$5s^24d^1$	59	Pr	[Xe]$6s^24f^3$
20	Ca	[Ar]$4s^2$	40	Zr	[Kr]$5s^24d^2$	60	Nd	[Xe]$6s^24f^4$

Atomic Interaction

- When two neutral atoms are brought close to each other, they experience attractive and or repulsive force.
- Attractive force is due to electrostatic attraction between electrons of one atom and the nucleus of the other.
- Repulsive force arises due to repulsion between electrons and nuclei of the atoms.
- The net force, F_N (Fig) acting on the atoms is the summation of attractive and repulsive forces.
- The distance, at which the attraction and repulsion forces are equal and the net force is zero, is the equilibrium interatomic distance, r_o . The atoms have lowest energy at this position.

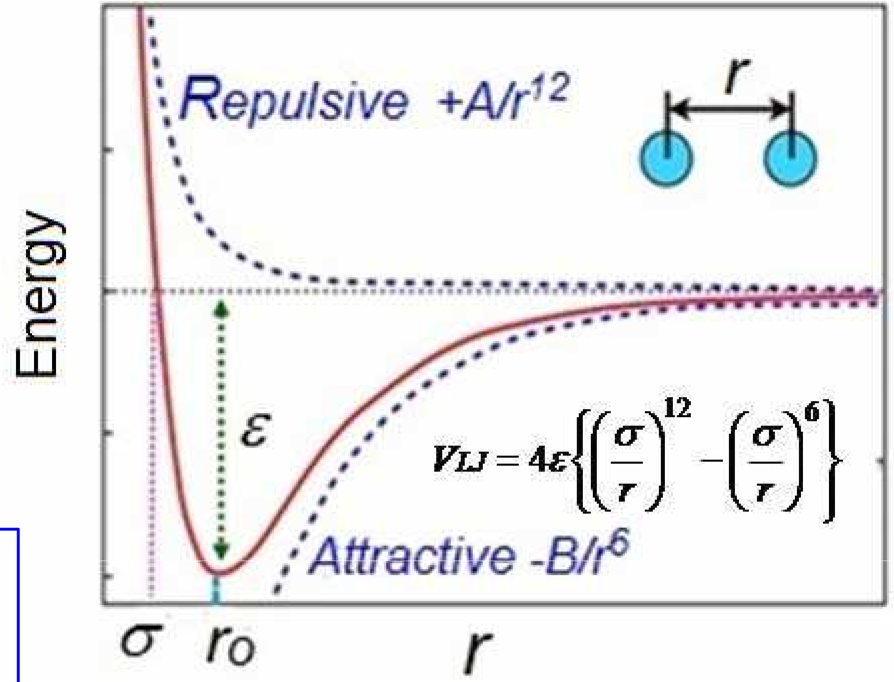
- Attraction is predominant above r_o and repulsion is dominant below r_o.



Atomic Interaction

The interaction energy between the pair of atoms is given by the Lennard-Jones potential, V_r or V_{LJ}

$$V_{LJ} = 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\}$$



Lennard-Jones potential

- σ is the distance at which the interaction energy is zero.ε is the depth of the potential well and is a measure of the bonding energy between two atoms.

- L-J potential can be also expresses in the simplified form as $V_{LJ} = A/r^{12} - B/r^{6}$ and hence, is also known as 6-12 potential.
- A/r^{12} is predominant at short distances and hence, represents the short-range repulsive potential due to overlap of electron orbital’s and $-B/r^{6}$ is dominant at longer distance and hence, is the long range attractive potential.

Atomic Bonding

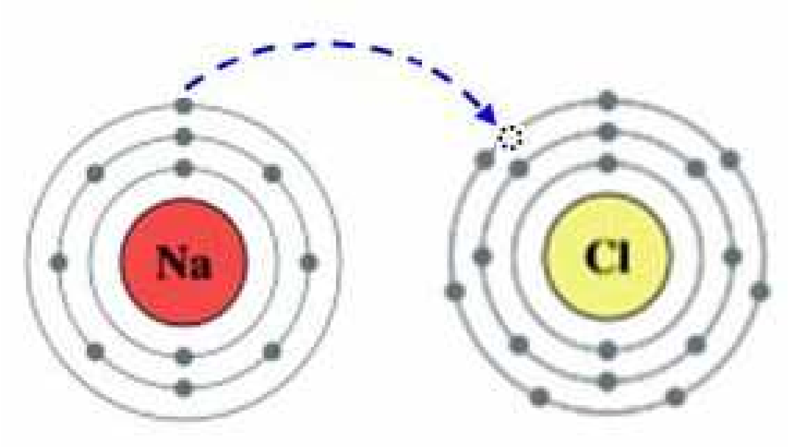
- The mechanisms of bonding between the atoms are based on the foregoing discussion on electrostatic inter- atomic interaction.
- The types of bond and bond strength are determined by the electronic structures of the atoms involved.
- The valence electrons take part in bonding. The atoms involved acquire, loose or share valence electrons to achieve the lowest energy or stable configuration of noble gases.
- Atomic bonding can be broadly classified as i) primary bonding ii) secondary bonding

- **Primary Bonds**
  - **Ionic**
  - **Covalent**
  - **Metalic**
- **Secondary Bonds**
  - **Vanderwaals**
  - **Hydrogen**

- Majority of the engineering materials consist of one of these bonds. Many properties of the materials depend on the specific kind of bond and the bond energy.

Ionic Bond

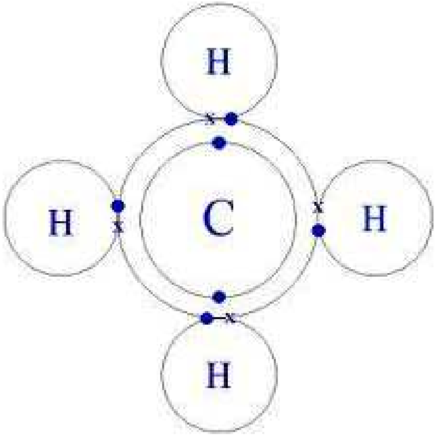
- Ionic bonds are generally found in compounds composed of metal and non-metal and arise out of electrostatic attraction between oppositely charged atoms (ions).
- Number of electron in outer shell is 1 in Na and 7 in Cl . Therefore, Na will tend to reject one electron to get stable configuration of Ne and Cl will accept one electron to obtain Ar configuration.
- The columbic attraction between Na+ and Cl^{-} ions thus formed will make an ionic bond to produce NaCl.



- Some other examples are CaF_2 , CsCl, MgO, Al_2O_3

Covalent Bond

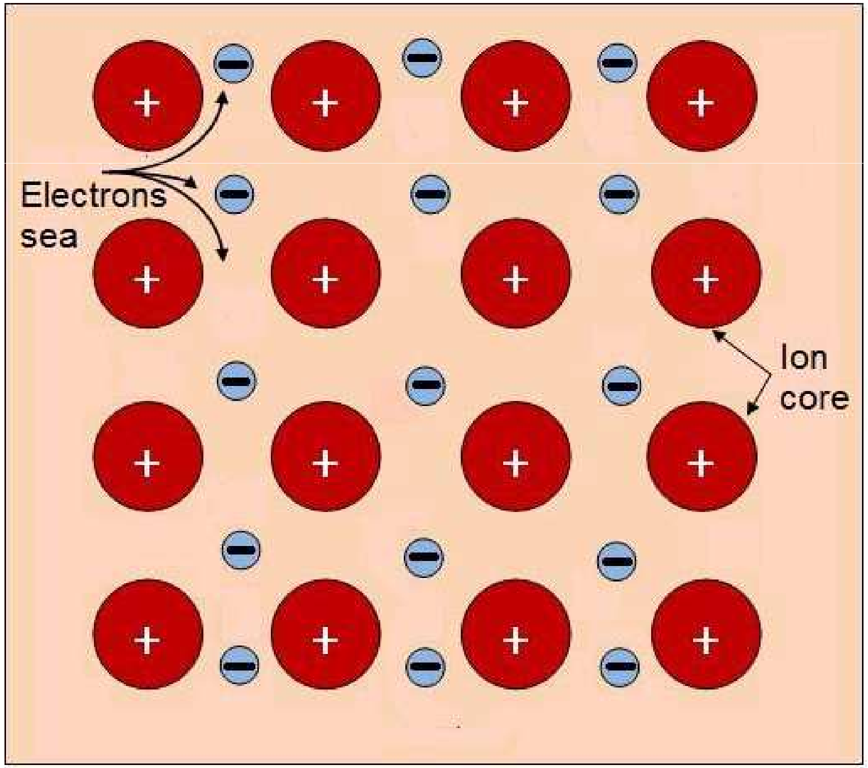
- In this type of bonding, atoms share their valence electrons to get a stable configuration.
- Methane (CH_4): Four hydrogen atoms share their valence electrons with one carbon atom and the carbon atom in turn shares one valence electron with each of the four hydrogen atoms. In the process both H and C atoms get stable configuration and form a covalent bond.



- Covalent bonds are formed between atoms of similar electro negativity.
- C atoms in diamond are covalently bonded to each other.
- Si also has valency of four and forms SiC through covalent bonding with C atoms.

Metallic Bond

- In metals the valence electrons are not really bound to one particular atom, instead they form a sea or cloud of valence electrons which are shared by all the atoms. The remaining electrons and the nuclei form what is called the ion core which is positively charged. The metallic bond arises out of the columbic attraction between these two oppositely charged species – the electron cloud and the ion cores.

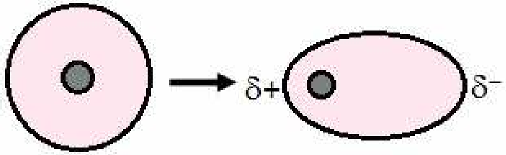


Characteristics of primary bonds

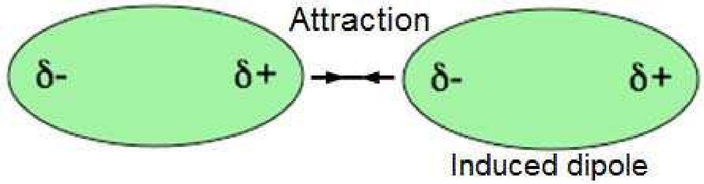
- Ionic and covalent bonds posses high bond energy : 450-1000 KJ/mole
- High bond strength in ionic and covalent solids results in high melting point, high strength and hardness. e.g. diamond
- As the electrons are tightly bound to the atoms they are generally poor conductors of heat and electricity.
- Are brittle in nature
- Most of the ceramics consist of covalent (SiC) or ionic bonds (Al_2O_3) or a mix of both and hence, exhibit all the properties described above.
- Metallic bonds on the other hand provide good thermal and electrical conductivities as the valence electrons are free to move.
- The metallic bond energy is 68 kJ/mol (Hg) on the lower side and 850 kJ/mol (W, tungsten) on the higher side.
- Bond strength increases with atomic number as more electrons are available to form the bonds with the ion cores. As a result melting point, hardness and strength increases with atomic number.
- Metals are ductile as the free moving electrons provides agility to the bonds and allows plastic deformation.

Vanderwaals bonding

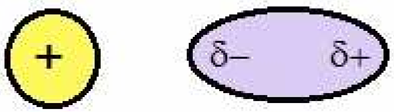
- Vanderwaals bonding between molecules or atoms arise due to weak attraction forces between dipoles.
- The natural oscillation of atoms leading to momentary break down of charge symmetry can generate temporary dipoles.



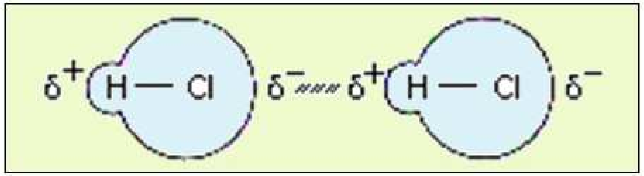
- Dipoles can induce dipoles and attraction between opposites ends of the dipoles leads to weak bonding.



- An ion can also induce a dipole

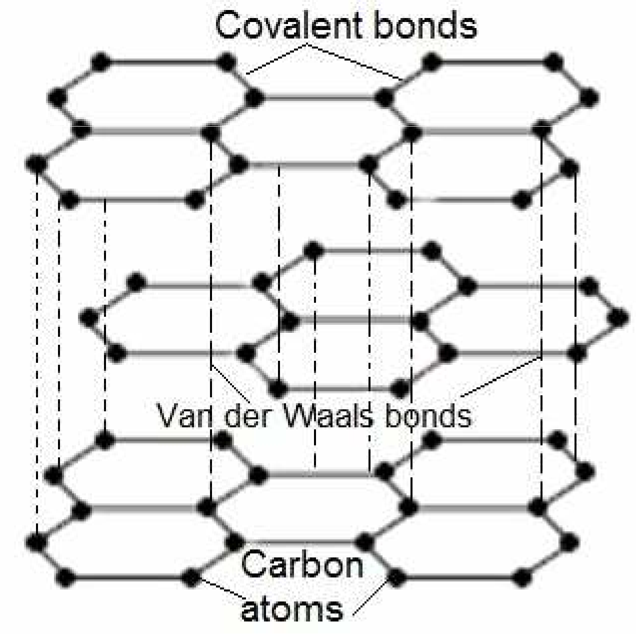


- Some molecules like HCl have permanent dipoles due to asymmetrical arrangement of +ve and –ve charges.



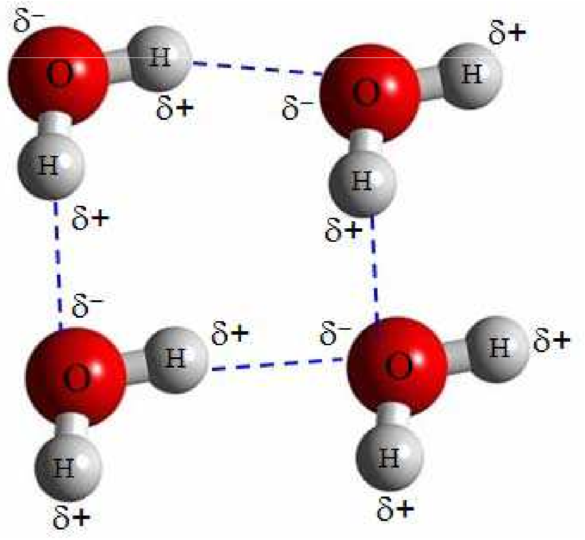
Vanderwaals bonding

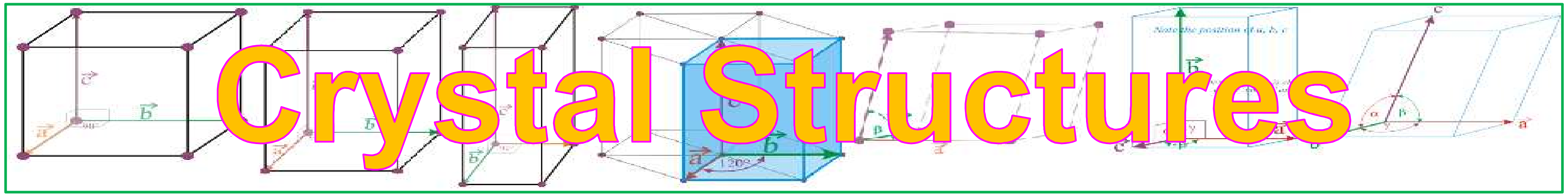
- Van der Waals bonding is much weaker compared to primary bonds. Bond energy lies in the range of 2 – 10 kJ/mol
- Molecules in liquid and gas are held by weak Vanderwaals forces.
- The atomic layers in graphite are held together by weak vanderwaals bonds. Therefore, the layers can move easily over each other and this imparts the lubricating property graphite is known for.



Hydrogen bonding

- ❑ Hydrogen bond is a type of secondary bond found in molecules containing hydrogen as a constituent.
- ❑ The bond originates from electrostatic interaction between hydrogen and another atom of high electro-negativity such as fluorine or oxygen.
- ❑ The strength of hydrogen bonds is in the range of 10 - 50 kJ/mol.
- ❑ Water molecules, for example, are connected by hydrogen bonds (dashed lines in the picture).





Crystal Structures

Avala Lava Kumar* : Suneeti Purohit : Gautam Behera

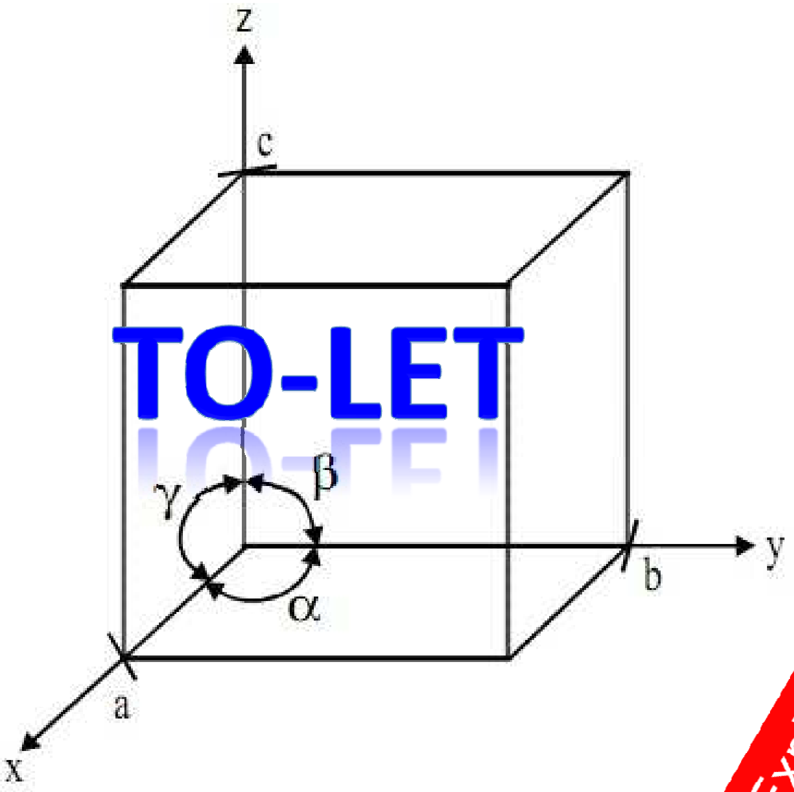
Department of Metallurgical & Materials Engineering (MME)

Veer Surendra Sai University of Technology (VSSUT), Burla -768018

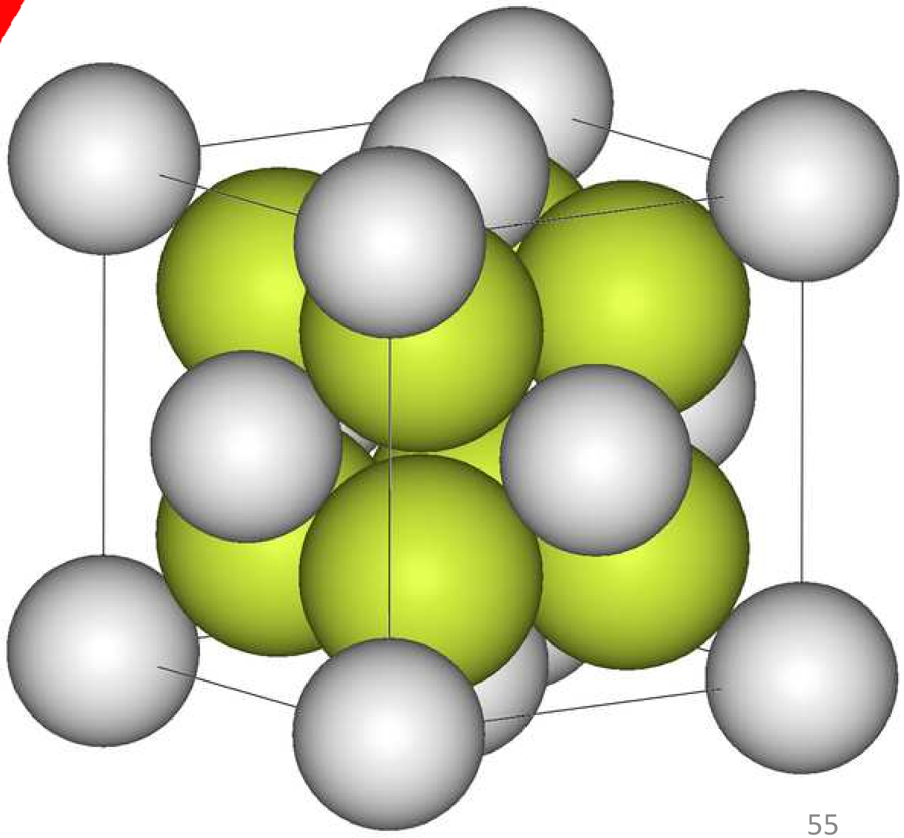
**E-mail : lavakumar.vssut@gmail.com*


To Let
Contact : 9999999999

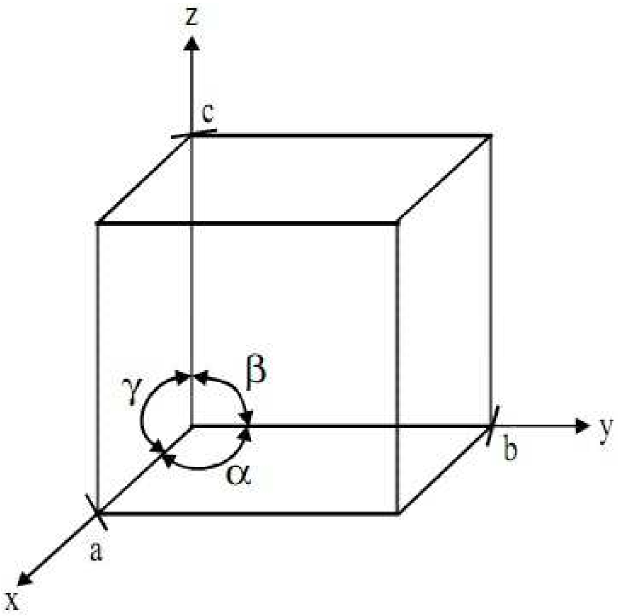

maps UK



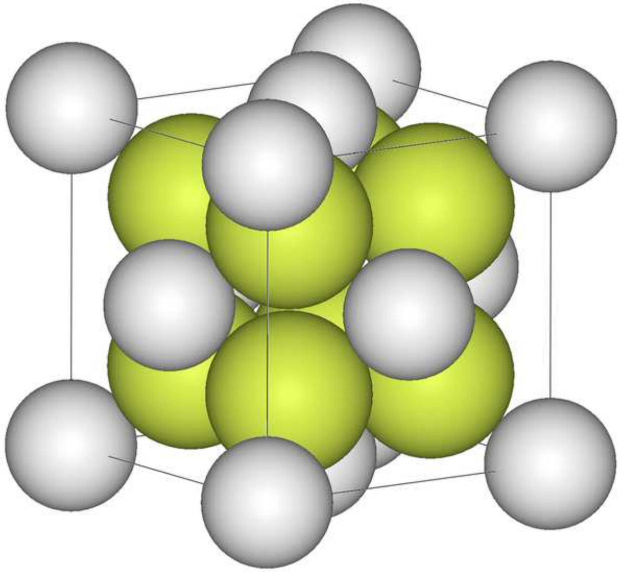
Crude Explanation/Imagination




To Let
Contact : 9575678843


z
c
γ
β
α
y
b
a
x


maps UK



Why study crystal structures?

- When we look around much of what we see is non-crystalline (organic things like wood, paper, sand; concrete walls, etc. → some of the things may have some crystalline parts!).
- But, many of the common 'inorganic' materials are '*usually**' crystalline:
  - Metals: Cu, Zn, Fe, Cu-Zn alloys
  - Semiconductors: Si, Ge, GaAs
  - Ceramics: Alumina (Al_2O_3), Zirconia (Zr_2O_3), SiC, $SrTiO_3$
- Also, the usual form of crystalline materials (say a Cu wire or a piece of alumina) is polycrystalline and special care has to be taken to produce single crystals
- Polymeric materials are *usually* not 'fully' crystalline
- The crystal structure directly influences the properties of the material

Why study crystallography?

- Gives a terse (concise) representation of a large assemblage of species
- Gives the 'first view' towards understanding of the properties of the crystal

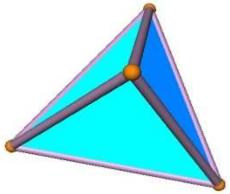
* *Many of the materials which are usually crystalline can also be obtained in an amorphous form*

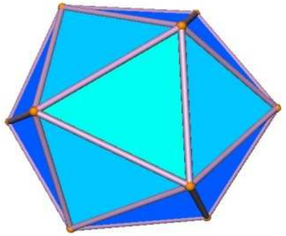
History

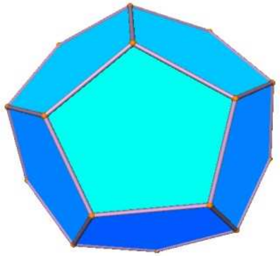
- In 387B.C. scientist called “PLATO” most famous student of Socrates thought that whole universe is made up of five solids. Whole universe is periodic arrangement of five solids named as Platonic Solids.
- Tetrahedron - 4 *faces* - *Fire*
- Hexahedron - 6 *faces* - *Earth*
- Octahedron - 8 *faces* - *Air*
- Dodecahedron - 12 *faces* - *GOD*
- Icosahedron - 20 *faces* - *Water*

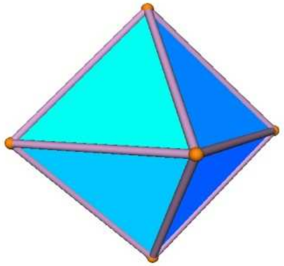
He had a some philosophical thought; in the universe we have 5 elements made up of these five solids

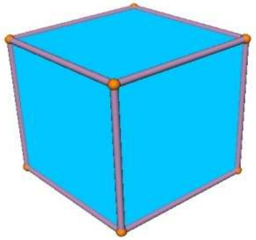
- In icosahedron, we will get best packing as for we concerned. But only problem is, if we try to translate it in 3D we can’t get continuous structure, without any voids left. This voids in crystallography is called *frustation.*
- Long back people thought, it is not possible to have solids with Icosahedron packing; but it is possible when Quasicrystals are discovered in 1984. (Al-Mg)


Tetrahedron

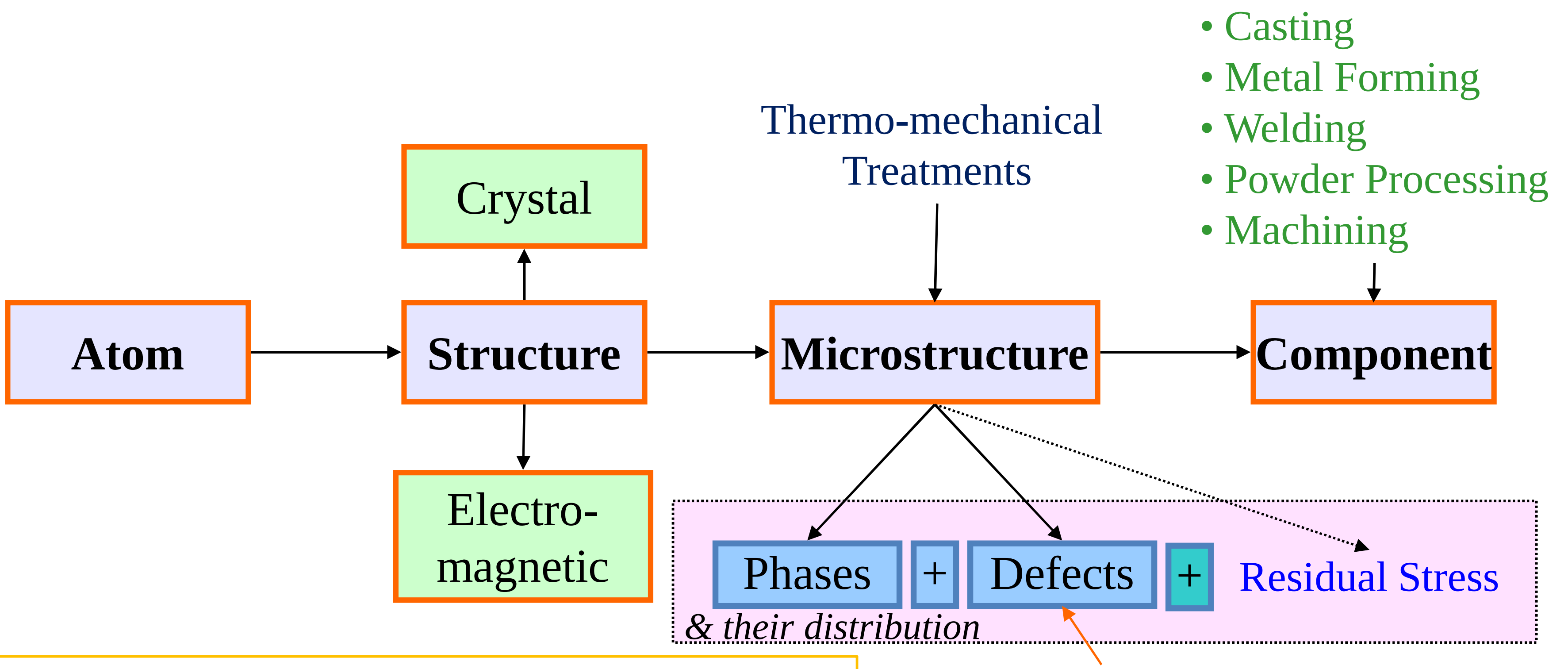

Icosahedron


Dodecahedron


Octahedron


Cube

Different levels of structures



- Casting
- Metal Forming
- Welding
- Powder Processing
- Machining

Thermo-mechanical Treatments

Crystal

Atom

Structure

Microstructure

Component

Electro-magnetic

Phases + Defects + Residual Stress

& their distribution

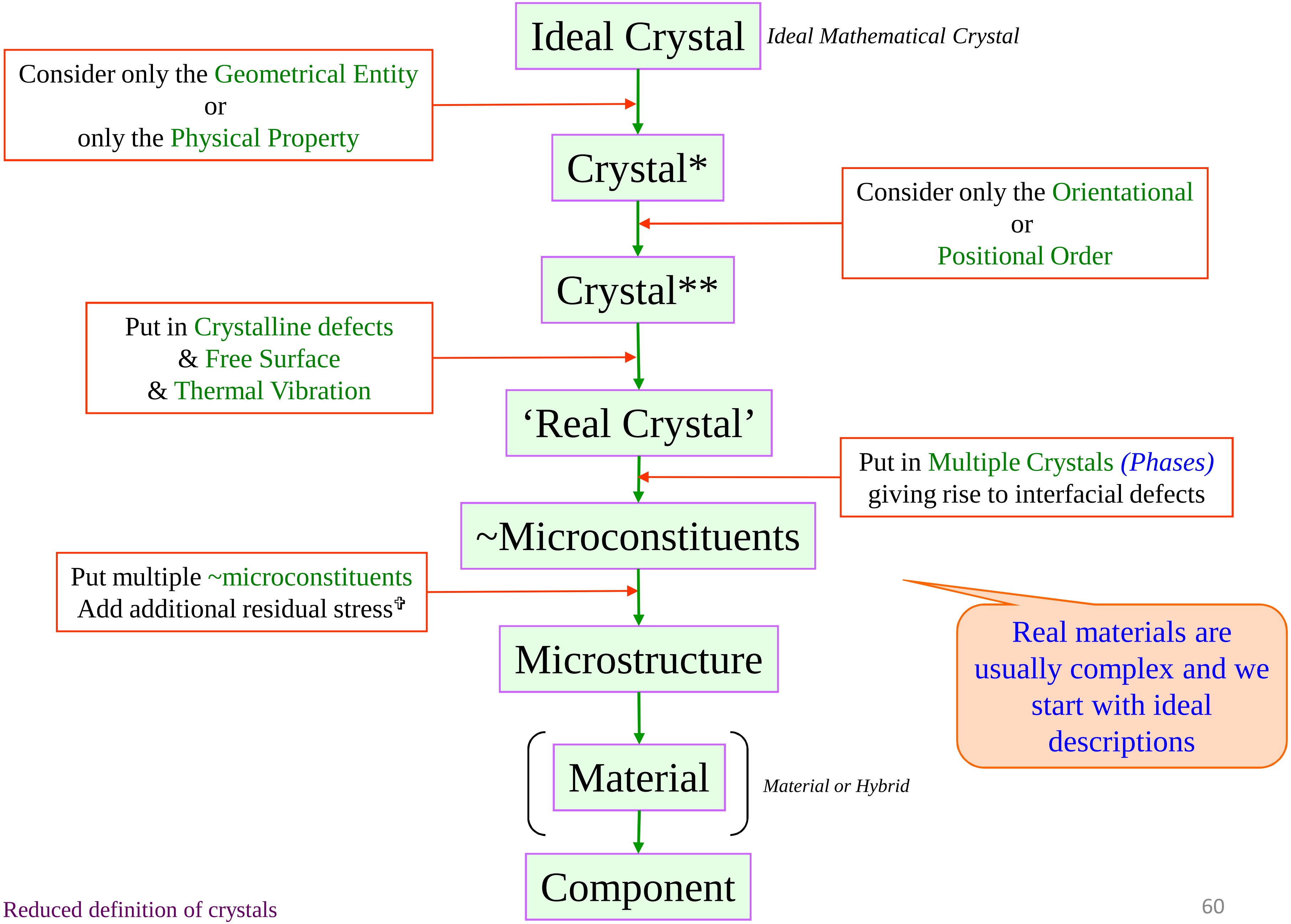
In brief we have different levels of structures

- *Electronic structure*
- *Atomic structure*
- *Crystal structure*
- *Microstructure*
- *Macro structure*
- *Nanostructure*

- Vacancies
- Dislocations
- Twins
- Stacking Faults
- Grain Boundaries
- Voids
- Cracks

Processing determines shape and microstructure of a component

Ideal Crystals → Real Crystals → Microstructures → Material → Component



Ideal Crystal

Ideal Mathematical Crystal

Consider only the Geometrical Entity
or
only the Physical Property

Crystal*

Consider only the Orientational
or
Positional Order

Crystal**

Put in Crystalline defects
& Free Surface
& Thermal Vibration

'Real Crystal'

Put in Multiple Crystals *(Phases)*
giving rise to interfacial defects

~Microconstituents

Put multiple ~microconstituents
Add additional residual stress✞

Microstructure

Real materials are usually complex and we start with ideal descriptions

Material

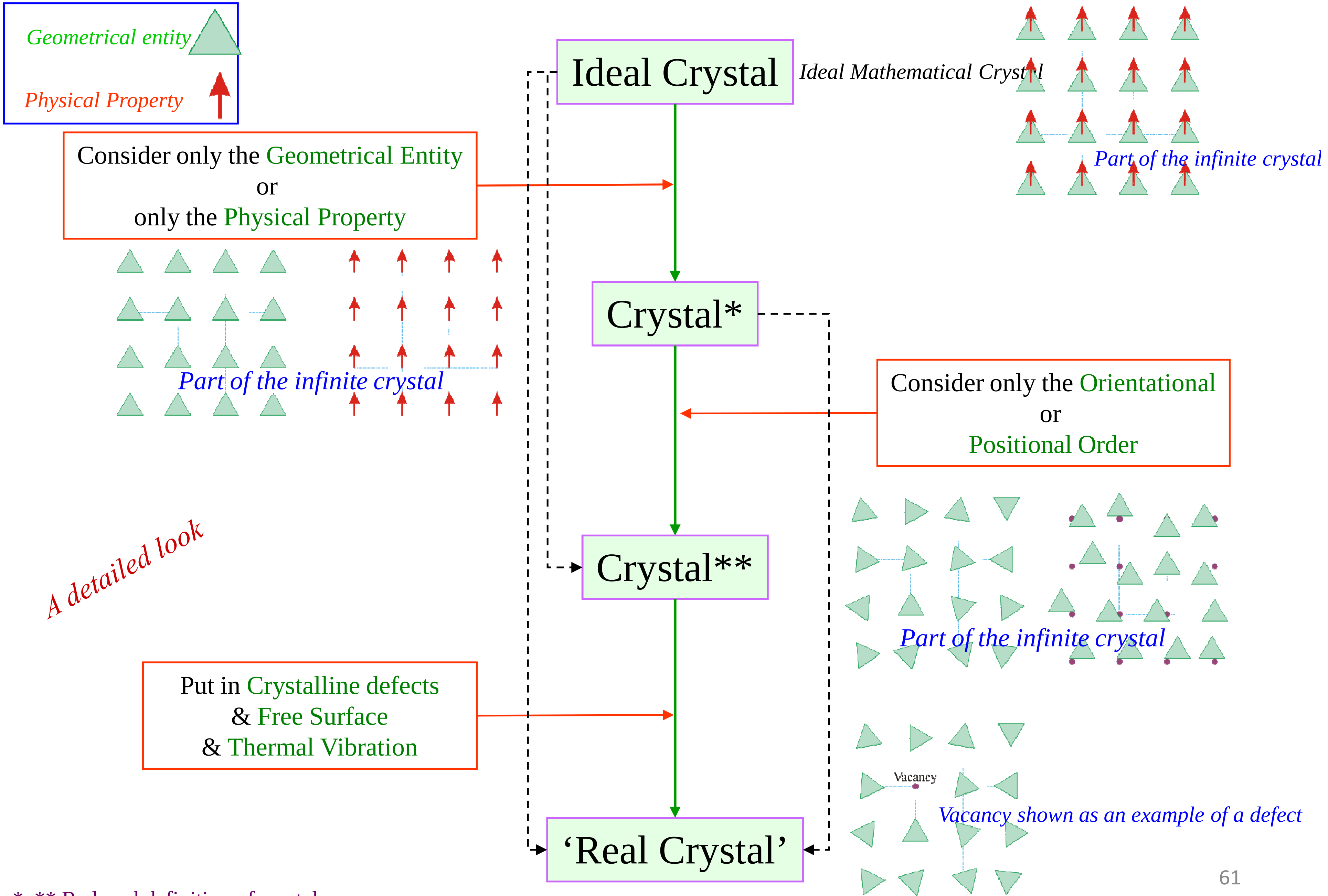
Material or Hybrid

Component

*, ** Reduced definition of crystals

✞ That which is NOT associated with defects *(crystalline or interfacial) → e.g. thermal residual stresses*

Ideal Crystals → Real Crystals → Microstructures → Material → Component



Geometrical entity

Physical Property

Ideal Crystal

Ideal Mathematical Crystal

Part of the infinite crystal

Consider only the Geometrical Entity
or
only the Physical Property

Part of the infinite crystal

Crystal*

Consider only the Orientational
or
Positional Order

Part of the infinite crystal

A detailed look

Crystal**

Put in Crystalline defects
& Free Surface
& Thermal Vibration

Vacancy shown as an example of a defect

‘Real Crystal’

*, ** Reduced definition of crystals

CRYSTAL

A 3D translationally periodic arrangement of atoms in a space is called a crystal.

LATTICE

A 3D translationally periodic arrangement of points in a space is called a crystal.

Crystal

A 3D translationally periodic arrangement of ***atoms*** in a space is called a crystal.

Lattice

A 3D translationally periodic arrangement of ***points*** in a space is called a lattice.

What is the relation between the two ?

Crystal = lattice + motif

Motif or basis: an atom or a group of atoms associated with each lattice point

Crystal = Lattice + Motif

Motif or Basis:
typically an atom or a group of atoms associated with each lattice point

- Lattice ➢ the underlying periodicity of the crystal
- Basis ➢ Entity associated with each lattice points

- Lattice ➢ how to repeat
- Motif ➢ what to repeat

Lattice

Translationally periodic arrangement of points

Crystal

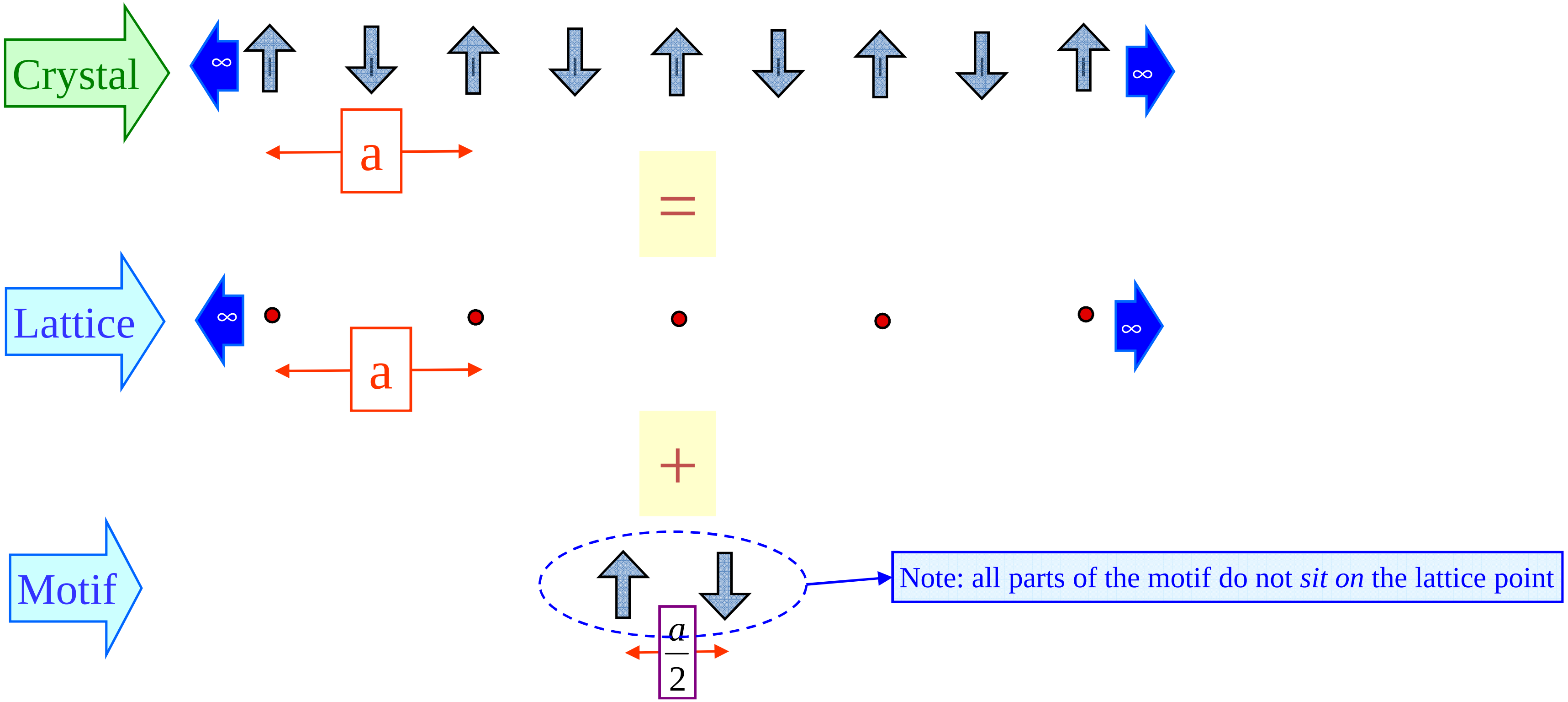
Translationally periodic arrangement of motifs

Crystal =

Lattice *(Where to repeat)*

\+

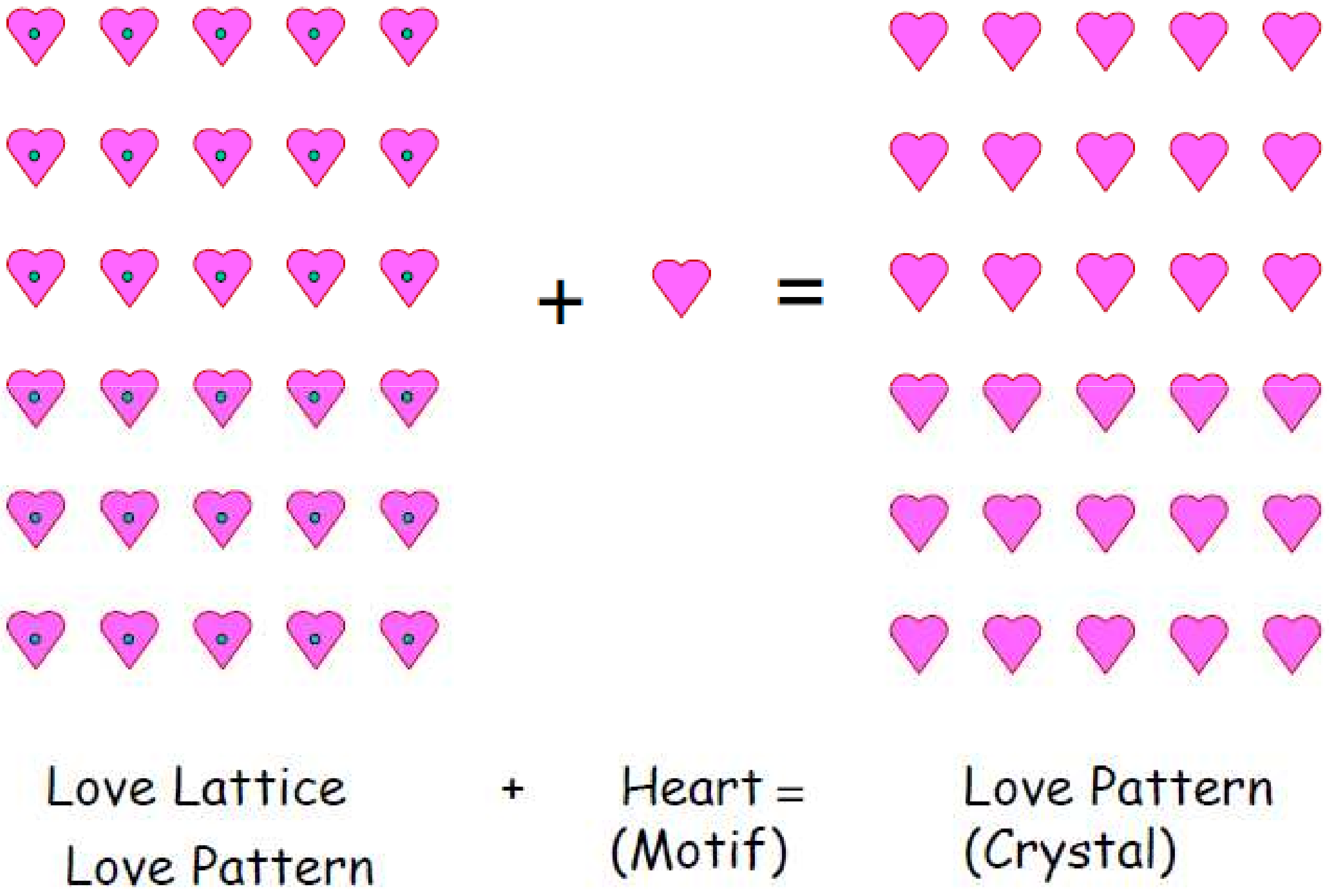
Motif *(What to repeat)*



Note: all parts of the motif do not *sit on* the lattice point

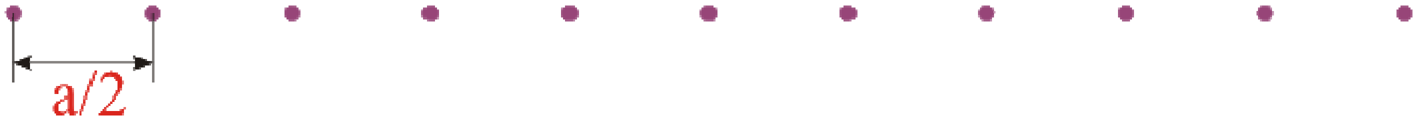
Motifs are associated with lattice points
→ they need NOT *sit* physically at the lattice point

Crystal = Lattice + Motif

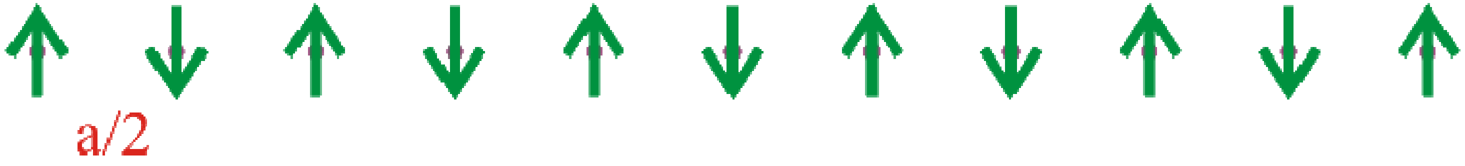


Example

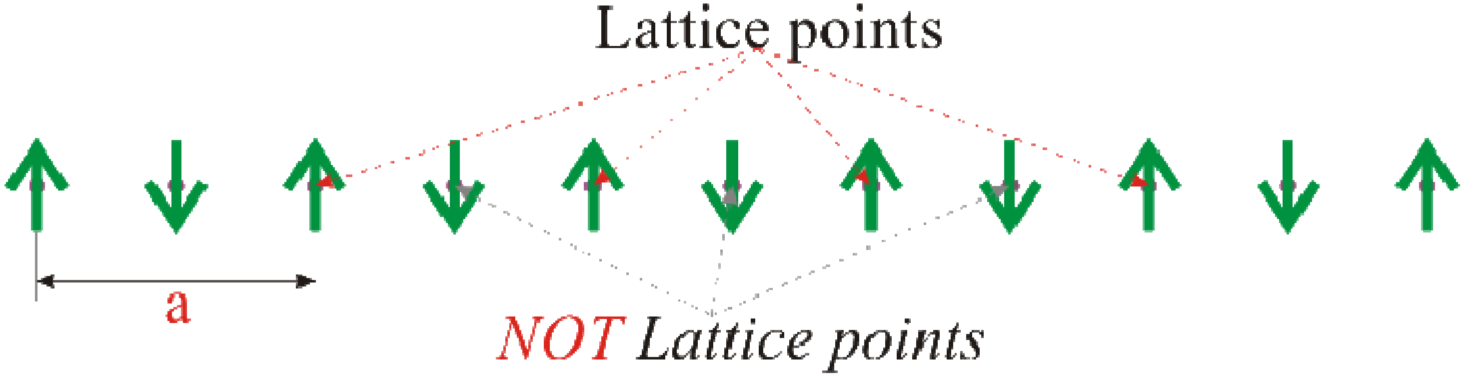
Let us construct the crystal considered before starting with an infinite array of points spaced a/2 apart



Put arrow marks pointing up and down alternately on the points:



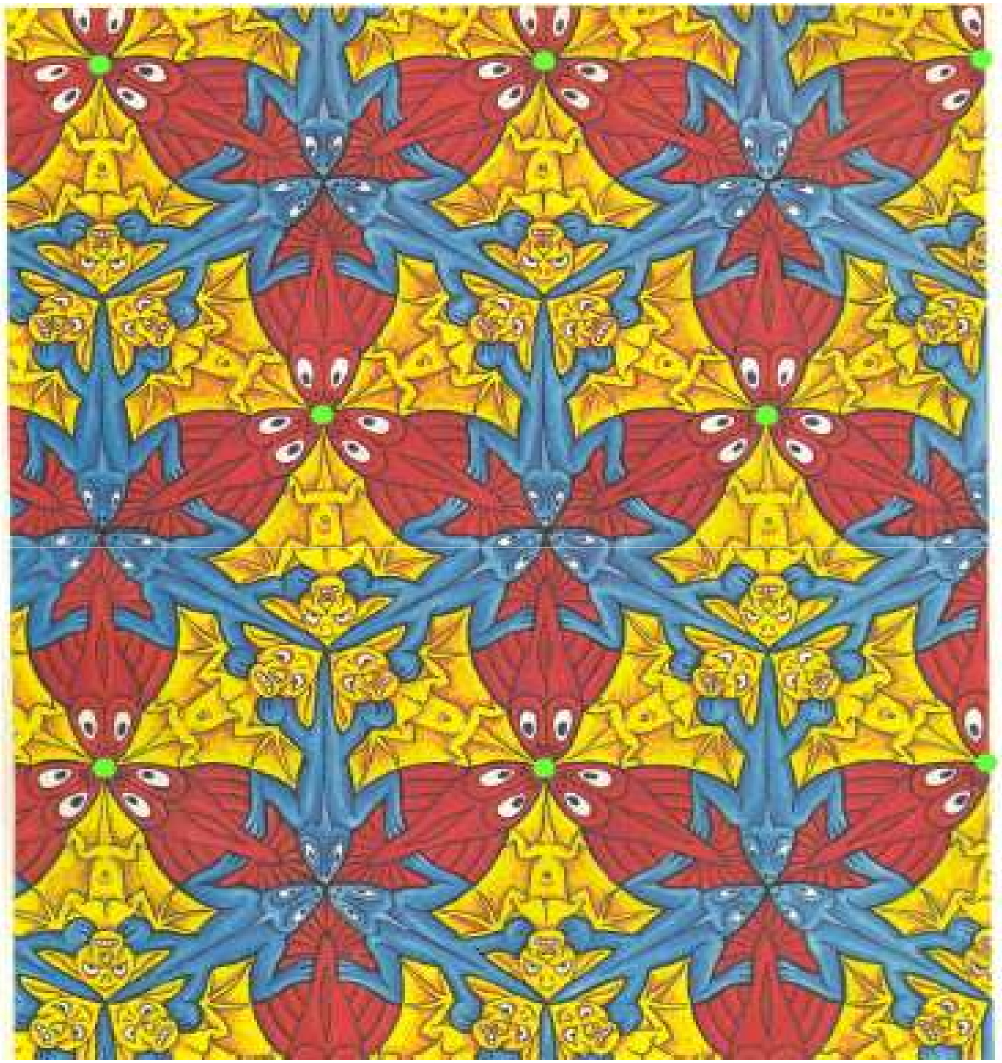
What we get is a crystal of lattice parameter 'a' and not 'a/2'! → *as this lattice parameter is a measure of the repeat distance!*

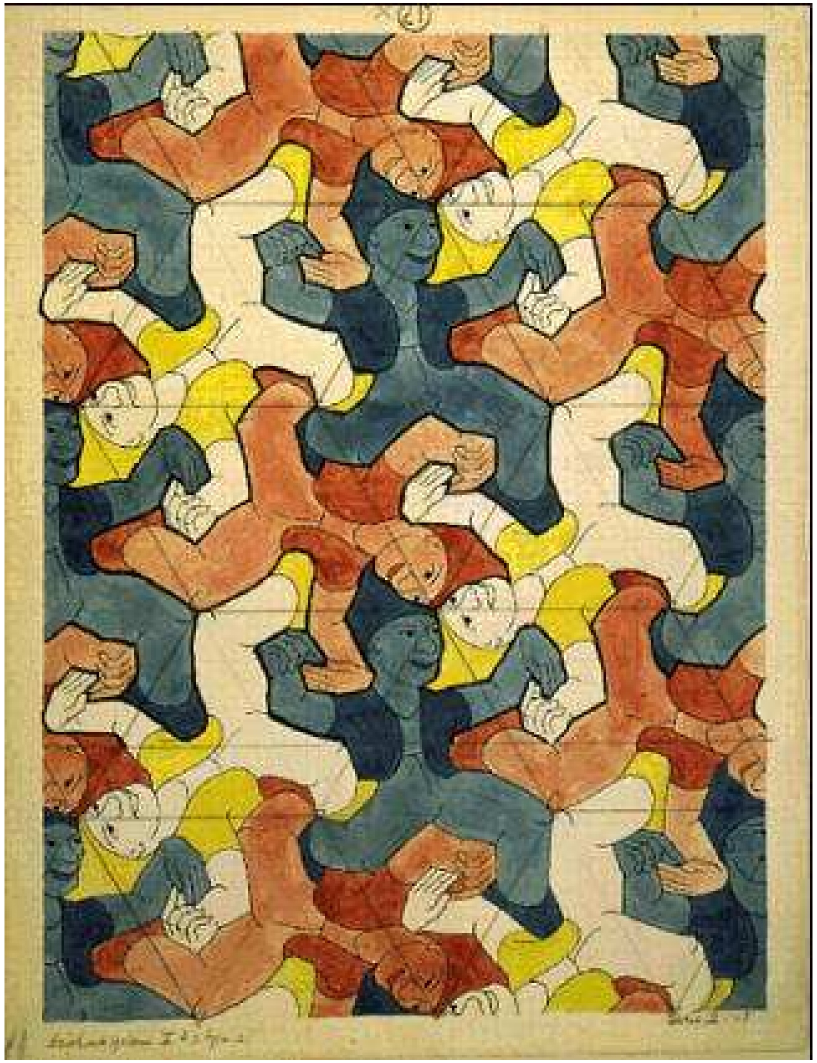


And the motif is:
↑ + ↓

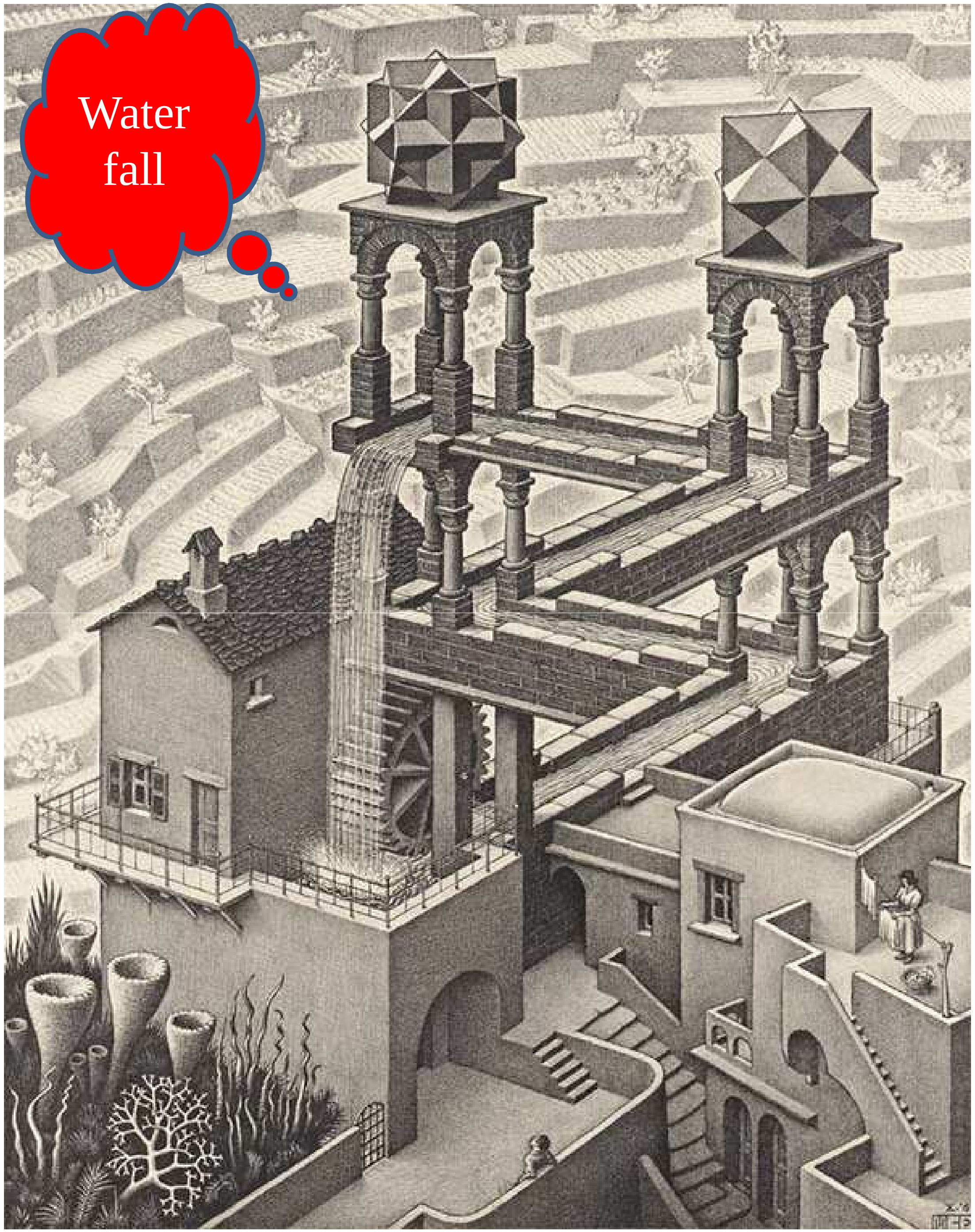
Note: we could have alternately chosen the centres of bottom arrows as lattice points!

M.C. Esher : Art with Science

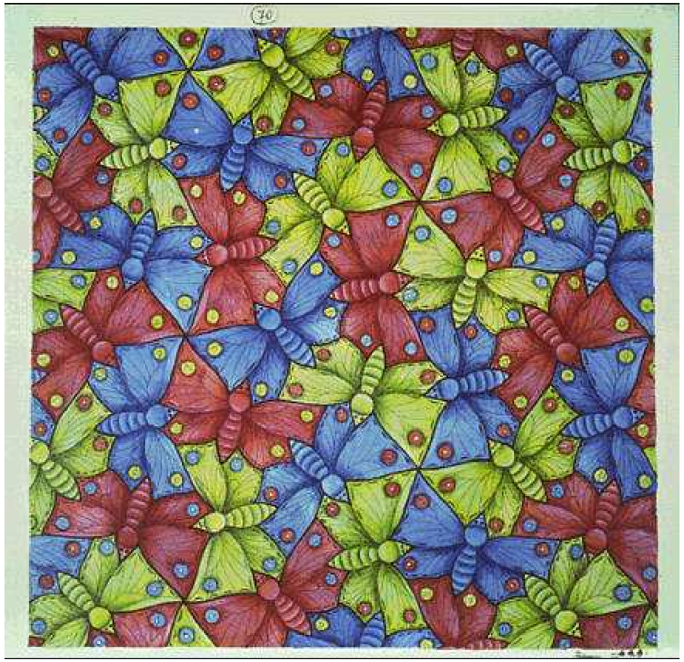




Every periodic pattern (and hence a Crystal) has a unique lattice associate with it.

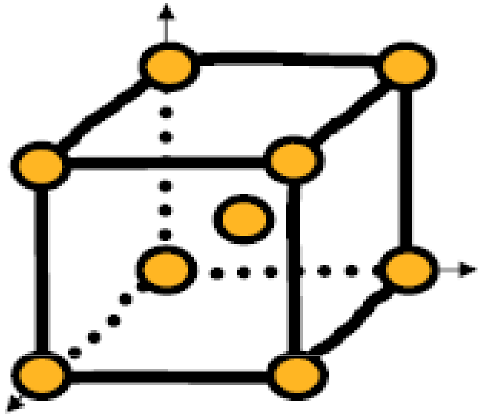


Water fall



Interesting Fact…!

Monatomic Body-centered cubic (BCC) crystal

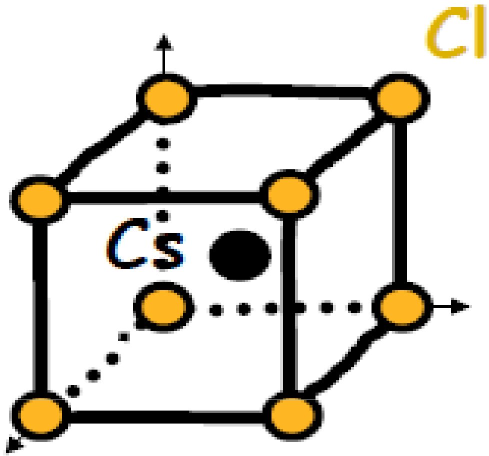


Corner and body centered have the same neighborhood

Lattice: BCC

Motif : 1 atom 000

CsCl crystal



Corner and body centered do not have the same neighborhood

~~**BCC**~~

FEYMAN !

Lattice : simple cubic

Motif : two atom Cl (0,0,0) Cs (½, ½, ½)

Space Lattice

A lattice is also called a Space Lattice

An array of points such that every point has ***identical surroundings***

- **In Euclidean space ⇒ infinite array**
- **We can have 1D, 2D or 3D arrays (lattices)**

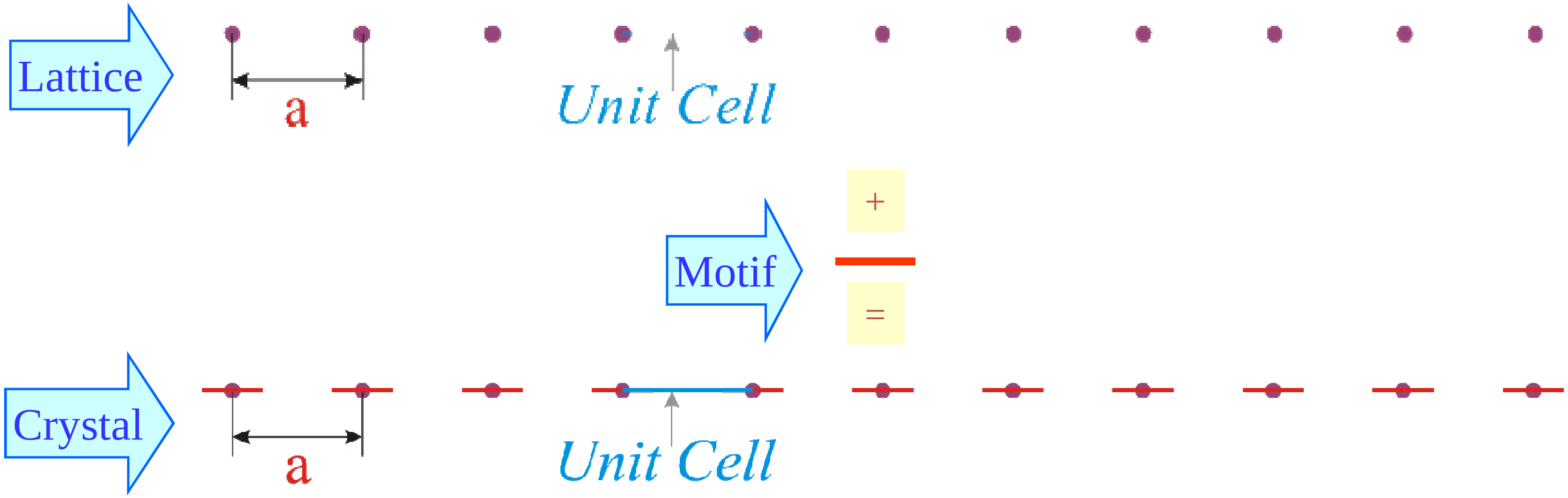
or

Translationally periodic arrangement of points in space is called a lattice

Making a 1D Crystal

- ❑ Some of the concepts are best illustrated in lower dimensions → hence we shall construct some 1D and 2D crystals before jumping into 3D
- ❑ A strict 1D crystal = 1D lattice + 1D motif
- ❑ The only kind of 1D motif is a line segment

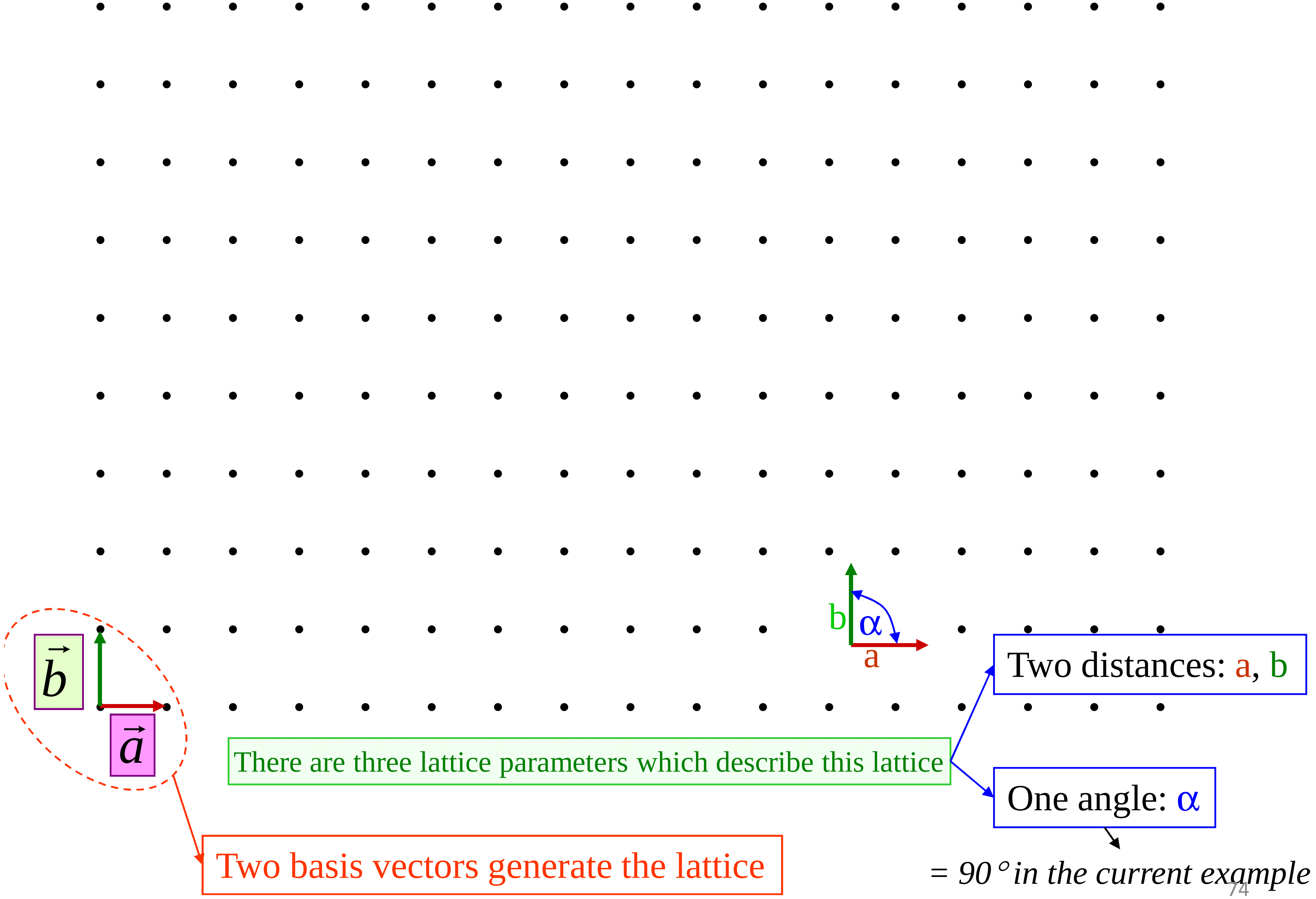
- ❑ An unit cell is a representative unit of the structure *(finite part of a infinite structure)*
  - ➢ which when translationally repeated gives the whole structure



2D Lattices

- ❑ 2D lattices can be generated with two basis vectors
- ❑ They are infinite in two dimensions
- ❑ There are five distinct 2D lattices:
  - 1➢ Square
  - 2➢ Rectangle
  - 3➢ Centered Rectangle
  - 4➢ 120° Rhombus
  - 5➢ Parallelogram (general)
- ❑ Four (4) Unit Cell shapes in 2D can be used for 5 lattices as follows:
  - ➢ Square → ($a = b$, $\alpha = 90°$)
  - ➢ Rectangle → (a, b, $\alpha = 90°$)
  - ➢ 120° Rhombus → ($a = b$, $\alpha = 120°$)
  - ➢ Parallelogram (general) → (a, b, α)
- ❑ It is clear some of them require more parameters to describe than others
- ❑ Some of them have special constraints on the angle
- ❑ Can we put them in some order?

2D Lattices



There are three lattice parameters which describe this lattice

Two distances: a, b

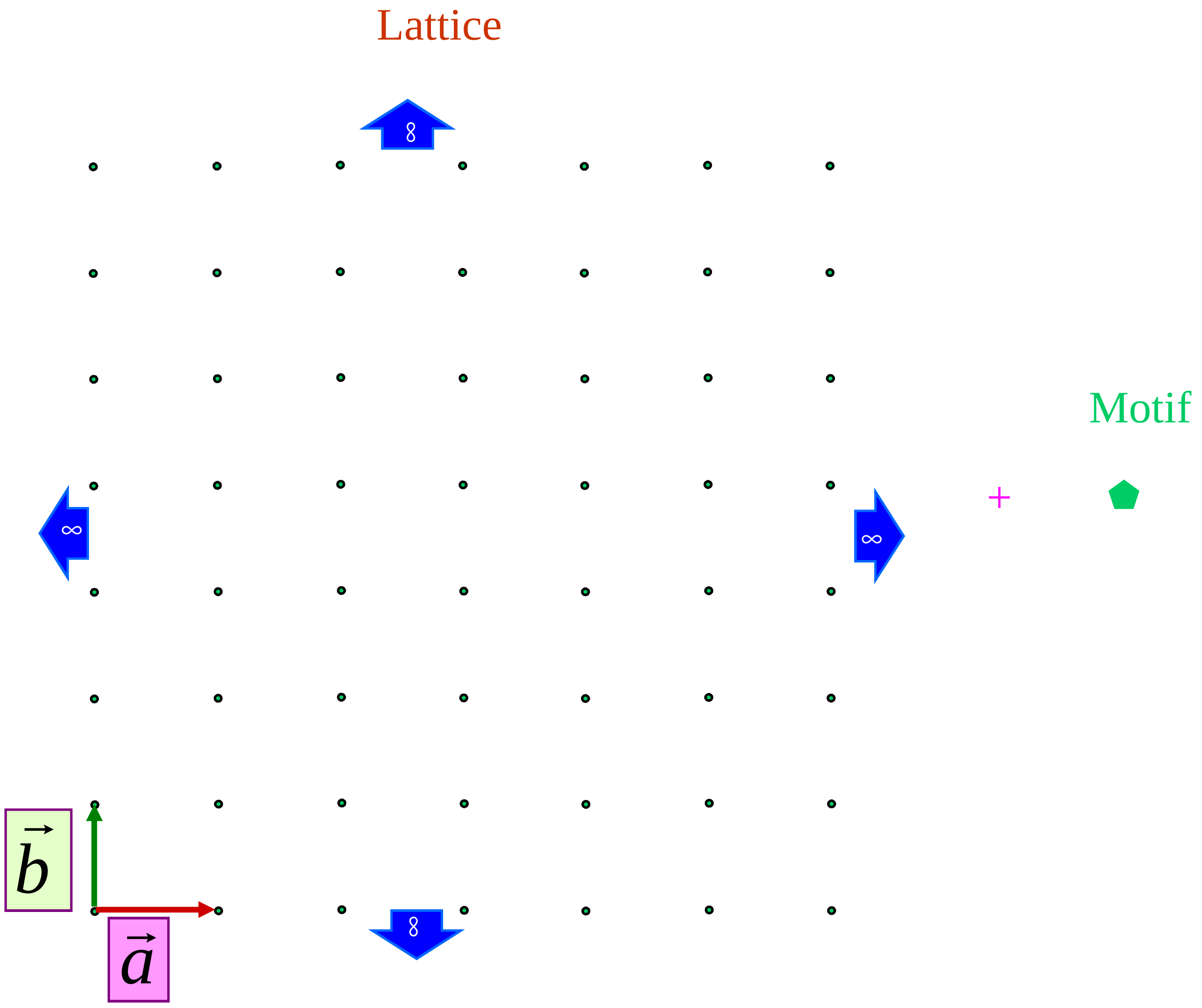
One angle: α

= 90° in the current example

Two basis vectors generate the lattice

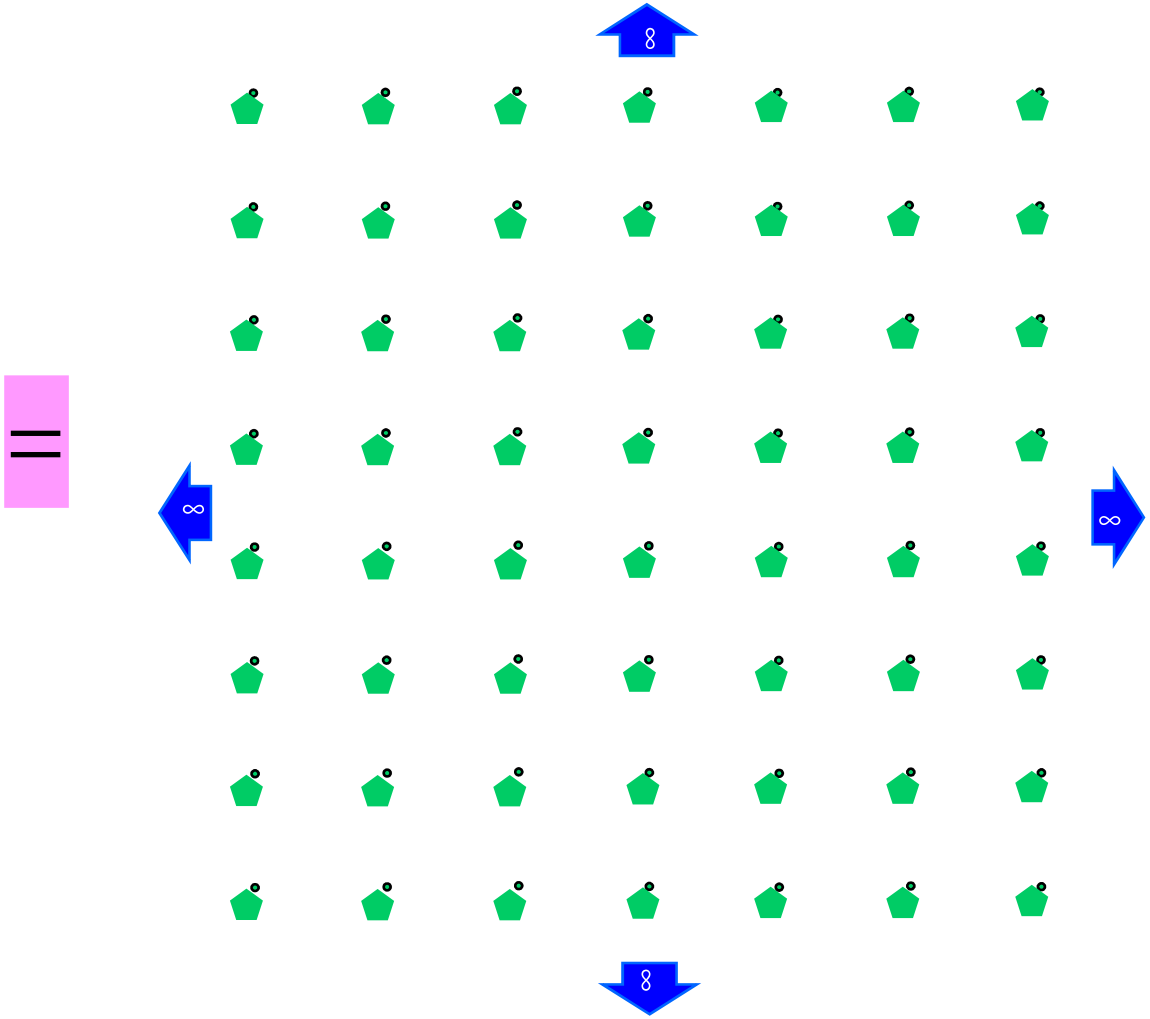
Making a 2D Crystal

- ☐ Some aspects we have already seen in 1D → but 2D many more concepts can be clarified in 2D



2D crystal = 2D lattice + 2D motif

Making a 2D Crystal

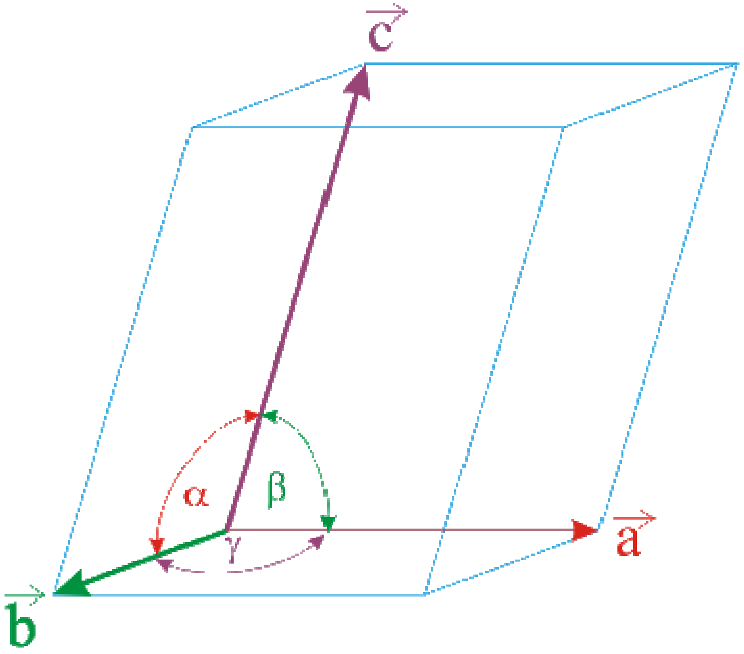


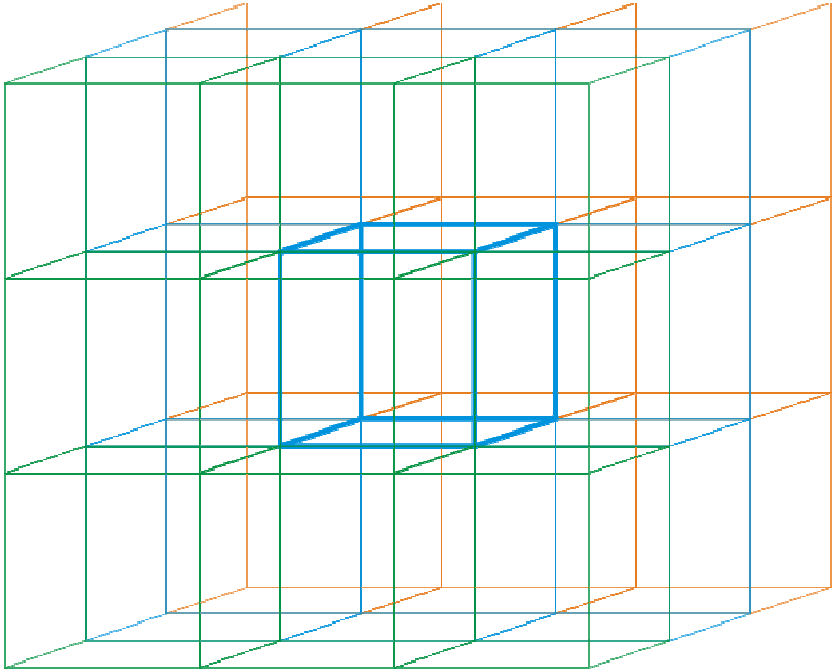
As before there are many ways of associating the motif with a lattice point (one of these is shown)

❉Note:
Each motif is identically oriented *(orientationally ordered)*
and
is associated exactly at the same position with each lattice point *(positionally ordered)*

3D Lattices

- ❑ 3D lattices can be generated with three basis vectors
- ❑ They are infinite in three dimensions
- ❑ 3 basis vectors generate a 3D lattice
- ❑ The unit cell of a general 3D lattice is described by 6 numbers (in special cases all these numbers need not be independent) → 6 lattice parameters
  - ➢ 3 distances (a, b, c)
  - ➢ 3 angles (α, β, γ)

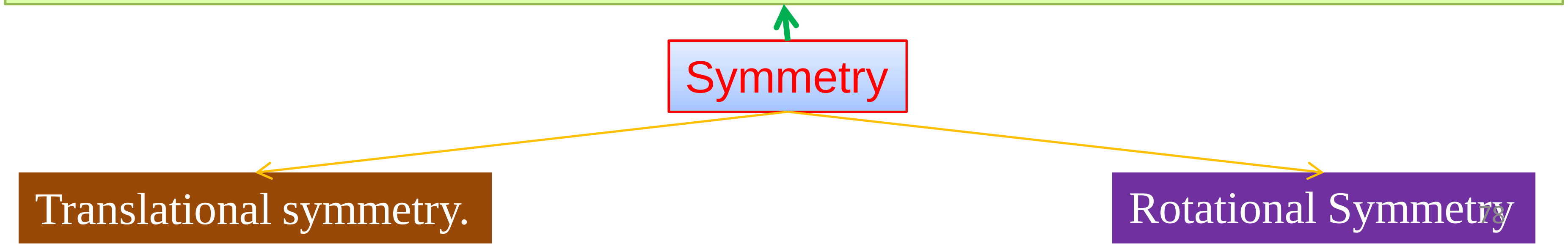




Making a 3D Crystal

- 3D crystal = 3D lattice + 3D motif
- There are 14 distinct lattices possible in 3D called the Bravais lattices
- Lattices can be constructed using translation alone
- The definition (& classification) of Crystals is based on symmetry and NOT on the geometry of the unit cell.
- Crystals based on a particular lattice can have symmetry:
  - equal to that of the lattice or
  - *lower than that of the lattice*
- Based on symmetry crystals are classified into seven types/categories/systems known as the SEVEN CRYSTAL SYSTEMS
- We can *put* all possible crystals into 7 boxes based on symmetry

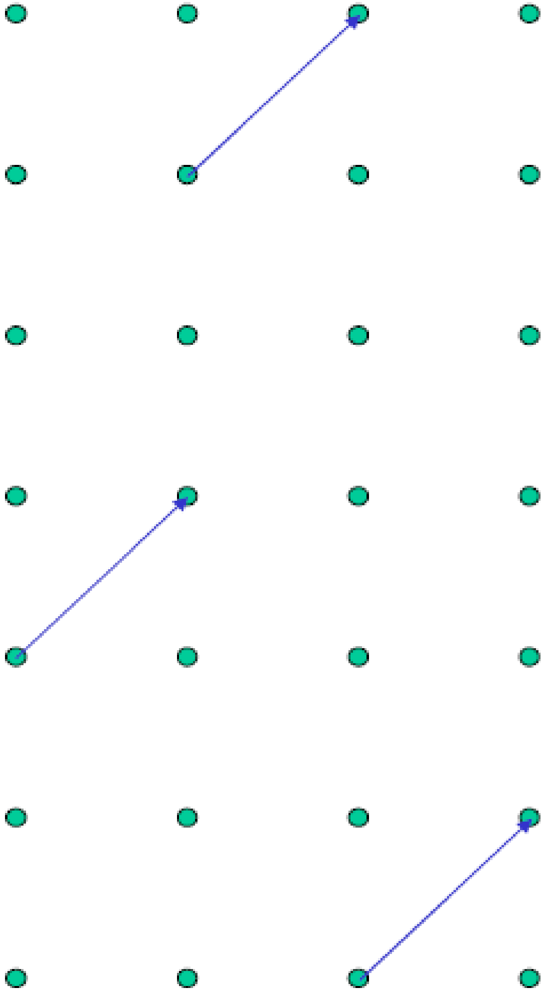
If an object is brought into self coincidence after some operation it is said to possess symmetry with respect to that operation


Symmetry

Translational symmetry.

Rotational Symmetry

Translational symmetry



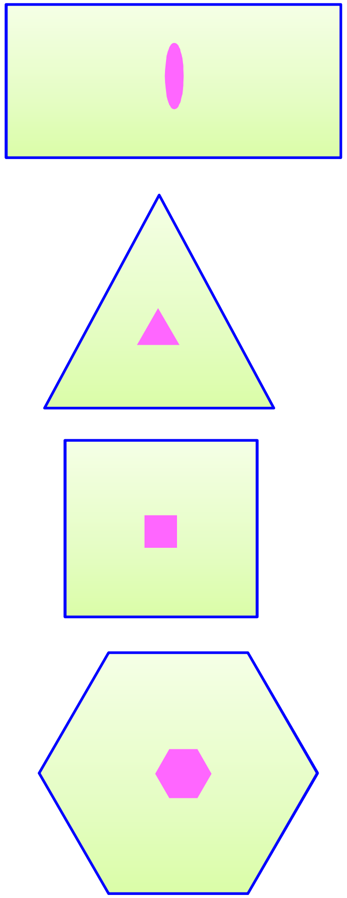
Lattice also have **translational symmetry**

In fact this is the defining symmetry of a lattice

Rotation Axis

If an object come into self-coincidence through smallest non-zero rotation angle of θ then it is said to have an n-fold rotation axis where

$$n = \frac{360^0}{\theta}$$

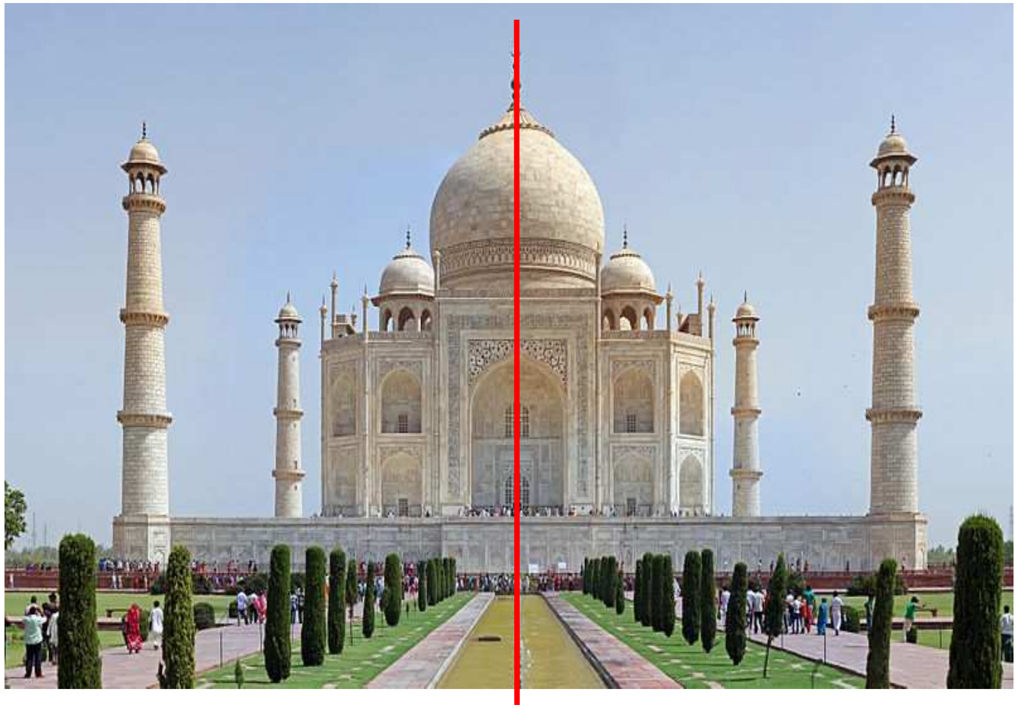


θ=180°	n=2	2-fold rotation axis
θ=120°	n=3	3-fold rotation axis
θ=90°	n=4	4-fold rotation axis
θ=60°	n=6	6-fold rotation axis

Examples of Rotational Symmetry

Angles	180°	120°	90°	72 °	60°	45°
Fold	2	3	4	5	6	8
Graphic Symbol	⬮	▲	■	⬟	⬢	⯃

Reflection (or mirror symmetry)



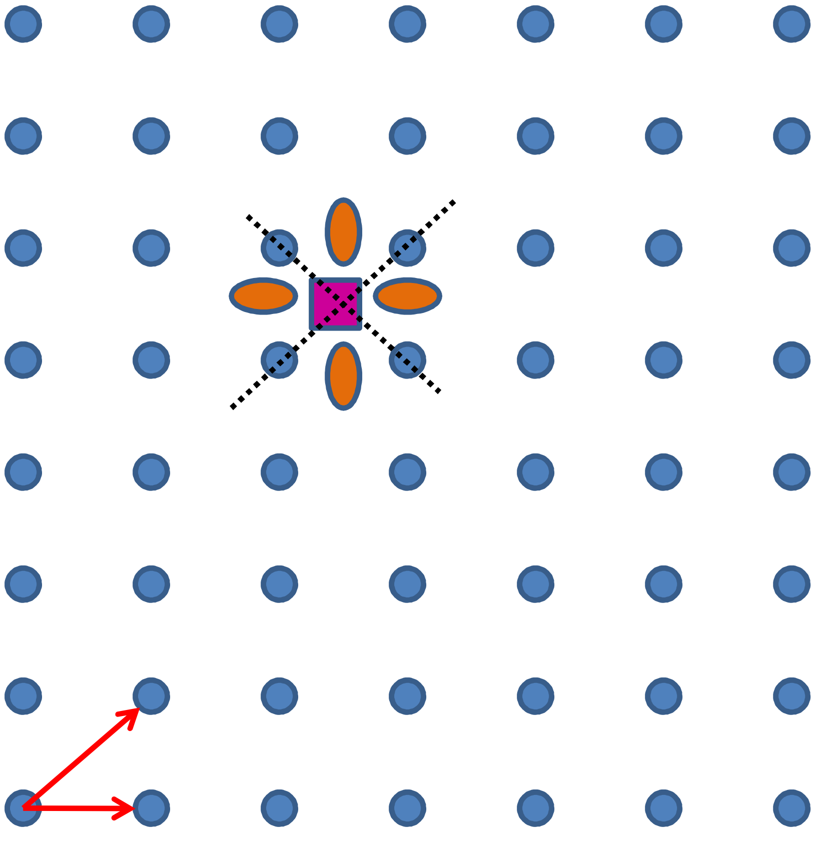
Symmetry of lattices

Lattices have….!

Translational Symmetry

Rotational Symmetry

Reflection Symmetry



What are the symmetries of the 7 crystal systems?

	Characteristic symmetry
Cubic	Four 3-fold rotation axes *(two will generate the other two)*
Hexagonal	One 6-fold rotation axis (or roto-inversion axis)
Tetragonal	(Only) One 4-fold rotation axis (or roto-inversion axis)
Trigonal	(Only) One 3-fold rotation axis (or roto-inversion axis)
Orthorhombic	(Only) Three ⊥ 2-fold rotation axes (or roto-inversion axis)
Monoclinic	(Only) One 2-fold rotation axis (or roto-inversion axis)
Triclinic	None *(only translational symmetry)*

We have stated that basis of definition of crystals is 'symmetry' and hence the classification of crystals is also based on symmetry

The essence of the required symmetry is listed in the table

- *more symmetries may be part of the point group in an actual crystal*

Note: translational symmetry is always present in crystals (i.e. even in triclinic crystal)

14 Bravais Lattices divided into 7 Crystal Systems

A Symmetry based concept

'Translation' based concept

	Crystal System	Lattice Parameters	Bravais Lattices			
			P	I	F	C
1	Cubic	(a = b = c, $\alpha = \beta = \gamma = 90°$)	✓	✓	✓	
2	Tetragonal	(a = b ≠ c, $\alpha = \beta = \gamma = 90°$)	✓	✓		
3	Orthorhombic	(a ≠ b ≠ c, $\alpha = \beta = \gamma = 90°$)	✓	✓	✓	✓
4	Hexagonal	(a = b ≠ c, $\alpha = \beta = 90°$, $\gamma = 120°$)	✓			
5	Trigonal	(a = b = c, $\alpha = \beta = \gamma \neq 90°$)	✓			
6	Monoclinic	(a ≠ b ≠ c, $\alpha = \gamma = 90° \neq \beta$)	✓			✓
7	Triclinic	(a ≠ b ≠ c, $\alpha \neq \beta \neq \gamma$)	✓			

Why are some of the entries missing?

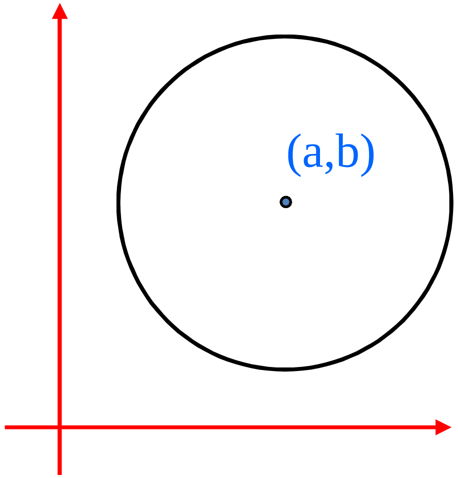
- Why is there no C-centred cubic lattice?
- Why is the F-centred tetragonal lattice missing?
- ….?

P	Primitive
I	Body Centred
F	Face Centred
C	A/B/C- Centred

If the definition of Crystals is based on symmetry and the existence of 7 crystal systems is also base on symmetry; *then how come we have statements like: $a = b = c$, $\alpha = \beta = \gamma = 90°$ is a cubic crystal?*

- ☐ This is an important point and requires some clarification
- ☐ Though the definition of crystals (e.g. cubic crystals) are based on symmetry and NOT on the geometry of the unit cell it is true that if we *already* have cubic crystal it is most *preferred/logical* to use parameters like $a = b = c$, $\alpha = \beta = \gamma = 90°$
- ☐ The next slide explains as to why a set of coordinate axis is more preferred for certain geometrical entities using the example of a circle

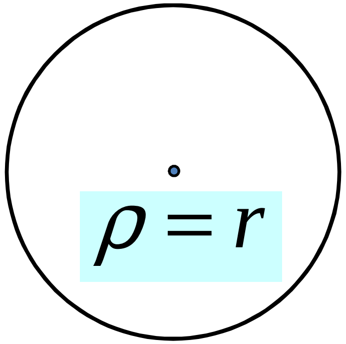
Concept of symmetry and choice of axes



$$(x-a)^2+(y-b)^2=r^2$$

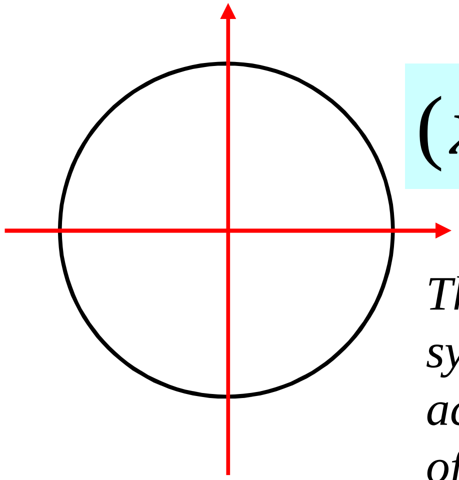
The centre of symmetry of the object does not coincide with the origin

Polar coordinates (ρ, θ)



$$\rho = r$$

$$(x)^2+(y)^2=r^2$$



The type of coordinate system chosen is not according to the symmetry of the object

The circle is described equally well by the three equations; but, in the polar coordinate system (with centre of the circle coinciding with the origin), the equation takes the most elegant (simple) form

Our choice of coordinate axis does not alter the symmetry of the object (or the lattice)!

Bravais Lattice: various viewpoints

- *A lattice is a set of points* constructed by translating a single point in discrete steps by a set of *basis vectors.*

  In three dimensions, there are 14 unique **Bravais** lattices *(distinct from one another)* in three dimensions. All crystalline materials recognized till now fit in one of these arrangements.

- In geometry and crystallography, a **Bravais lattice** is an infinite set of points generated by a set of discrete translation operations.

- A Bravais lattice looks exactly the same no matter from which point in the lattice one views it.

  An important property of a lattice

- *Bravais concluded that there are only* ***14*** *possible Space Lattices (with Unit Cells to represent them). These belong to* ***7*** *Crystal systems.*

- There are 14 Bravais Lattices which are the Space Group symmetries of lattices

A derivation of the 14 Bravais lattices or the existence of 7 crystal systems will not be shown in this course

Symmetry → Crystal System → Conventional unitcell

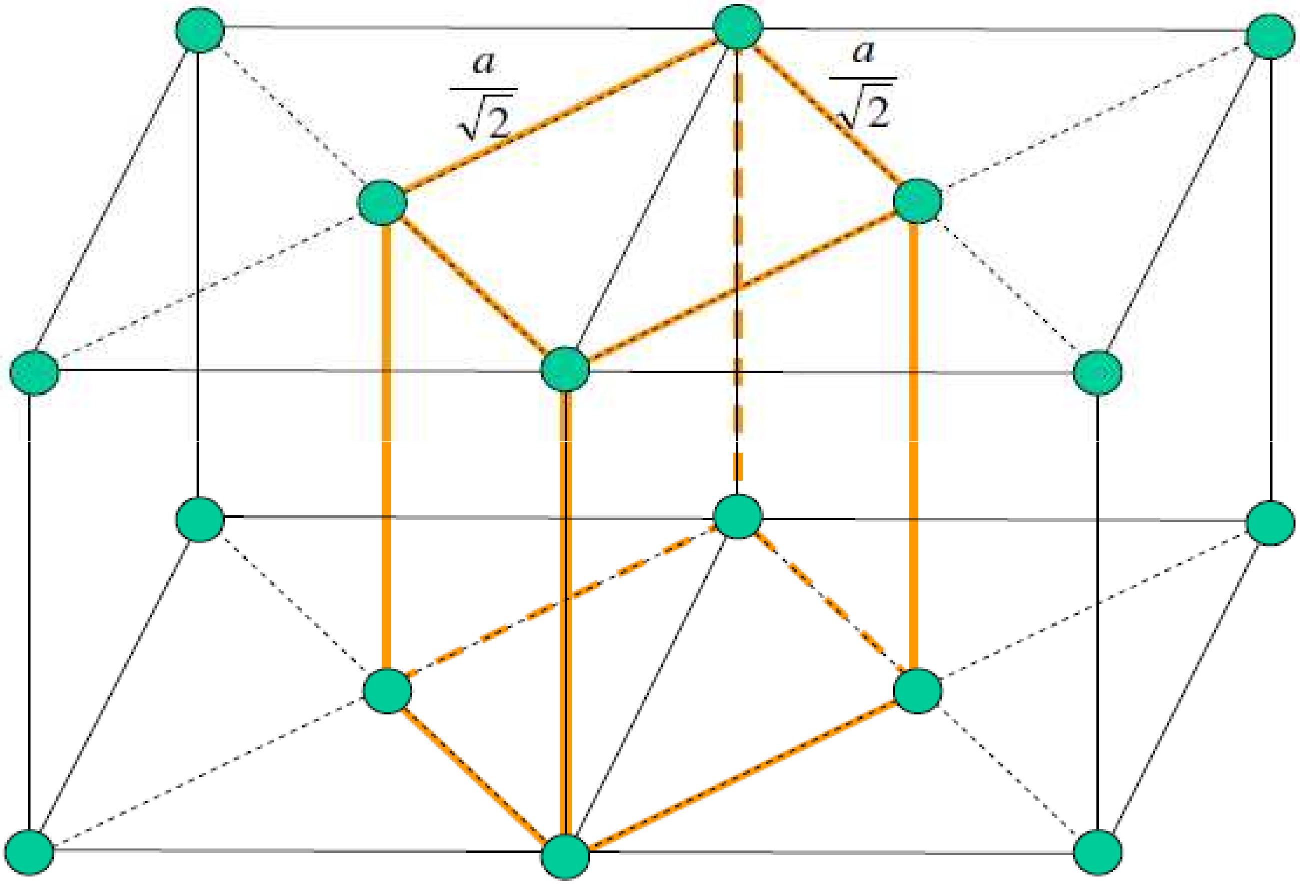
Symmetry operation	Used as UC for crystal:	Lattice Parameters
4 ▲	Cubic	$(a = b = c, \alpha = \beta = \gamma = 90°)$
1 ■	Tetragonal	$(a = b \neq c, \alpha = \beta = \gamma = 90°)$
3 ⬮	Orthorhombic	$(a \neq b \neq c, \alpha = \beta = \gamma = 90°)$
1 ⬢	Hexagonal	$(a = b \neq c, \alpha = \beta = 90°, \gamma = 120°)$
1 ▲	Trigonal	$(a = b = c, \alpha = \beta = \gamma \neq 90°)$
1 ⬮	Monoclinic	$(a \neq b \neq c, \alpha = \gamma = 90° \neq \beta)$
None	Triclinic	$(a \neq b \neq c, \alpha \neq \beta \neq \gamma)$

14 Bravais Lattices classified in Seven Crystal systems

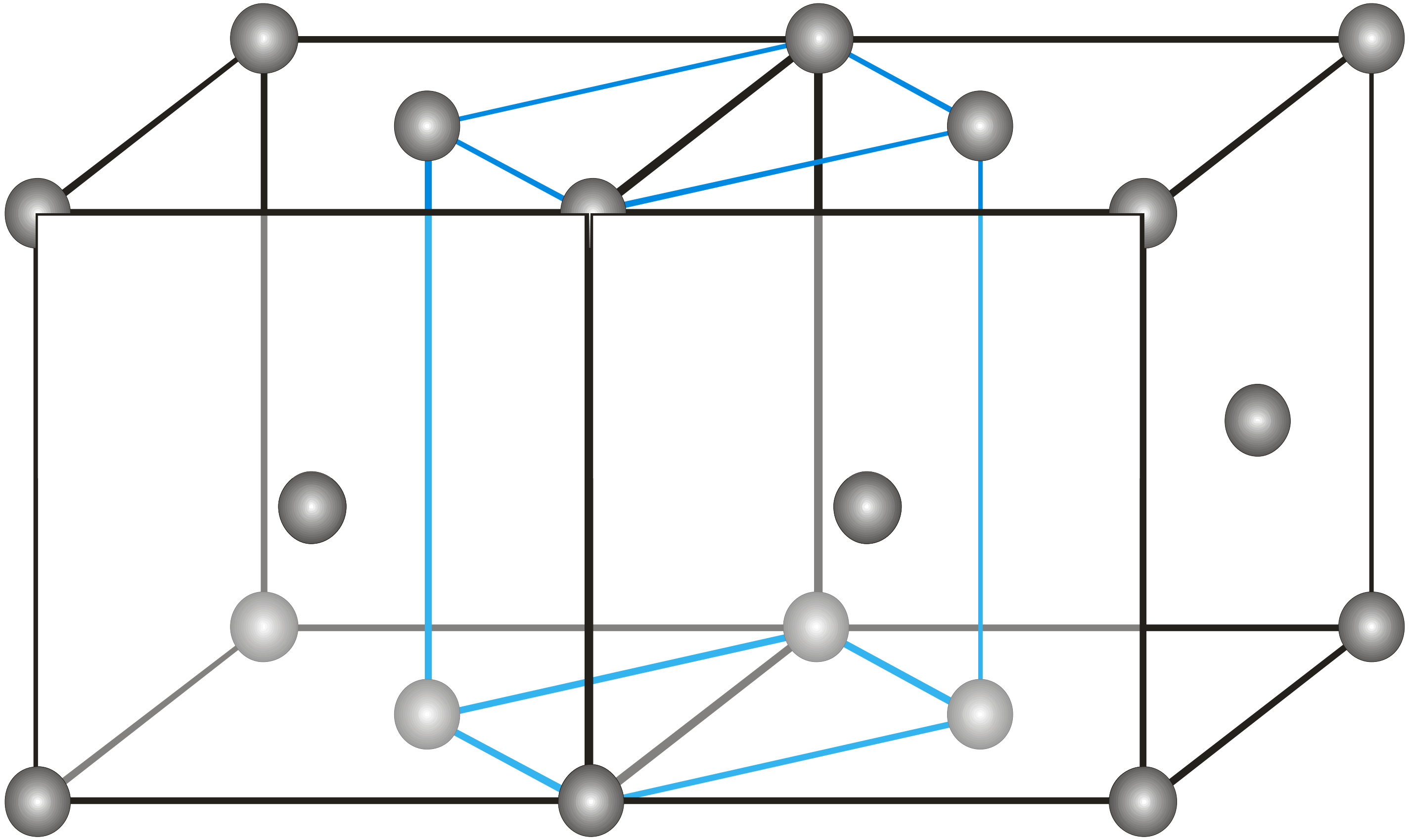
Cubic system	**Bravais lattices**			
1. Cubic	P	I	F	**?**
2. Tetragonal	P	I		
3. Orthorhombic	P	I	F	C
4. Hexagonal	P			
5. Trigonal	P			
6. Monoclinic	P			C
7. Triclinic	P			

P : Primitive, I : In Center, F: Face Center, C: End Center

End centre cubic not in the Bravais crystal ?

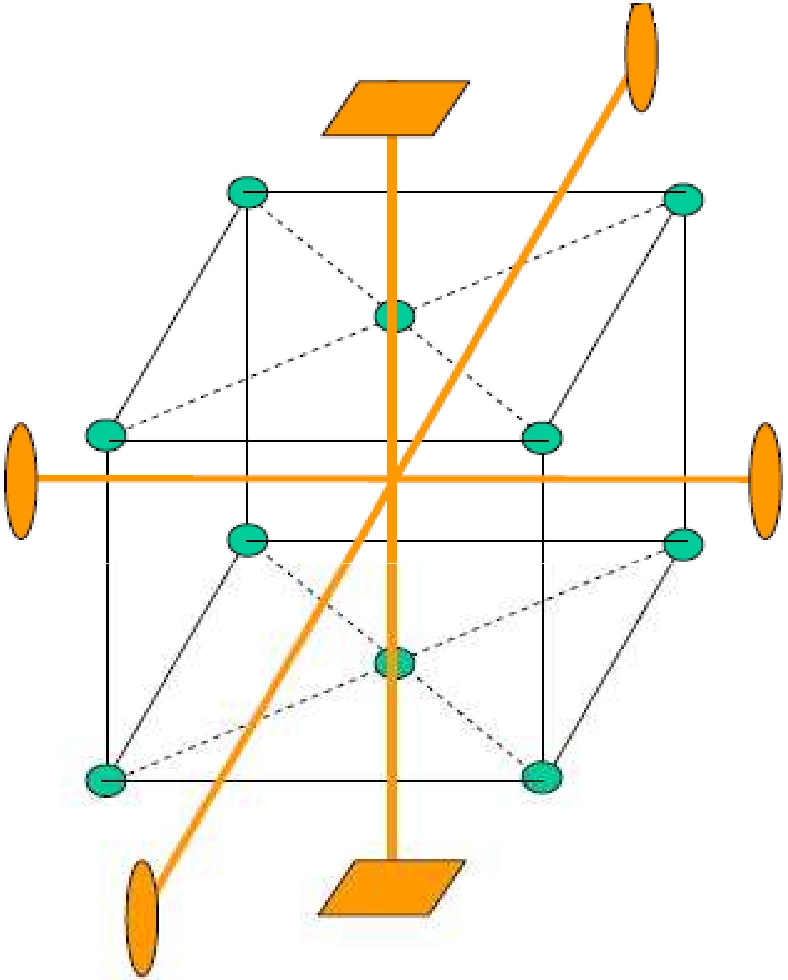


Face centre cubic in the Bravais list ?

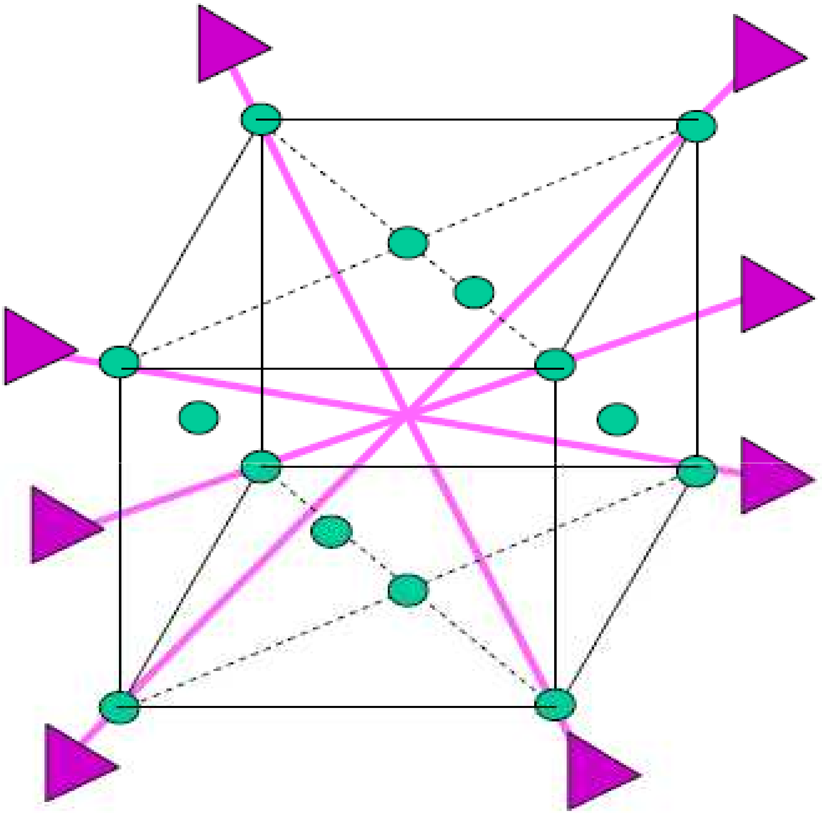


Cubic F = Tetragonal I ??? !

Tetragonal symmetry Cubic symmetry



Cubic C = Tetragonal P



Cubic F ≠ Tetragonal

IMPORTANT

Crystals and Crystal Systems are defined based on Symmetry

& NOT

Based on the Geometry of the Unit Cell

Example

Cubic Crystal

- Does NOT imply $a = b = c$ & $\alpha = \beta = \gamma$
- It implies the existence of two 3-fold axis in the structure

IMPORTANT

If lattices are based on just translation
(Translational Symmetry (t))
then how come other Symmetries *(especially rotational)* come into the picture while choosing the Crystal System & Unit Cell for a lattice?

Example

Why do we say that End Centred Cubic Lattice does not exist?

- Isn't it sufficient that $a = b = c$ & $\alpha = \beta = \gamma$ to call something cubic?

(why do we put End Centred Cubic in Simple Tetragonal?)

Answer

- The issue comes because we want to put 14 Bravais lattices into 7 boxes *(the 7 Crystal Systems; the Bravais lattices have 7 distinct symmetries)* and further assign Unit Cells to them
- The Crystal Systems are defined based on Symmetries *(Rotational, Mirror, Inversion etc. → forming the Point Groups)* and NOT on the geometry of the Unit Cell
- The Choice of Unit Cell is based on Symmetry & Size (& Convention)

(in practice the choice of unit cell is left to us! → but what we call the crystal is not!!)

Continued…

ONCE MORE:

- When we say End Centred Cubic →

  End Centred is a type of Lattice *(based on translation)*

  &

  Cubic is a type of Crystal *(based on other symmetries)*

  &

  Cubic also refers to a shape of Unit Cell *(based on lattice parameters)*

To emphasize:

- The word Cubic (e.g. in a cubic crystal) refers to 3 things →

  A type of Lattice *(based on translation)*

  &

  A type of Crystal *(based on other symmetries)*

  &

  A shape of Unit Cell *(based on lattice parameters)*

Arrangement of lattice points in the Unit Cell & No. of Lattice points / Cell

		Position of lattice points	Effective number of Lattice points / cell
1	P	8 Corners	= [8 × (1/8)] = 1
2	I	8 Corners + 1 body centre	= [1 (for corners)] + [1 (BC)] = 2
3	F	8 Corners + 6 face centres	= [1 (for corners)] + [6 × (1/2)] = 4
4	A/ B/ C	8 corners + 2 centres of opposite faces	= [1 (for corners)] + [2 × (1/2)] = 2

14 Bravais Lattices divided into 7 Crystal Systems

A Symmetry based concept

'Translation' based concept

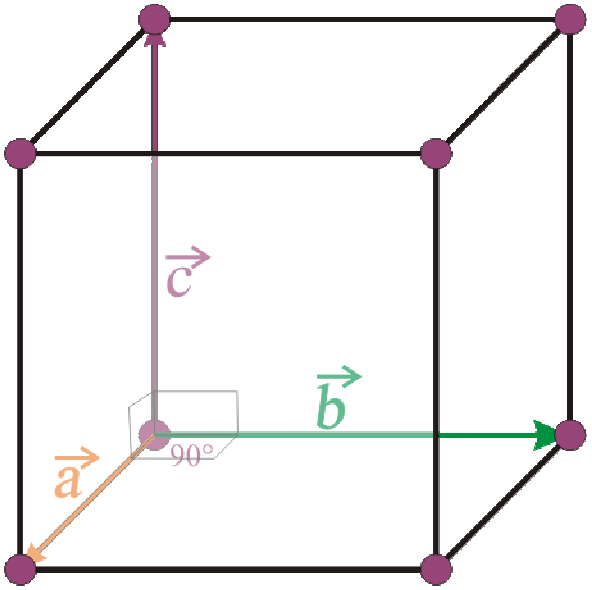
	Crystal System	Lattice Parameters	Bravais Lattices			
			P	I	F	C
1	Cubic	$(a = b = c, \alpha = \beta = \gamma = 90°)$	✓	✓	✓	
2	Tetragonal	$(a = b \neq c, \alpha = \beta = \gamma = 90°)$	✓	✓		
3	Orthorhombic	$(a \neq b \neq c, \alpha = \beta = \gamma = 90°)$	✓	✓	✓	✓
4	Hexagonal	$(a = b \neq c, \alpha = \beta = 90°, \gamma = 120°)$	✓			
5	Trigonal	$(a = b = c, \alpha = \beta = \gamma \neq 90°)$	✓			
6	Monoclinic	$(a \neq b \neq c, \alpha = \gamma = 90° \neq \beta)$	✓			✓
7	Triclinic	$(a \neq b \neq c, \alpha \neq \beta \neq \gamma)$	✓			

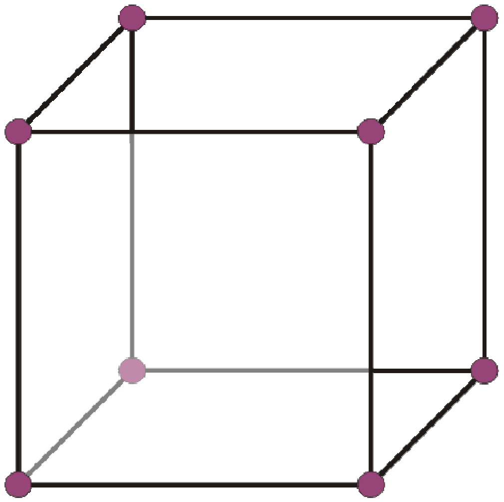
Why are some of the entries missing?

- Why is there no C-centred cubic lattice?
- Why is the F-centred tetragonal lattice missing?
- ….?

P	Primitive
I	Body Centred
F	Face Centred
C	A/B/C- Centred

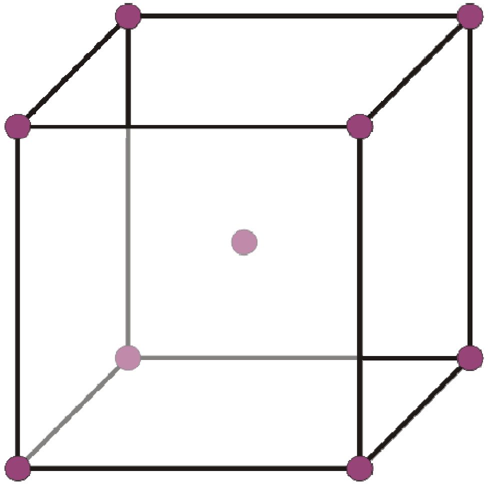
			P	I	F	C
1	Cubic	Cube	✓	✓	✓	




P

$a = b = c$

$\alpha = \beta = \gamma = 90°$

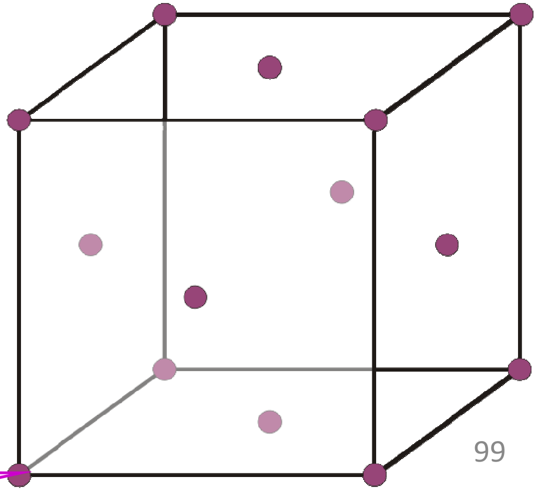

I

- Elements with Cubic structure →

  SC: F, O, Po

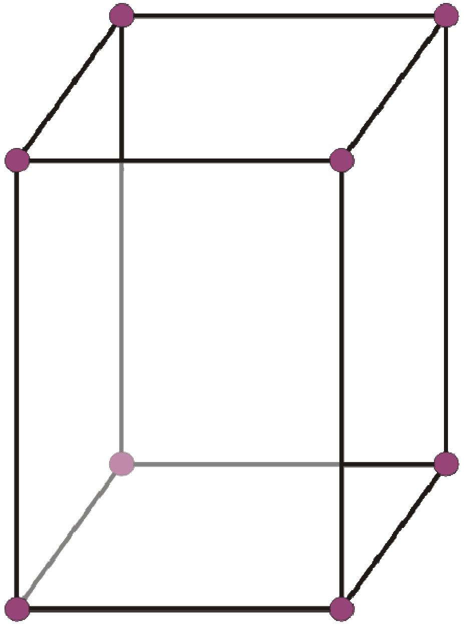
  BCC: Cr, Fe, Nb, K, W, V

  FCC: Al, Ar, Pb, Ni, Pd, Pt, Ge

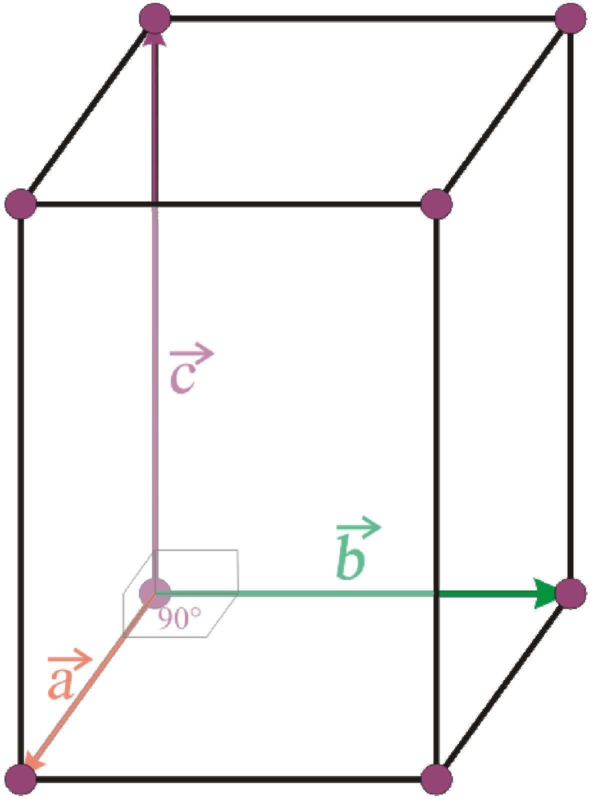

F

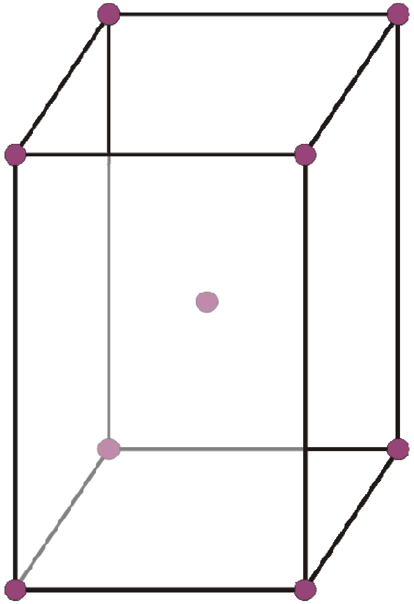
Lattice point

			P	I	F	C
2	Tetragonal	Square Prism (general height)	✓	✓		



P





I

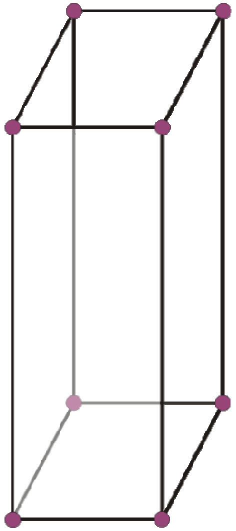
$$a = b \neq c$$

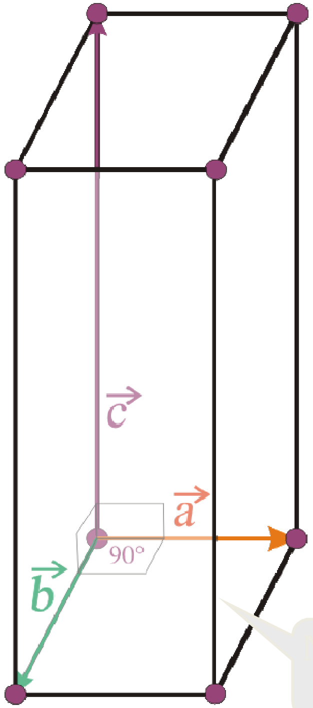
$$\alpha = \beta = \gamma = 90^\circ$$

- Elements with Tetragonal structure → In, Sn

			P	I	F	C
3	Orthorhombic	Rectangular Prism (general height)	✓	✓	✓	✓

P





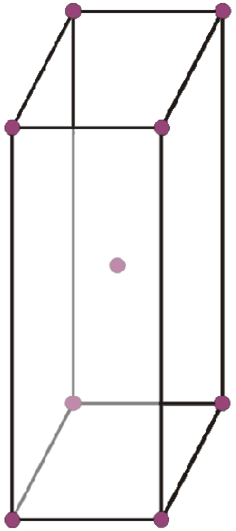
Note the position of ‘a’ and ‘b’

One convention

$a < b < c$

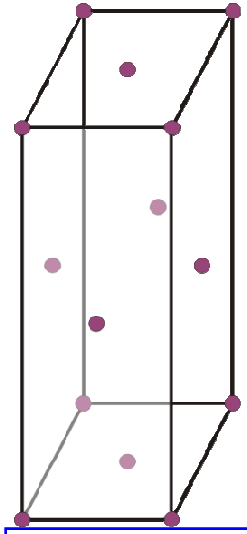
$a \neq b \neq c$

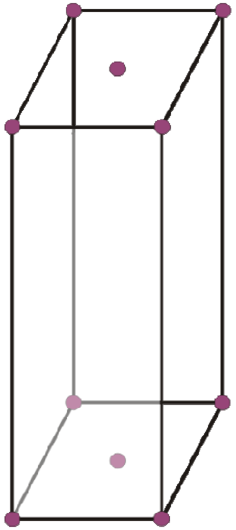
$\alpha = \beta = \gamma = 90°$



I

F

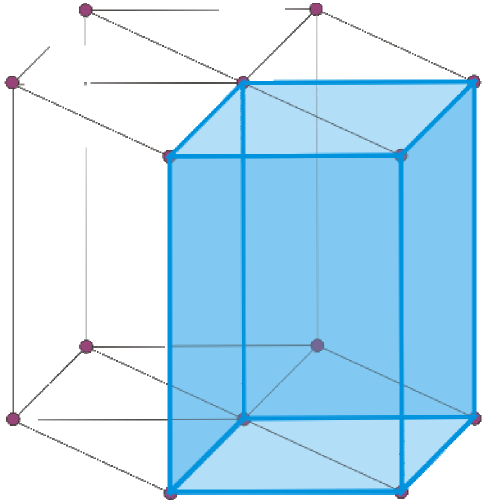




C

- Elements with Orthorhombic structure → Br, Cl, Ga, I, Su

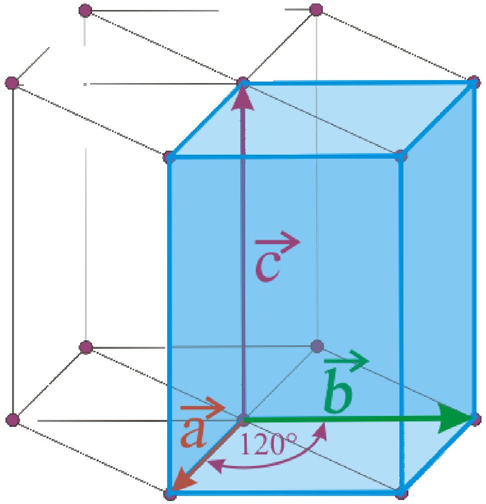
			P	I	F	C
4	Hexagonal	120° Rhombic Prism	✓			



A single unit cell *(marked in blue) along with a 3-unit cells forming a hexagonal prism*

$$a = b \neq c$$

$$\alpha = \beta = 90^\circ,\ \gamma = 120^\circ$$

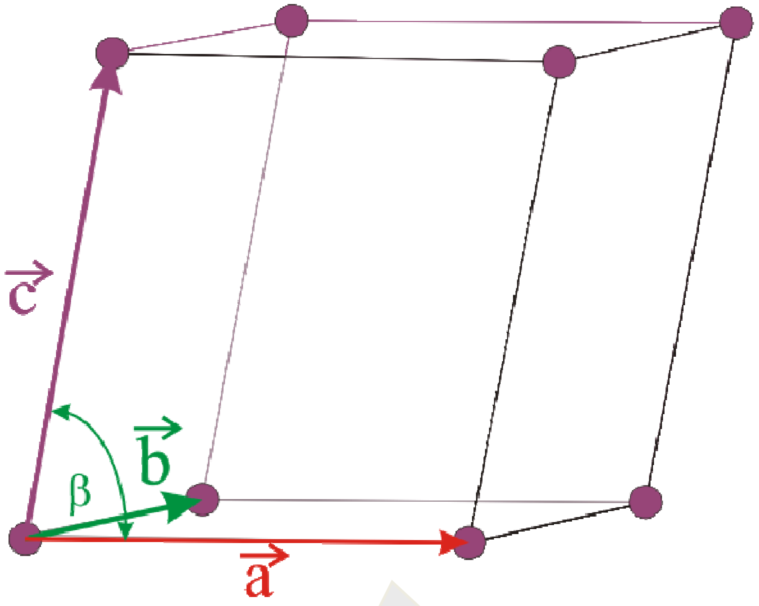


- Elements with Hexagonal structure → Be, Cd, Co, Ti, Zn

Note: there is only one type of hexagonal lattice *(the primitive one)*

What about the HCP?
(Does it not have an additional atom somewhere in the middle?)

			P	I	F	C
5	Trigonal / *Rhombohedral*	Parallelepiped (Equilateral, Equiangular)	✓			



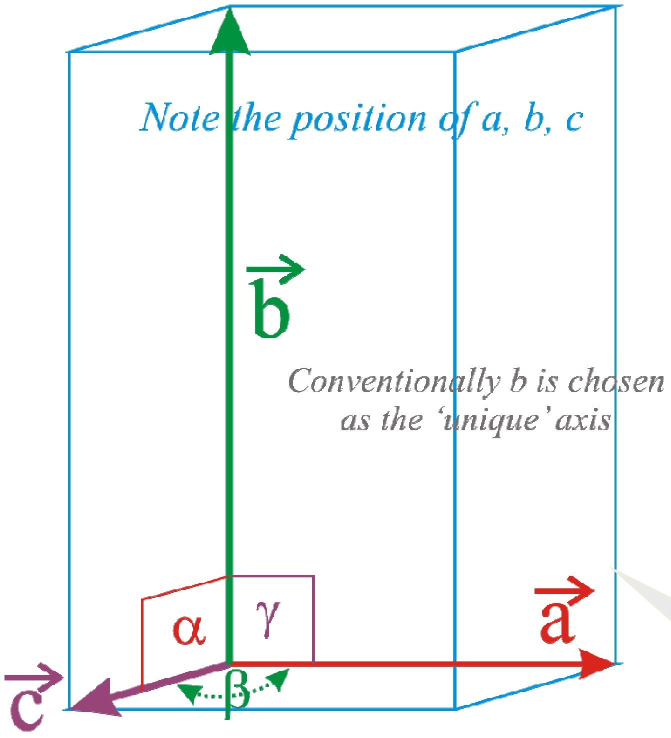
Note the position of the origin and of ‘a’, ‘b’ & ‘c’

$$\boxed{a = b = c}$$

$$\boxed{\alpha = \beta = \gamma \neq 90^\circ}$$

- Elements with Trigonal structure → As, B, Bi, Hg, Sb, Sm

			P	I	F	C
6	Monoclinic	Parallogramic Prism	✓			✓



Note the position of a, b, c

Conventionally b is chosen as the 'unique' axis

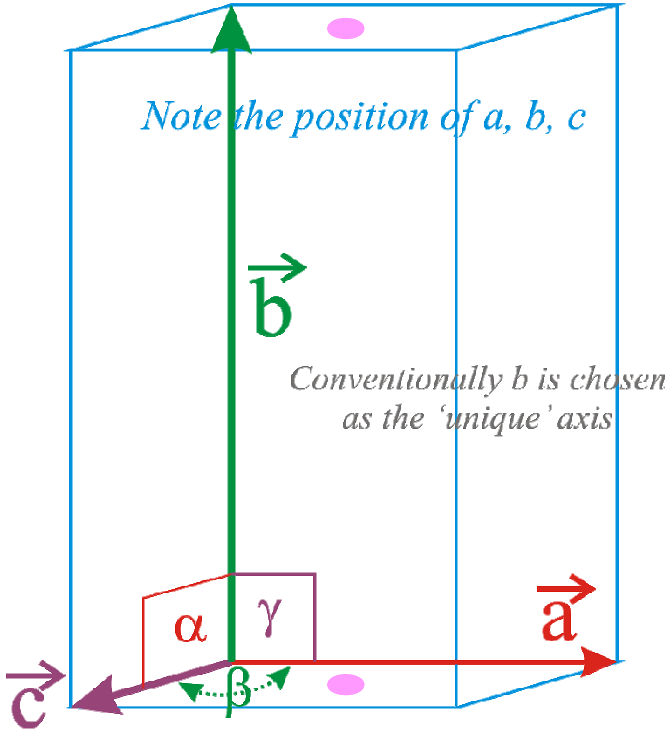
Note the position of 'a', 'b' & 'c'

One convention

$a < b < c$

$a \neq b \neq c$

$\alpha = \gamma = 90° \neq \beta$

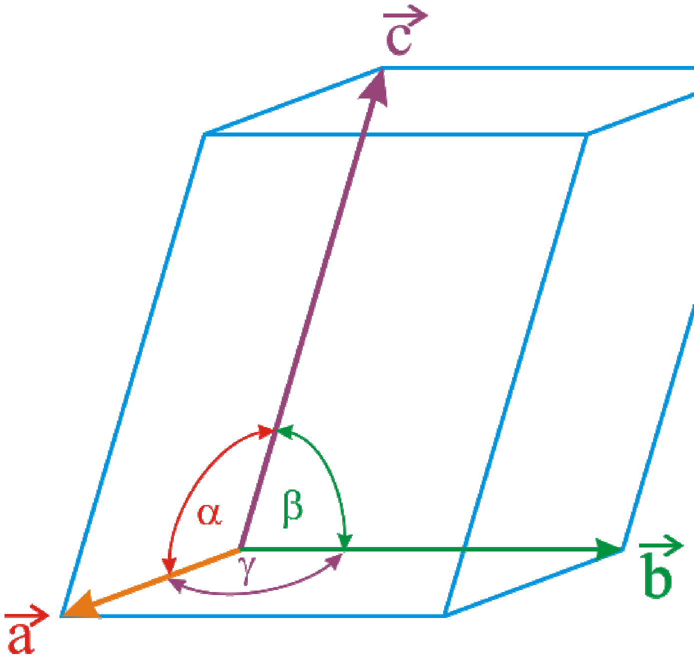


Note the position of a, b, c

Conventionally b is chosen as the 'unique' axis

- Elements with Monoclinic structure → P, Pu, Po

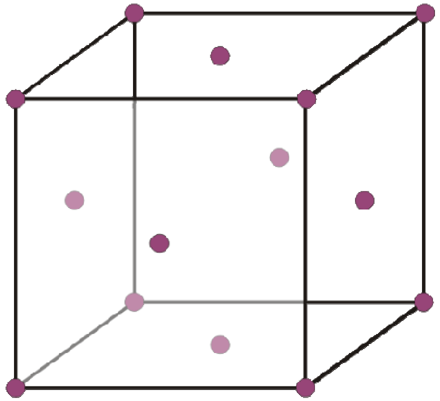
			P	I	F	C
7	Triclinic	Parallelepiped (general)	✓			



$$\boxed{a \neq b \neq c}$$

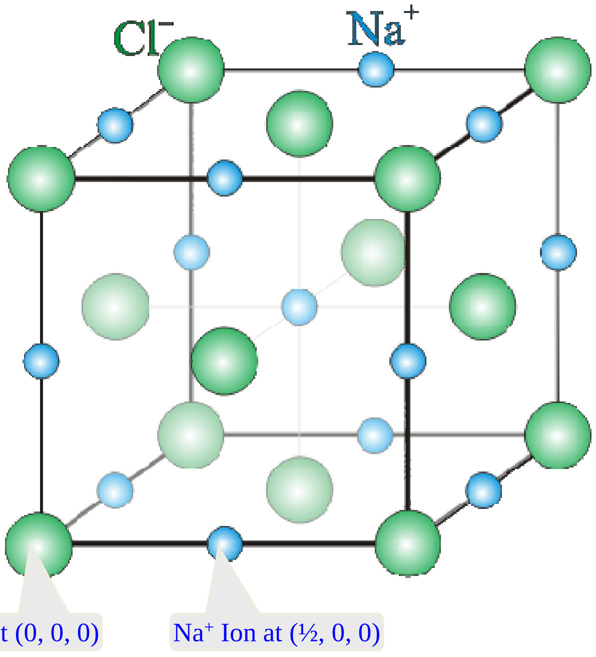
$$\boxed{\alpha \neq \beta \neq \gamma}$$

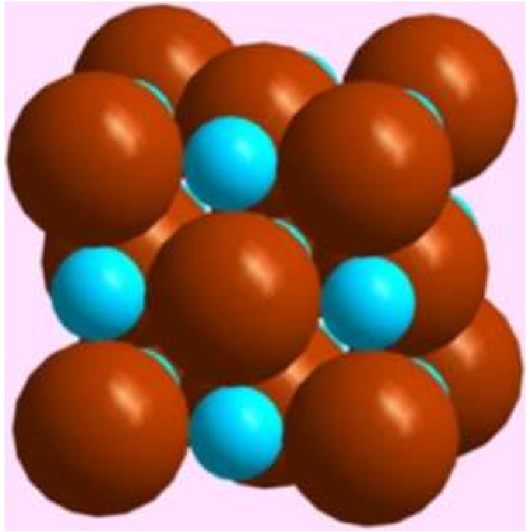
Face Centred Cubic (FCC) Lattice + Two Ion Motif



=

NaCl Crystal



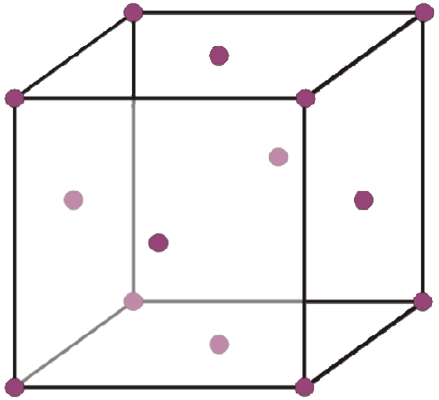


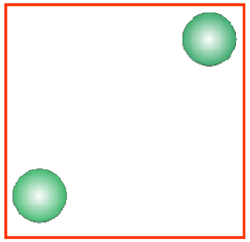
Note: This is not a close packed crystal *Has a packing fraction of ~0.67* *(using rigid sphere model)*

Face Centred Cubic (FCC) Lattice +

Two Carbon atom Motif

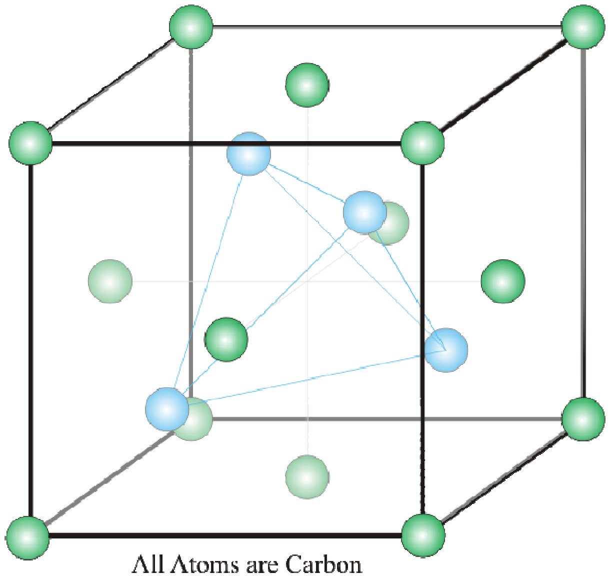
(0,0,0) & (¼, ¼, ¼)



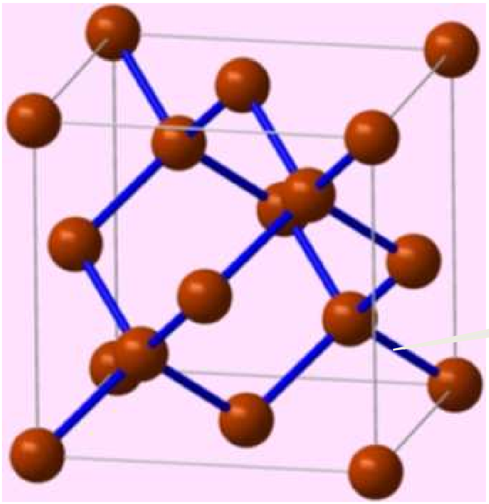


=

Diamond Cubic Crystal



All Atoms are Carbon
(coloured differently for better visibility)



Tetrahedral bonding of C
(sp^3 hybridized)

It requires a little thinking to convince yourself that the two atom motif actually sits at all lattice points!

Q & A

❑ What is a crystal?

➢ Crystal = Lattice + Motif

➢ An array of entities in space, having at least translational symmetry

❑ What constitutes a motif?

➢ A geometrical entity or a physical property or a combination of both can serve a motif

❑ How is the classification of crystals made into the 7 crystal system?

➢ The classification is purely based on symmetry

➢ E.g. if a crystal has only one 4-fold axis then it would be classified as a tetragonal crystal

➢ This classification is not based on geometry of the unit cell *(as commonly perceived)*

➢ Ofcourse if one has a cubic crystal, then it will be referred to the cubic axis system

❑ What are the 14 Bravais lattices?

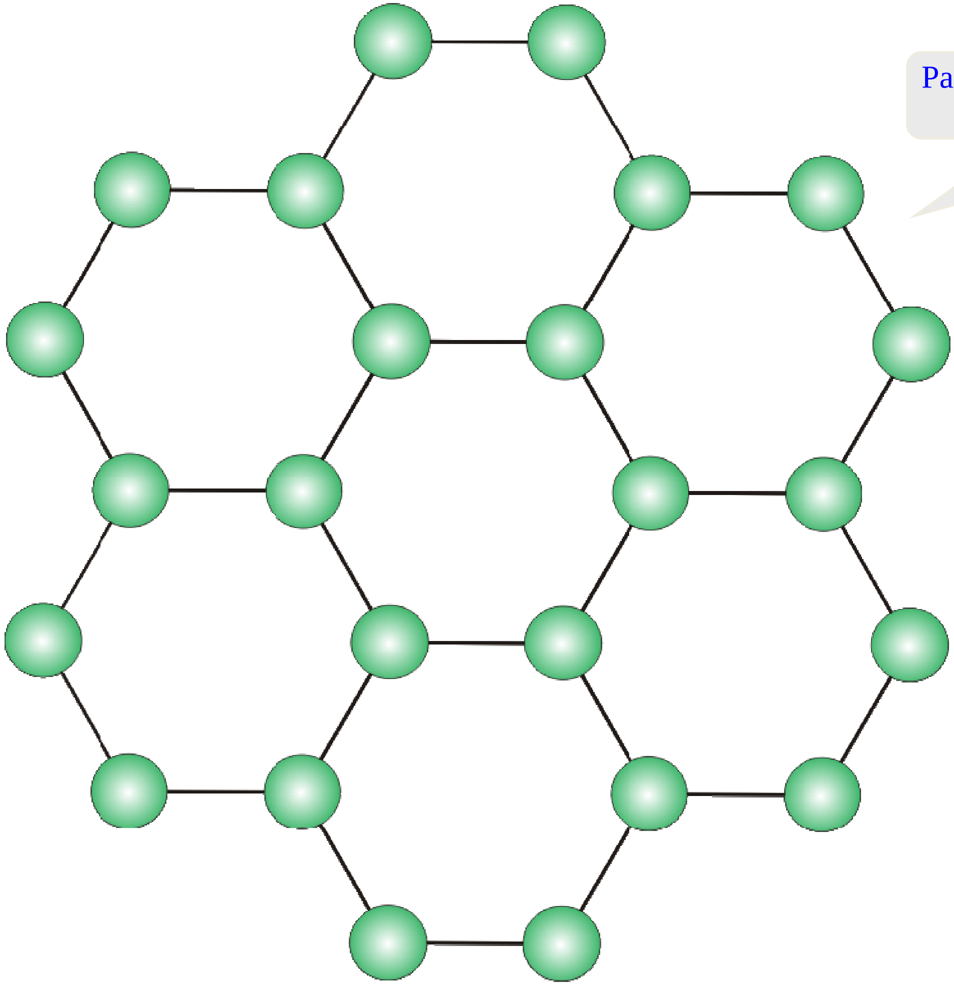
➢ There are only 14 different ways in which points can be arranged in 3D space such that each point has identical surrounding

Q & A

- What is a cubic crystal? *(or more formally, 'define a cubic crystal')*
  - A cubic crystal is one having Four 3-fold axes of rotational symmetry
  - It may or may not have 4-fold axes of symmetry!
  - If you *have* a cubic crystal, then you *may (i.e. may not also!)* chose axes like: $a = b = c$; $\alpha = \beta = \gamma = 90^o$ (but then you are allowed to make other choices!)
  - A cubic crystal should be defined based on symmetry and not the geometry of the unit cell.
- What is the relation between the 7 crystal systems and the 14 Bravais lattices?
  - Based on symmetry the 14 Bravais lattices can be put into 7 boxes → the 7 crystal systems
  - E.g. all lattices with two/four 3-fold axes are put into the box labeled 'cubic'

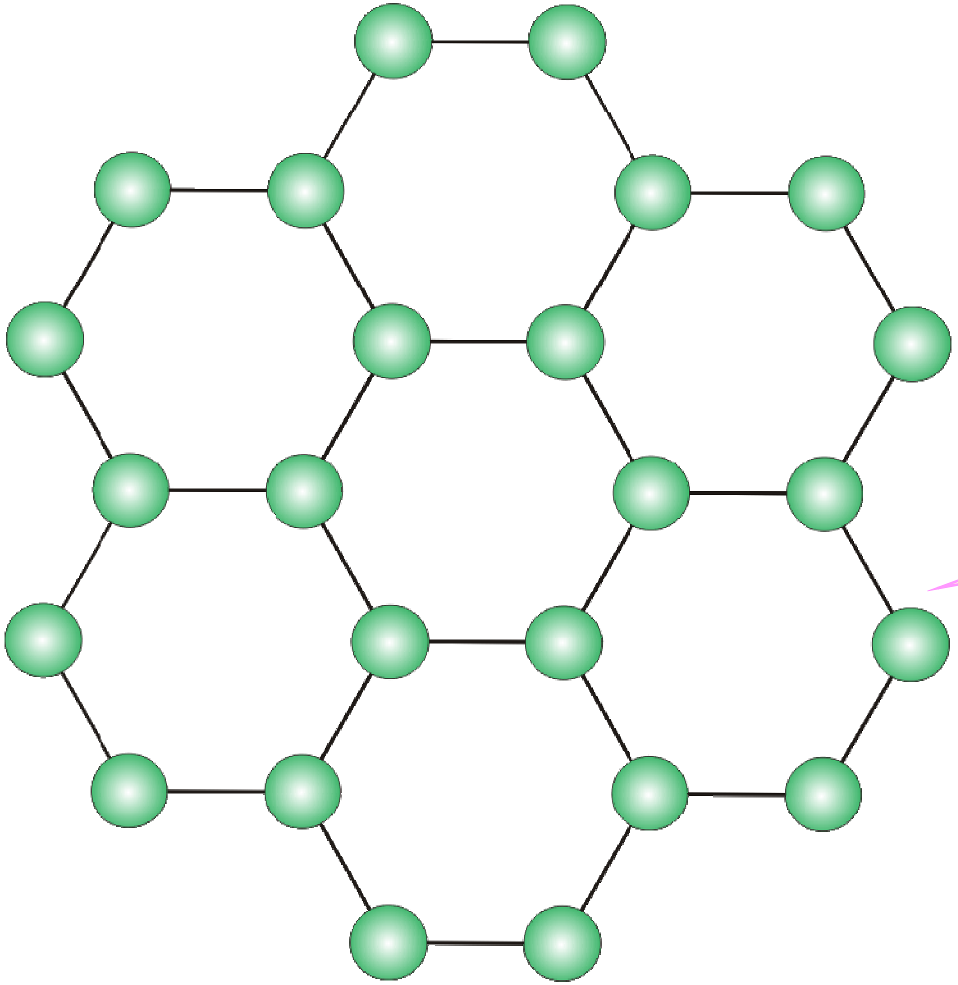
Solved Example

- Does the array of points at the centres of the Carbon atoms in the graphene sheet as shown below form a lattice?
- Describe the crystal in terms of a lattice and a motif
- What is the unit cell?

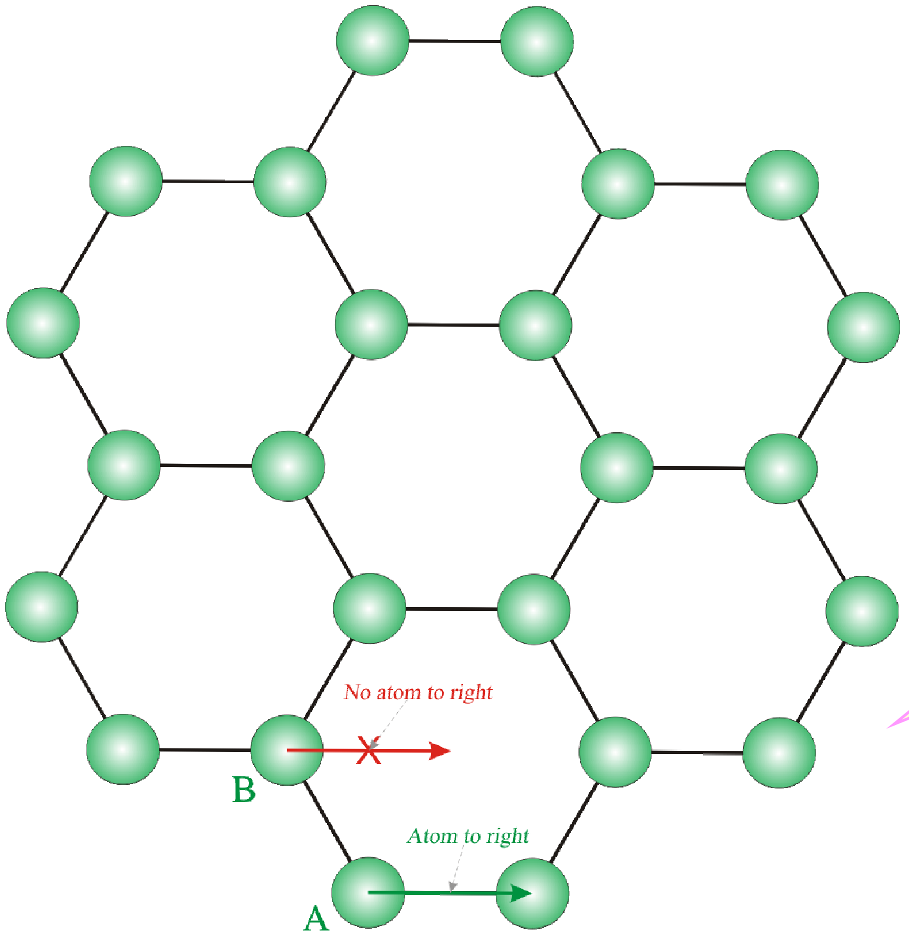


Part of the hexagonal array of C atoms which forms the Graphene structure

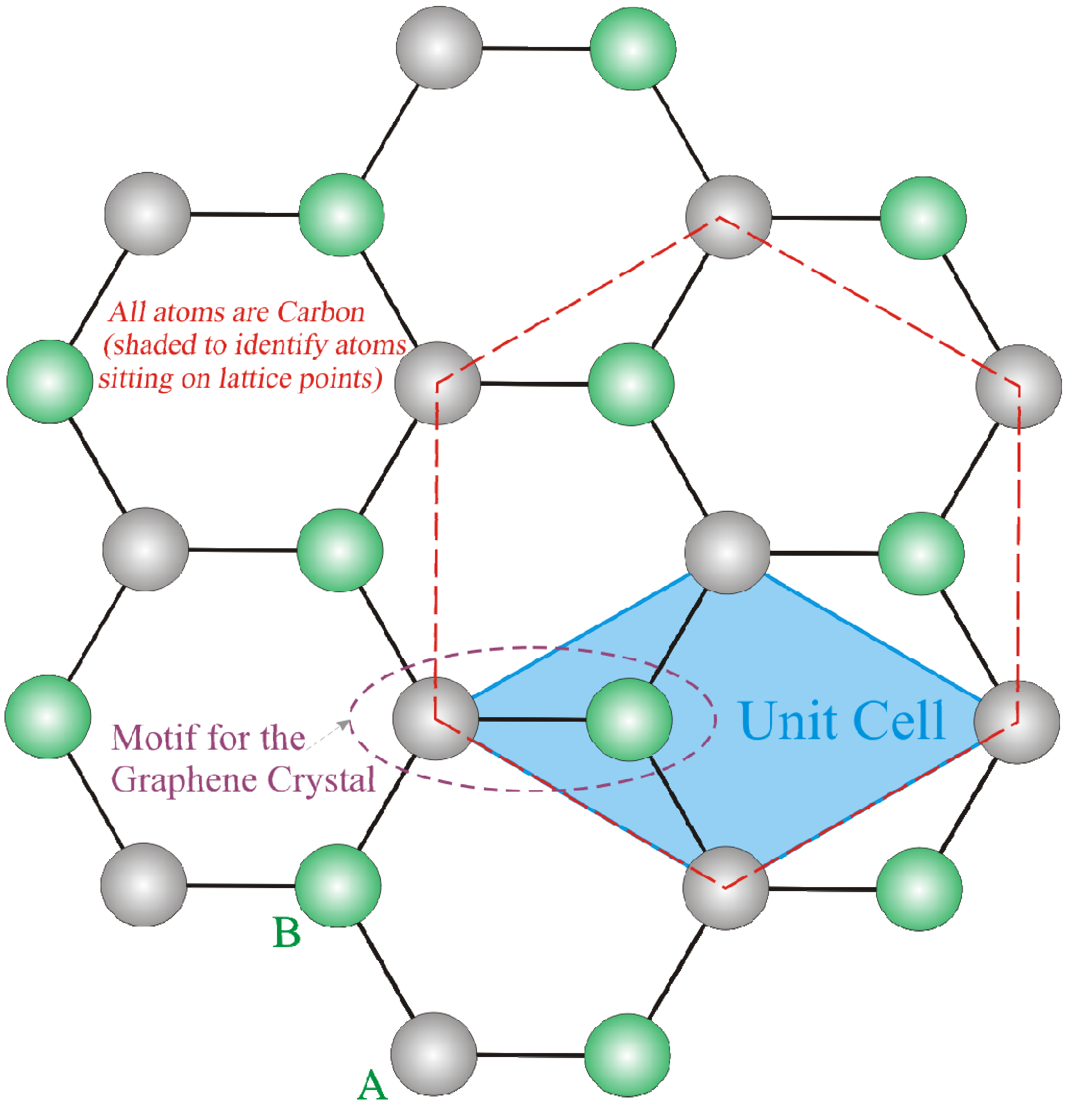
The answer is NO!



Not all carbon positions form a lattice



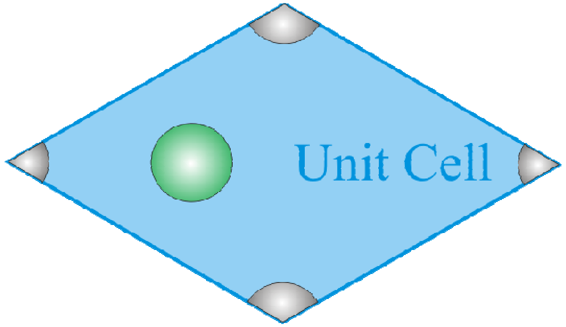
As atoms A & B do not have identical surrounding both cannot be lattice points

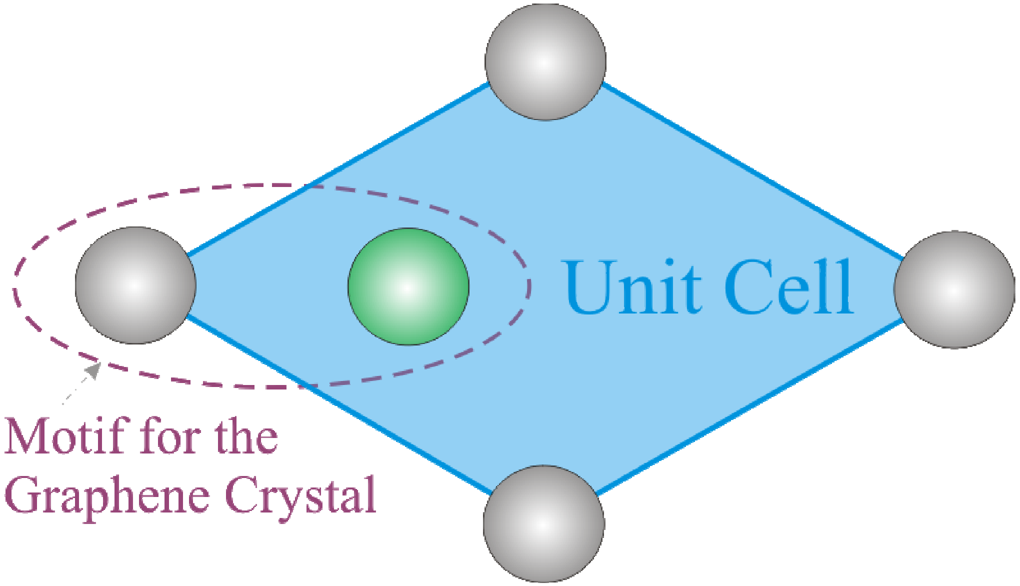


Crystal = Lattice + Motif

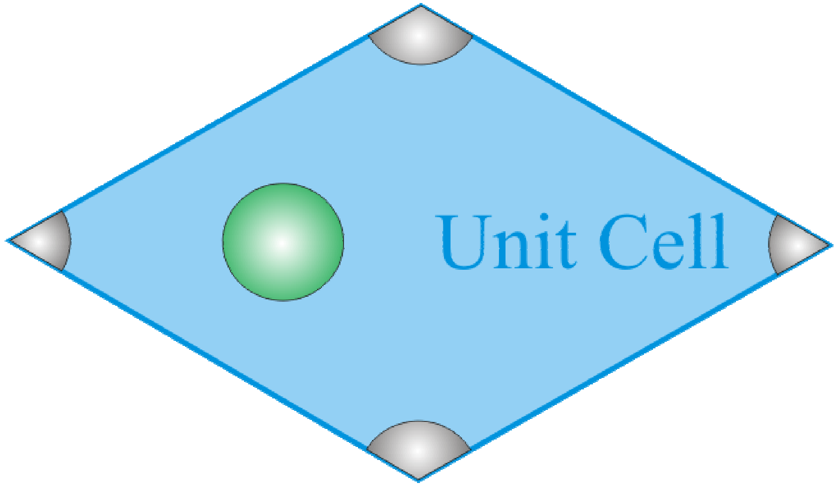
Grey atoms sit on the lattice positions

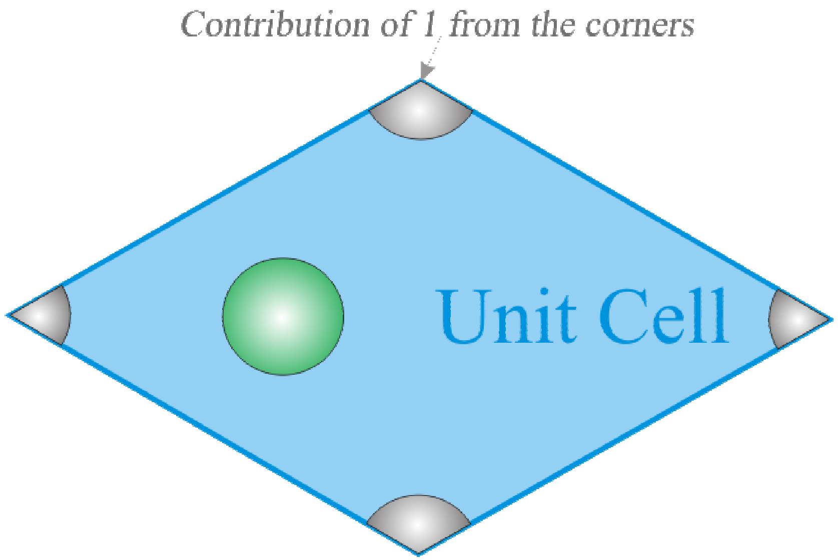
Motif = 1 grey + 1 green
(in positions as shown)





Primitive unit cell



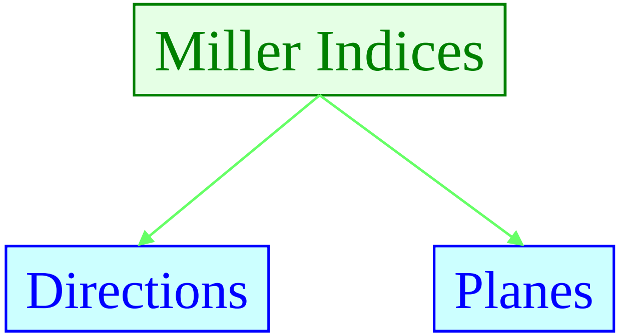


MILLER INDICES

- ☐ PLANES
- ☐ DIRECTIONS

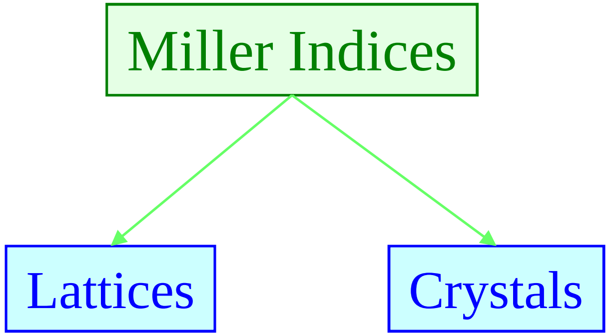
From the law of rational indices developed by French Physicist and mineralogist
Abbé René Just Haüy
and popularized by
William Hallowes Miller

- Miller indices are used to specify directions and planes.
- These directions and planes could be in lattices or in crystals.
- *(It should be mentioned at the outset that special care should be given to see if the indices are in a lattice or a crystal).*
- The number of indices will match with the dimension of the lattice or the crystal: in 1D there will be 1 index and 2D there will be two indices etc.
- Some aspects of Miller indices, especially those for planes, are not intuitively understood and hence some time has to be spent to familiarize oneself with the notation.


Miller Indices

Directions

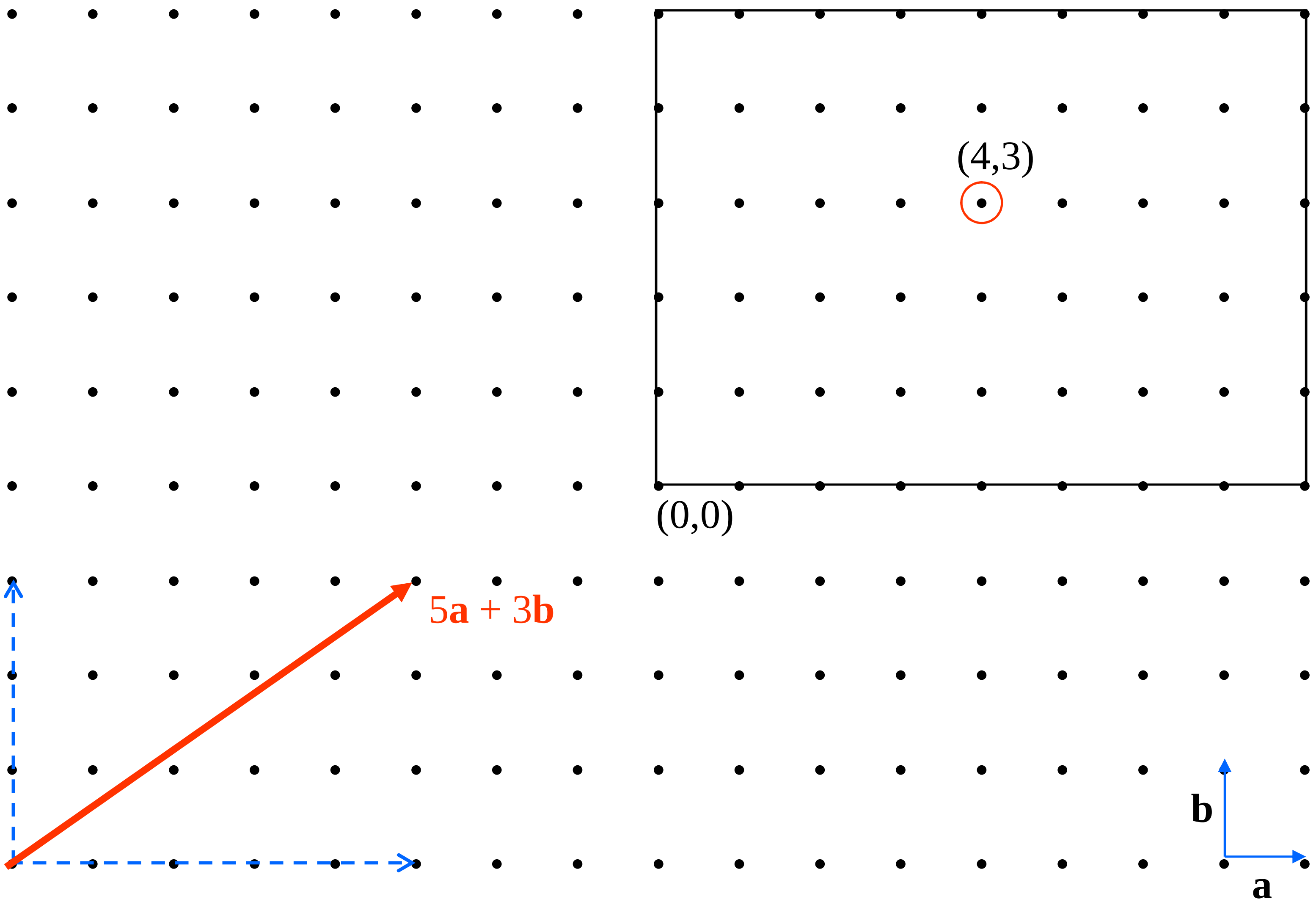
Planes


Miller Indices

Lattices

Crystals

Miller Indices for directions in 2D



Miller indices → [53]

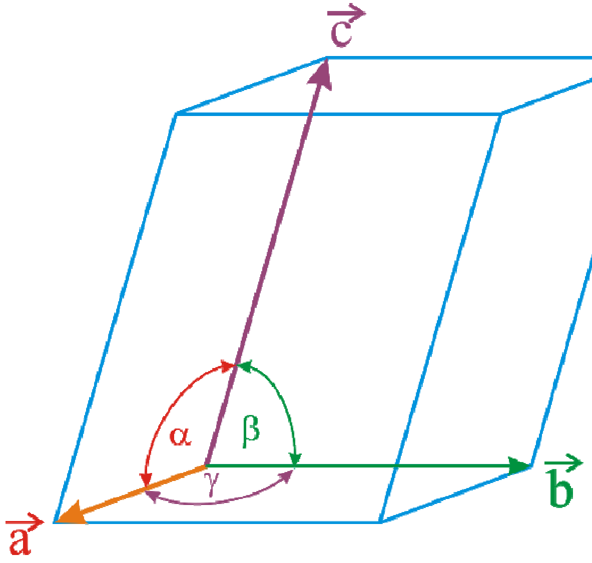
Miller indices for DIRECTIONS in 3D

A vector **r** passing from the origin to a lattice point can be written as: $\mathbf{r} = r_1\,\mathbf{a} + r_2\,\mathbf{b} + r_3\,\mathbf{c}$

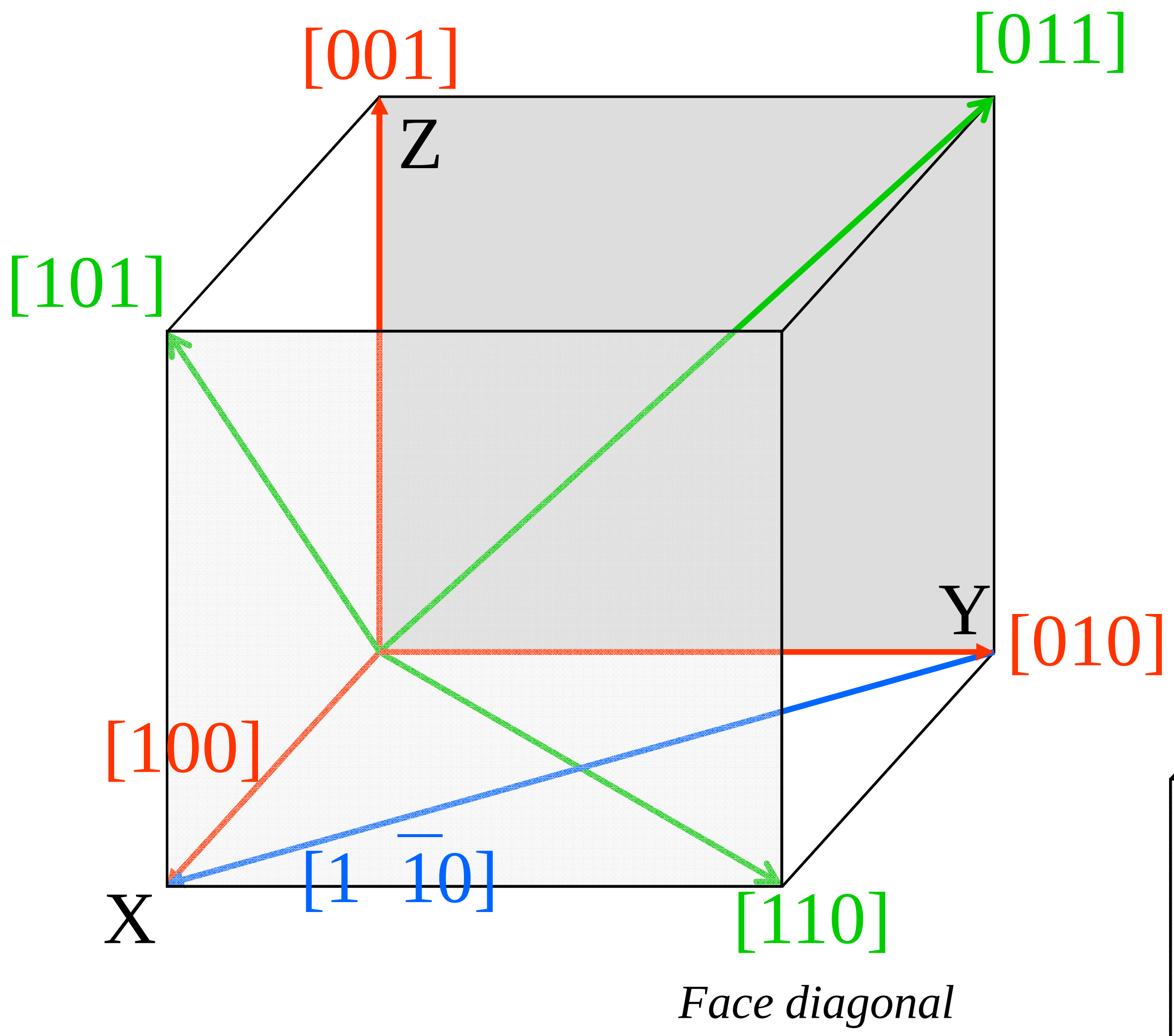
$$r = r_1\,\vec{a} + r_2\,\vec{b} + r_3\,\vec{c}$$

Where, **a**, **b**, **c** → basic vectors

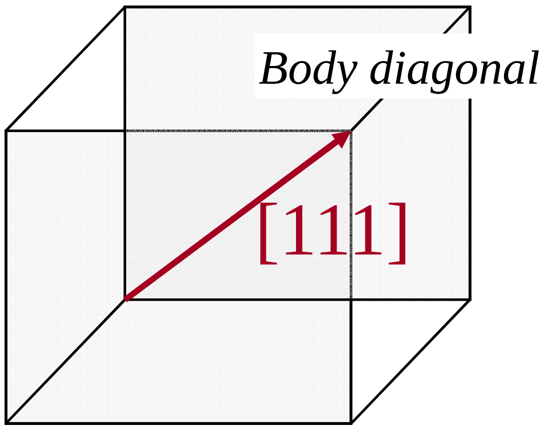
- Basis vectors are unit lattice translation vectors which define the coordinate axis *(as in the figure below)*.
- *Note their length is not 1 unit! (like for the basis vectors of a coordinate axis).*



Important directions in 3D represented by Miller Indices (cubic lattice)



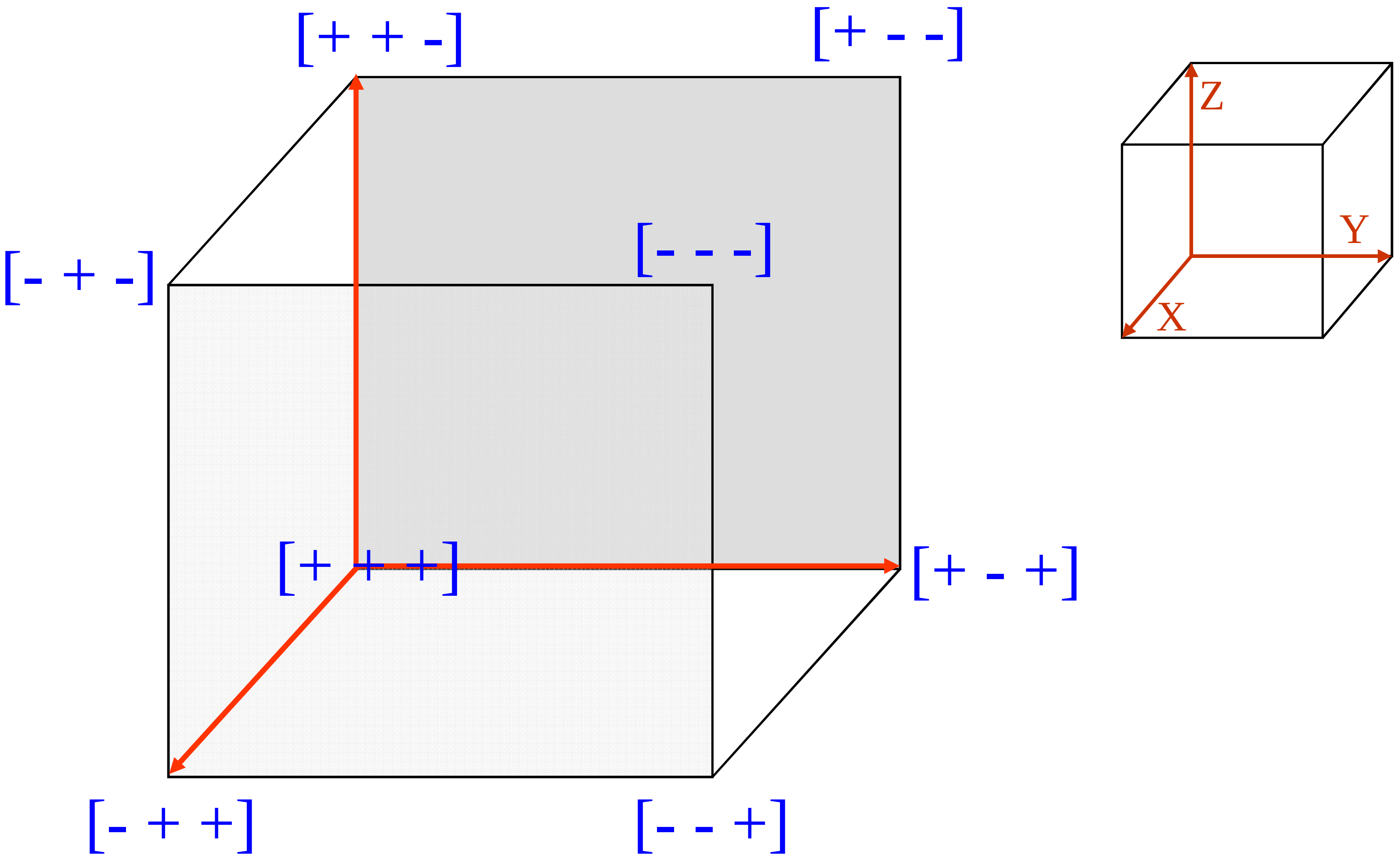
Memorize these



Procedure as before:

- (Coordinates of the final point – coordinates of the initial point)
- Reduce to smallest integer values

Possible coordinates in 3D



If you have confusion while selecting origin in negative indices refer this figure

Family of directions

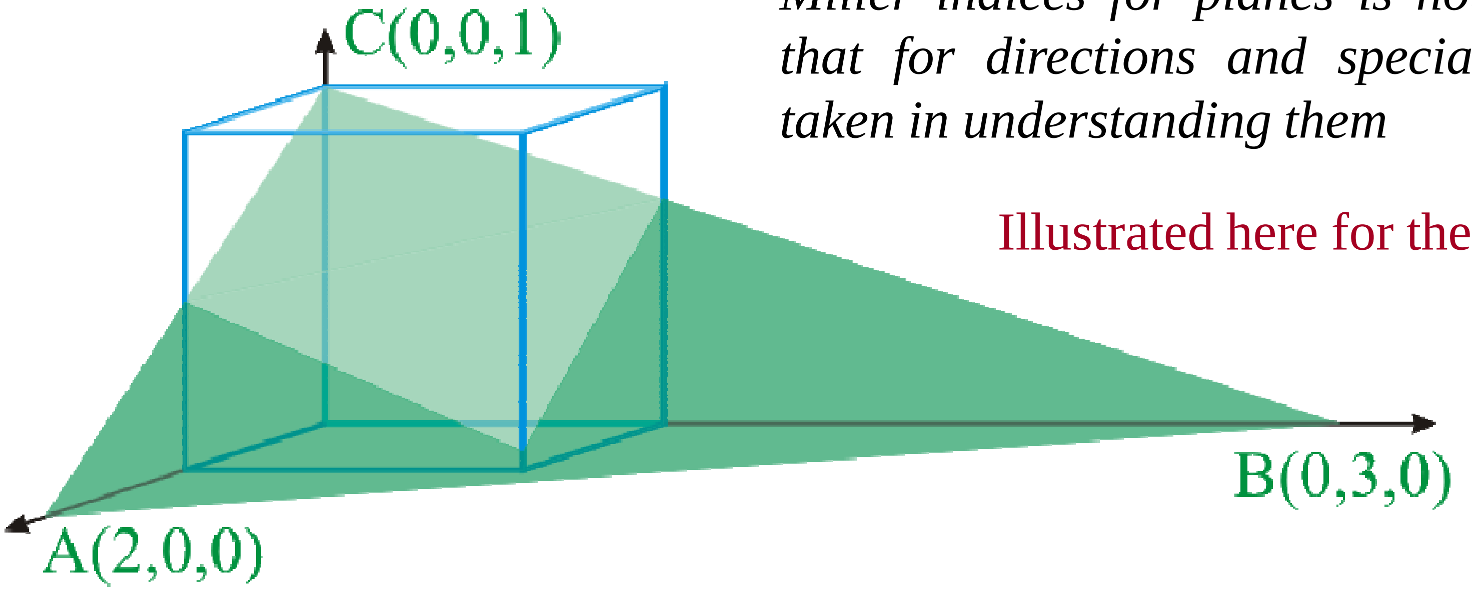
- ❑ A set of directions related by symmetry operations of the lattice or the crystal is called a family of directions
- ❑ A family of directions is represented (Miller Index notation) as: <u v w>

Index	Members in family for **cubic lattice**	Number
<100>	$[100],[\bar{1}00],[010],[0\bar{1}0],[001],[00\bar{1}]$	3 x 2 = 6
<110>	$[110],[\bar{1}10],[1\bar{1}0],[\bar{1}\bar{1}0],[101],[\bar{1}01],[10\bar{1}],[\bar{1}0\bar{1}],[011],[0\bar{1}1],[01\bar{1}],[0\bar{1}\bar{1}]$	6 x 2 = 12
<111>	$[111],[\bar{1}11],[1\bar{1}1],[11\bar{1}],[\bar{1}\bar{1}1],[\bar{1}1\bar{1}],[1\bar{1}\bar{1}],[\bar{1}\bar{1}\bar{1}]$	4 x 2 = 8

the ‘negatives’ (opposite direction)

Symbol	Alternate symbol		
[ ]		→	Particular direction
< >	[[ ]]	→	Family of directions

Miller Indices for PLANES

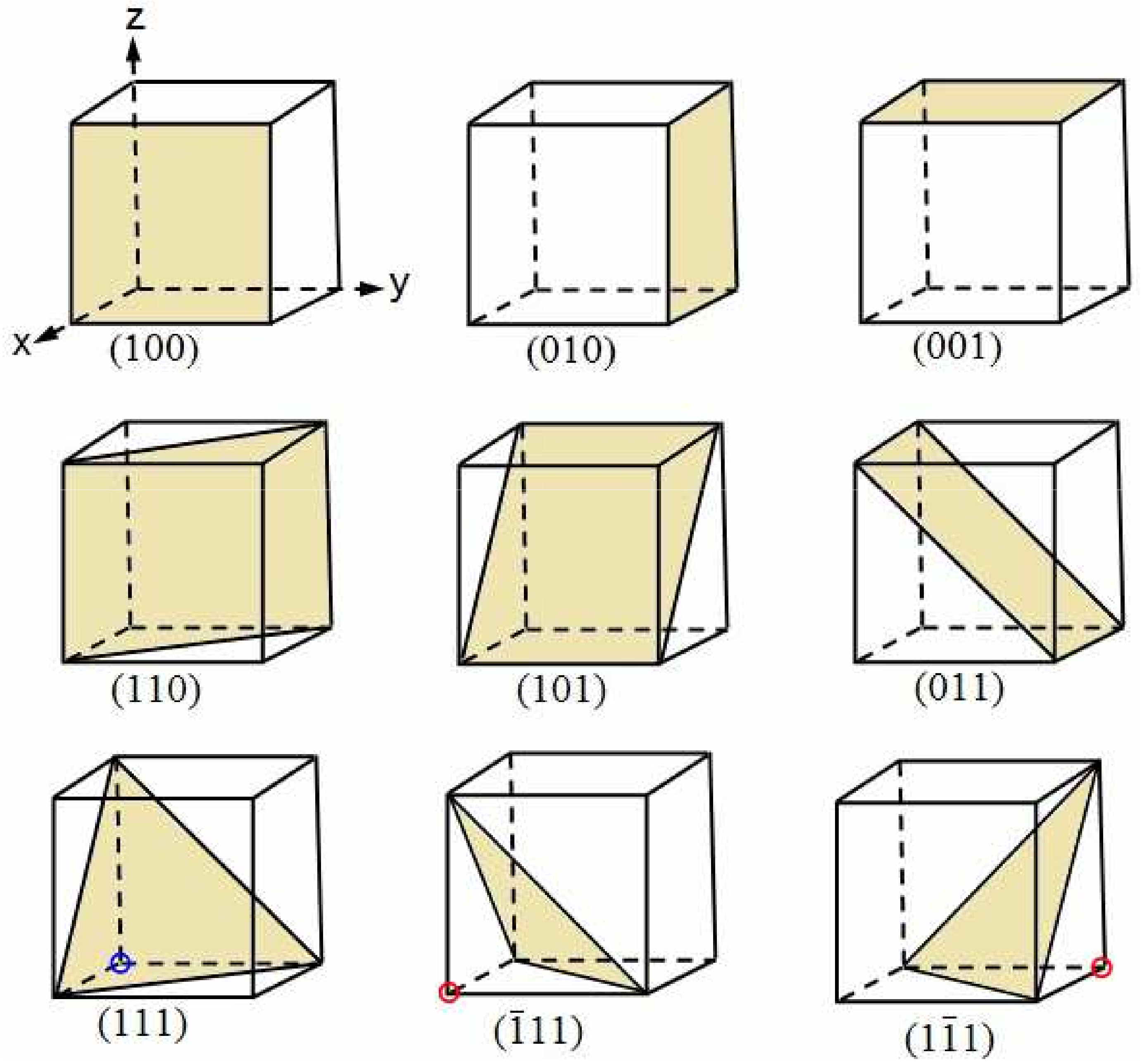


Miller indices for planes is not as intuitive as that for directions and special care must be taken in understanding them

Illustrated here for the cubic lattice

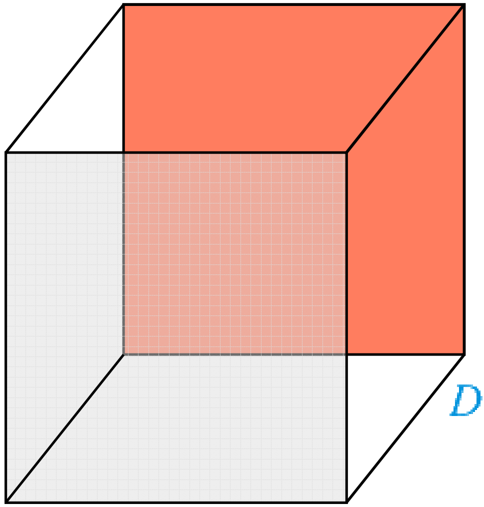
- ☐ Find intercepts along axes → 2 3 1
- ☐ Take reciprocal → 1/2 1/3 1
- ☐ Convert to smallest integers in the same ratio → 3 2 6
- ☐ Enclose in parenthesis → (326)

Important Planes in 3D represented by Miller Indices (cubic lattice)

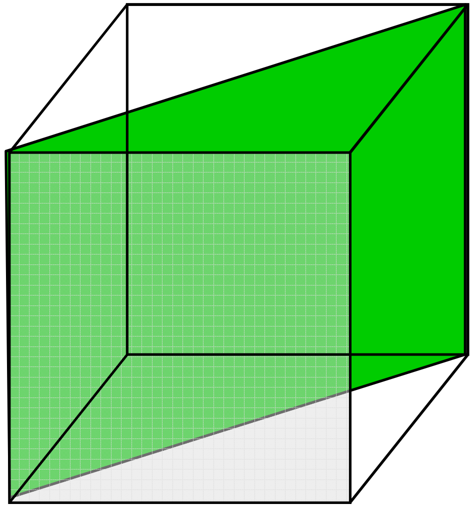


- ❑ A set of planes related by symmetry operations of the lattice or the crystal is called a family of planes
- ❑ All the points which one should keep in mind while dealing with directions to get the members of a family, should also be kept in mind when dealing with planes

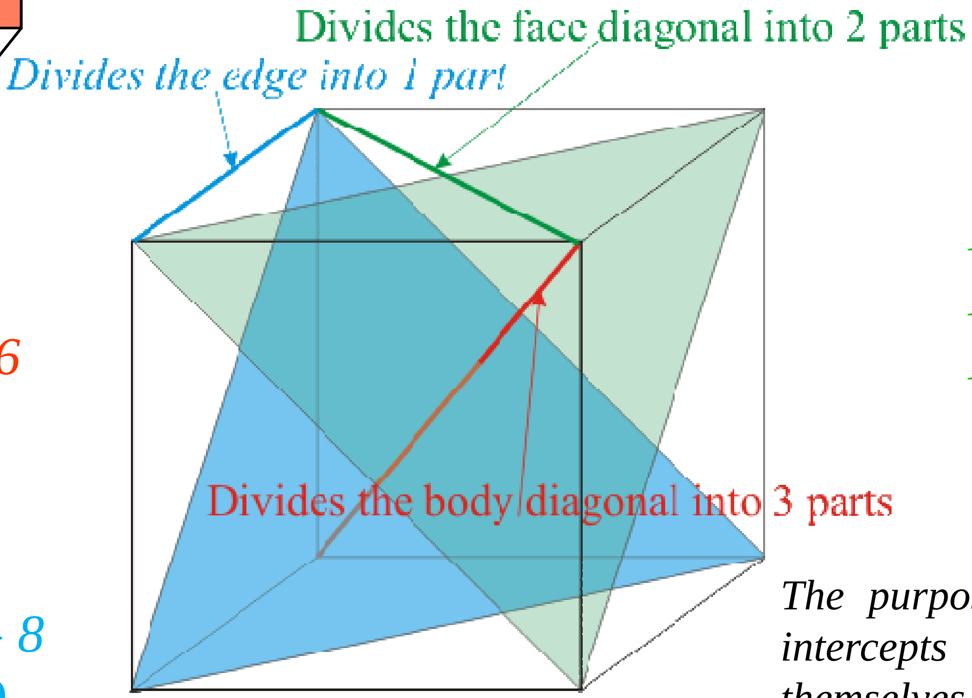
Family of planes



Intercepts → 1 ∞ ∞
Plane → (100)
Family → {100} → 6



Intercepts → 1 1 ∞
Plane → (110)
Family → {110} → 6



Divides the face diagonal into 2 parts

Divides the edge into 1 part

Divides the body diagonal into 3 parts

Intercepts → 1 1 1
Plane → (111)
Family → {111} → 8
(Octahedral plane)

The purpose of using reciprocal of intercepts and not intercepts themselves in Miller indices becomes clear → the ∞ are removed

Points about planes and directions

- ❑ Unknown direction → [uvw]
- ❑ Unknown plane → (hkl)
- ❑ Double digit indices should be separated by commas → (12,22,3)
- ❑ In cubic lattices/crystals [hkl] ⊥ (hkl)

Interplanar spacing (d_{hkl}) in cubic lattice (& crystals)

$$d_{hkl}^{\text{cubic lattice}} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

	Symbol		Alternate symbols		
Direction	[ ]	[uvw]		→	Particular direction
	< >	<uvw>	[[ ]]	→	Family of directions
Plane	( )	(hkl)		→	Particular plane
	{ }	{hkl}	(( ))	→	Family of planes

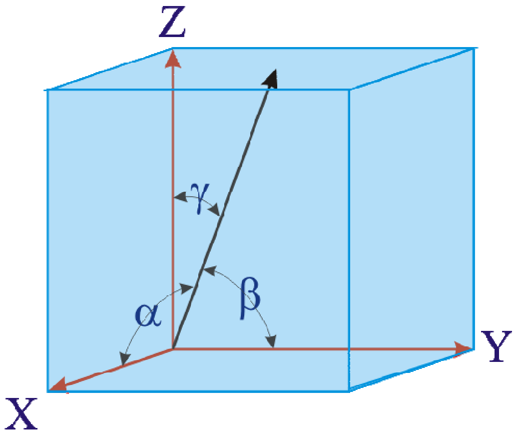
Note…!

- ❑ A direction in 3D can be specified by three angles- or the hree direction cosines.
- ❑ There is one equation connecting the three direction cosines:

$$Cos^2\alpha + Cos^2\beta + Cos^2\gamma = 1$$

- ❑ This implies that we required only two independent parameters to describe a direction. *Then why do we need three Miller indices?*
- ❑ The Miller indices prescribe the direction as a vector having a particular length (i.e. this prescription of length requires the additional index)
- ❑ Similarly three Miller indices are used for a plane (hkl) as this has additional information regarding interplanar spacing. E.g.:

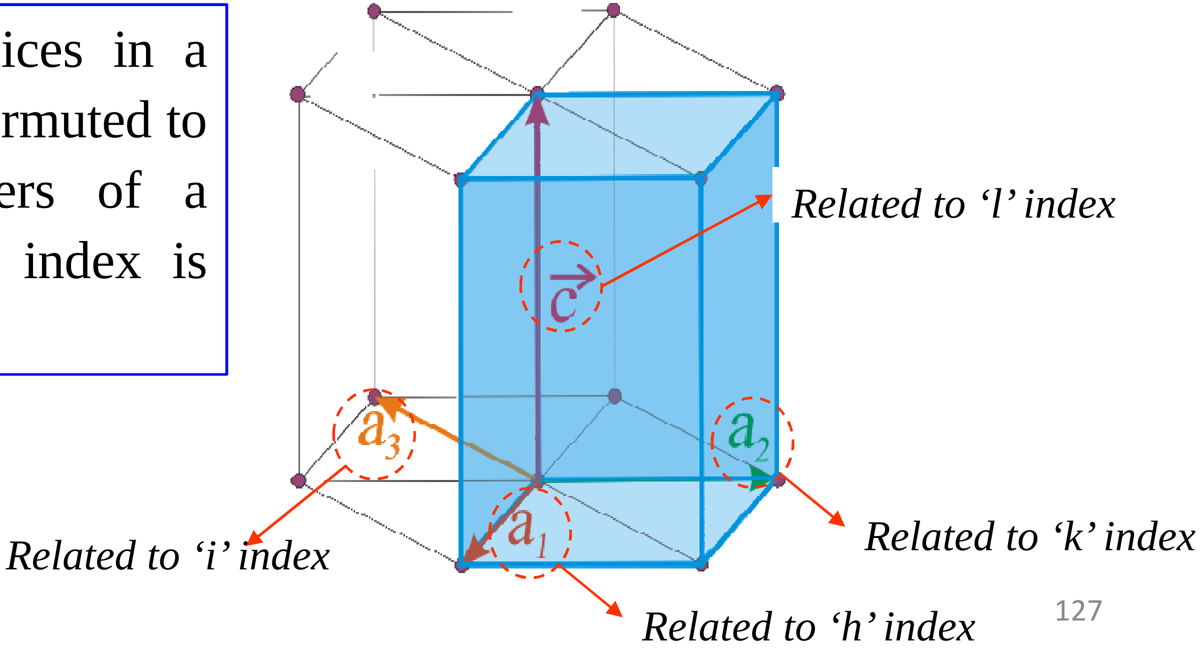
$$d_{hkl}^{cubic\ lattice} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$



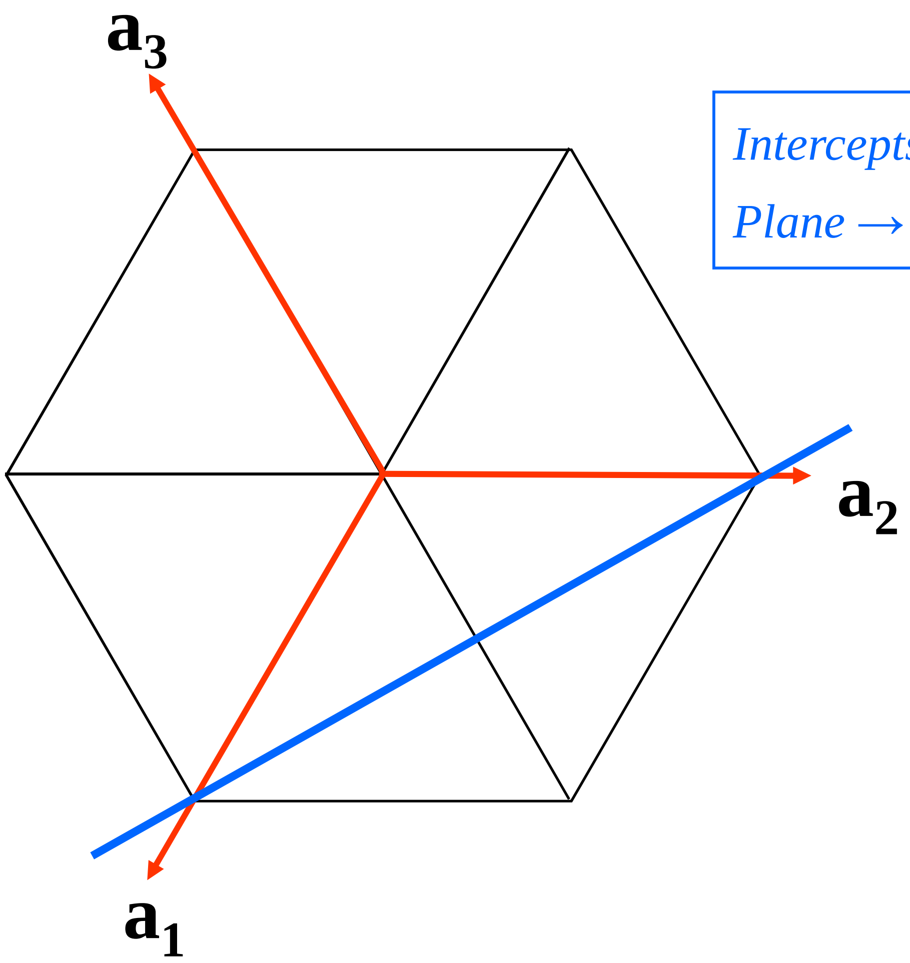
Hexagonal crystals → Miller-Bravais Indices : PLANES

- ☐ Directions and planes in hexagonal lattices and crystals are designated by the 4-index Miller-Bravais notation
- ☐ In the four index notation:
  - ➢ the first three indices are a symmetrically related set on the basal plane
  - ➢ the third index is a *redundant one* (which can be derived from the first two) and is introduced to make sure that members of a family of directions or planes have a set of numbers which are identical
  - ➢ the fourth index represents the ‘c’ axis *(⊥ to the basal plane)*

- ☐ Hence the first three indices in a hexagonal lattice can be permuted to get the different members of a family; while, the fourth index is kept separate.



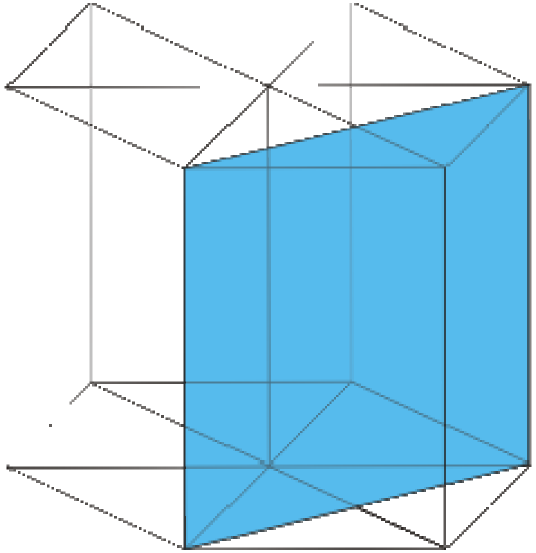
Hexagonal crystals → Miller-Bravais Indices : PLANES



Intercepts → 1 1 - ½ ∞

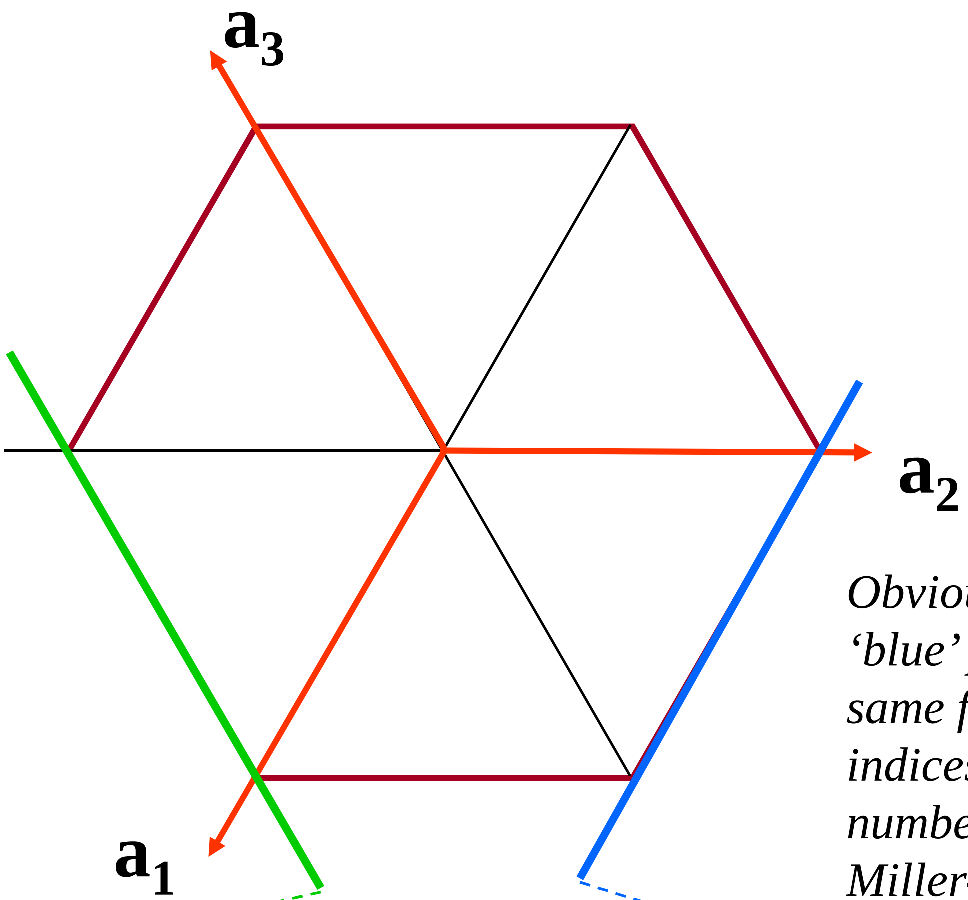
Plane → $(1\ 1\ \bar{2}\ 0)$

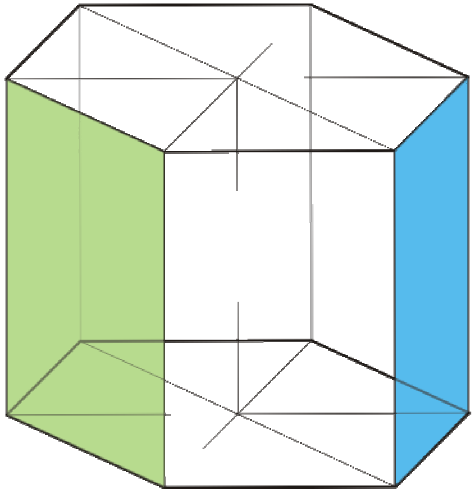
(h k i l)
i = −(h + k)



In general three indices point is denoted as miller indices i.e., (h k l). But hexagonal crystals we are using 4 indices point is denoted by miller-bravais indices i.e., (h k i l)The use of the 4 index notation is to bring out the equivalence between crystallographically equivalent planes and directions.

Hexagonal crystals → Miller-Bravais Indices : PLANES





Obviously the 'green' and 'blue' planes belong to the same family and first three indices have the same set of numbers (as brought out by the Miller-Bravais system)

Intercepts → 1 -1 ∞ ∞

Miller → (1 $\bar{1}$ 0)

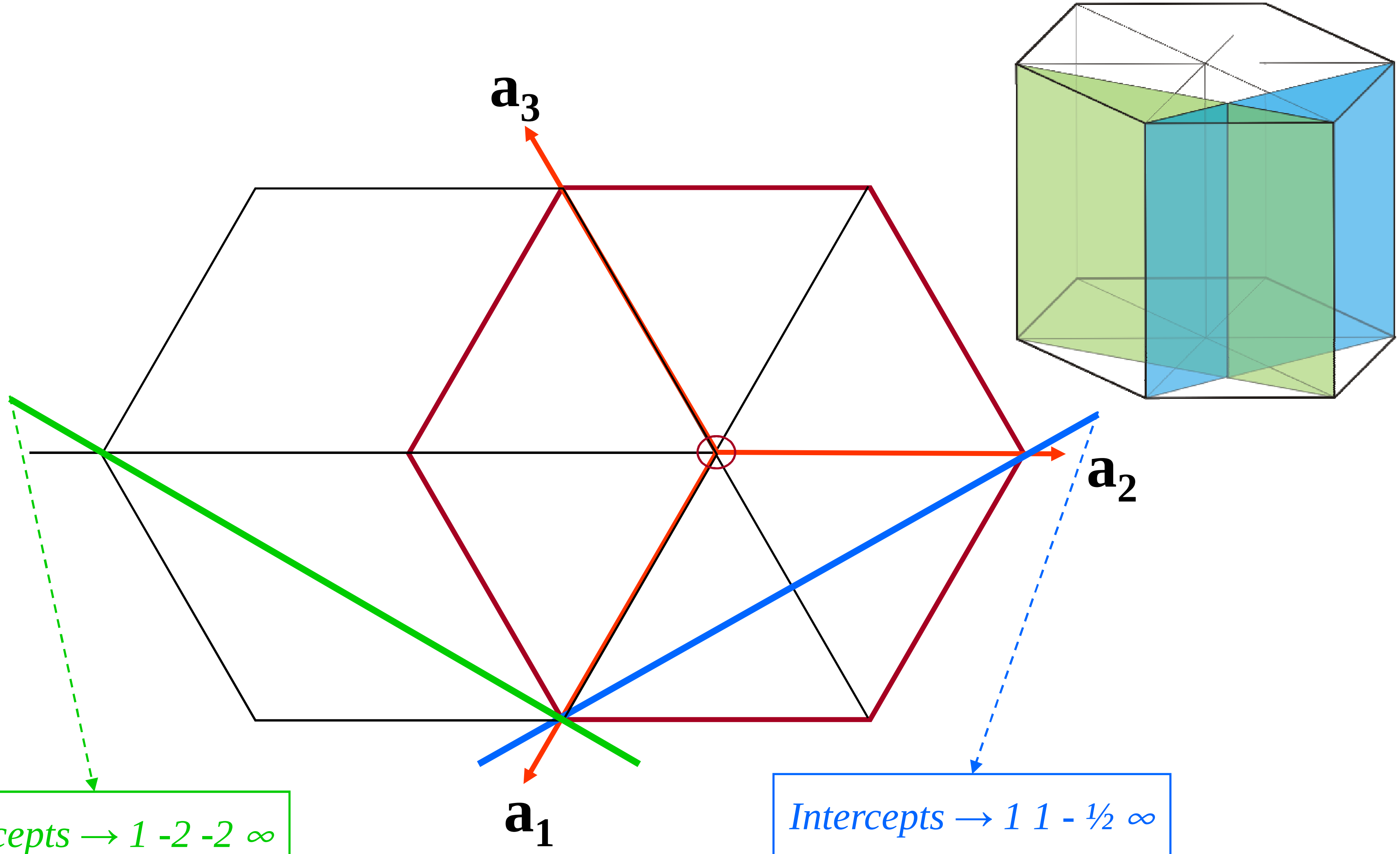
Miller-Bravais → (1 $\bar{1}$ 0 0)

Intercepts → ∞ 1 -1 ∞

Miller → (0 1 0)

Miller-Bravais → (0 1 $\bar{1}$ 0)

Hexagonal crystals → Miller-Bravais Indices : PLANES



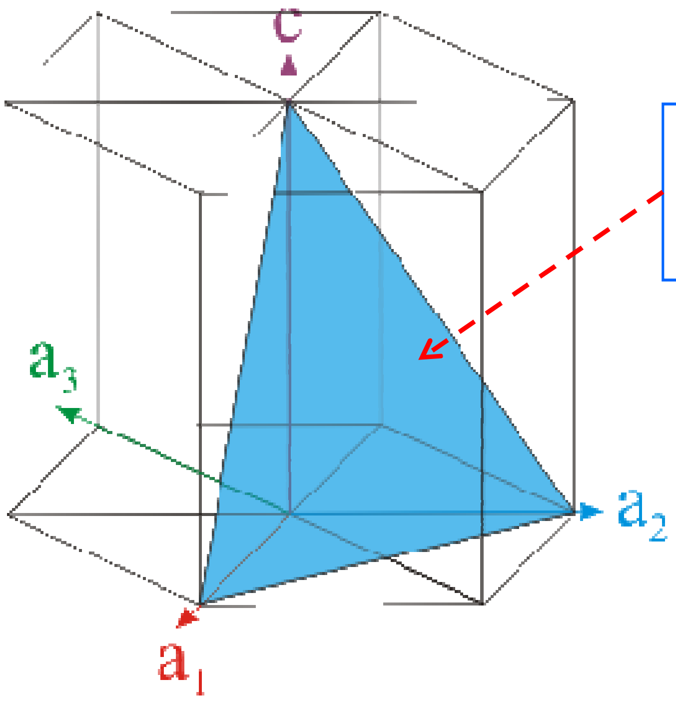
Intercepts → 1 -2 -2 ∞

Plane → (2 $\bar{1}$ $\bar{1}$ 0)

Intercepts → 1 1 - ½ ∞

Plane → (1 1 $\bar{2}$ 0)

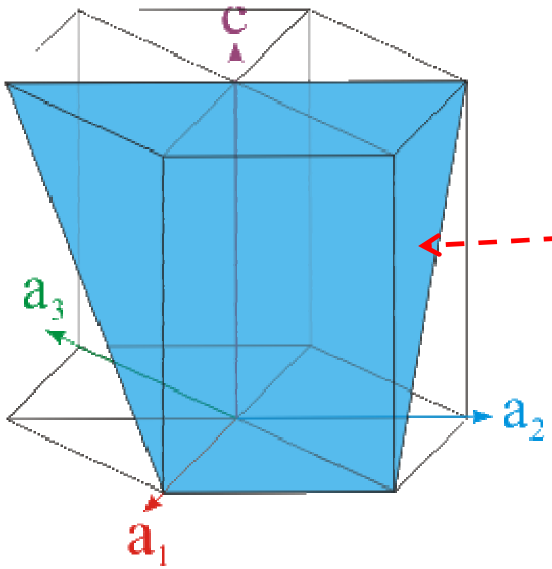
Hexagonal crystals → Miller-Bravais Indices : PLANES



Intercepts → 1 1 - ½ 1

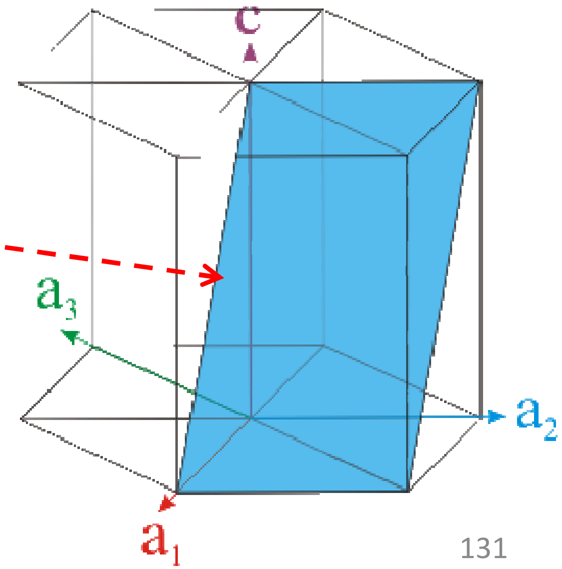
Plane → $(1\ 1\ \bar{2}\ 1)$

Both planes contain same intercepts. The common thing in these planes is $\mathbf{a_2}$ axis is infinite



Intercepts → $1\ \infty\ -1\ 1$

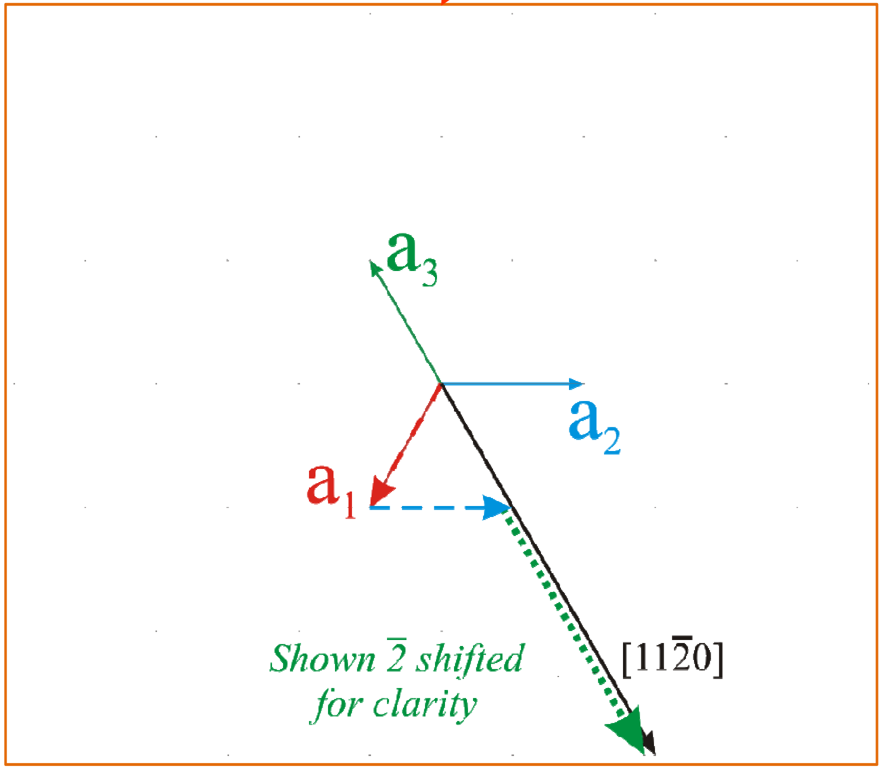
Plane → $(1\ 0\ \bar{1}\ 1)$



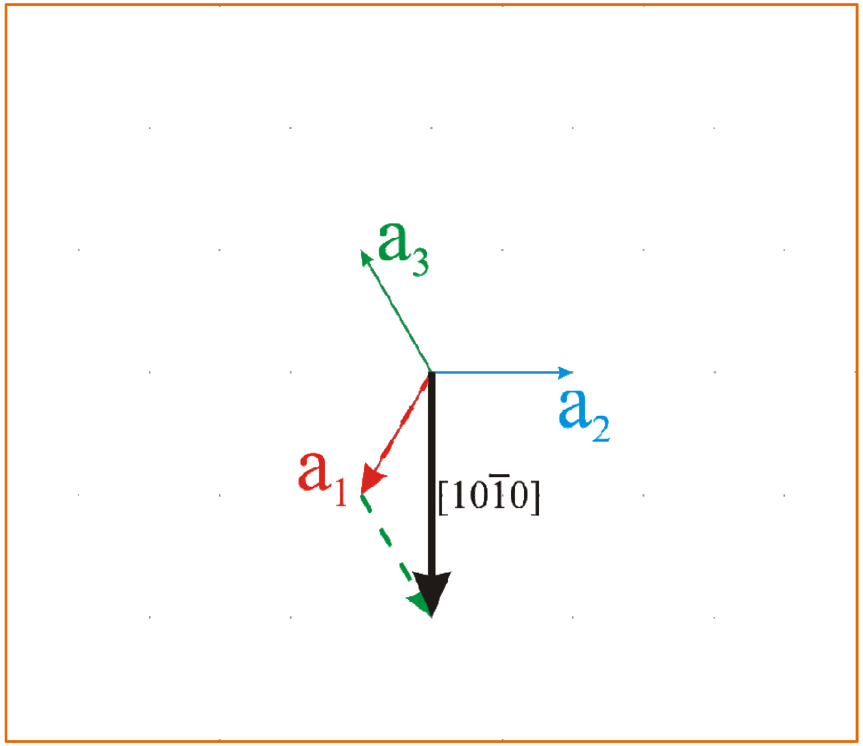
Hexagonal crystals → Miller-Bravais Indices : DIRECTIONS

Drawing the $[11\bar{2}0]$ *direction*

- Trace a path along the basis vectors as required by the direction. In the current example move 1unit along a_1, 1unit along a_2 and –2 units along a_3.
- Directions are projected onto the basis vectors to determine the components and hence the Miller-Bravais indices can be determined as in the table.



Drawing the $[10\bar{1}0]$ direction



Hexagonal crystals → Miller-Bravais Indices : DIRECTIONS

Transformation between 3-index *[UVW]* and 4-index *[uvtw]* notations

$$U = u - t$$

$$V = v - t$$

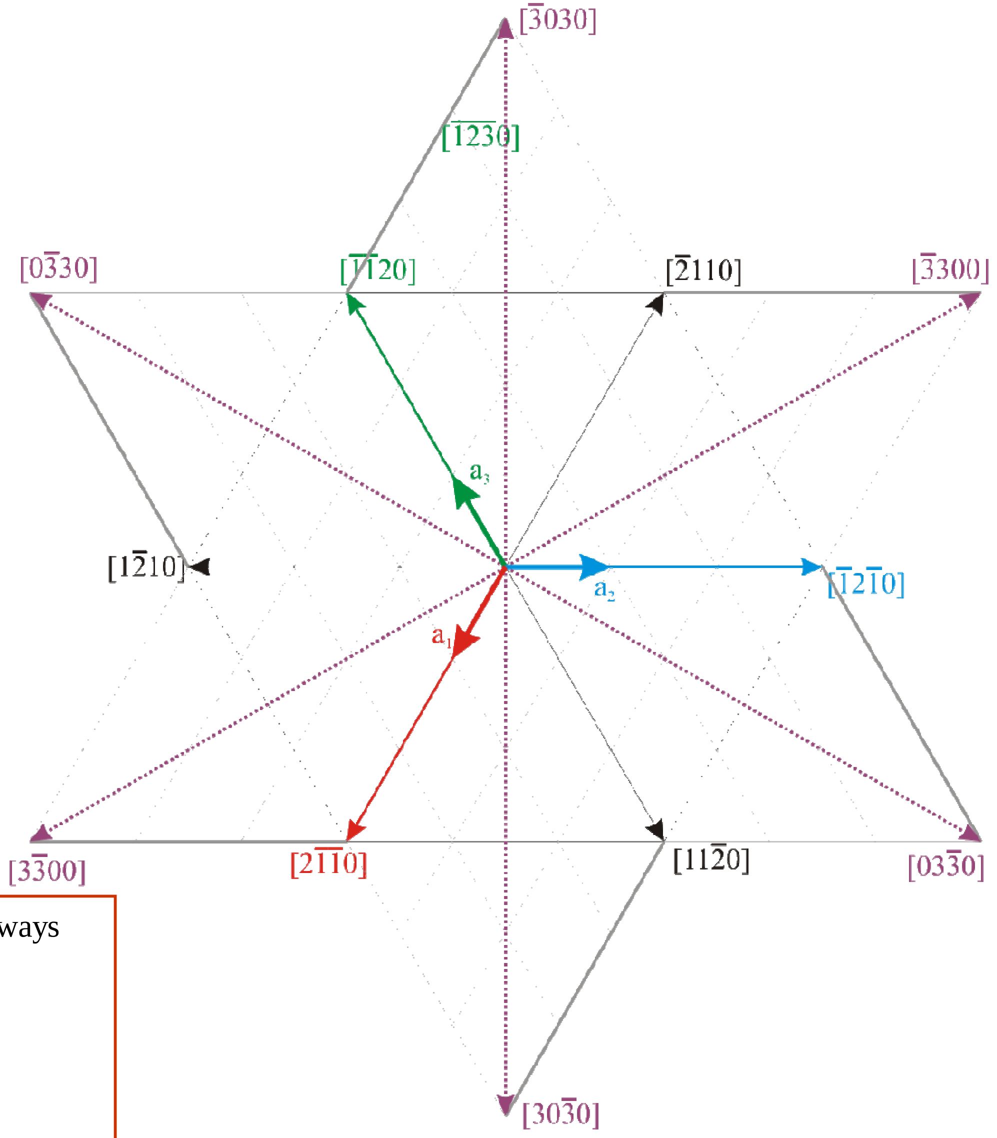
$$W = w$$

$$u = \frac{1}{3}(2U - V)$$

$$t = -(u + v)$$

$$v = \frac{1}{3}(2V - U)$$

$$w = W$$



- Directions in the hexagonal system can be expressed in many ways
- 3-indices:
  By the three vector components along a_1, a_2 and c:
  $r_{UVW} = Ua_1 + Va_2 + Wc$
- In the three index notation equivalent directions may not seem equivalent; while, in the four index notation the equivalence is brought out.

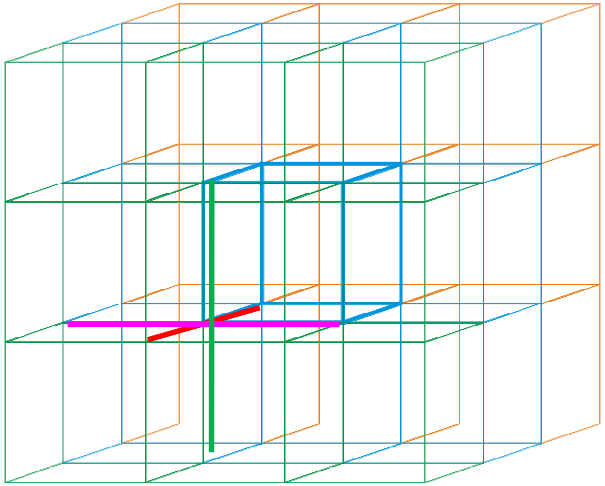
Directions ⊥ Planes

- Cubic system: (hkl) ⊥ [hkl]
- Tetragonal system: only special planes are ⊥ to the direction with same indices:
  [100] ⊥ (100), [010] ⊥ (010), [001] ⊥ (001), [110] ⊥ (110)
  ([101] not ⊥ (101))
- Orthorhombic system:
  [100] ⊥ (100), [010] ⊥ (010), [001] ⊥ (001)
- Hexagonal system: [0001] ⊥ (0001)
  (this is for a general c/a ratio; for a Hexagonal crystal with the special c/a ratio = √(3/2) the cubic rule is followed)
- Monoclinic system: [010] ⊥ (010)
- Other than these a general [hkl] is NOT ⊥ (hkl)

COORDINATION NUMBER

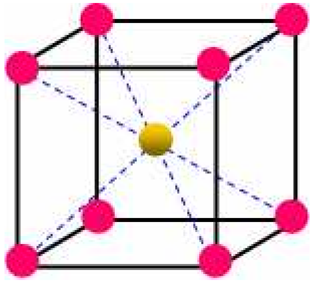
Coordination number is defined as the total number of nearest neighboring atoms

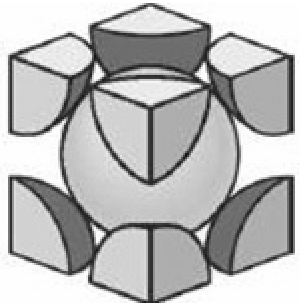
Simple cubic



The coordination number of simple cubic crystal is '6' It is shown in figure. In this figure we are considered one corner and drawn 3 lines connecting to six points.

Body Centered cubic



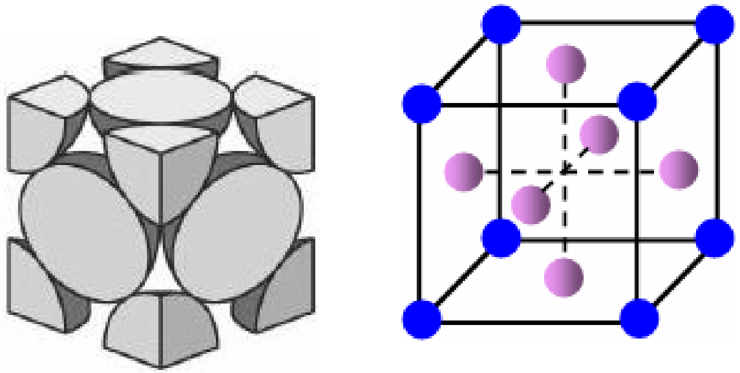


The coordination number of BCC crystal is 8. The body centered atom is in contact with all the eight corner atoms. Each corner atom is shared by eight unit cells and hence, each of these atoms is in touch with eight body centered atoms.

COORDINATION NUMBER

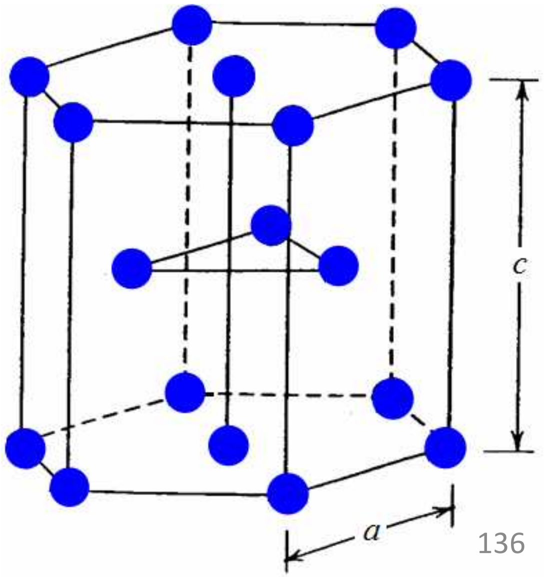
Face Centered cubic

In the FCC lattice each atom is in contact with 12 neighbor atoms. FCC coordination number Z = 12 . For example, the face centered atom in the front face is in contact with four corner atoms and four other face-centered atoms behind it (two sides, top and bottom) and is also touching four face-centered atoms of the unit cell in front of it.



Hexagonal close pack structure

In Hexagonal lattice Z = 12. The center atom of the top face is in touch with six corner atoms, three atoms of the mid layer and other three atoms of the mid layer of the unit cell above it.



Average number of atoms per unit cell

		Position of atoms	Effective number of atoms
1	SC	8 Corners	= [8 × (1/8)] = 1
2	BCC	8 Corners + 1 body centre	= [1 (for corners)] + [1 (BC)] = 2
3	FCC	8 Corners + 6 face centres	= [1 (for corners)] + [6 × (1/2)] = 4
4	HCP	12 corners (6 bottom+6 top) + 2 atoms at face centers + 3 atoms in the interior	= [12 × (1/6)] + [2 × (1/2)] + [3 (interior)] = 6

Atomic packing factor

Atomic packing factor (APF) or packing efficiency indicates how closely atoms are packed in a unit cell and is given by the ratio of volume of atoms in the unit cell and volume of the unit cell.

$$APF = \frac{Volumeofatoms}{Volumeofunitcell}$$

Simple Cubic

In a simple cubic structures, the atoms are assumed to be placed in such a way that any two adjacent atoms touch each other. If ‘a’ is the lattice parameter of simple cubic structure and ‘r’ the radius of atoms. From the figure it is clear that

Atomic radius (r) $= {}^{a}\!/_{2}$

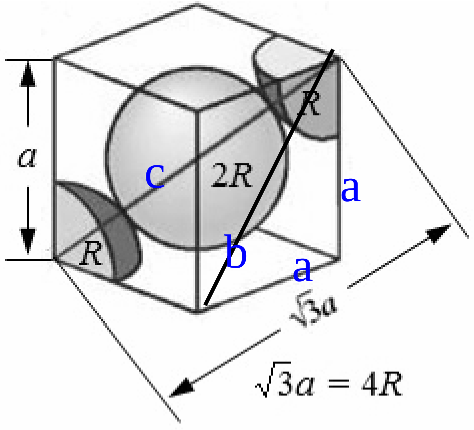
$$APF = \frac{Avg.noofatomsperunitcell \times Volumeofanatom}{Volumeoftheunitcell}$$

$$APF = \frac{1 \times \frac{4}{3}\Pi r^3}{a^3} = \frac{\frac{4}{3}\Pi r^3}{(2r)^3} = \frac{4\Pi}{24} \times 100 = 0.52 = 52\%$$

Atomic packing factor

Body Centered Cubic

In body centered cubic structures the center atom touches the corner atoms as shown in Figure



From the figure

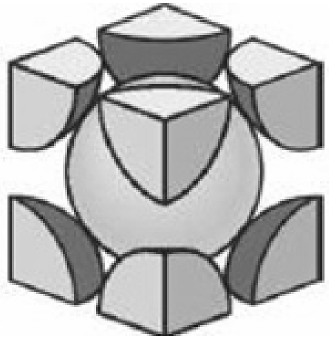
$$b^2 = a^2 + a^2 = 2a^2$$

$$c^2 = b^2 + a^2 \rightarrow c^2 = 2a^2 + a^2$$

$$c^2 = 3a^2 \rightarrow (4r)^2 = 3a^2 \rightarrow r^2 = \frac{3a^2}{16}$$

$$r = \frac{\sqrt{3}a}{4}, a = \frac{4r}{\sqrt{3}}$$

r = atomic radius
a = lattice parameter



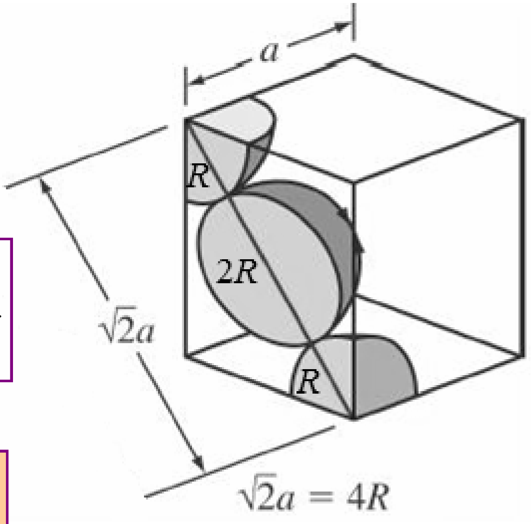
$$APF = \frac{2 \times \frac{4}{3} \prod r^3}{a^3} = \frac{2 \times \frac{4}{3} \prod \left(\frac{\sqrt{3}a}{4} \right)^3}{a^3} = \frac{8 \times 3\sqrt{3} \prod a^3}{3 \times 64a^3}$$

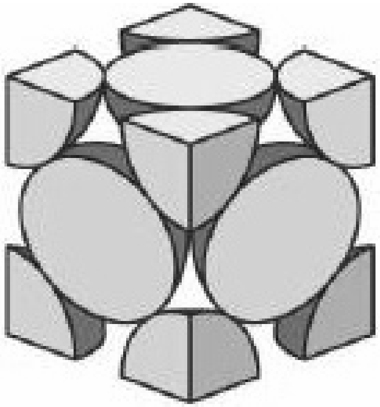
$$APF = 0.68(or)68\%$$

Atomic packing factor

Face Centered Cubic

From this figure; first we can calculate atomic radius:





$$(4r)^2 = a^2 + a^2 \rightarrow 16r^2 = 2a^2 \rightarrow r^2 = \frac{2a^2}{16}$$

$$r = \frac{a\sqrt{2}}{4} = \frac{a}{2\sqrt{2}}$$

$$a = \frac{4r}{\sqrt{2}} \rightarrow 4r = \sqrt{2}a$$

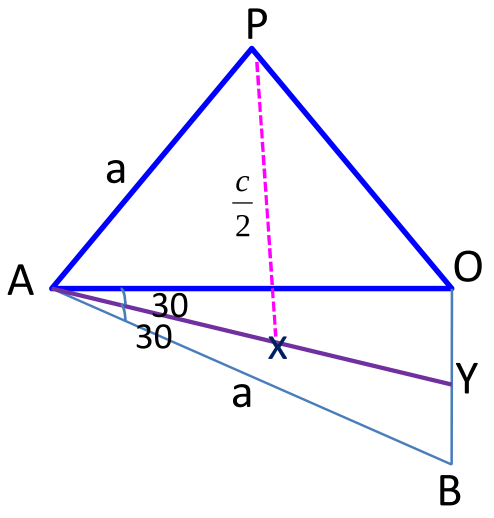
$$APF = \frac{4\times\frac{4}{3}\prod r^3}{a^3} = \frac{4\times\frac{4}{3}\prod\left(\frac{a}{2\sqrt{2}}\right)^3}{a^3} = \frac{16\times 2\sqrt{2}\prod a^3}{3\times 64a^3} = 0.74$$

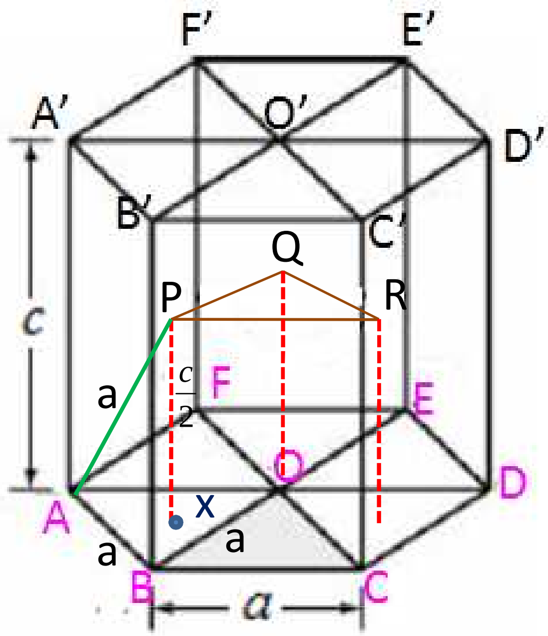
$$APF_{FCC} = 0.74(or)74\%$$

Atomic packing factor

Hexagonal Close Packed Structure

Consider any one triangle
Let us consider ΔAOB;
‘P’ is center of triangle
APOB - Tetrahedron





In the Δ AYB

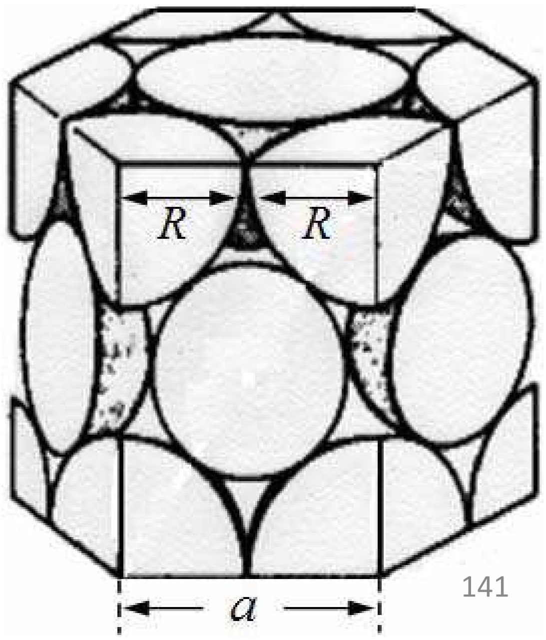
$$Cos30^0 = \frac{AY}{AB}$$

The distance between any neighboring atoms is ‘a’ from the figure ‘AB’ = a

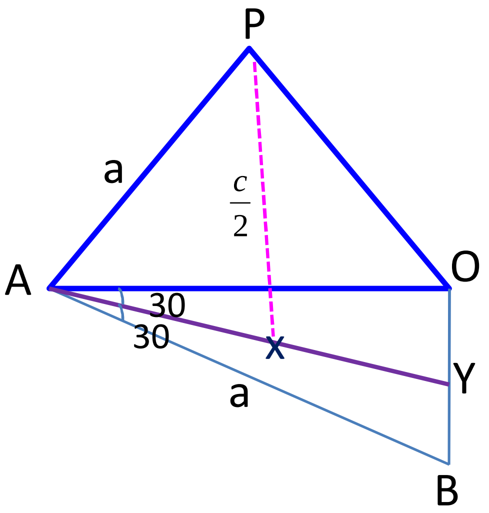
$$AY = AB\cos 30^0 = \frac{a\sqrt{3}}{2}$$

From the figure ‘Ax’ is orthocenter; so,

$$Ax = \frac{2}{3}AY = \frac{2}{3}\times\frac{a\sqrt{3}}{2} = \frac{a}{\sqrt{3}}$$



Hexagonal Close Packed Structure



Consider Δ APx

$$(AP)^2 = (Ax)^2 + (xP)^2$$

$$a^2 = \frac{a^2}{3} + \frac{c^2}{4} \rightarrow a^2 - \frac{a^2}{3} = \frac{c^2}{4} \rightarrow \frac{c^2}{4} = \frac{2a^2}{3}$$

$$\boxed{\frac{c^2}{a^2} = \frac{8}{3} \rightarrow \frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633}$$

$$APF = \frac{Avg.no of atoms per unit cell \times Volume of an atom}{Volume of the unit cell}$$

$$APF = \frac{6 \times \frac{4}{3} \prod r^3}{Volume of the unit cell}$$

In cubic a=b=c, so volume is a^3 but in this case, it is H.C.P so here a=b≠c

Volume of unitcell = Area of base of hexagonal × Height

Hexagonal Close Packed Structure

$$\text{Volume of unitcell} = \text{Area of base of hexagonal} \times \text{Height}$$

$$Volume of unitcell = 6 \times area of \Delta AOB \times c$$

$$Volume of unitcell = 6 \times \frac{1}{2} \times OB \times AY \times c$$

$$Volume of unitcell = 6 \times \frac{1}{2} \times a \times \frac{a\sqrt{3}}{2} \times c = ca^2 \frac{3\sqrt{3}}{2}$$

$$APF = \frac{6 \times \frac{4}{3} \prod r^3}{ca^2 \frac{3\sqrt{3}}{2}}$$

$$APF = \frac{6 \times \frac{4}{3} \prod r^3}{ca^2 \frac{3\sqrt{3}}{2}} = \frac{6 \times \frac{4}{3} \prod \times \frac{a^3}{8}}{ca^2 \frac{3\sqrt{3}}{2}} = \frac{2 \prod a}{c \times 3\sqrt{3}} = 0.74$$

$$APF_{HCP} = 0.74(or)74\%$$

Summary on PACKING FRACTION / Efficiency

$$\text{Packing Fraction} = \frac{\text{Volume occupied by atoms}}{\text{Volume of Cell}}$$

	SC*	BCC*	CCP	DC	HCP
Relation between atomic radius (r) and lattice parameter (a)	a = 2r	$\sqrt{3}a = 4r$	$\sqrt{2}a = 4r$	$\frac{\sqrt{3}}{4}a = 2r$	a = 2r $c = 4r\sqrt{\frac{2}{3}}$
Atoms / cell	1	2	4	8	2
Lattice points / cell	1	2	4	4	1
No. of nearest neighbours	6	8	12	4	12
Packing fraction	$\frac{\pi}{6}$	$\frac{\sqrt{3}\pi}{8}$	$\frac{\sqrt{2}\pi}{6}$	$\frac{\sqrt{3}\pi}{16}$	$\frac{\sqrt{2}\pi}{6}$
	~ 0.52	~ 0.68	~ 0.74	~ 0.34	~ 0.74

* *Crystal formed by monoatomic decoration of the lattice*

Density

- The usual density is mass/volume
- In materials science various other kinds of density and occupation ratios are defined. These include:
  - Linear density: mass/length [kg/m]
    atoms/length [/m] *or number/length*
    length occupied/length [m/m]
  - Areal density: mass/area [kg/m^2]
    atoms/area [/m^2] *or number/area*
    area occupied/area [m^2/m^2]
  - Volume density: mass/volume [kg/m^3]
    atoms/volume [/m^3] *or number/volume*
    volume occupied/volume [m^3/m^3]
- The volume occupied/volume of space [m^3/m^3] is also called the packing fraction
- In this context other important quantities include:
  - Length/area [m/m^2] → e.g. length of dislocation lines per unit area of interface (interfacial dislocations)
  - Length/volume [m/m^3] → e.g. length of dislocation lines per unit volume of material
  - Area/volume [m^2/m^3] → e.g. grain boundary area per unit volume of material
- The 'useful' way to write these quantities is to NOT factor out the common terms: i.e. write [m/m^3] '*as it is*' and *not as* [1/m^2]

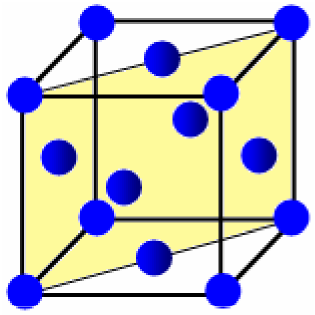
Planar density

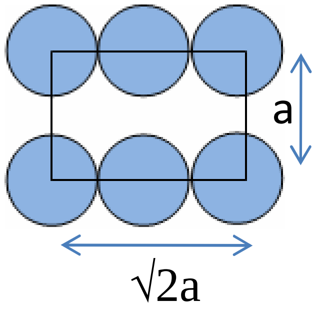
Planar density (PD) refers to density of atomic packing on a particular plane.

$$PlanarDensity = \frac{Numberofatomsonaplane}{Areaofplane}$$

For example, there are 2 atoms (1/4 x 4 corner atoms + 1/2 x 2 side atoms) in the {110} planes in the FCC lattice.
Planar density of {110} planes in the FCC crystal

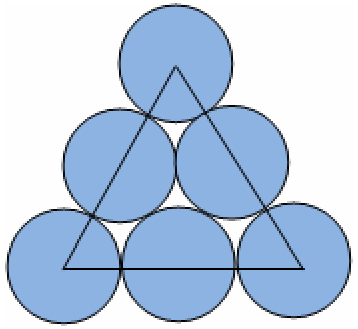
$$PD_{(110)} = \frac{2}{a\sqrt{2}a} = \frac{\sqrt{2}}{a^2}$$

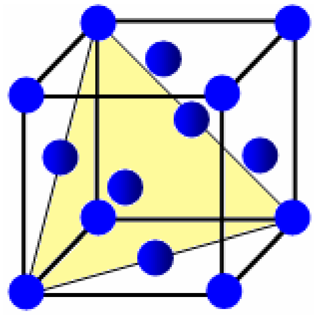




In the {111} planes of the FCC lattice there are 2 atoms (1/6 x 3 corner atoms + 1/2 x 3 side atoms).
Planar density of {111} planes in the FCC crystal

$$PD_{(111)} = \frac{2}{\frac{1}{2}\sqrt{2}a \times \sqrt{2}a\frac{\sqrt{3}}{2}} = \frac{4}{\sqrt{3}a^2}$$



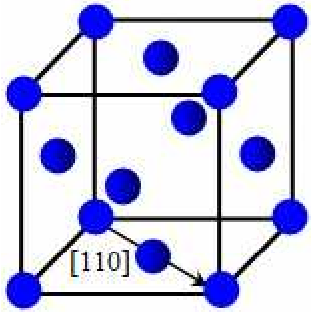


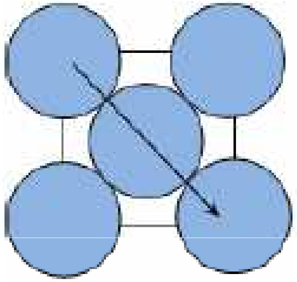
This is higher than {110} and any other plane. Therefore, {111} planes are most densely packed planes in the FCC crystal

Linear density

Linear density (LD) is the number of atoms per unit length along a particular direction

$$LinearDensity = \frac{Numberofatomsonthedirectionvector}{Lengthofthedirectionvector}$$





<110> directions in the FCC lattice have 2 atoms (1/2 x 2 corner atoms + 1 center atom) and the length is

$$LD_{[110]} = \frac{2}{\sqrt{2}a} = \frac{\sqrt{2}}{a}$$

This is the most densely packed direction in the FCC lattice

Theoretical density

Theoretical density calculation from crystal structure

Theoretical density $\boxed{\rho = \frac{nA}{V_C N_A}}$

n = number of atoms in the unit cell
A = atomic weight
V_C = Volume of unitcell
N_A = Avogadro's number (6.023×10^{23})

Calculate the theoretical density of Aluminum (Al)

Given : Al is FCC structure; Lattice parameter is $4.05A^0$; n=4;
Atomic weight of Al is 26.98 g/mol

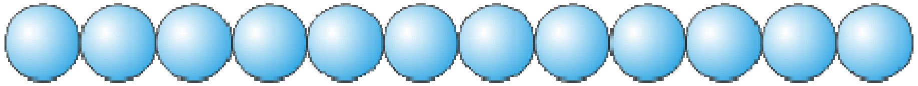
$$\boxed{\rho = \frac{4\times 26.98}{(4.05\times 10^{-8})^3 \times 6.023\times 10^{23}} = 2.697 g/cc}$$

CCP=FCC

Closed Packed Structures : FCC

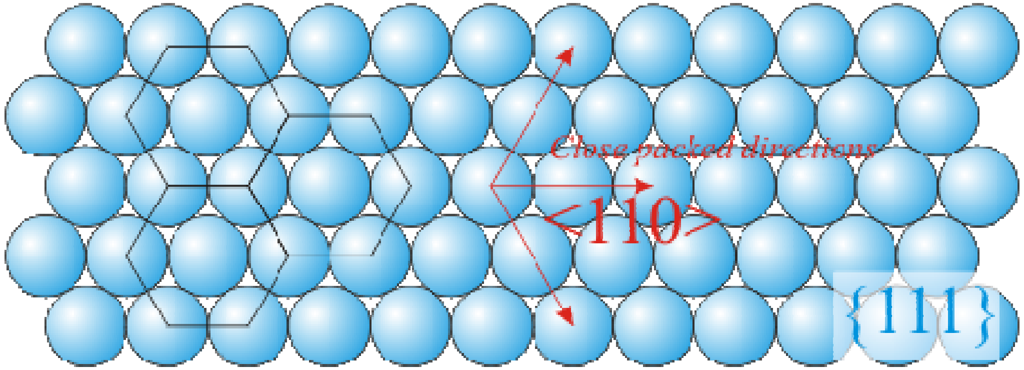
CCP=FCC

Start with a row of atoms *(close packed in 1D)*



Monatomic decoration of FCC lattice

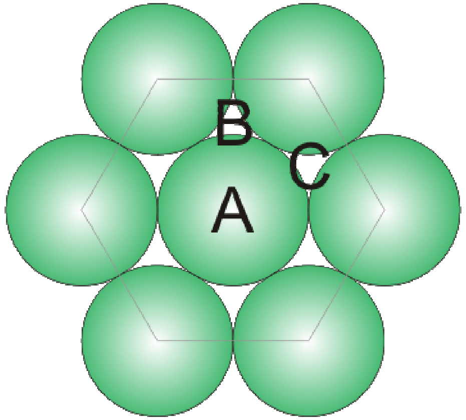
Make a 2D hexagonal close packed array (the A layer)

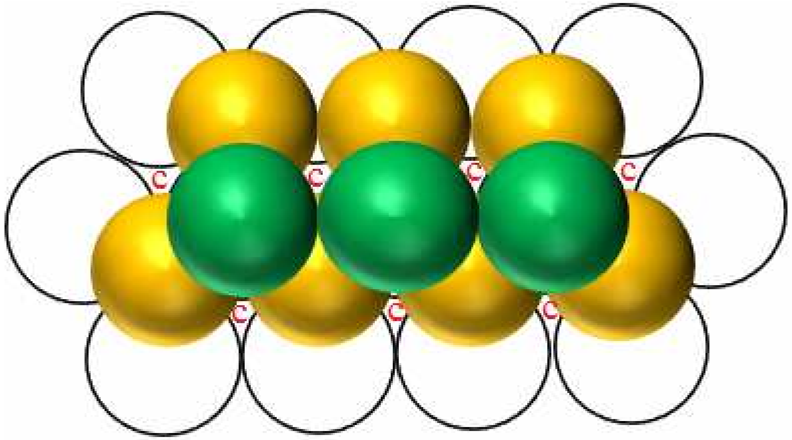


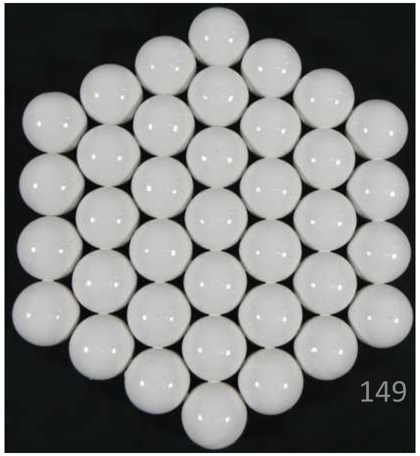
There is only one way of doing so!

- This is a close packed layer with close packed directions (like <110> directions represented using cubic indices)
- As we shall see this becomes the {111} plane in the FCC crystal

To build the next layer → leading to the 3D structure, there are 2 stable positions where atoms can be put → called the B and C positions. If atoms are put in the B position than we cannot put atoms in the C position (no space!)



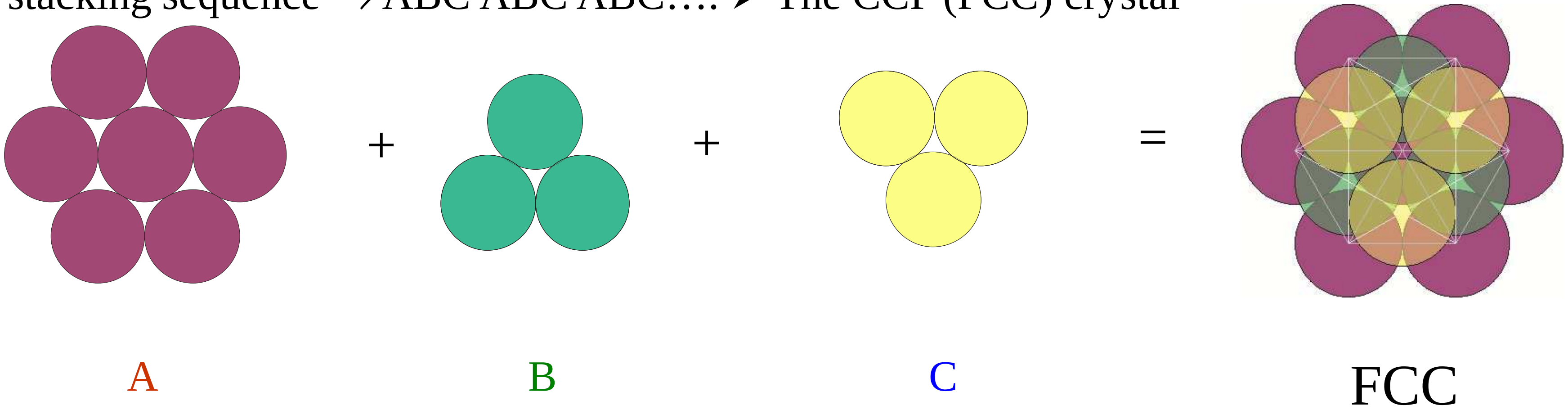


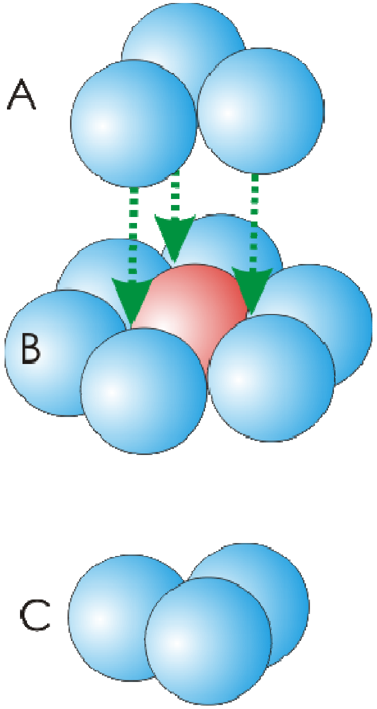


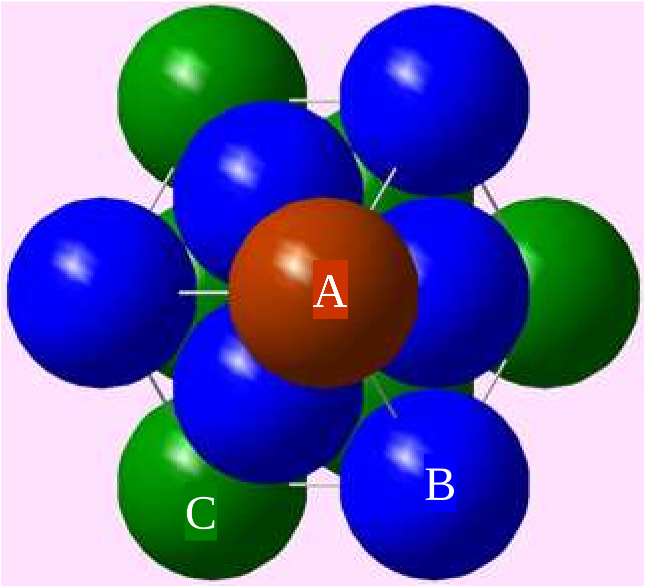
Closed Packed Structures : FCC

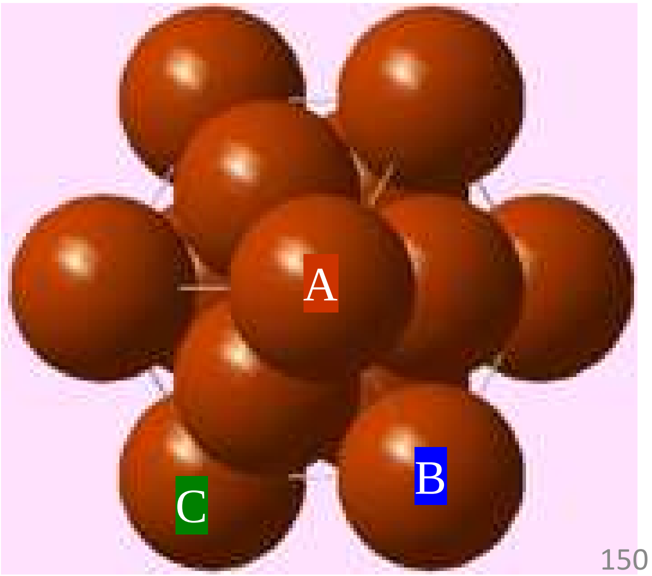
CCP=FCC

Putting atoms in the B position in the II layer and in C positions in the III layer we get a stacking sequence → ABC ABC ABC…. ➢ The CCP (FCC) crystal





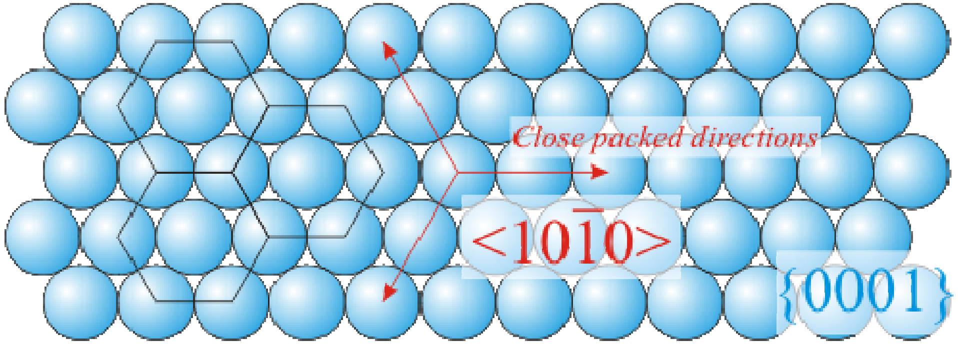




Closed Packed Structures : HCP

An alternate packing (one amongst an infinite possibilities) is where in the III layer coincides with the I layer → giving rise to a AB AB AB … packing → The Hexagonal Close Packed Crystal *(this arrangement is close packed only for ideal c/a ratio; i.e. for 'hard sphere' packing)*

As before we make a 2D hexagonal close packed array (the A layer)



- This is a close packed layer with close packed directions (like $<10\bar{1}0>$ directions)
- As we shall see this becomes the {0001} plane in the HCP crystal

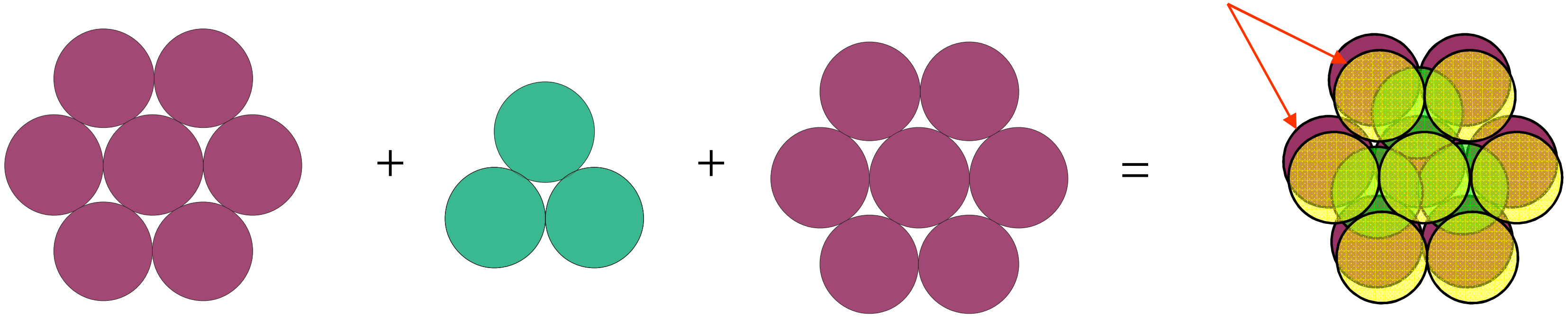
Metals which adopt HCP structure ➢

Mg, Zn, Ti, Co, Be, Cd, Zr, Y, Sc, Tc, Ru, Gd, Tb, Dy, Ho, Er, Tm, Lu, Hf, Re, Os, Tl

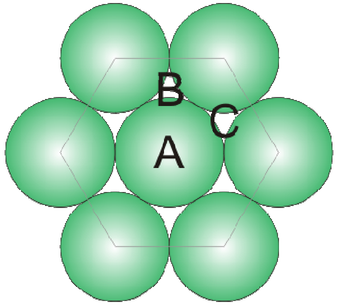
Closed Packed Structures : HCP

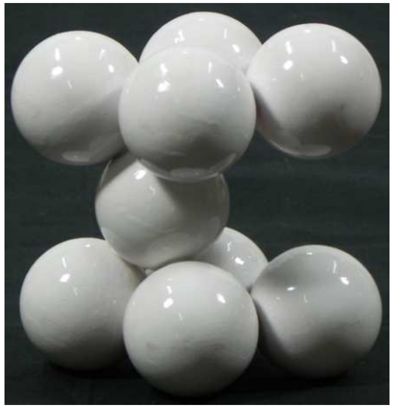
HCP

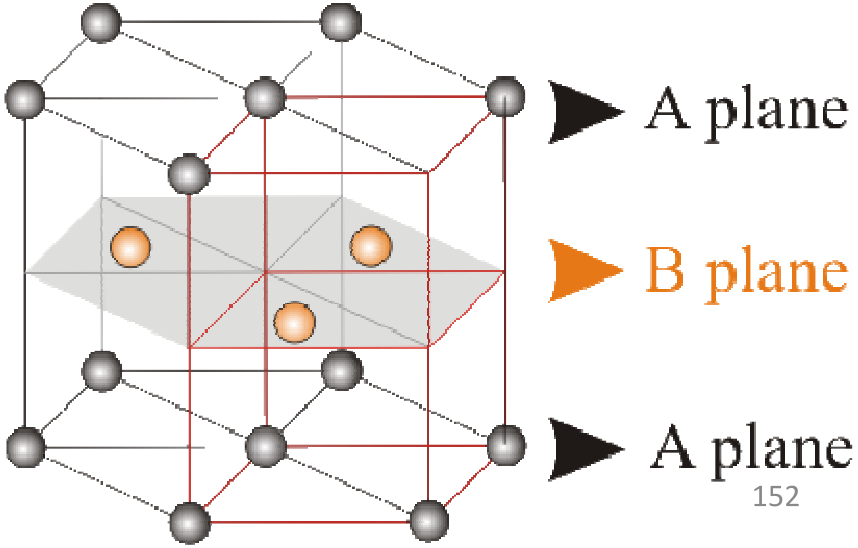
Shown displaced for clarity



The C position is vacant and we can pass a line through this position without intersecting any atoms
As we shall see in one of the upcoming slides that this is special line







Structure-Property Correlation

- Aluminum (Al) is ductile while iron (Fe) and magnesium (Mg) are not. This can be explained from their crystal structures.
- Al is FCC where as Fe is BCC and Mg is HCP.
- Plastic deformation in metals takes place mainly by a process called slip. Slip can broadly be visualized as sliding of crystal planes over one another. Slip occurs on most densely packed planes in the most closely packed directions lying on that plane.
- The slip plane and the direction together is called a Slip system
- In FCC, {111} planes are close-packed and there are four unique {111} planes. Each of these planes contains three closely packed <110> directions. Therefore, there are 4 x 3 = 12 slip systems
- In HCP, the basal plane, (0001) is the close-packed and it contains three <11$\bar{2}$0> directions. Hence, number of slip system = 1 x 3 = 3
- Slip in more number of slip systems allows greater plastic deformation before fracture imparting ductility to FCC materials.
- Close-packed planes are also planes with greatest interplanar spacing and this allows slip to take place easily on these planes.
- BCC structure on the other hand has 48 possible slip systems. However, there is no close-packed plane. Hence, plastic deformation before fracture is not significant. Slip might occur in {110}, {112} and {123} planes in the <111> directions.

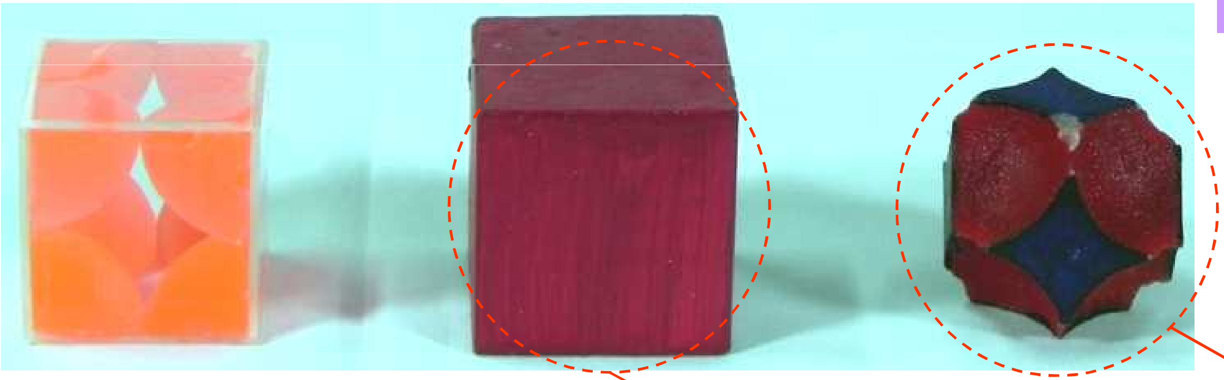
VOIDS IN CRYSTALS

- We have already seen that as spheres cannot fill entire space → the packing fraction (PF) < 1 (for all crystals)
- This implies there are voids between the atoms. Lower the PF, larger the volume occupied by voids.
- These voids have complicated shapes; but we are mostly interested in the largest sphere which can fit into these voids→ hence the plane faced polyhedron *version* of the voids is only (typically) considered.
- **The size and distribution of voids in materials play a role in determining aspects of material behavior → e.g. solubility of interstitials and their diffusivity**
- In the close packed crystals (FCC, HCP) there are two types of voids → tetrahedral and octahedral voids *(identical in both the structures as the voids are formed between two layers of atoms)*
- In the 'BCC crystal' the voids do NOT have the shape of the regular tetrahedron or the regular octahedron

Void in Simple Cube

- ❑ The simple cubic crystal (monoatomic decoration of the simple cubic lattice) has large void in the centre of the unit cell with a coordination number of 8.
- ❑ The actual space of the void in *very complicated* (right hand figure below) and the polyhedron version of the void is the cube (as cube is the coordination polyhedron around a atom sitting in the void)

$$\frac{r_x}{r} = (\sqrt{3} - 1) = 0.732$$



True Unit Cell of SC crystal

Polyhedral model (Cube)

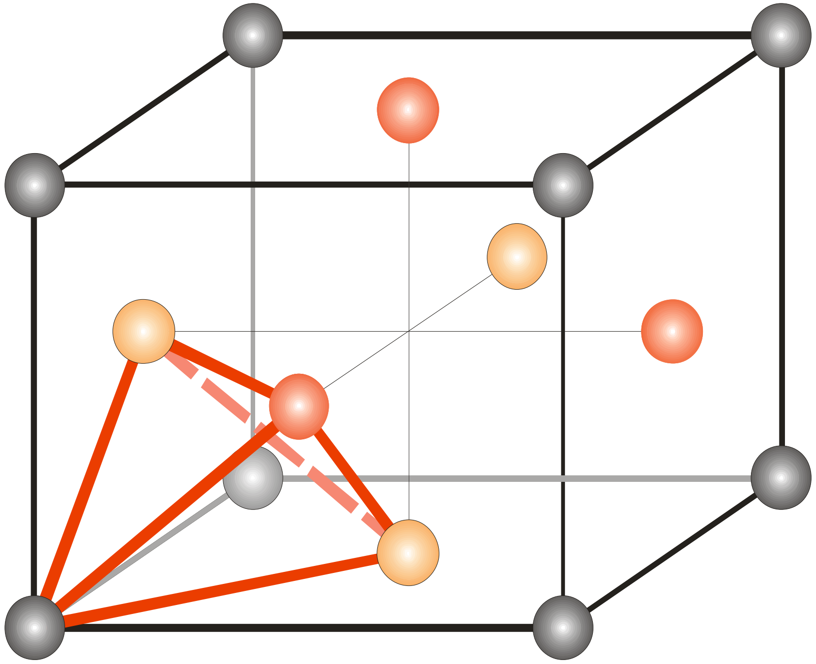
Actual shape of the void (space)!

- Later on we will talk about tetrahedral and octahedral voids in FCC, BCC & HCP crystals:
- note that there are **NO** *such tetrahedral and octahedral voids* in SC crystals and the only polyhedral void is CUBIC (i.e. coordination number of 8)

FCC = CCP

VOIDS in FCC

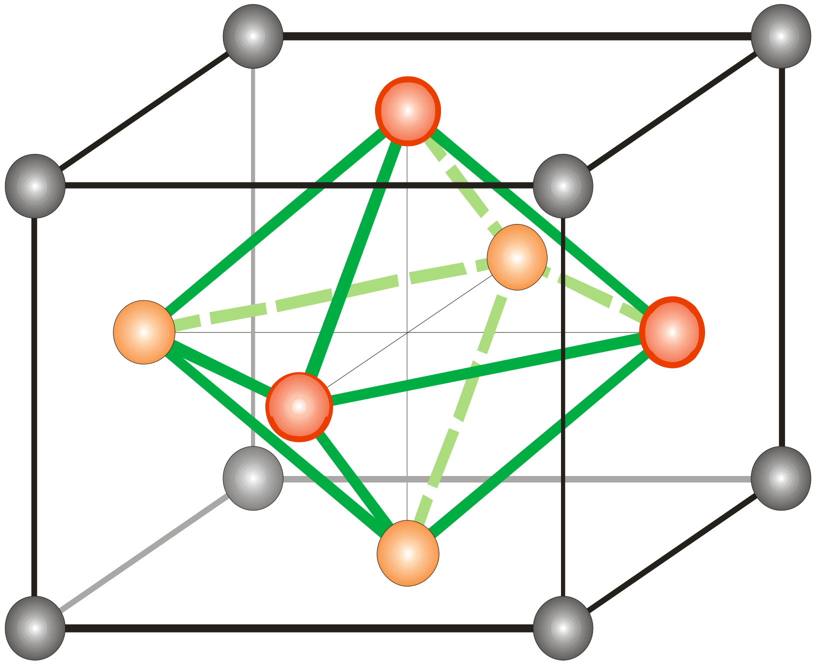
- Tetrahedral — TV
- Octahedral — OV



¼ way along body diagonal
{¼, ¼, ¼}, {¾, ¾, ¾}
+ face centering translations

$$V_{tetrahedron} = \frac{1}{24} V_{cell}$$

$r_{void} / r_{atom} = 0.225$



At body centre
{½, ½, ½}
+ face centering translations

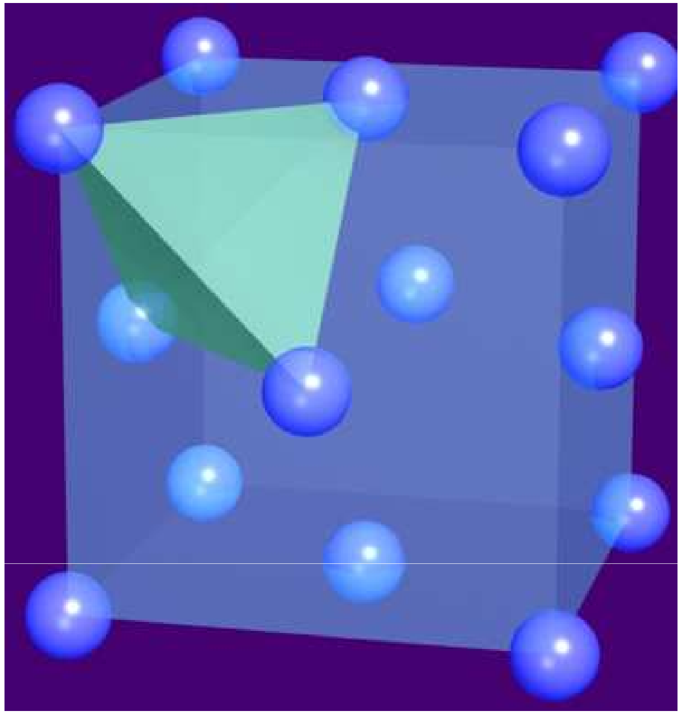
$$V_{octahedron} = \frac{1}{6} V_{cell}$$

$r_{Void} / r_{atom} = 0.414$

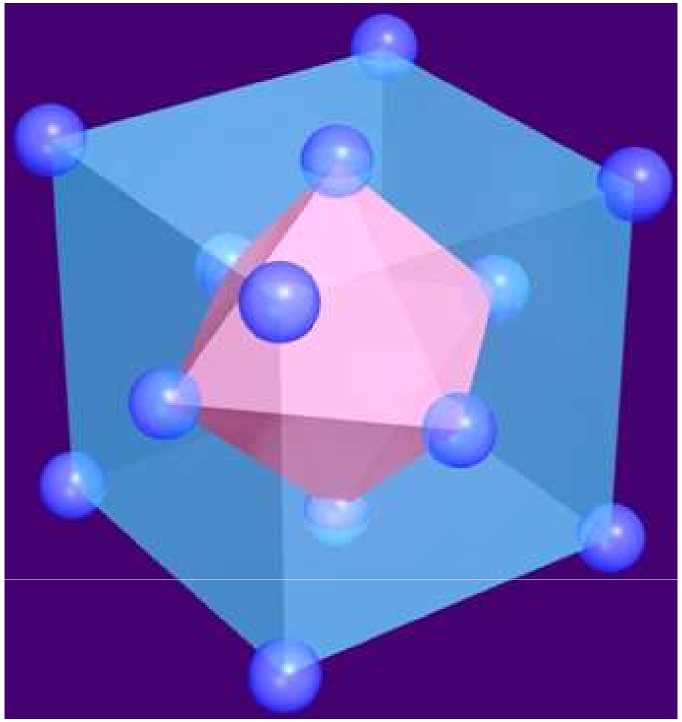
Note: Atoms are coloured differently but are the same

FCC

Tetrahedral TV



Octahedral OV



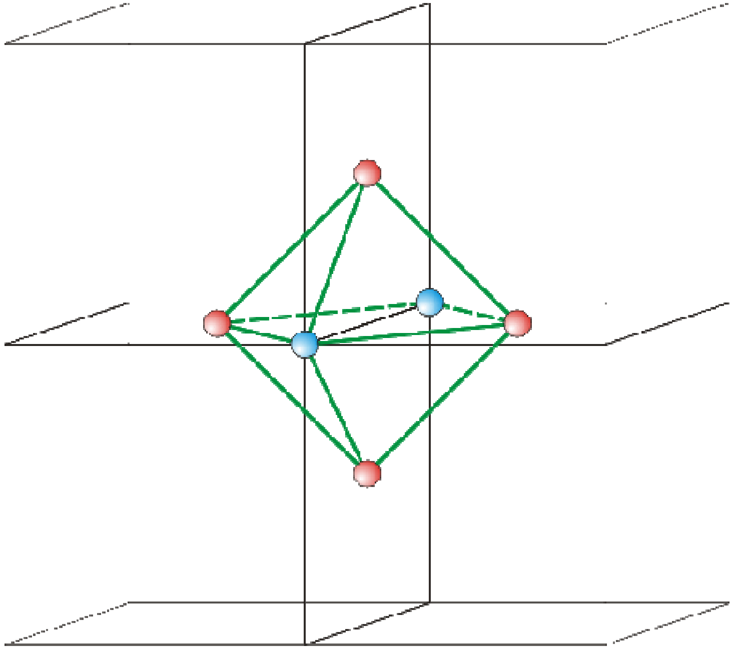
Actual shape of void

- Actual shape of the void is as shown below. This shape is very completed and we use the polyhedral version of the void- i.e. tetrahedral and octahedral voids.

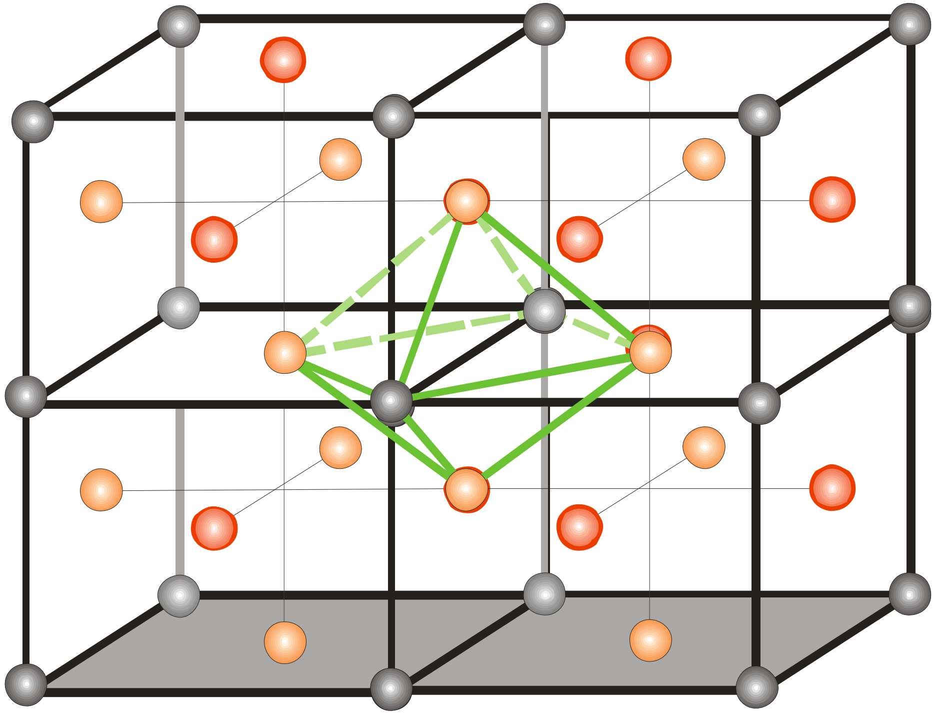
Position of some of the atoms w.r.t to the void

Once we know the position of a void then we can use the symmetry operations of the crystal to locate the other voids. This includes lattice translations

FCC- OCTAHEDRAL



Site for octahedral void



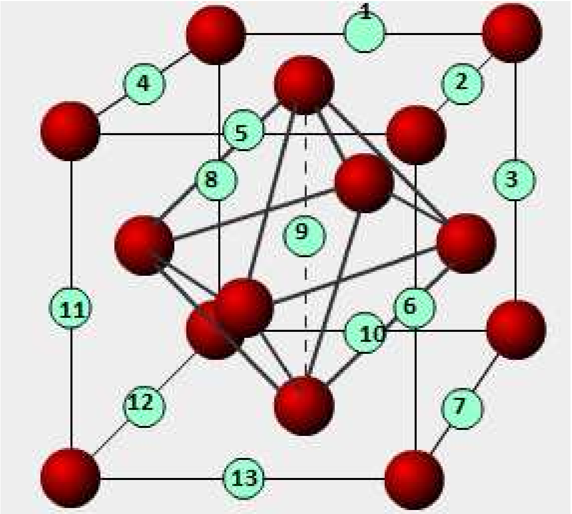
{½, ½, ½} + {½, ½, 0} = {1, 1, ½} ≡ {0, 0, ½}

Equivalent site for an octahedral void

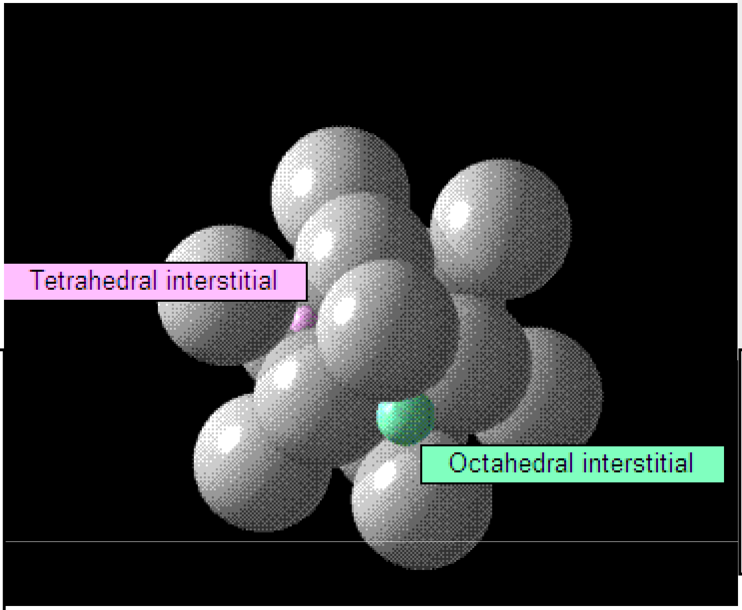
Face centering translation

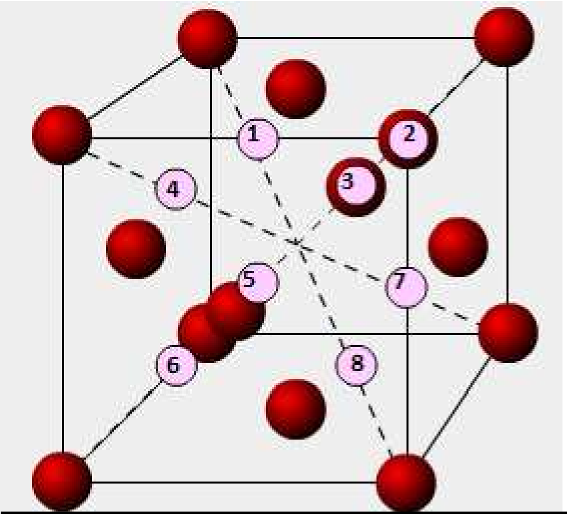
Note: Atoms are coloured differently but are the same

Calculations



There is one octahedral site at the centre of the FCC cell (½,½,½) and one on each of the twelve cell edges (½,0,0).





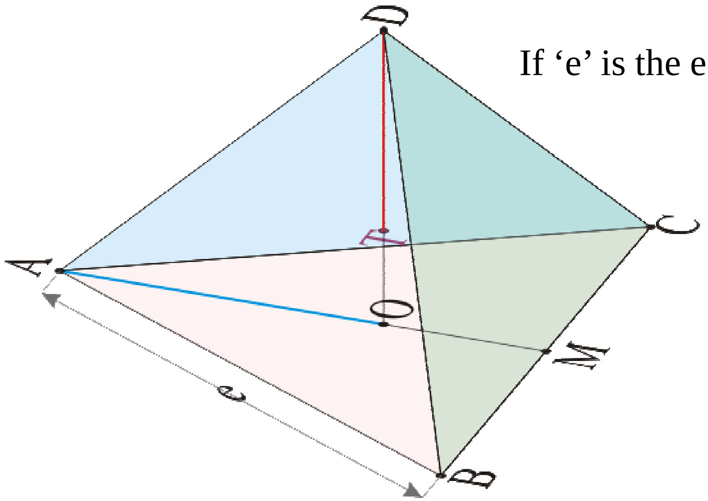
There are eight tetrahedral sites in the FCC unitcell (¼,¼,¼).

FCC voids	Position	Voids / cell	Voids / atom
Tetrahedral	¼ way from each vertex of the cube along body diagonal <111> → ((¼, ¼, ¼))	8	2
Octahedral	• Body centre: 1 → (½, ½, ½) • Edge centre: (12/4 = 3) → (½, 0, 0)	4	1

Size of the largest atom which can fit into the tetrahedral void of FCC

The distance from the vertex of the tetrahedron to the centroid (DT) is the distance spanned by radius of the atom and the radius of the interstitial sphere.

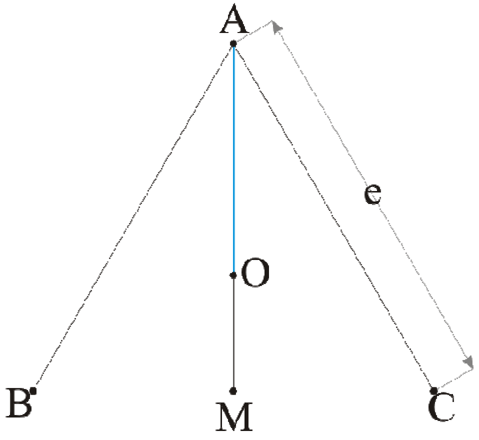
$DT = r + x$ ⟶ Radius of the interstitial atom (sphere)



If ‘e’ is the edge length of the tetrahedron then CV = (√6/4)e → *see below in triangle ABC*

$$DT = \frac{\sqrt{6}}{4}e = r + x \qquad e = 2r \qquad \frac{\sqrt{6}}{2}r = r + x$$

$$\frac{x}{r} = \left(\frac{\sqrt{6}}{2} - 1\right) \sim 0.225$$



In triangle ABC

$$e^2 = \frac{e^2}{4} + AM^2$$

$$AM = \frac{\sqrt{3}}{2}e$$

$$AO = \frac{2}{3}AM = \frac{2}{3}\frac{\sqrt{3}}{2}e = \frac{e}{\sqrt{3}}$$

In tetrahedron ABCD

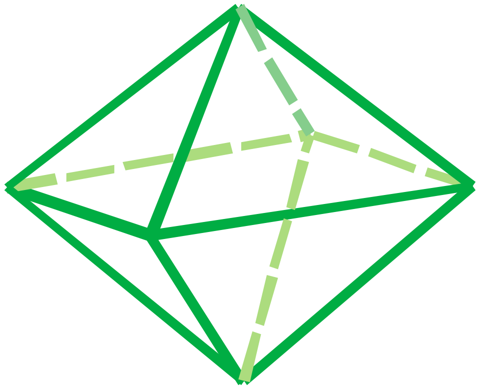
$$AD^2 = e^2 = AO^2 + DO^2$$

$$e^2 = \frac{e^2}{3} + DO^2 \qquad DO = e\sqrt{\frac{2}{3}}$$

$$DT = \frac{3}{4}DO$$

$$DT = \frac{3}{4}\sqrt{\frac{2}{3}}e = \frac{\sqrt{6}}{4}e$$

Size of the largest atom which can fit into the Octahedral void of FCC



$$2r + 2x = a$$

$$\sqrt{2}a = 4r$$

$$\frac{x}{r} = \left(\sqrt{2} - 1\right) \sim 0.414$$

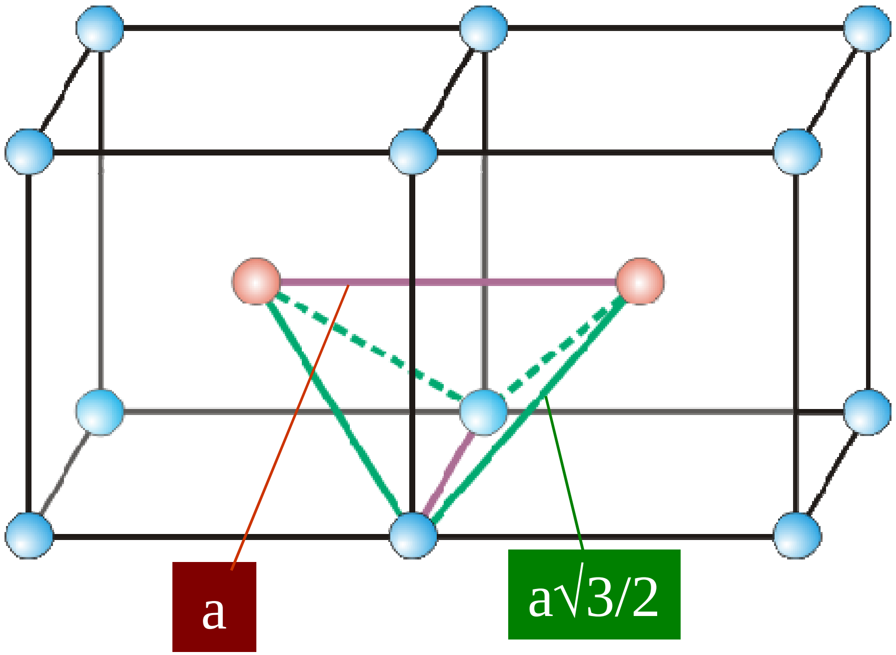
Thus, the octahedral void is the bigger one and interstitial atoms (which are usually bigger than the voids) would prefer to sit here

Voids in BCC crystal

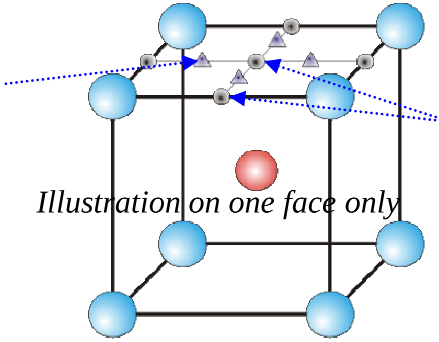
- There are NO voids in a 'BCC crystal' which have the shape of a regular polyhedron *(one of the 5 Platonic solids)*
- The voids in BCC crystal are: distorted 'octahedral' and distorted tetrahedral
→ the correct term should be *non-regular* instead of *distorted.*
- However, the 'distortions' are 'pretty regular' as we shall see
- The distorted octahedral void is in a sense a *'linear void'*
→ *an sphere of correct size sitting in the void touches only two of the six atoms surrounding it*
- Carbon prefers to sit in this smaller 'octahedral void' for reasons which we shall see soon

VOIDS in BCC Crystal

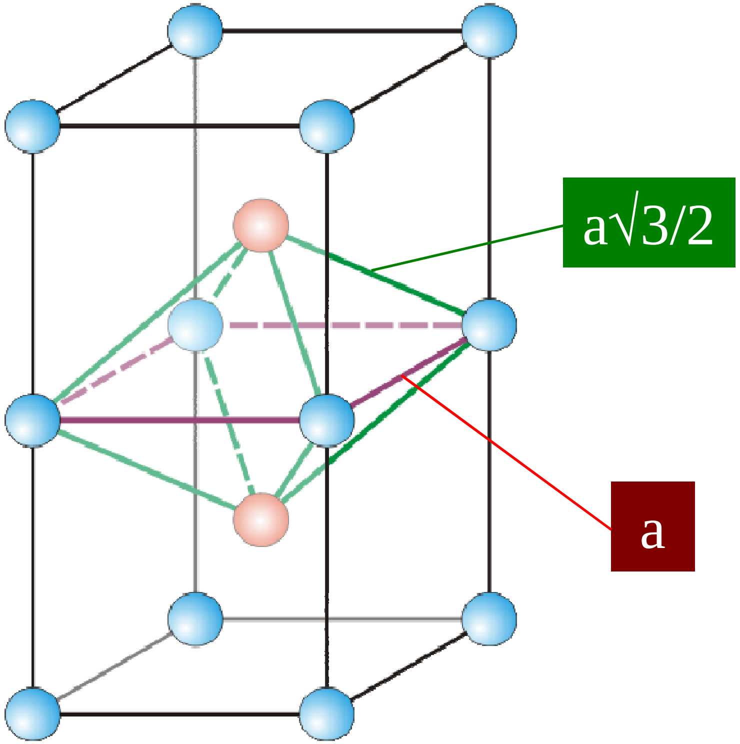
Distorted TETRAHEDRAL



Coordinates of the void:
{½, 0, ¼} *(four on each face)*



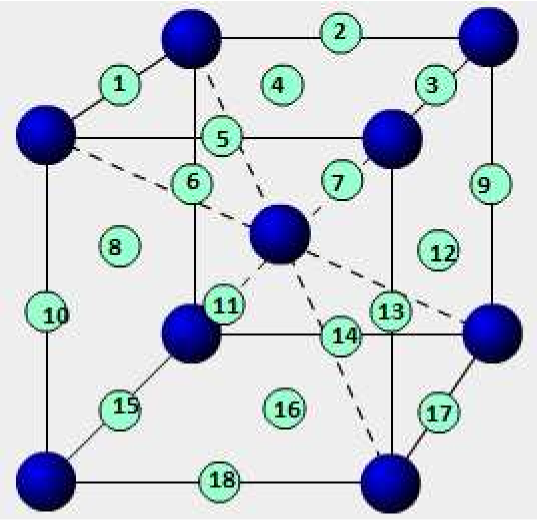
Distorted OCTAHEDRAL**



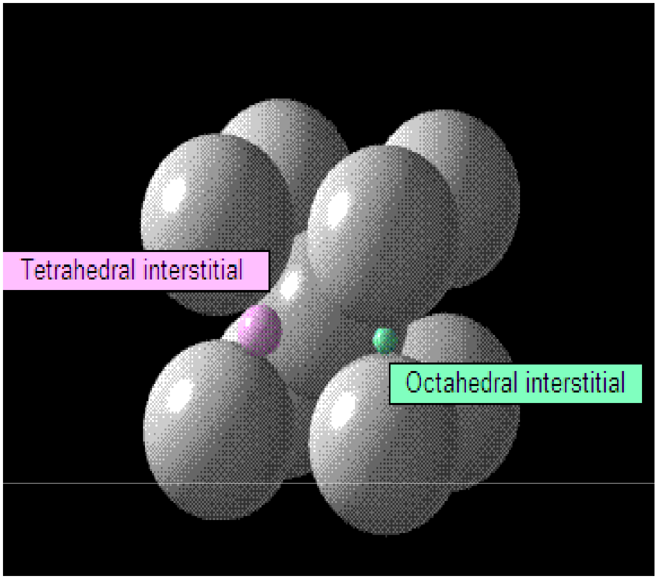
Coordinates of the void:
{½, ½, 0} (+ BCC translations: {0, 0, ½})

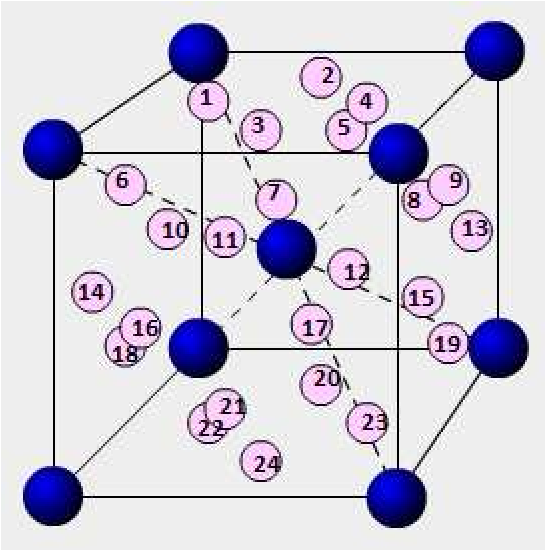
*** Actually an atom of correct size touches only the top and bottom atoms*

Calculations



There is one octahedral site on each of the six BCC cell faces (½,½,0) and one on each of the twelve cell edges (½,0,0)

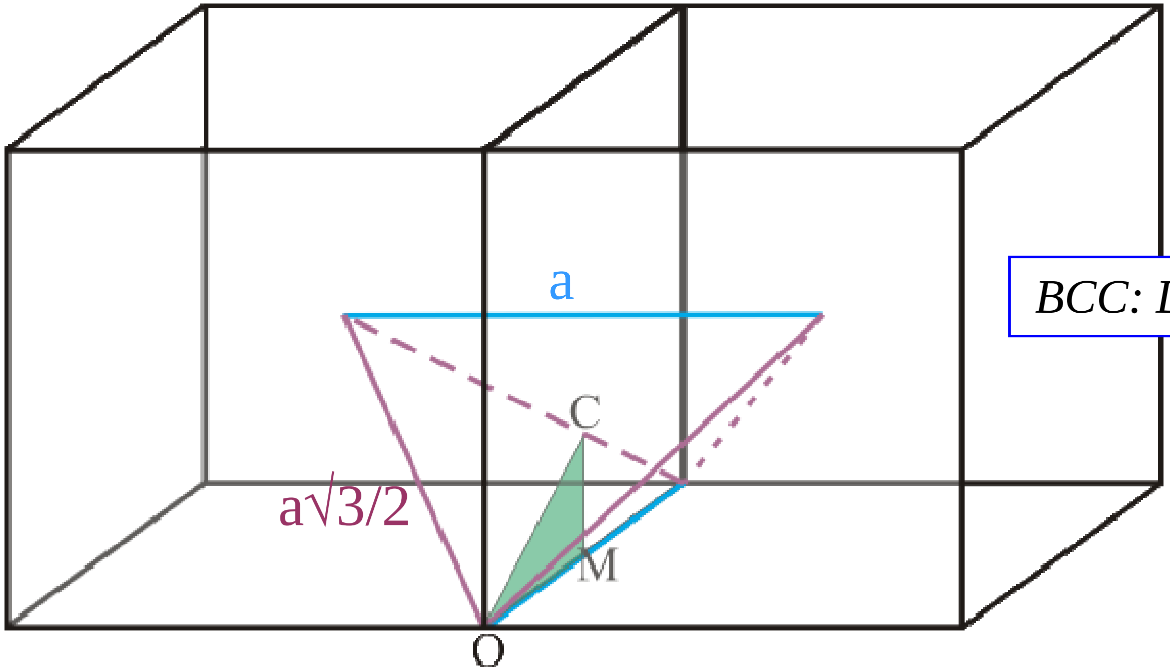




There are four tetrahedral sites on each of the six BCC cell faces (½,¼,0).

BCC voids	Position	Voids / cell	Voids / atom
Distorted Tetrahedral	• Four on each face: [(4/2) × 6 = 12] → (0, ½, ¼)	12	6
Non-regular Octahedral	• Face centre: (6/2 = 3) → (½, ½, 0) • Edge centre: (12/4 = 3) → (½, 0, 0)	6	3

Calculation of the size of the distorted tetrahedral void



BCC: Distorted Tetrahedral Void

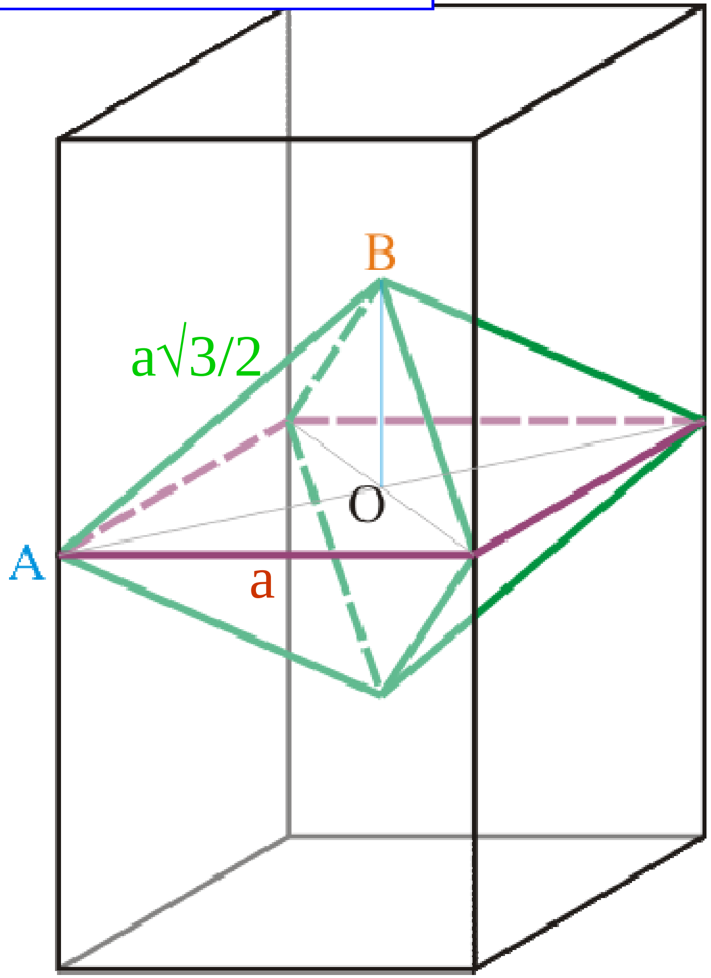
From the right angled triange OCM: $OC = \sqrt{\frac{a^2}{16} + \frac{a^2}{4}} = \frac{\sqrt{5}}{4} a = r + x$

For a BCC structure: $\sqrt{3}a = 4r \ \ (a = \frac{4r}{\sqrt{3}})$

$$\frac{\sqrt{5}}{4}\frac{4r}{\sqrt{3}} = r + x \ \Rightarrow \ \frac{x}{r} = \left(\sqrt{\frac{5}{3}} - 1\right) = 0.29$$

Calculation of the size of the distorted octahedral void

Distorted Octahedral Void



$$OB = \frac{a}{2} = 0.5a \qquad OA = \frac{\sqrt{2}a}{2} = .707a$$

As the distance OA > OB the atom in the void touches only the atom at B (body centre).
⇒ void is *actually* a 'linear' void*

This implies:

$$OB = r + x = \frac{a}{2}$$

$$r + x = \frac{4r}{2\sqrt{3}} \qquad BCC: \sqrt{3}a = 4r$$

$$\frac{x}{r} = \left(\frac{2\sqrt{3}}{3} - 1 \right) = 0.1547$$

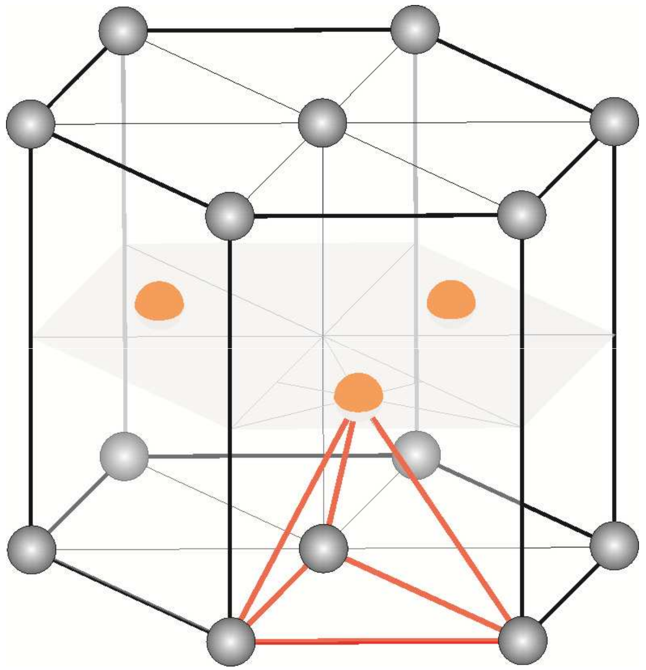
* Point regarding 'Linear Void'

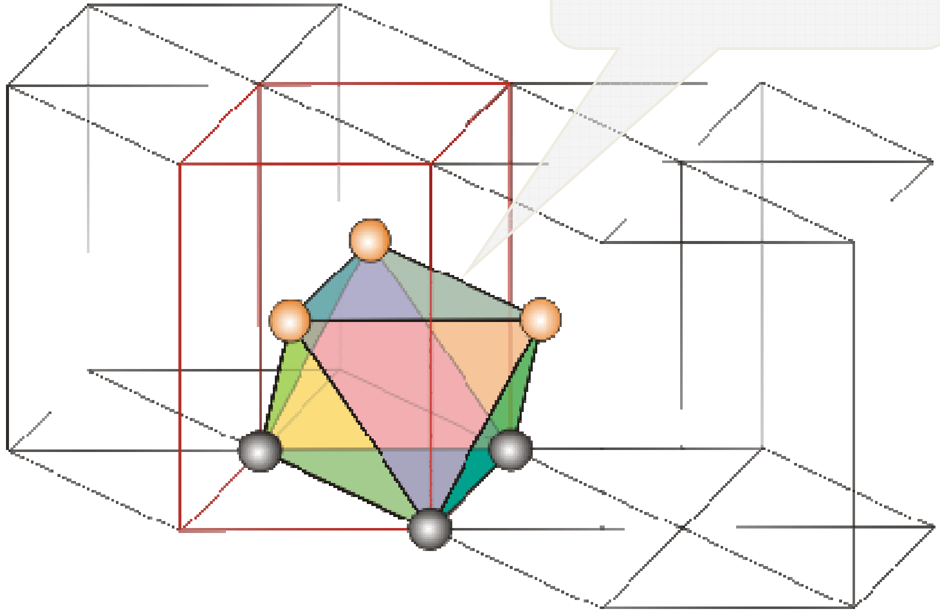
- Because of this aspect the OV along the 3 axes can be differentiated into OV_x, OV_y & OV_z
- Similarly the TV along x,y,z can be differentiated

VOIDS in HCP Crystals

TETRAHEDRAL

OCTAHEDRAL





This void extends across 3 conventional unit cells and hence is difficult to visualize

Coordinates : $(0,0,\tfrac{3}{8}), (0,0,\tfrac{5}{8}), (\tfrac{2}{3},\tfrac{1}{3},\tfrac{1}{8}), (\tfrac{2}{3},\tfrac{1}{3},\tfrac{7}{8})$

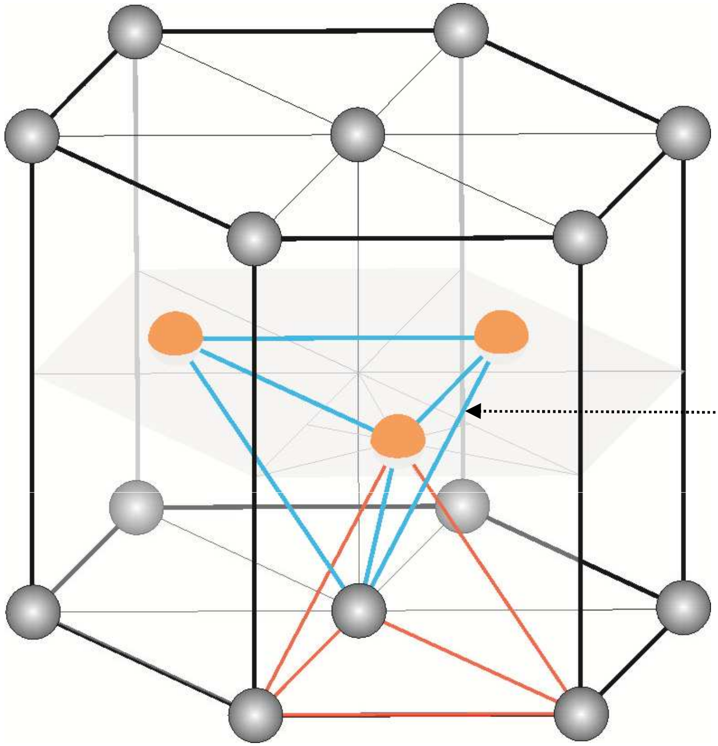
Coordinates: $(\tfrac{1}{3}\ \tfrac{2}{3},\tfrac{1}{4}), (\tfrac{1}{3},\tfrac{2}{3},\tfrac{3}{4})$

- These voids are identical to the ones found in FCC *(for ideal c/a ratio)*
- When the c/a ratio is non-ideal then the octahedra and tetrahedra are distorted *(non-regular)*

Important Note: often in these discussions an ideal c/a ratio will be assumed (without stating the same explicitly)

Note: Atoms are coloured differently but are the same

VOIDS in HCP Crystals



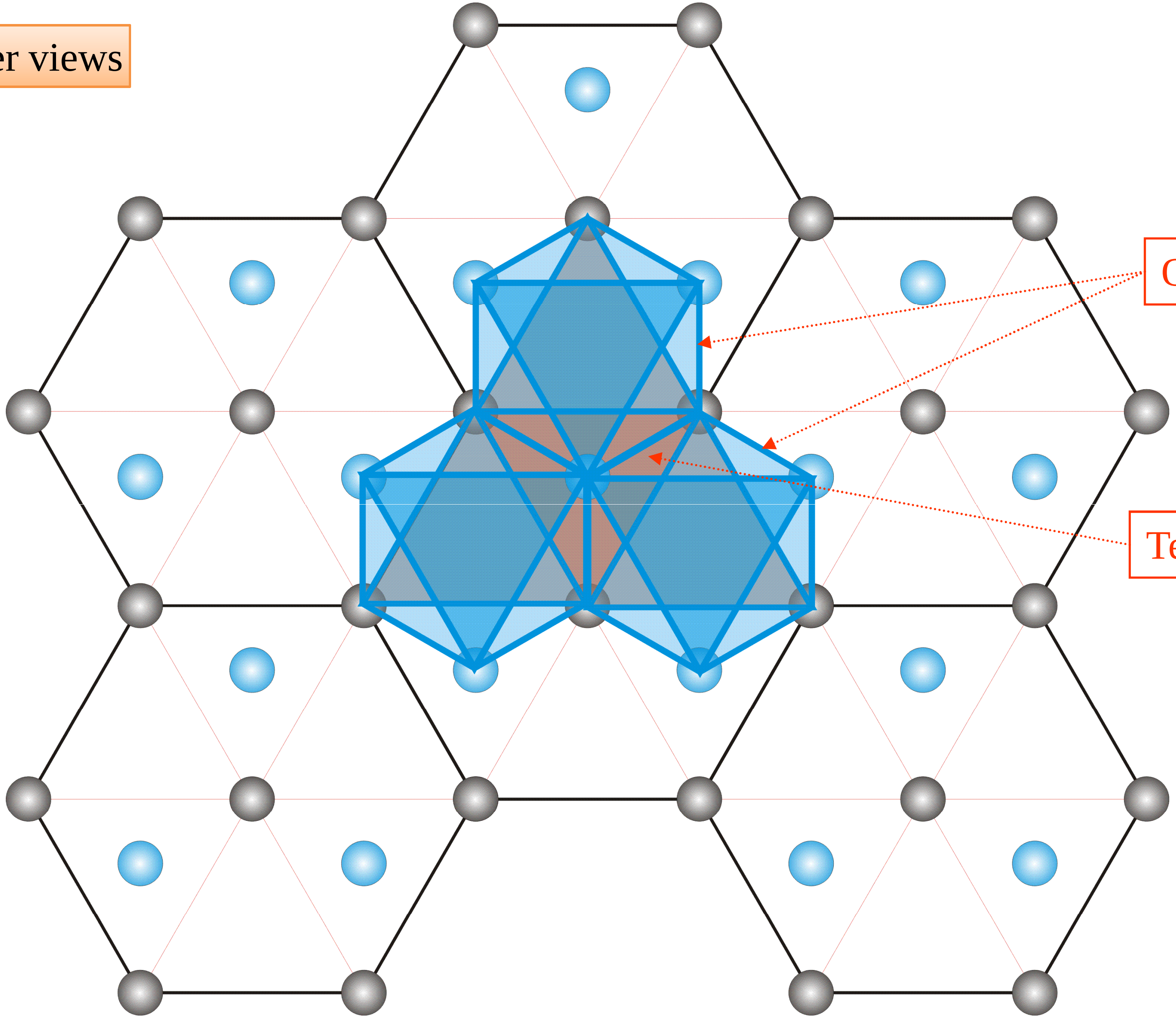
The other orientation of the tetrahedral void

Octahedral voids occur in 1 orientation, tetrahedral voids occur in 2 orientations

Note: Atoms are coloured differently but are the same

VOIDS in HCP Crystals

Further views



Octahedral voids

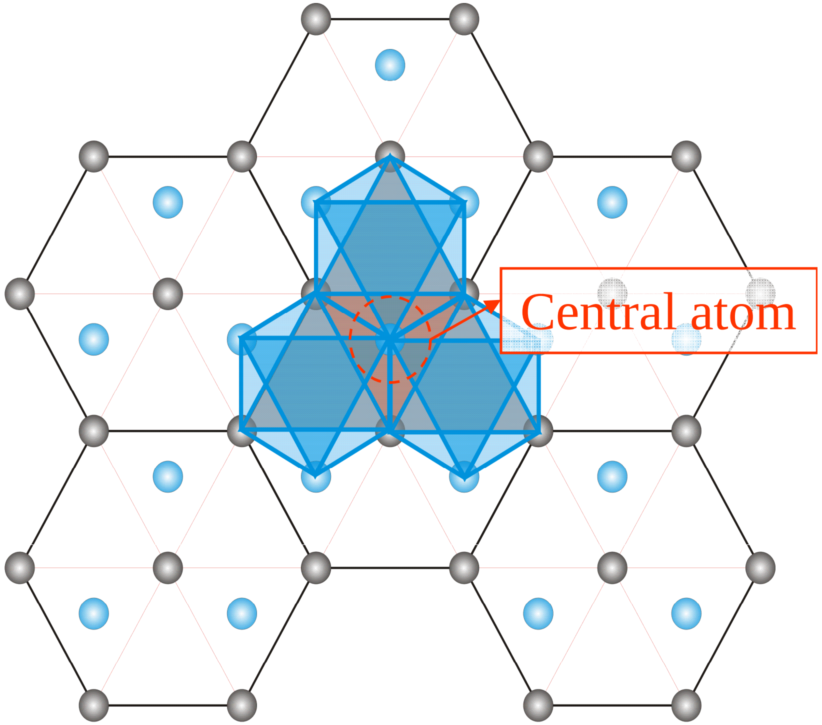
Tetrahedral void

Note: Atoms are coloured differently but are the same

VOIDS in HCP Crystals

Voids/atom: FCC ≡ HCP

→ as we can go from FCC to HCP (and vice-versa) by a twist of 60° around a central atom of two void layers *(with axis ⊥ to figure)*



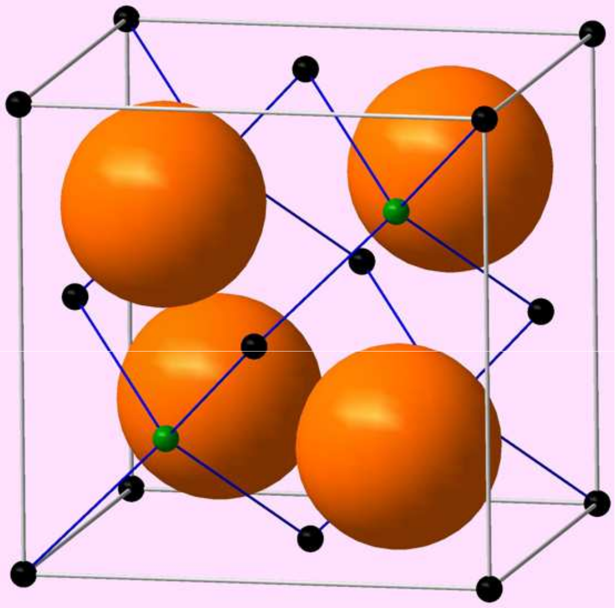
Atoms in HCP crystal: (0,0,0), (⅔, ⅓,½)

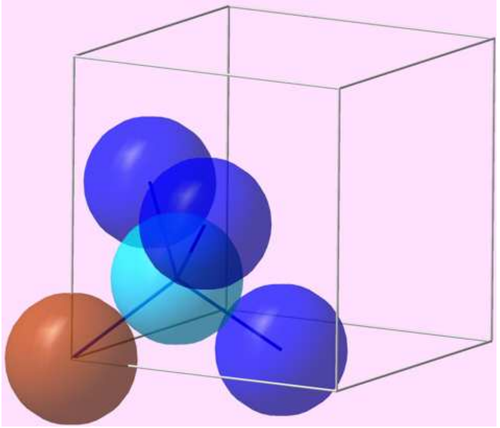
Check below

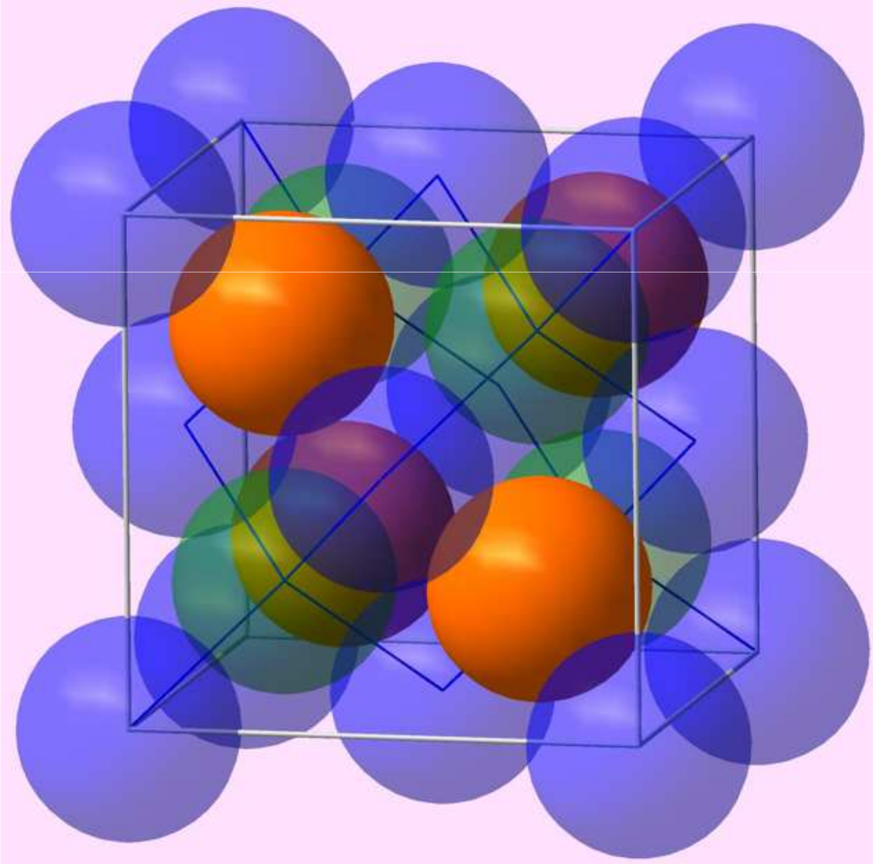
HCP voids	Position	Voids / cell	Voids / atom
Tetrahedral	(0,0,3/8), (0,0,5/8), (⅔, ⅓,1/8), (⅔,⅓,7/8)	4	2
Octahedral	• (⅓ ⅔,¼), (⅓,⅔,¾)	2	1

Voids in Diamond Cubic crystal

- In the DC structure out of the family of 8 (¼, ¼, ¼) type positions only 4 are occupied [(¼, ¼, ¼), (¾, ¾, ¼), (¼, ¾, ¾), (¾, ¼, ¾)].
- The other four are like void positions- which are all tetrahedral in nature.







Summary of void sizes

	r_{void} / r_{atom}			
	SC	**BCC**	**FCC**	**DC**
Octahedral (CN = 6)	*Not present*	0.155 *(non-regular)*	0.414	*Not present*
Tetrahedral (CN = 4)	*Not present*	0.29 *(non-regular)*	0.225	1 (½,½,½) & (¼, ¼, ¼)
Cubic (CN = 8)	0.732	*Not present*	*Not present*	*Not present*

- ❑ Voids should not be confused with vacancies- vacancies are due to missing atoms or ions in crystals.
- ❑ Holes should also not be confused with voids- holes are ‘missing electrons’ from the valence band of a solid.
- ❑ Voids have complicated shapes- we usually use a polyhedral version – the coordination polyhedron around a sphere of ‘correct size’.
- ❑ Sometimes, as in the case of ‘octahedral void’ in the BCC- the second nearest neighbors are also included in constructing the coordination polyhedron.

SOLIDIFICATION

Avala Lava Kumar : Suneeti Purohit : Gautam Behera

Department of Metallurgical & Materials Engineering (MME)

Veer Surendra Sai University of Technology (VSSUT), Burla -768018

E-mail : lavakumar.vssut@gmail.com

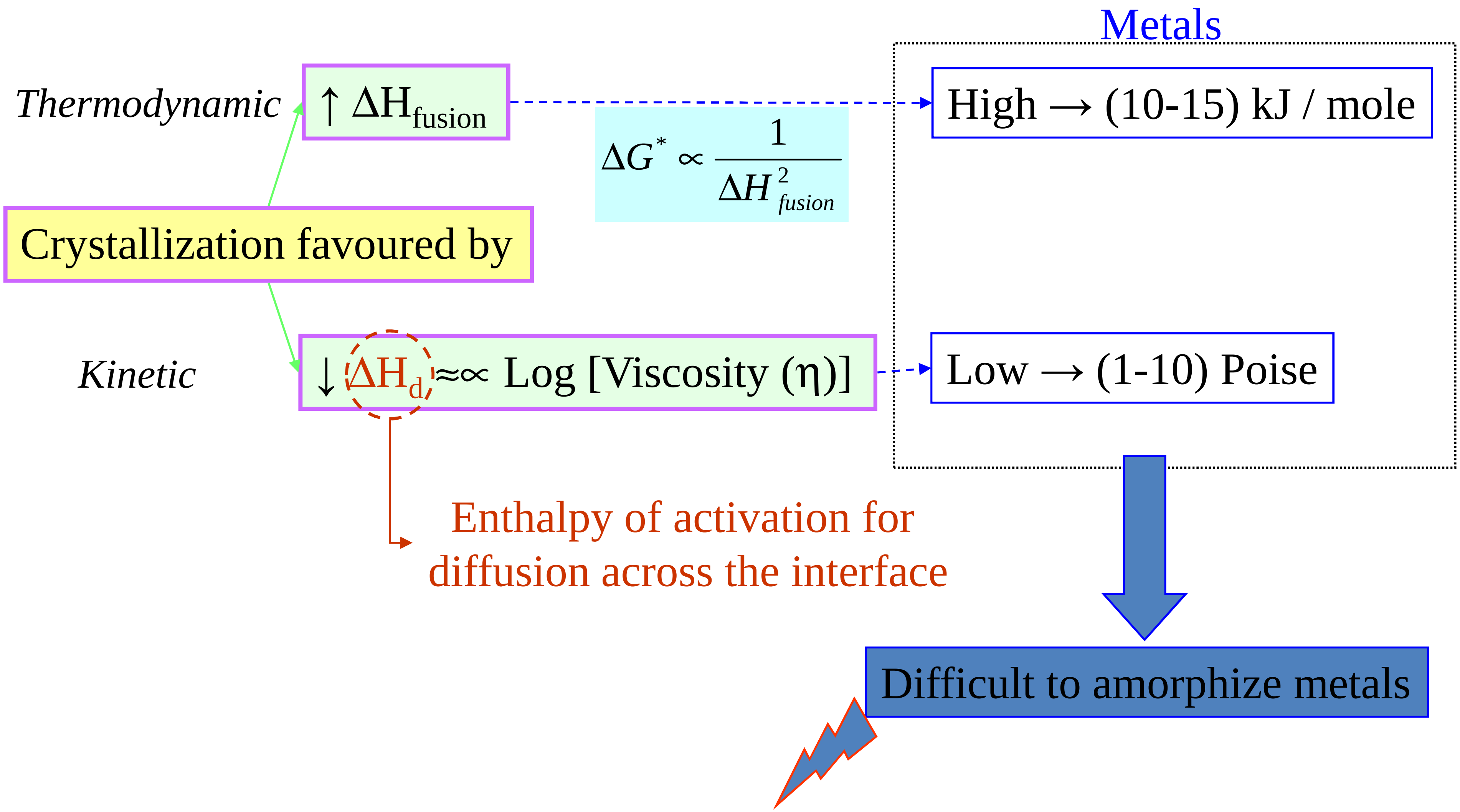
Introduction

- ☐ Three states of matter are distinguishable: gas, liquid, and solid
- ☐ In the gaseous state the metal atoms occupy a great deal of space because of their rapid motion. The atoms move independently and are usually widely separated so that the attractive forces between atoms are negligible. The arrangement of atoms in a gas is one of complete disorder.
- ☐ At some lower temperature, the kinetic energy of the atoms has decreased so that the attractive forces become large enough to bring most of the atoms together in a liquid. And there is a continual interchange of atoms between the vapor and liquid across the liquid surface.
- ☐ The attractive forces between atoms in a liquid may be demonstrated by the application of pressure. A gas may be easily compressed into a smaller volume, but it takes a high pressure to compress a liquid. There is, however, still enough free space in the liquid to allow the atoms to move about irregularly.
- ☐ As the temperature is decreased, the motions are less vigorous and the attractive forces pull the atoms closer together until the liquid solidifies. Most materials contract upon solidification, indicating a closer packing of atoms in the solid state.
- ☐ The atoms in the solid are not stationary but are vibrating around fixed points, giving rise to the orderly arrangement of crystal structures.

Mechanism of Crystallization

- Crystallization is the transition from the liquid to the solid state and occurs in two stages:
  - Nuclei formation
  - Crystal Growth
- Although the atoms in the liquid state do not have any definite arrangement, it is possible that some atoms at any given instant are in positions exactly corresponding to the space lattice they assume when solidified.
- These chance aggregates or groups are not permanent but continually break up and reform at other points.
- The higher the temperature, the greater the kinetic energy of the atoms and the shorter the life of the group. When the temperature, of the liquid is decreased, the atom movement decreases, lengthening the life of the group, and more groups will be present at the same time.
- *Atoms in a material have both kinetic and potential energy. Kinetic energy is related to the speed at which the atoms move and is strictly a function of temperature. The higher the temperature, the more active are the atoms and the greater is their kinetic energy. Potential energy, on the other hand, is related to the distance between atoms. The greater the average distance between atoms, the greater is their potential energy.*

Mechanism of Crystallization



Crystallization favoured by

Thermodynamic $\uparrow \Delta H_{fusion}$

$$\Delta G^* \propto \frac{1}{\Delta H^2_{fusion}}$$

Kinetic $\downarrow \Delta H_d \approx\propto \text{Log [Viscosity } (\eta)]$

Enthalpy of activation for diffusion across the interface

Metals

High ⟶ (10-15) kJ / mole

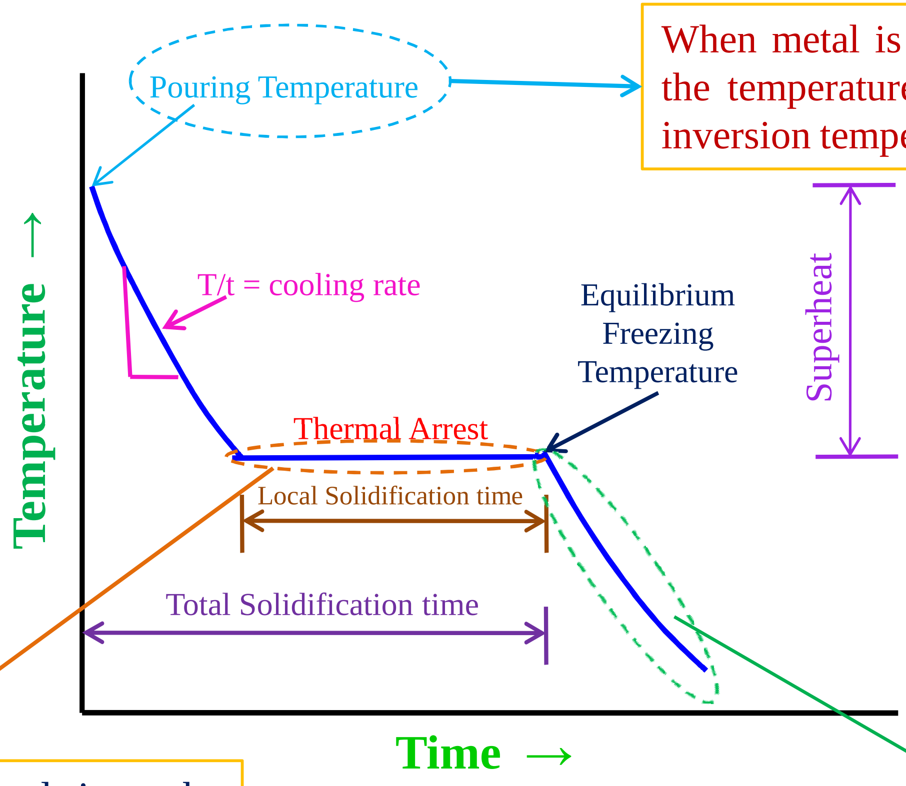
Low ⟶ (1-10) Poise

Difficult to amorphize metals

Very fast cooling rates ~10^6 K/s are used for the amorphization of alloys

⟶ *splat cooling, melt-spinning.*

Solidification (or) Freezing



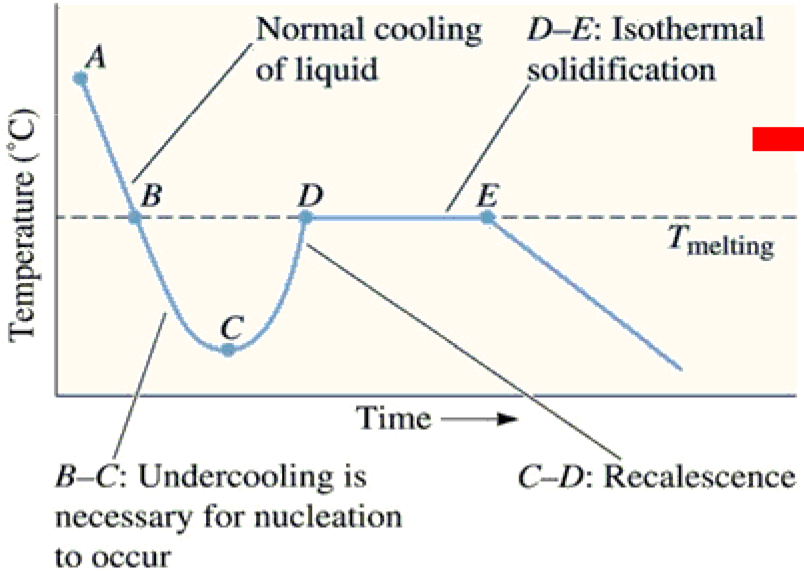
When metal is poured into the mould, the temperature will be as high as its inversion temperature.

It gets cooled when poured into the mould and molten metal in the liquid form will solidify. This time is called local solidification time

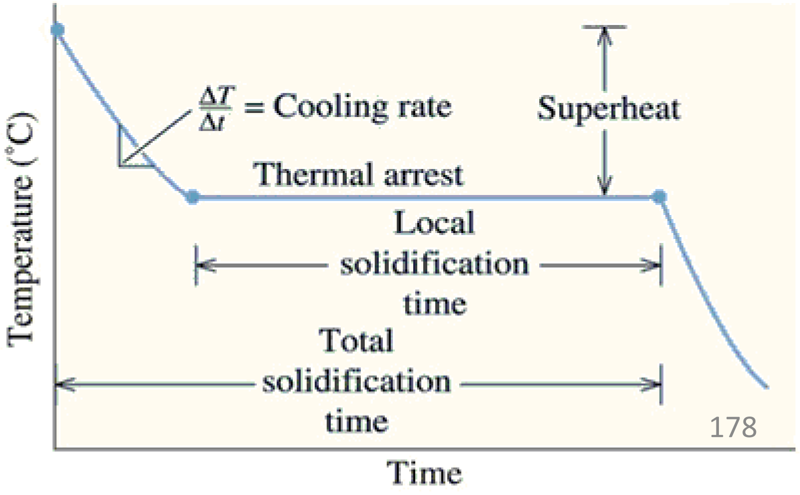
The solidified metal in the mould (called casting) gets cooled in the mould to the temperature of the surroundings

Cooling Curves

- Recalescence : The increase in temperature of an undercooled liquid metal as a result of the liberation of heat during nucleation.
- Thermal Arrest : A plateau on the cooling curve during the solidification of a material caused by the evolution of the latent heat of fusion during solidification.
- Total Solidification Time : The time required for the casting to solidify completely after the casting has been poured.
- Local Solidification Time : The time required for a particular location in a casting to solidify once nucleation has begun.



Cooling curve for a pure metal that has not been well inoculated. Liquid cools as specific heat is removed (betweens points *A* and *B*). Undercooling is thus necessary (between points *B* and *C*). As the nucleation begins (point *C*), latent heat of fusion is released causing an increase in the temperature of the liquid. This process is known as recalescence (point *C* to point *D*). Metal continues to solidify at a constant temperature (T melting). At point *E*, solidification is complete. Solid casting continues to cool from the point.



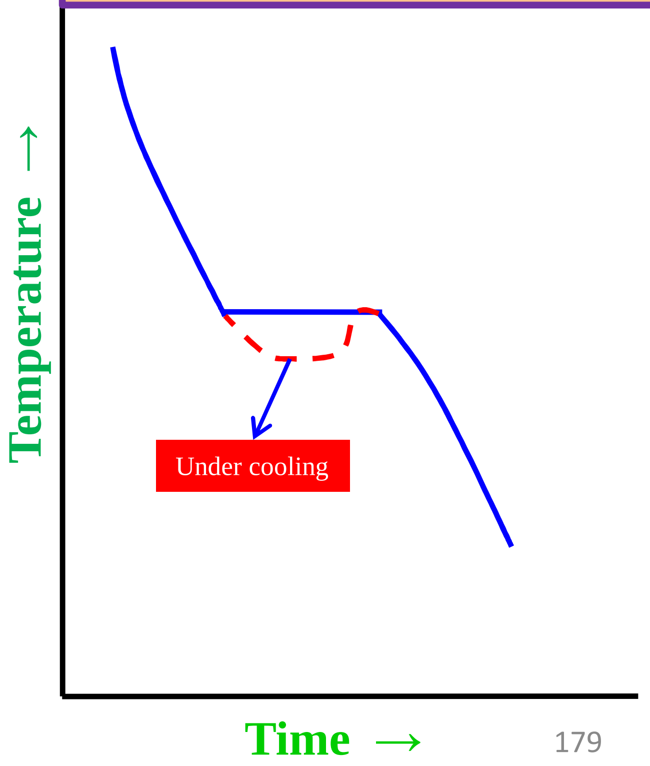
Cooling curve for a well inoculated, but otherwise pure metal. No undercooling is needed. Recalescence is not observed. Solidification begins at the melting temperature

Solidification of pure metal : Super cooling

- ☐ In a pure metal at its freezing point where both the liquid and solid states are at the same temperature. The kinetic energy of the atoms in the liquid and the solid must be the same, but there is a significant difference in potential energy.
- ☐ The atoms in the solid are much closer together, so that solidification occurs with a release of energy. This difference in potential energy between the liquid and solid states is known as the *latent heat of fusion.*

- ☐ However, energy is required to establish a surface between the liquid and solid. In pure materials at the freezing point insufficient energy is released by the heat of fusion to create a stable boundary, and some under cooling is always necessary to form stable nuclei.
- ☐ Subsequent release of the heat of fusion will raise the temperature to the freezing point. The amount of undercooling required may be reduced by the presence of solid impurities which reduce the amount of surface energy required.

Cooling Curve for a pure metal



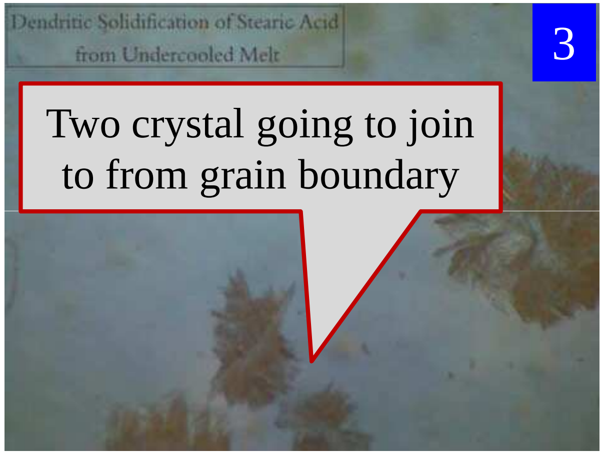
Solidification of pure metal

- When the temperature of the liquid metal has dropped sufficiently below its freezing point, stable aggregates or nuclei appear spontaneously at various points in the liquid. These nuclei, which have now solidified, act as centers for further crystallization.
- As cooling continues, more atoms tend to freeze, and they may attach themselves to already existing nuclei or form new nuclei of their own. Each nucleus grows by the attraction of atoms from the liquid into its space lattice.
- Crystal growth continues in three dimensions, the atoms attaching themselves in certain preferred directions, usually along the axes of the crystal this gives rise to a characteristic treelike structure which is called a dendrite.
- Since each nucleus is formed by chance, the crystal axes are pointed at random and the dendrites growing from them will grow in different directions in each crystal. Finally, as the amount of liquid decreases, the gaps between the arms of the dendrite will be filled and the growth of the dendrite will be mutually obstructed by that of its neighbors. This leads to a very irregular external shape.
- The crystals found in all commercial metals are commonly called grains because of this variation in external shape. The area along which crystals meet, known as the grain boundary, is a region of mismatch.

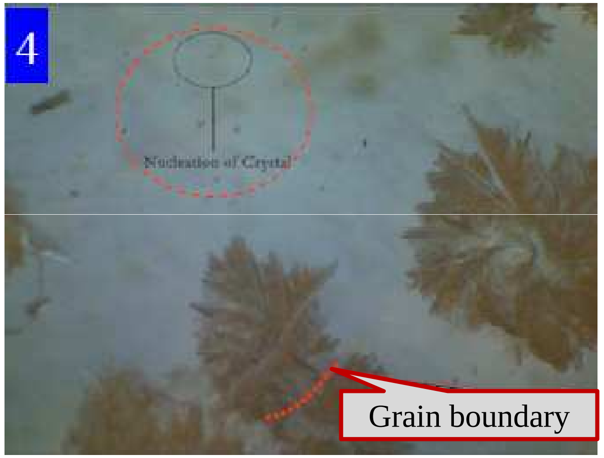
Liquid to Solid Phase Transformation : Solidification

Solid

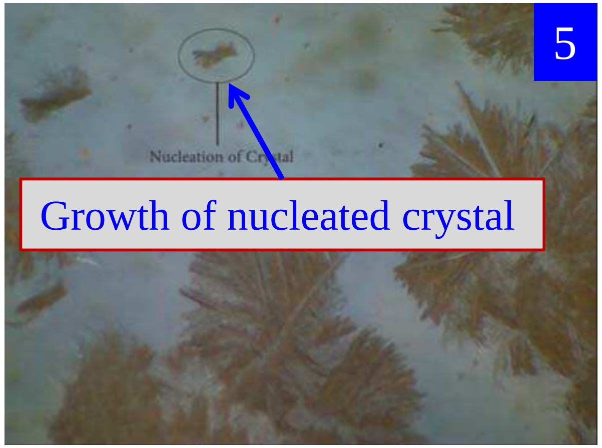
Growth of crystal



Two crystal going to join to from grain boundary

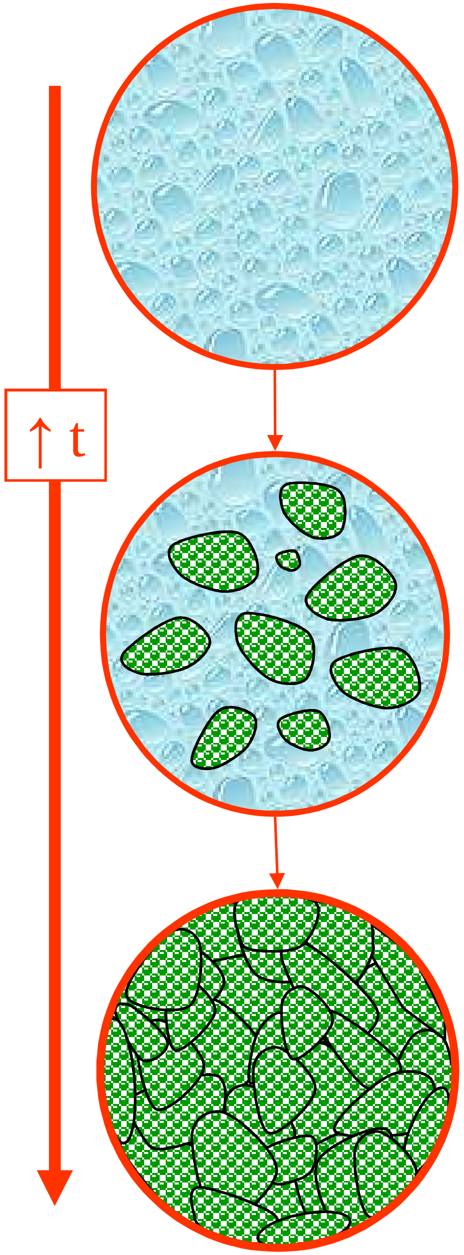


Grain boundary



Growth of nucleated crystal

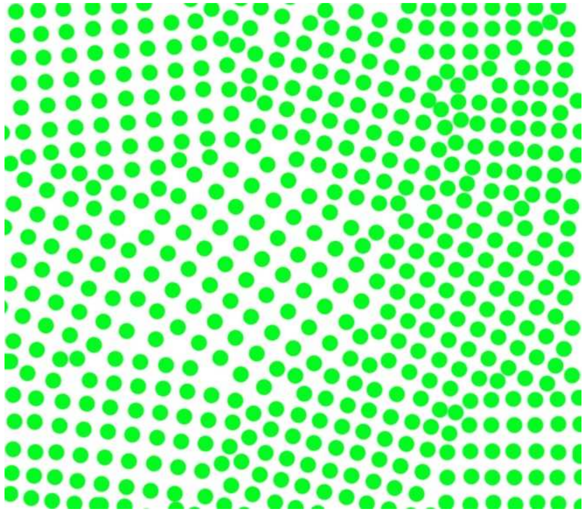
Solidification Complete

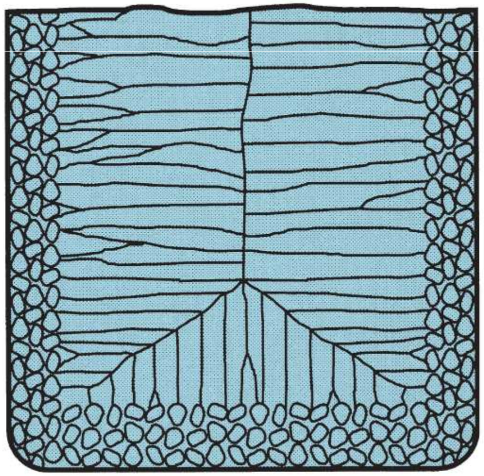


“For sufficient Undercooling”

Solidification of pure metal

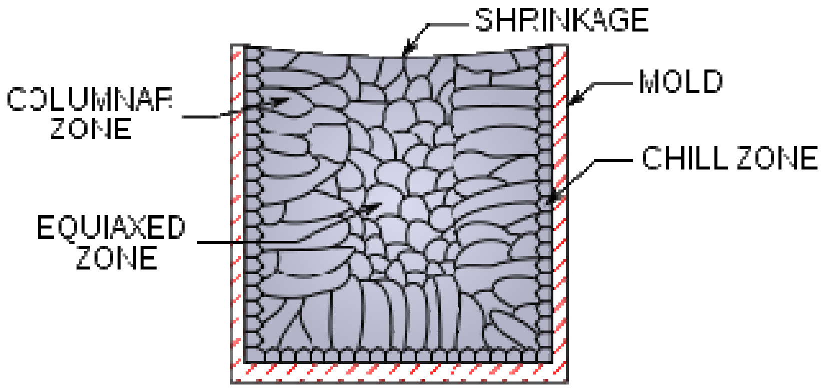
- This mismatch leads to a noncrystalline (amorphous) structure at the grain boundary with the atoms irregularly spaced.
- Since the last liquid to solidify is generally along the grain boundaries, there tends to be higher concentration of impurity atoms in that area. Figure (previous page) shows schematically the process of crystallization from nuclei to the final grains.
- Due to chilling action of mold wall, a thin skin of solid metal is formed at the wall surface immediately after pouring.
- Grain structure in a casting of a pure metal, showing randomly oriented grains of small size near the mold wall, and large columnar grains oriented toward the center of the casting.

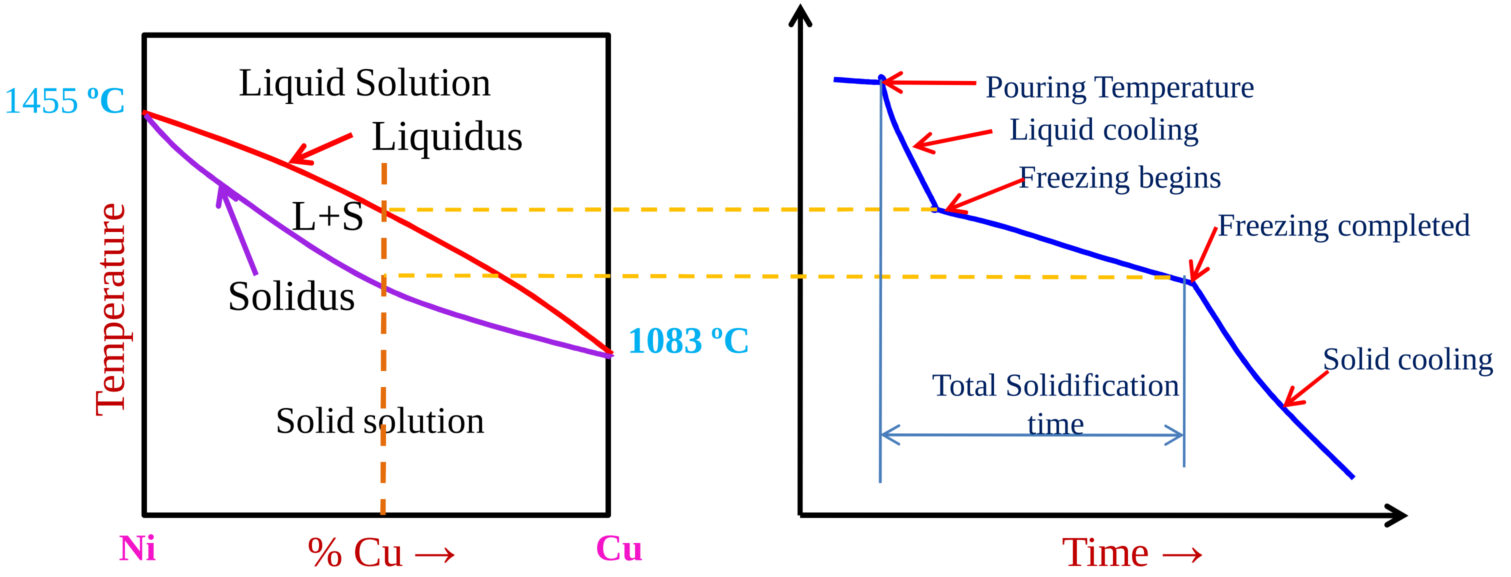




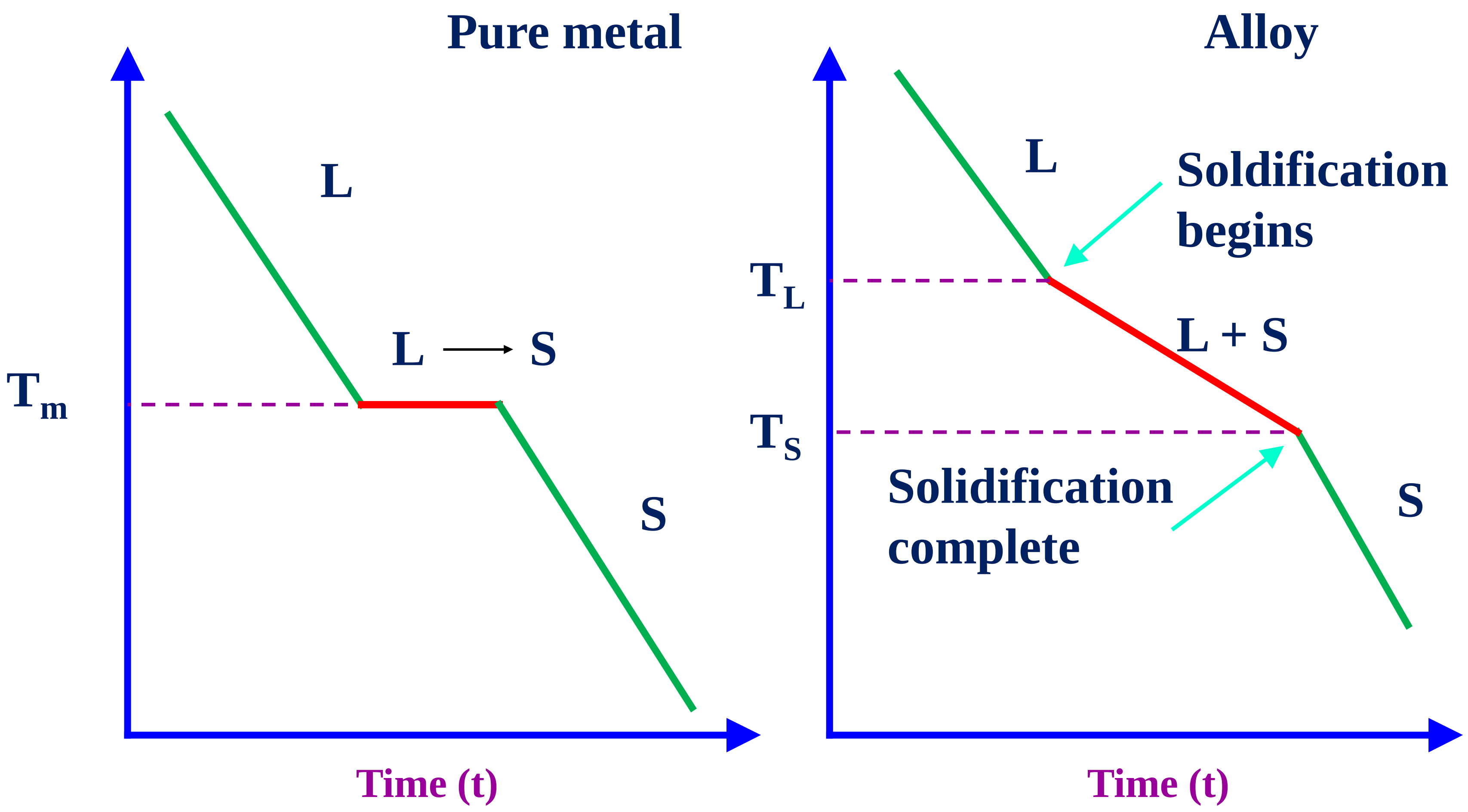
Solidification of Alloys

- ☐ Most alloys freeze over a temperature range
- ☐ Phase diagram for a Cu-Ni alloy system and cooling curve for different alloy systems.
- ☐ Characteristic grain structure in an alloy casting, showing segregation of alloying components in center of casting.





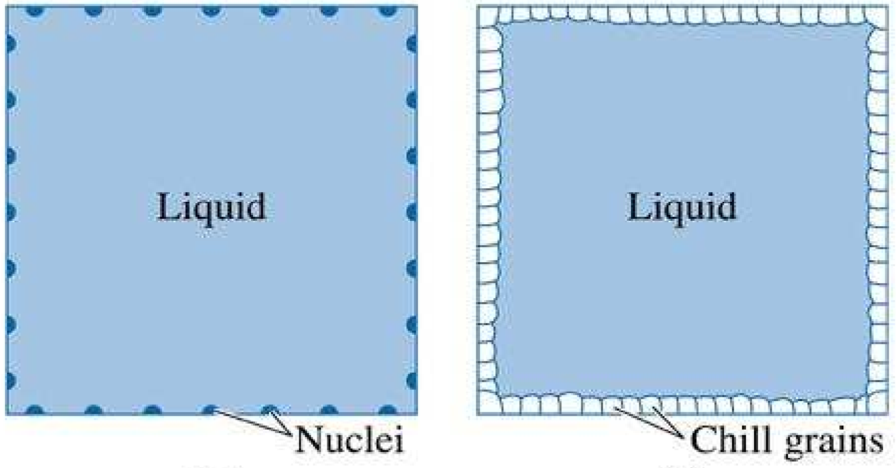
Comparison of cooling curves



Cast Structure

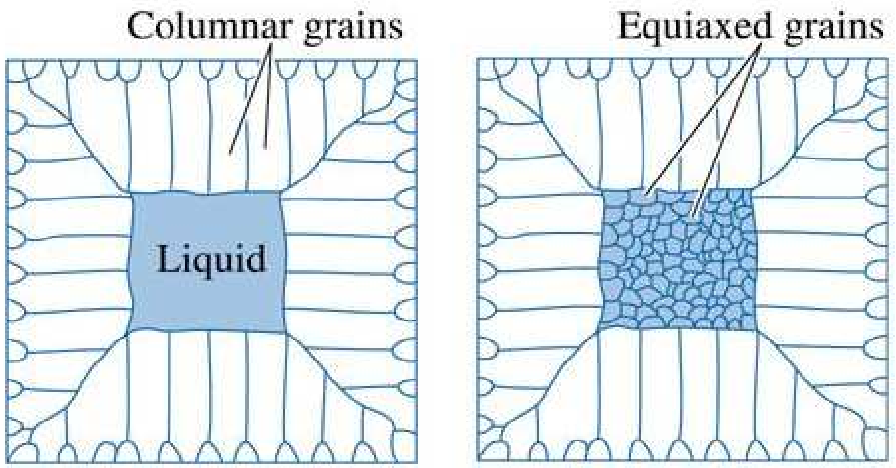
- Chill Zone: A region of small, randomly oriented grains that forms at the surface of a casting as a result of heterogeneous nucleation.
- Columnar Zone: A region of elongated grains having a preferred orientation that forms as a result of competitive growth during the solidification of a casting.
- Equiaxed Zone: A region of randomly oriented grains in the center of a casting produced as a result of widespread nucleation.

Figure: Development of the ingot structure of a casting during solidification:



Nucleation begins

Chill zone forms



preferred growth produces the columnar zone

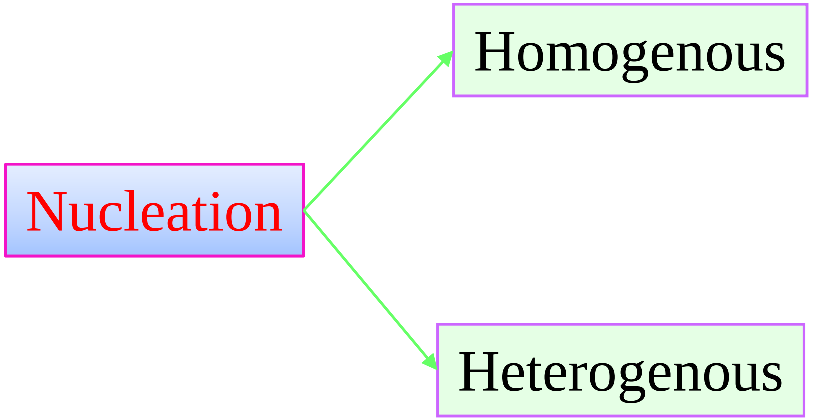
additional nucleation creates the equiaxed zone

Nucleation

Solidification = Nucleation + Growth

- Nucleation: localized formation of a distinct thermodynamic phase.
- Nucleation an occur in a gas, liquid or solid phase. Some examples of phases that may form via nucleation include:
  - In gas-creation of liquid droplets in saturated vapor
  - In liquid-formation of gaseous bubbles crystals (e.g., ice formation from water) or glassy regions.
  - In solid-Nucleation of crystalline, amorphous and even vacancy clusters in solid materials. Such solid state nucleation is important, for example, to the semi conductor industry.
- Most nucleation processes are physical, rather than chemical.
- There are two types of nucleation : homogeneous and heterogeneous. This distinction between them made according to the site at which nucleating events occur. For the homogeneous type, nuclei of the new phase form uniformly throughout the parent phase, where as for the heterogeneous type, nuclei form preferentially at structural inhomogeneities such as container surfaces insoluble impurities grain boundaries, dislocations and so on

Nucleation



- *It occurs spontaneously and randomly, but it requires superheating or supercooling of the medium.*

- Liquid → solid
  walls of container, inclusions
- Solid → solid
  inclusions, grain boundaries, dislocations, stacking faults

❑ The probability of nucleation occurring at point in the parent phase is same throughout the parent phase

❑ In heterogeneous nucleation there are some preferred sites in the parent phase where nucleation can occur

Nucleation

- Compared to the heterogeneous nucleation (which starts at nucleation sites on surfaces) homogeneous nucleation occurs with much more difficulty in the interior of a uniform substance. The creation of a nucleus implies the formation of an interface at the boundaries of a new phase.
- Liquids cooled below the maximum heterogeneous nucleation temperature (melting temperature) but which are above the homogeneous nucleation temperature. (pure substance freezing temperature) are cooled super cooled.
- An example of supercooling: pure water freezes at -42°C rather than at its freezing temperature °C.

Nucleation - *The physical process by which a new phase is produced in a material.*
Critical radius (r)* - *The minimum size that must be formed by atoms clustering together in the liquid before the solid particle is stable and begins to grow.*
Undercooling - *The temperature to which the liquid metal must cool below the equilibrium freezing temperature before nucleation occurs.*
Homogeneous nucleation - *Formation of a critically sized solid from the liquid by the clustering together of a large number of atoms at a high undercooling (without an external interface).*
Heterogeneous nucleation - *Formation of a critically sized solid from the liquid on an impurity surface.*

Mechanical Properties

Avala Lava Kumar : Suneeti Purohit : Gautam Behera

Department of Metallurgical & Materials Engineering (MME)

Veer Surendra Sai University of Technology (VSSUT), Burla -768018

E-mail : lavakumar.vssut@gmail.com

Mechanical properties of metals

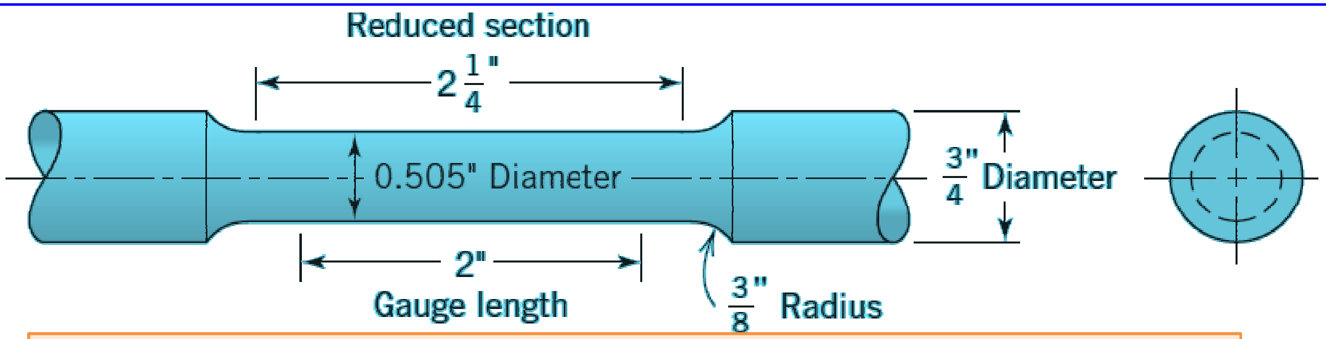
- The mechanical properties of a material reflects the relationship between its response or deformation to an applied load or force.
- Important mechanical properties are strength, hardness, ductility, and stiffness.
- These properties are ascertained by performing carefully designed laboratory experiments that replicate as nearly as possible the service conditions.
- Factors to be considered include the nature of the applied load and its duration, as well as the environmental conditions.
- It is possible for the load to be tensile, compressive, or shear, and its magnitude may be constant with time, or it may fluctuate continuously. Application time may be only a fraction of a second, or it may extend over a period of many years. Service temperature may be an important factor.

Concepts of Stress & Strain

Solids deform when they are subject to load (can be tensile, compressive or shear). They can maintain or lose their shape

Tension Tests

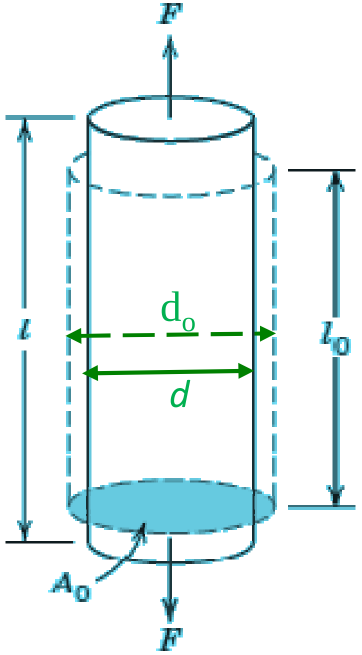
- ☐ Most common mechanical stress–strain tests which is used to ascertain several mechanical properties of materials.
- ☐ A specimen is deformed, usually to fracture, with a gradually increasing uniaxial tensile load applied along the long axis of a specimen.
- ☐ The tensile testing machine is designed to elongate the specimen at a constant rate, and to continuously and simultaneously measure the instantaneous applied load (with a load cell) and the resulting elongations (using an extensometer).
- ☐ The output of such a tensile test is recorded (usually on a computer) as ***load or force versus elongation***



A standard tensile specimen with circular cross section

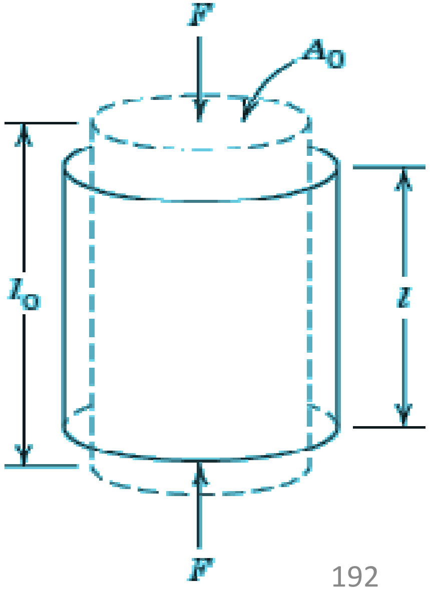
Concepts of Stress & Strain

- Engineering stress : Tensile stress $\sigma = \frac{F}{A_o}$ *SI Unit: Megapascals*
- Engineering strain : Tensile strain $\varepsilon = \frac{l - l_o}{l_o} = \frac{\Delta l}{l_o}$
- Lateral Strain : $\varepsilon_l = \frac{d - d_o}{d_o} = \frac{\Delta d}{d_o}$ *Strain is always dimensionless*
- Where l_o and d_o are the original dimensions before any load is applied; l and d are the instantaneous dimensions; Δl and Δd are changes in dimensions.



Compression Tests

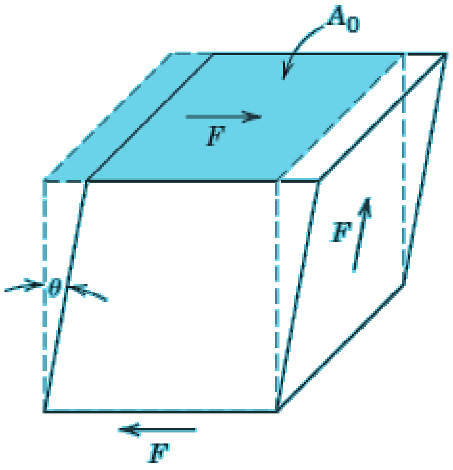
- Test is conducted in a manner similar to the tensile test, except that the force is compressive and the specimen contracts along the direction of the stress.
- By convention, a compressive force is taken to be negative, which yields a negative stress. Furthermore, since l_o is greater than l, compressive strains is also negative



Concepts of Stress & Strain

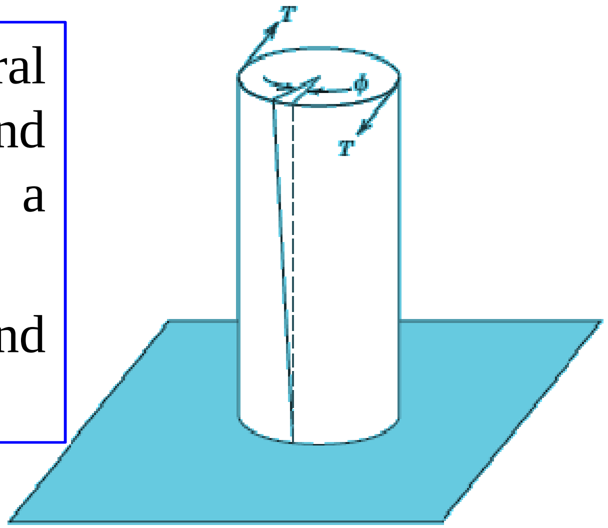
Shear Tests

- For tests performed using a pure shear force, the shear stress is computed according to
- Shear stress $\tau = \frac{F}{A_o}$ Shear strain $\gamma = \tan\theta$
- Where F is the load or force imposed parallel to the upper and lower faces, each of which has an area of A_0 . The shear strain γ is defined as the tangent of the strain angle θ.



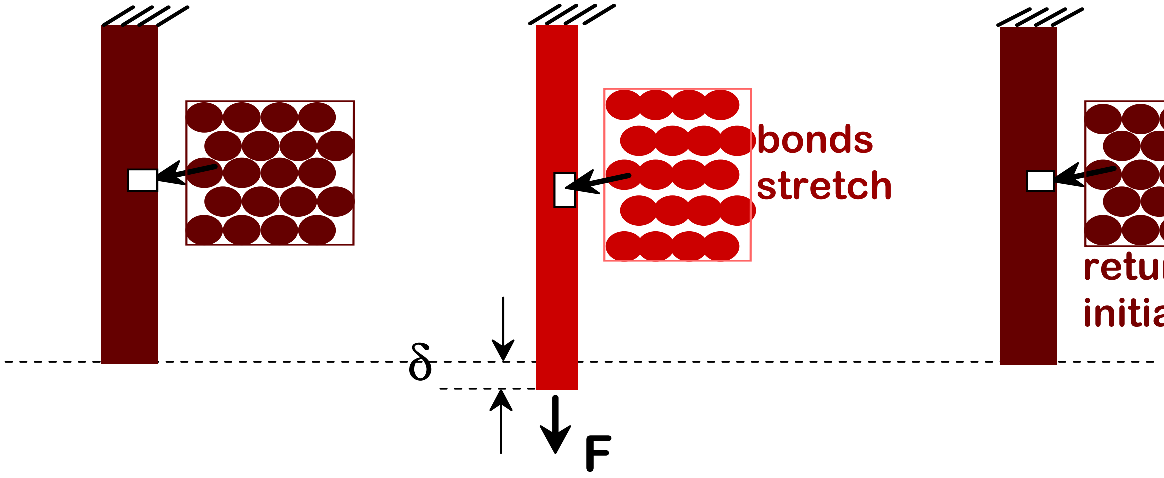
Torsional Tests

- Torsion is a variation of pure shear, wherein a structural member is twisted about the longitudinal axis of one end of the member relative to the other end producing a rotational motion .
- Shear stress τ is a function of the applied torque T and shear strain is related to the angle of twist φ.



Elastic Deformation

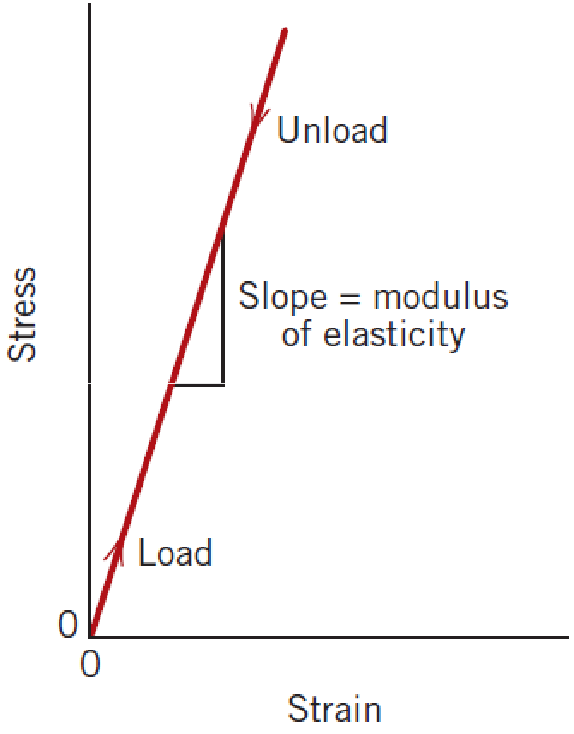
- ❑ Deformation in which stress and strain are proportional is called elastic deformation.
- ❑ Elastic deformation is non permanent reversible deformation- i.e. when load/forces are released the body returns to its original configuration (shape and size). It can be caused by tension/compression or shear forces.
- ❑ Usually in metals and ceramics elastic deformation is seen at low strains (< 10^{-3}).



- ❑ Elasticity can be linear or Non linear. Metals and ceramics usually show linear elastic behavior.
- ❑ Some materials (e.g., gray cast iron, concrete, and many polymers) exhibit non linear elasticity.

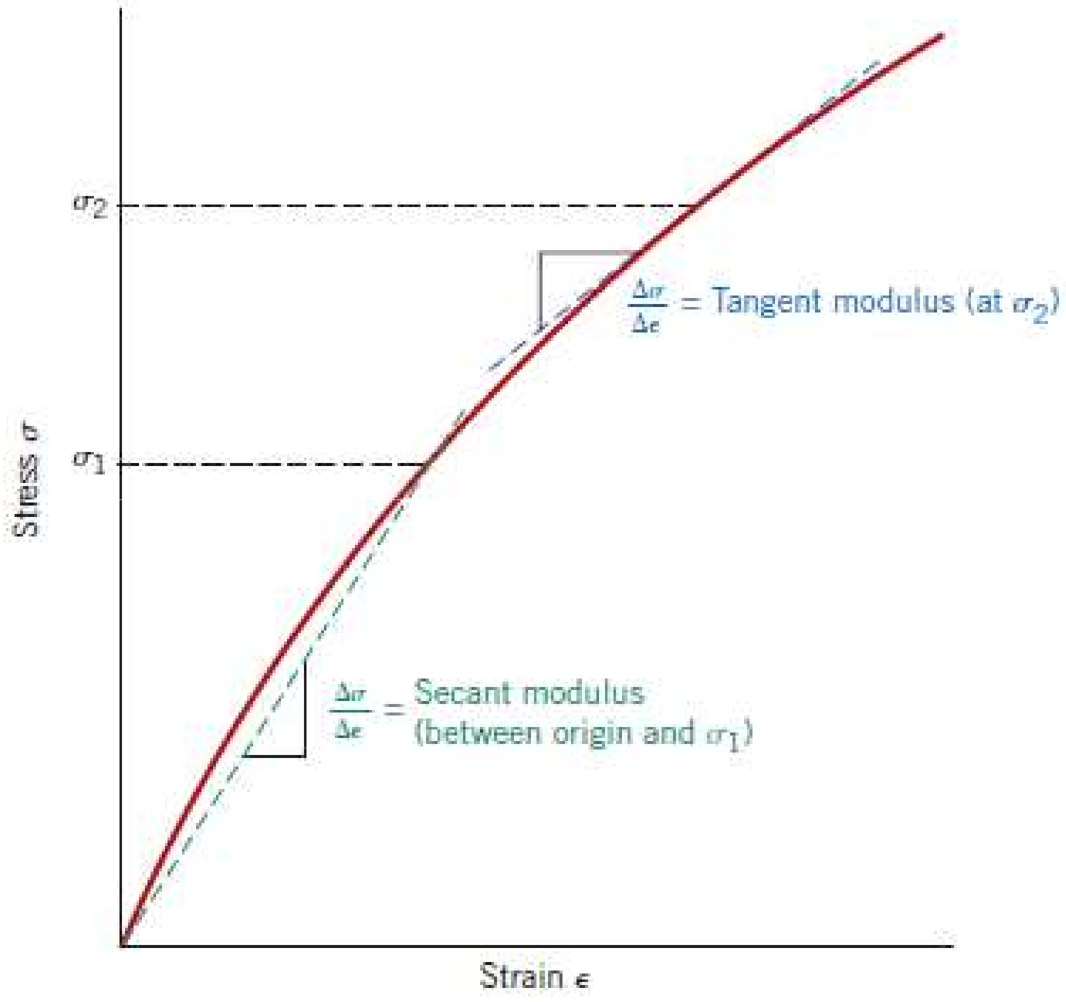
Elastic Stress-Strain Curve

- A **stress-strain** curve is a graph derived from measuring load (stress - σ) versus extension (strain - ε) for a sample of a material
- For most metals that are stressed in tension and at relatively low levels, stress and strain are proportional to each other i.e.
- The slope of this linear segment corresponds to the modulus of elasticity E.
- This is known as Hooke’s law, and the constant of proportionality E (Gpa or psi) is the **modulus of elasticity,** or **Young’s modulus.**
- This modulus may be thought of as stiffness, or a material’s resistance to elastic deformation. The greater the modulus, the stiffer the material, or the smaller the elastic strain that results from the application of a given stress.

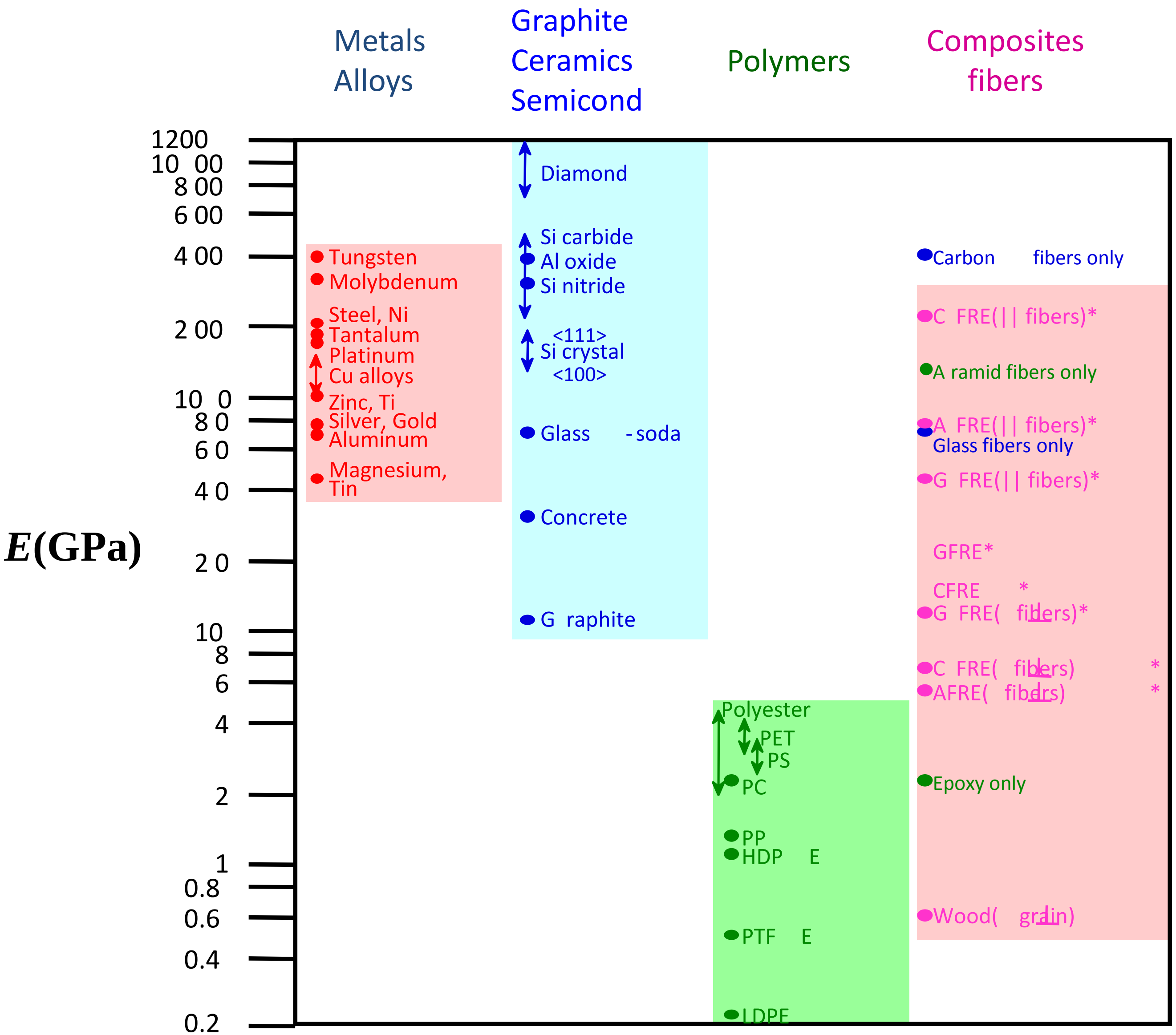


Elastic Stress-Strain Curve

- For materials showing non linear elasticity either tangent or secant modulus can be used to determine the modulus of elasticity.
- Tangent modulus is taken as the slope of the stress–strain curve at some specified level of stress, while secant modulus represents the slope of a secant drawn from the origin to some given point of the σ–ϵ curve.



Young's Moduli : Comparison



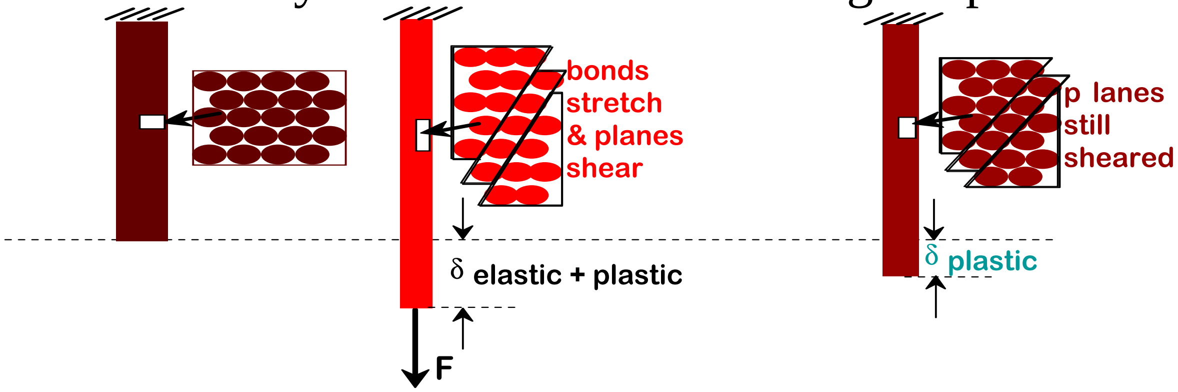
$E_{ceramics}$

$> E_{metals}$

$>> E_{polymers}$

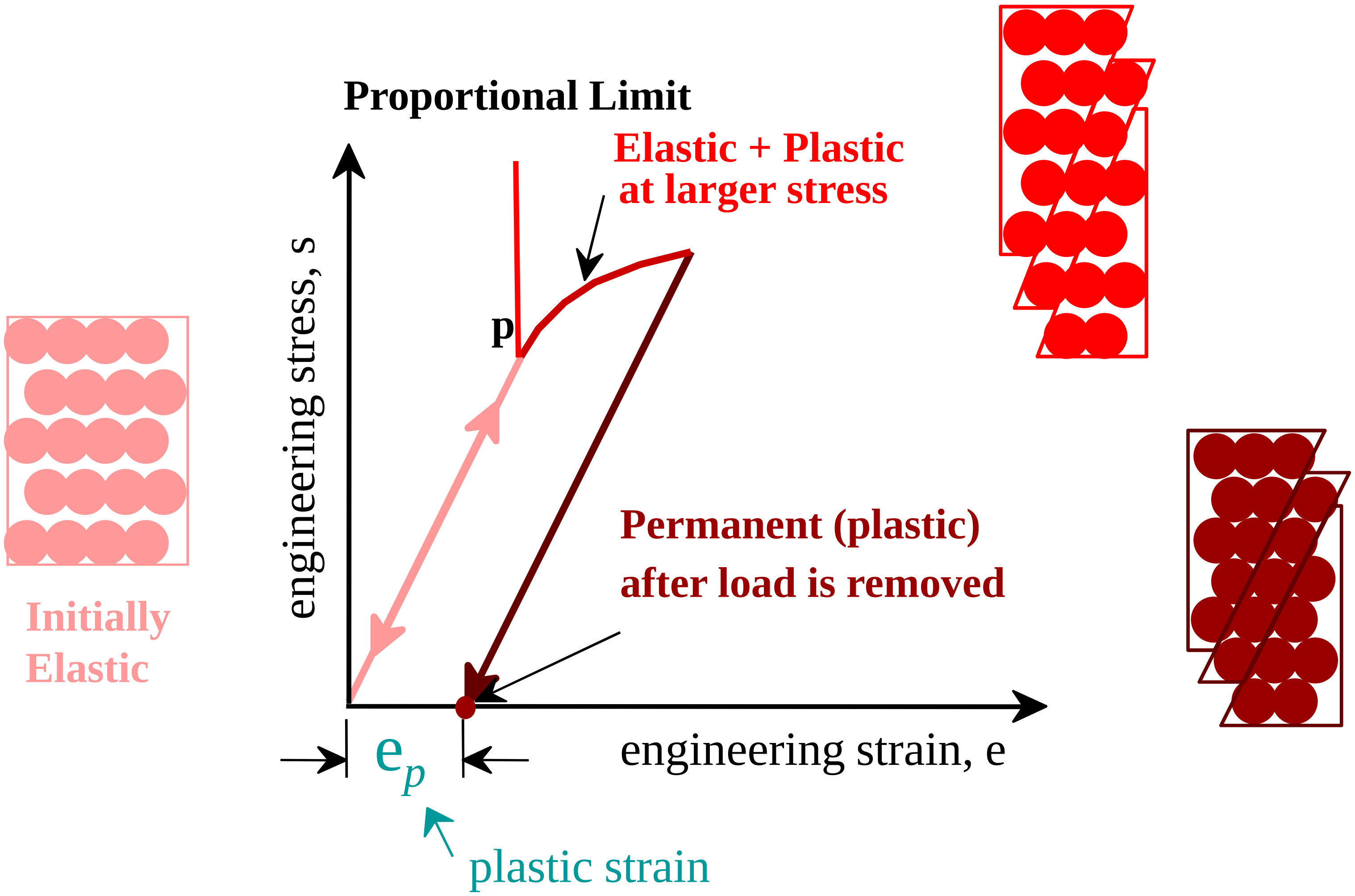
Plastic (Permanent) Deformation

- Plastic deformation in the broadest sense means permanent deformation in the absence of external constraints (forces, displacements).
- From an atomic perspective, plastic deformation corresponds to the breaking of bonds with original atom neighbors and then reforming bonds with new neighbors as large numbers of atoms or molecules move relative to one another; upon removal of the stress they do not return to their original positions.



- For most metallic materials, elastic deformation persists only to strains of about 0.005. As the material is deformed beyond this point, the stress is no longer proportional to strain (Hooke's law) and permanent/nonrecoverable/plastic deformation occurs.
- The transition from elastic to plastic is a gradual one for most metals; some curvature results at the onset of plastic deformation, which increases more rapidly with rising stress.

Schematic of Stress-Strain diagram showing plastic deformation resulting from Simple tension test at lower temperatures, i.e. T < Melt/3



Tensile Properties

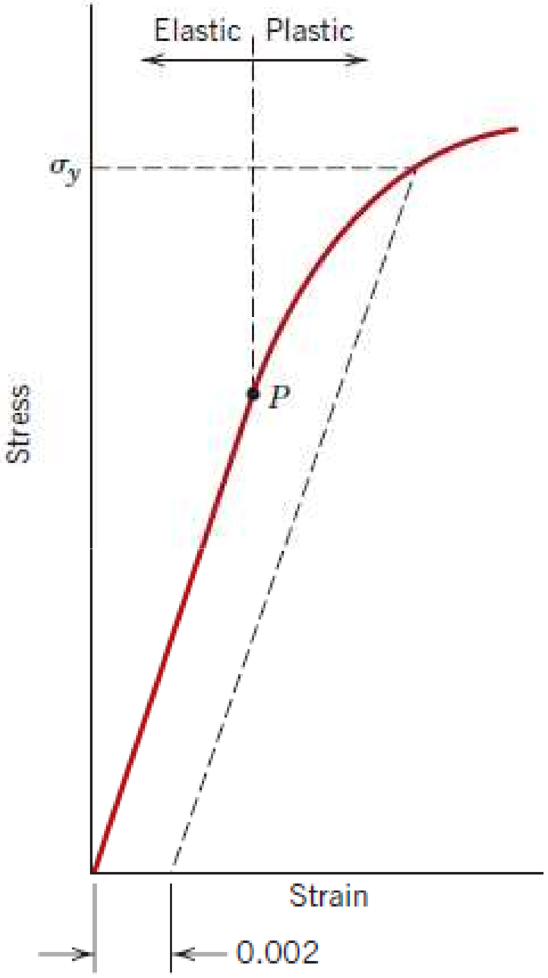
Yielding : Yielding is the beginning of plastic deformation

proportional limit : The point at which there is a deviation from the straight line 'elastic' regime

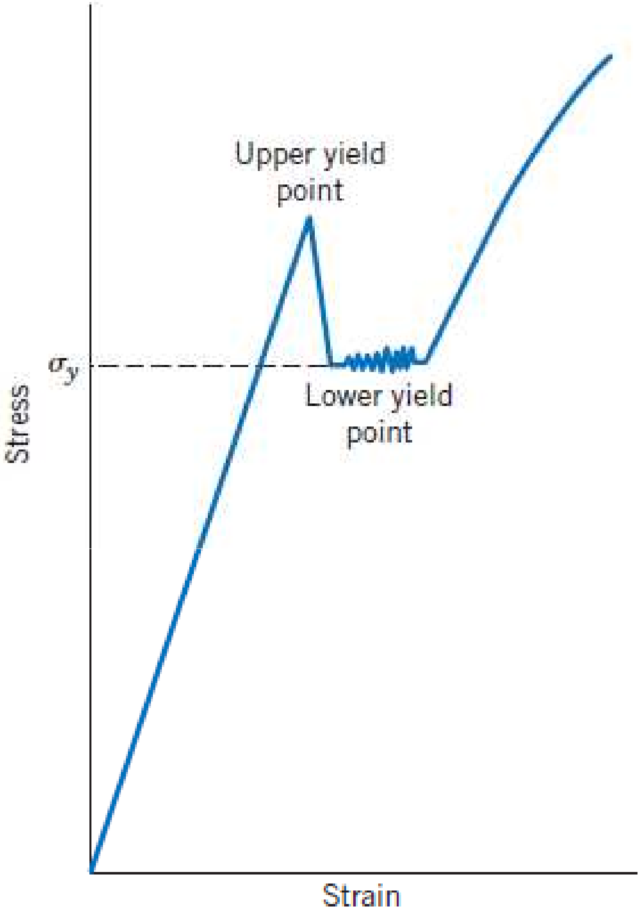
Yield Strength (σ_y)

- ❑ Stress at which noticeable plastic deformation has occurred.
- ❑ The magnitude of the yield strength for a metal is a measure of its resistance to plastic deformation.
- ❑ For metals that experience gradual elastic–plastic transition, a curve is drawn parallel to the elastic line at a given strain like 0.2% (= 0.002) to determine the yield strength.
- ❑ For materials having a nonlinear elastic region the yield strength is defined as the stress required to produce some amount of strain ($\epsilon = 0.005$)
- ❑ Some materials elastic–plastic transition is very well defined and occurs abruptly (yield point phenomenon). For these materials yield strength is taken as the average stress that is associated with the lower yield point

Tensile Properties

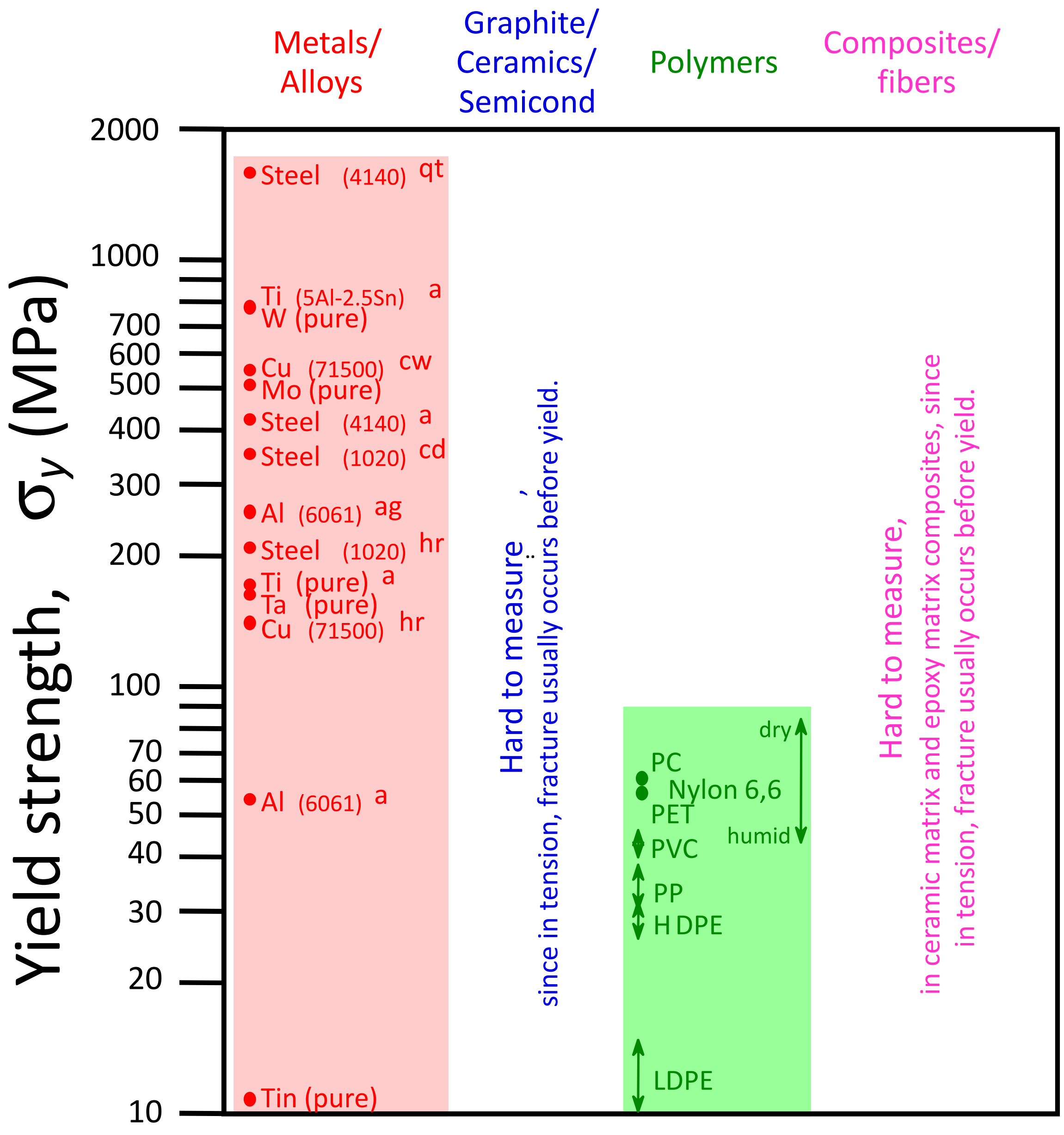


Typical stress– strain behavior for a metal showing elastic and plastic deformations, the proportional limit *P*, and the yield strength as determined using the 0.002 strain offset method.



Representative stress–strain behavior found for some steels demonstrating the yield point phenomenon.

Yield Strength : Comparison



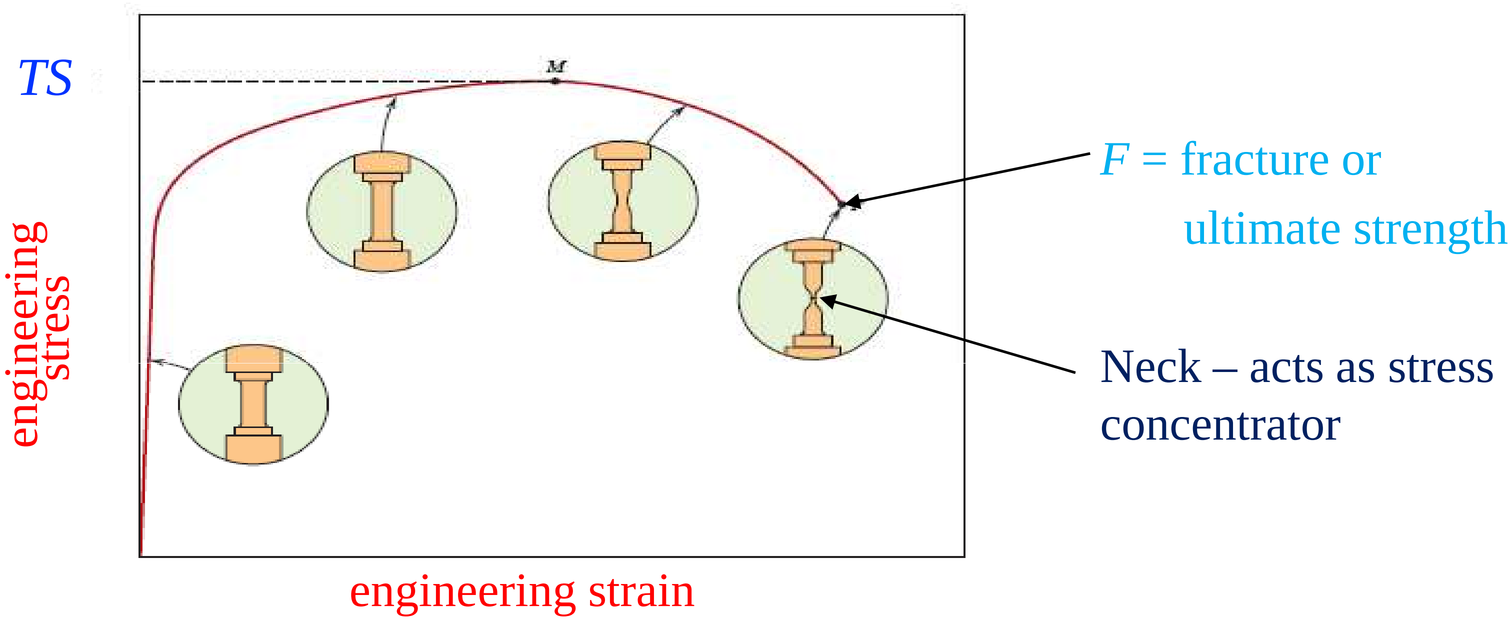
Room T values

a = annealed
hr = hot rolled
ag = aged
cd = cold drawn
cw = cold worked
qt = quenched & tempered

σy(ceramics)
>>σy(metals)
>> σy(polymers)

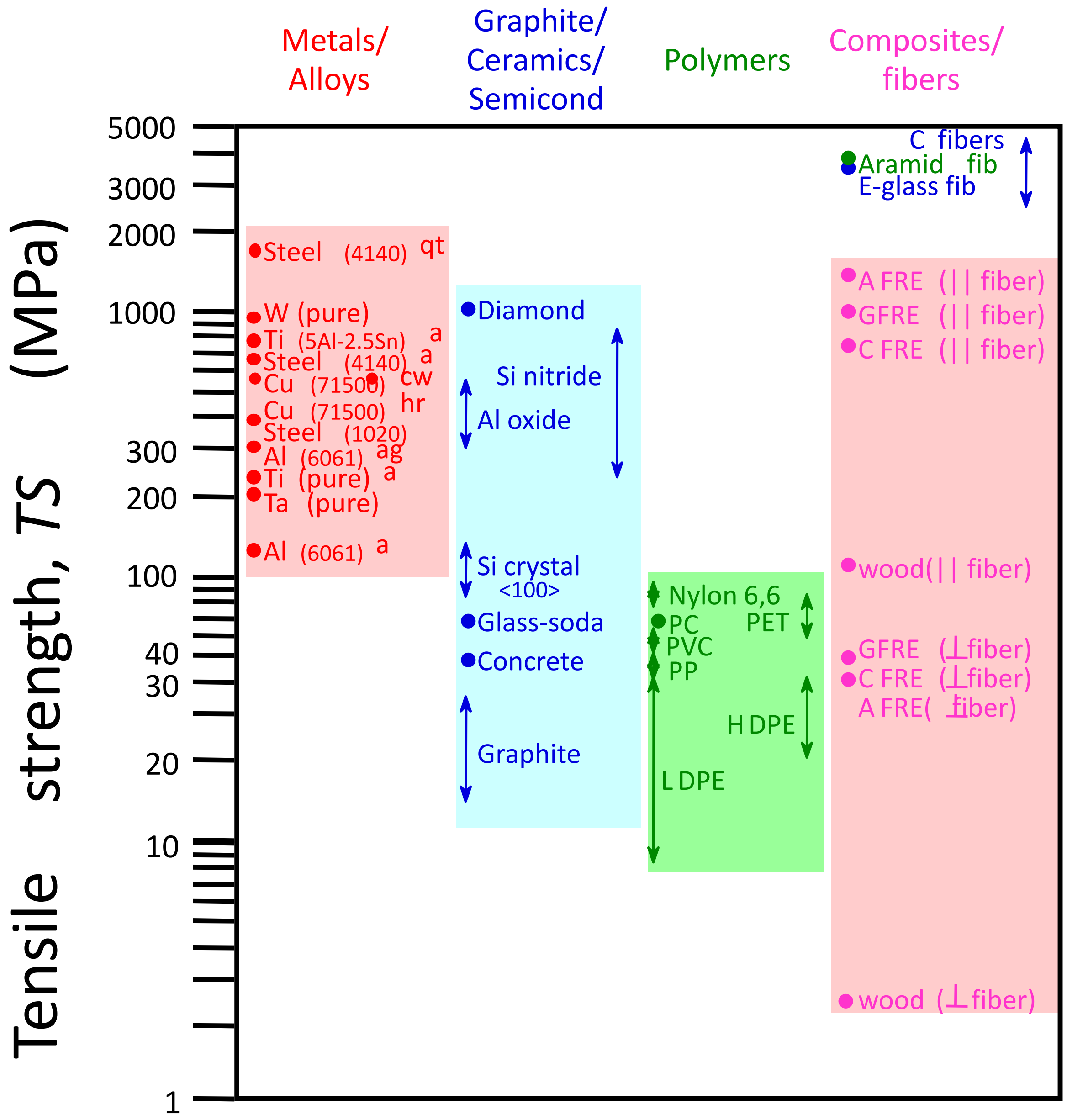
Tensile Strength (TS)

- The tensile strength TS (MPa or psi) is the stress at the maximum on the engineering stress–strain curve



- Metals : This is the point when noticeable necking starts.
- Ceramics : Crack propagation starts at this point.
- Polymers : Polymer backbones are aligned and about to break at this point.

Tensile Strength: Comparison



Room T values

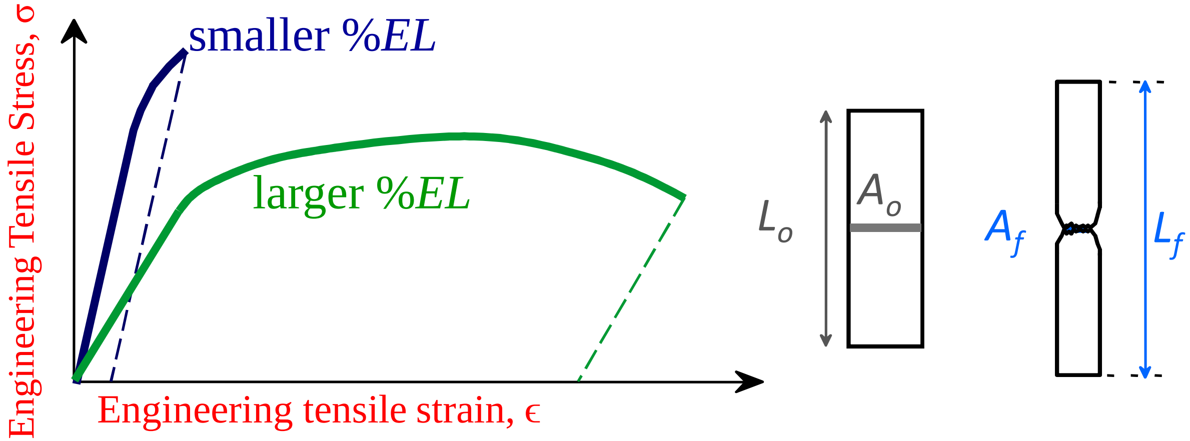
a = annealed
hr = hot rolled
ag = aged
cd = cold drawn
cw = cold worked
qt = quenched & tempered

AFRE, GFRE, & CFRE = aramid, glass, & carbon fiber-reinforced epoxy composites, with 60 vol% fibers.

Ductility, %Elongation

- Ductility may be expressed quantitatively as either *percent elongation or percent reduction in area.*
- The percent elongation %EL is the percentage of plastic strain at fracture

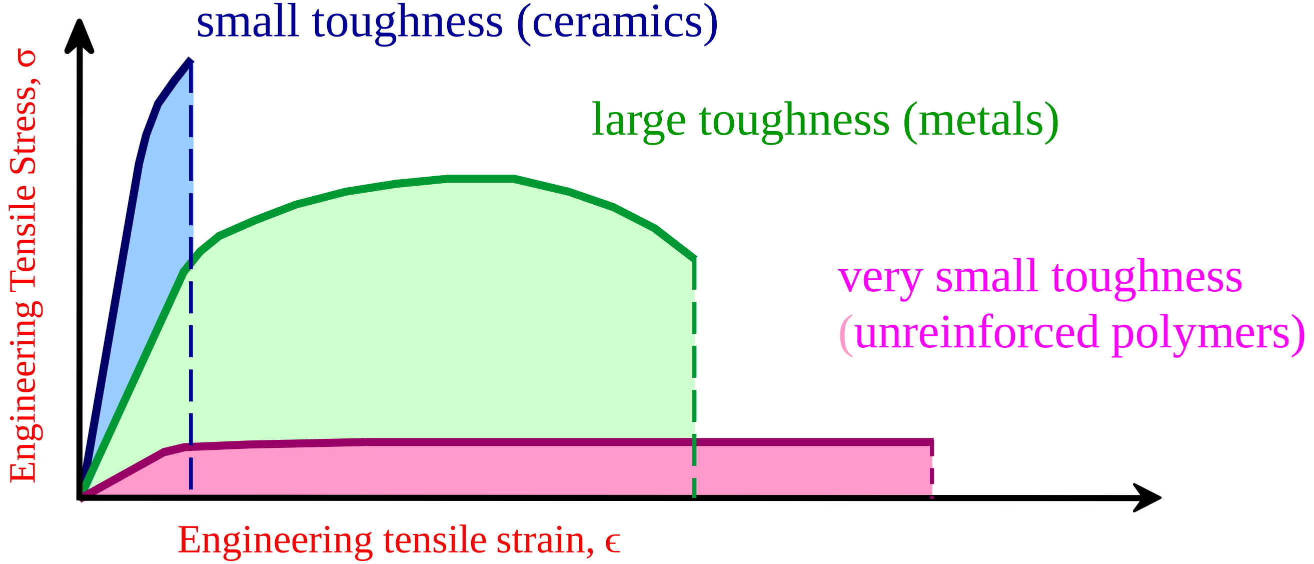
$$\%EL = \frac{L_f - L_o}{L_o} \text{ x } 100$$



- Another ductility measure: $\%RA = \frac{A_o - A_f}{A_o} \text{ x } 100$

Toughness

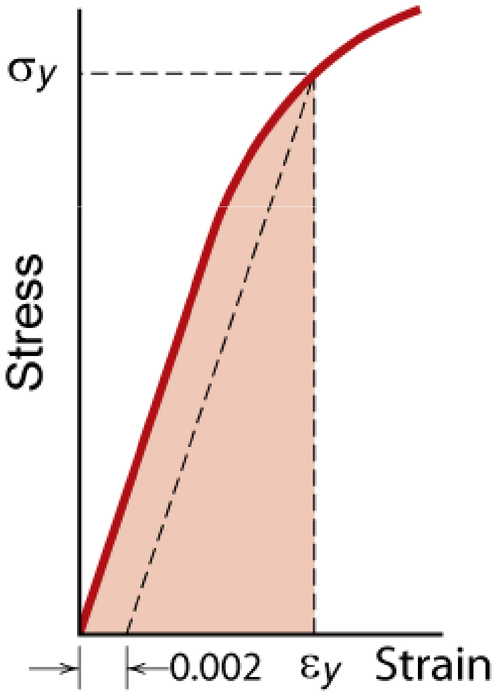
- ❑ Energy required to break a unit volume of material
- ❑ It can be approximated by the area under the stress-strain curve up to the point of fracture.



- ❑ For Brittle fracture: elastic energy
- ❑ For Ductile fracture: elastic + plastic energy

Resilience, U_r

- Resilience is the capacity of a material to absorb energy when it is deformed elastically and then, upon unloading, to have this energy recovered.
- Modulus of resilience U_r is the strain energy per unit volume required to stress a material from an unloaded state up to the point of yielding.



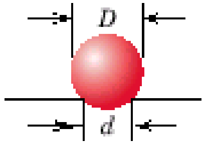
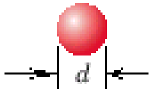
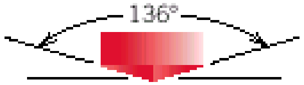
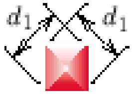
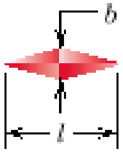
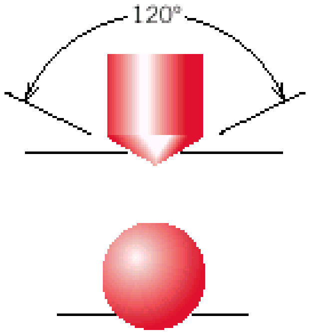
$$U_r = \int_0^{\varepsilon_y} \sigma d\varepsilon$$

If we assume a linear stress-strain curve this simplifies to

$$U_r \cong \frac{1}{2}\sigma_y \varepsilon_y$$

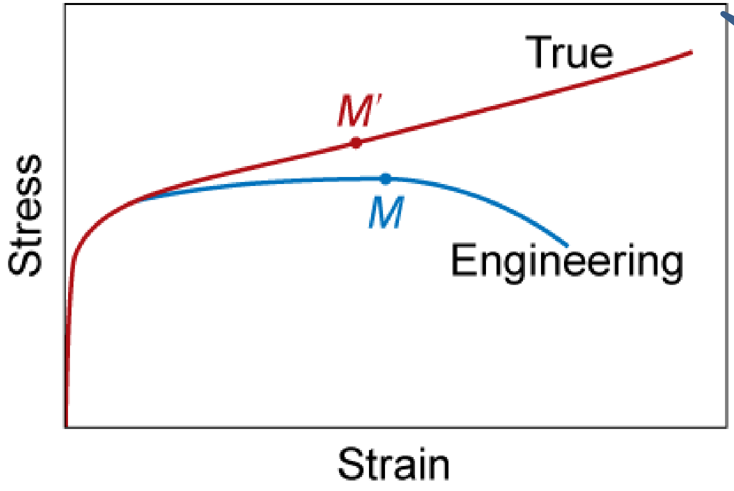
Hardness

- Resistance to permanently indenting the surface.
- Large hardness means:
  - ✓ resistance to plastic deformation or cracking in compression.
  - ✓ better wear properties

Test	Indenter	Shape of Indentation: Side View	Shape of Indentation: Top View	Load	Formula for Hardness Number[a]
Brinell	10-mm sphere of steel or tungsten carbide			P	$\mathrm{HB} = \dfrac{2P}{\pi D[D - \sqrt{D^2 - d^2}]}$
Vickers microhardness	Diamond pyramid			P	$\mathrm{HV} = 1.854P/d_1^2$
Knoop microhardness	Diamond pyramid			P	$\mathrm{HK} = 14.2P/l^2$
Rockwell and Superficial Rockwell	Diamond cone $\frac{1}{16}, \frac{1}{8}, \frac{1}{4}, \frac{1}{2}$ in. diameter steel spheres			60 kg 100 kg 150 kg 15 kg 30 kg 45 kg	Rockwell Superficial Rockwell

True Stress & Strain

- True stress : $\sigma_{True} = \dfrac{F}{A_i}$
- True strain : $\varepsilon_{True} = \ln \dfrac{l_i}{l_o}$
- The relation with Eng. Stress and Eng strain is $\begin{aligned} \sigma_T &= \sigma(1+\varepsilon) \\ \varepsilon_T &= \ln(1+\varepsilon) \end{aligned}$
- Necking begins at point M on the engineering curve, which corresponds to on the true curve. The “corrected” true stress–strain curve takes into account the complex stress state within the neck region.

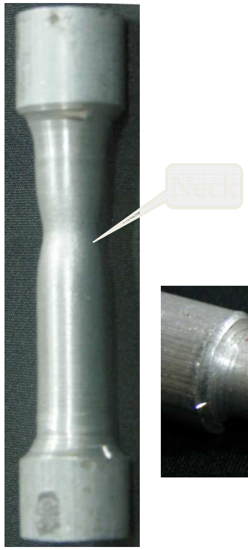


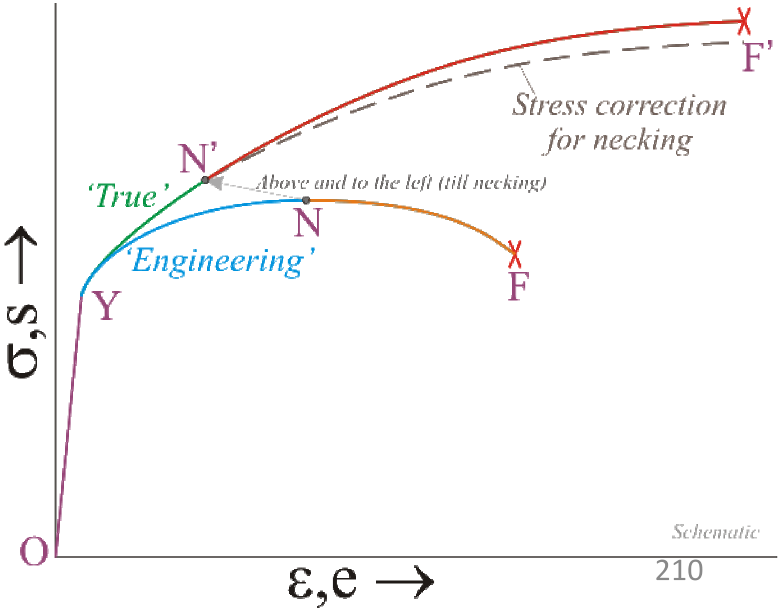
A comparison of typical tensile engineering stress–strain and true stress–strain behaviors

What happens after necking?

Following factors come in to picture due to necking:

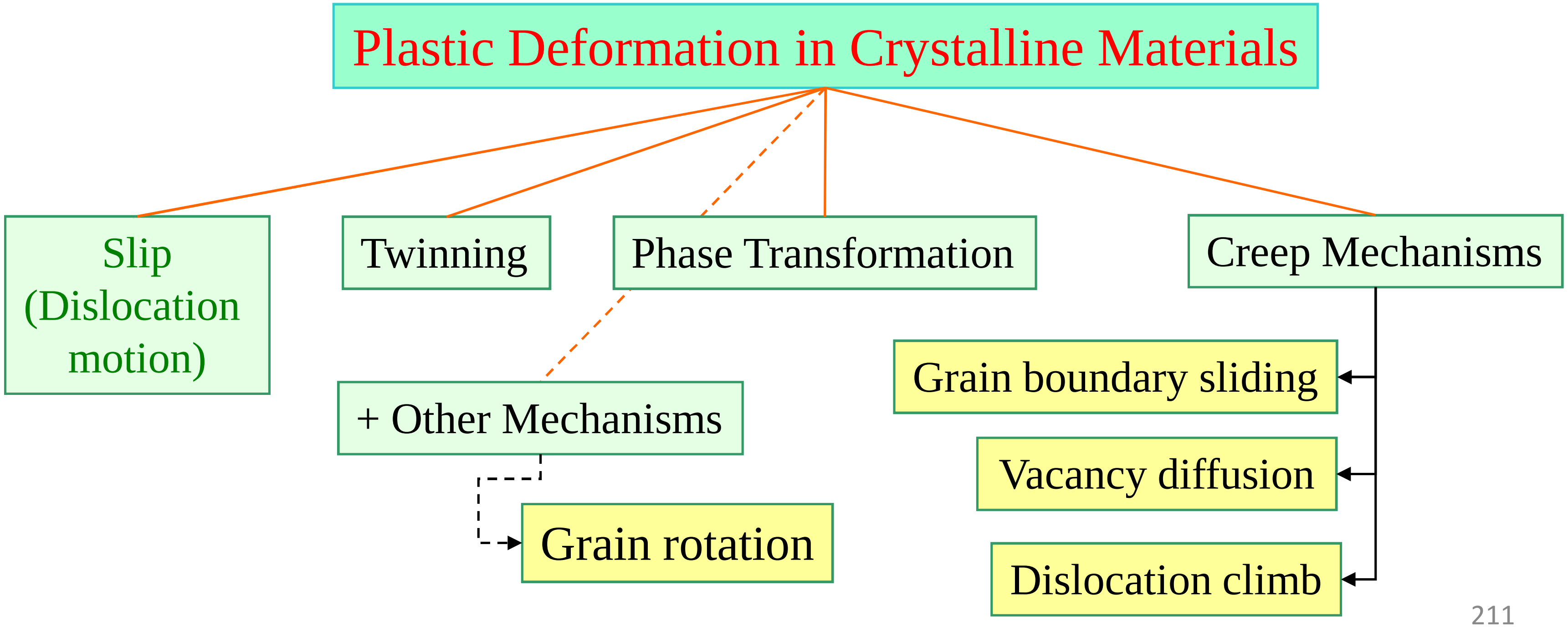
- Till necking the deformation is ~uniform along the whole gauge length.
- Till necking points on the σ-ε plot lie to the left and higher than the s-e plot (as below).
- After the onset of necking deformation is localized around the neck region.
- Formulae used for conversion of 'e' to 'ε' and 's' to 'σ' cannot be used after the onset of necking. $\boxed{\sigma = s(1+e)}$ $\boxed{\varepsilon = \ln(1+e)}$
- Triaxial state of stress develops and uniaxiality condition assumed during the test *breaks down.*
- Necking can be considered as an instability in tension.
- Hence, quantities calculated after the onset of necking (like fracture stress, σ_F) has to be corrected for: (i) triaxial state of stress, (ii) correct cross sectional area.





Mechanisms/modes of plastic deformation

- Plastic deformation in crystalline solid is accomplished by means of various processes mentioned below; among which slip is the most important mechanism.
- Plastic deformation of crystalline materials takes place by mechanisms which are very different from that for amorphous materials (glasses). *Plastic deformation in amorphous materials occur by other mechanisms including flow (~viscous fluid) and shear banding.*



Plastic Deformation in Crystalline Materials

Slip (Dislocation motion)

Twinning

Phase Transformation

Creep Mechanisms

+ Other Mechanisms

Grain rotation

Grain boundary sliding

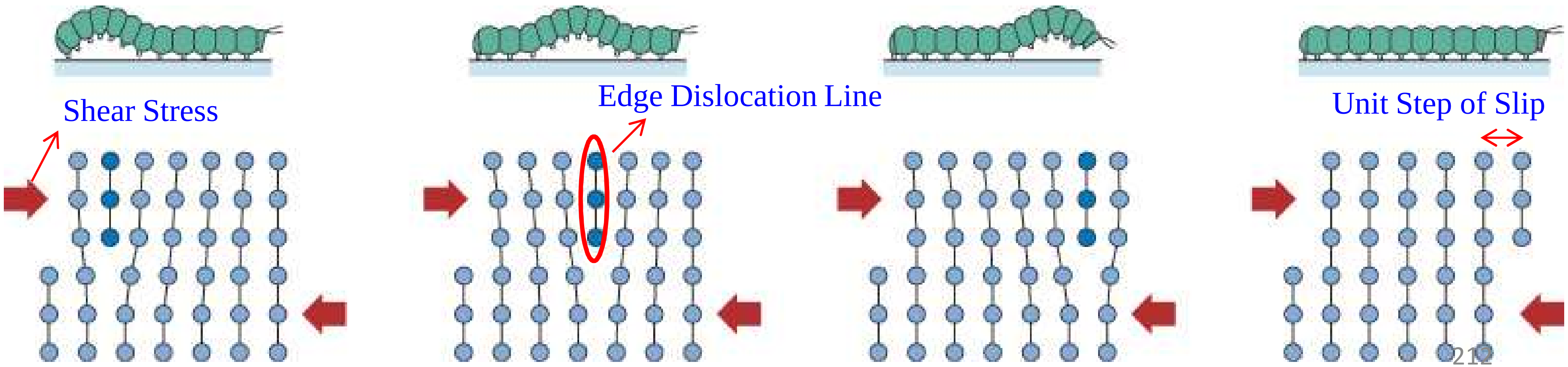
Vacancy diffusion

Dislocation climb

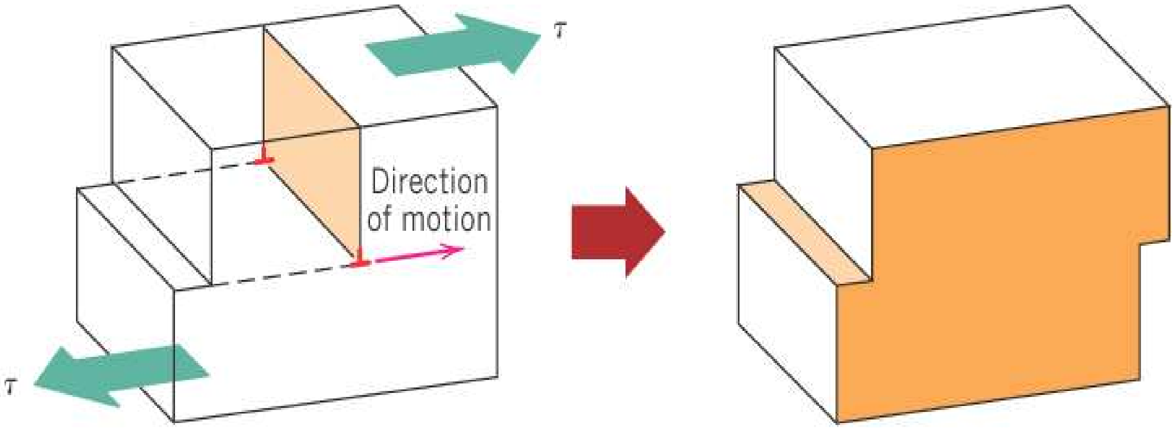
Plastic deformation by dislocation Motion (SLIP)

Basic concepts

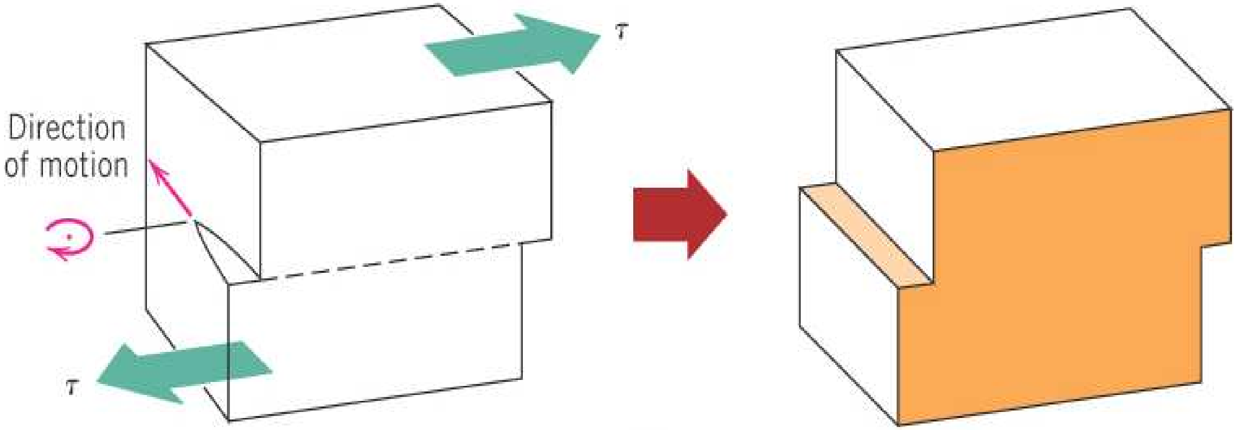
- SLIP is the most important mechanism of plastic deformation . At low temperatures (especially in BCC metals) twinning may also become important.
- At the fundamental level plastic deformation (in crystalline materials) by slip involves the motion of dislocations on the slip plane *(creating a step of Burgers vector).*
- Slip is caused by shear stresses (at the level of the slip plane). Hence, a purely hydrostatic state of stress cannot cause slip.
- A slip system consists of a slip direction lying on a slip plane.
- Slip is analogous to the mode of locomotion employed by a caterpillar



Direction of Dislocation Motion



Edge dislocation line moves **parallel** to applied stress



Screw dislocation line moves **perpendicular** to applied stress

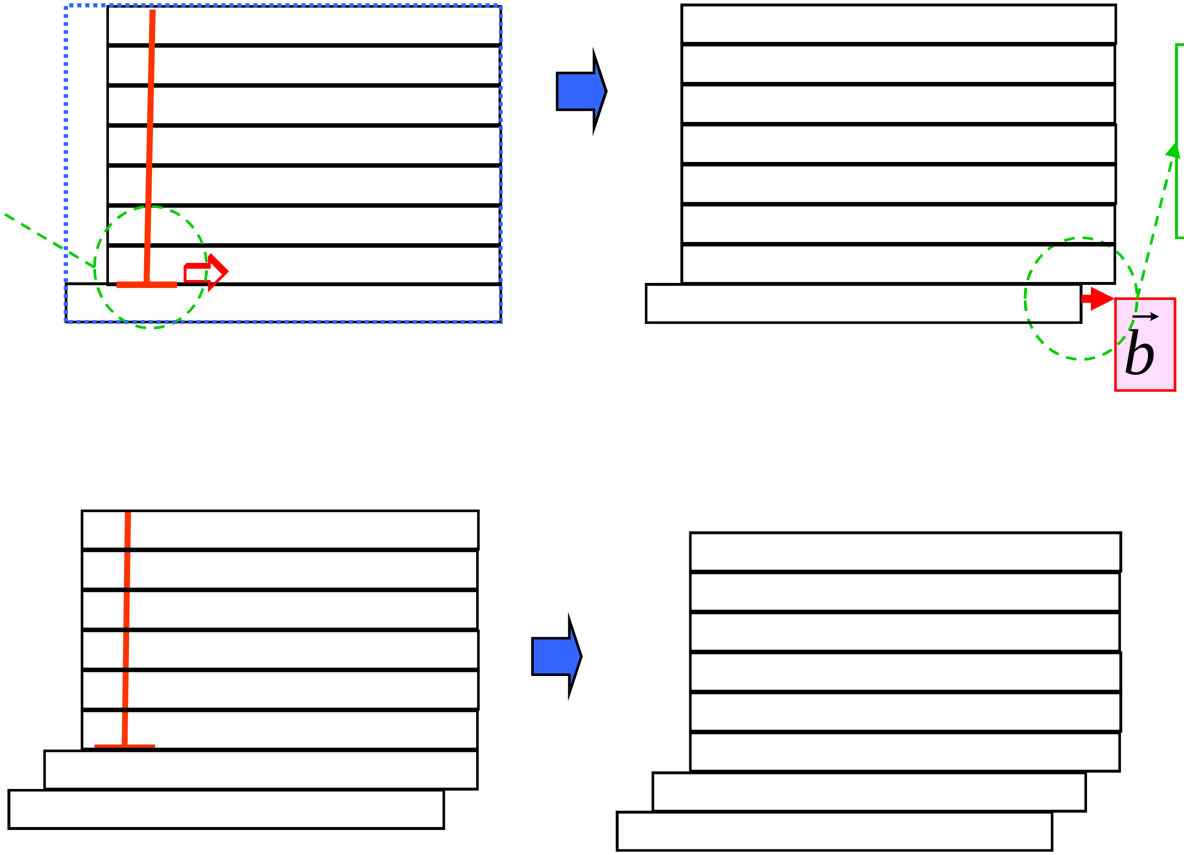
Slip systems

- Dislocations move more easily on specific planes and in specific directions.
- Ordinarily, there is a preferred plane (slip plane), and specific directions (slip direction) along which dislocations move. The combination of slip plane and slip direction is called the slip system.
- The slip system depends on the crystal structure of the metal.
- The slip plane is the plane that has the most dense atomic packing (the greatest planar density). The slip direction is most closely packed with atoms (highest linear density).
- In CCP, HCP materials the slip system consists of a close packed direction on a close packed plane.
- Just the existence of a slip system does not guarantee slip → slip is competing against other processes like twinning and fracture. If the stress to cause slip is very high (i.e. CRSS is very high), then fracture may occur before slip (like in brittle ceramics).
- For slip to occur in polycrystalline materials, 5 independent slip systems are required. Hence, materials which are ductile in single crystalline form, may not be ductile in polycrystalline form. CCP crystals (Cu, Al, Au) have excellent ductility.
- At higher temperatures more slip systems may become active and hence polycrystalline materials which are brittle at low temperature, may become ductile at high temperature.

Example of slip systems

Crystal	Slip plane(s)	Slip direction	Number of slip systems
FCC	{111}	½<110>	12
HCP	(0001)	$<11\bar{2}0>$	3
BCC	{110}, {112}, {123}	½[111]	48
NaCl (*Ionic)*	{110} {111} not a slip plane	½<110>	6
C (Diamond cubic)	{111}	½<110>	12
TiO2*(Rutile)*	{101}	$<10\bar{1}>$	
CaF_2, UO_2, ThO_2 *Fluorite*	{001}	$<1\bar{1}0>$	
CsCl	{110}	<001>	
NaCl, LiF, MgO *Rock Salt*	{110}	<110>	6
C, Ge, Si *Diamond cubic*	{111}	<110>	12
$MgAl_2O_4$ *Spinel*	{111}	$<1\bar{1}0>$	
Al_2O_3 *Hexagonal*	(0001)	$<11\bar{2}0>$	

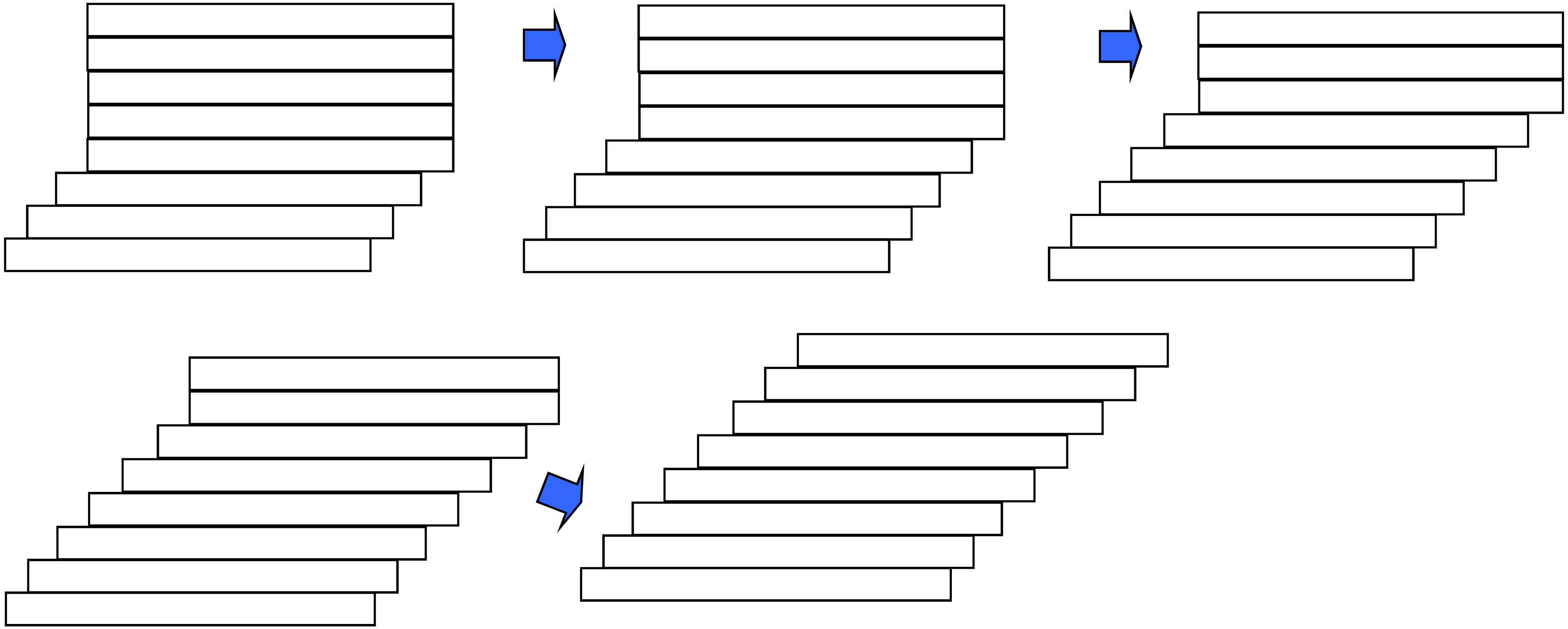
microscopic slip to macroscopic deformation



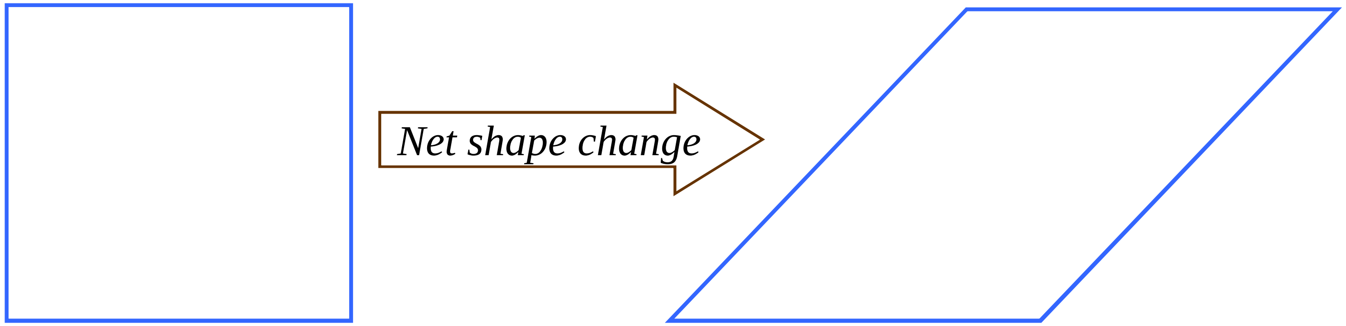
Dislocation formed by pushing in a plane

Step formed when dislocation leaves the crystal

Now visualize dislocations being punched in on successive planes → moving and finally leaving the crystal



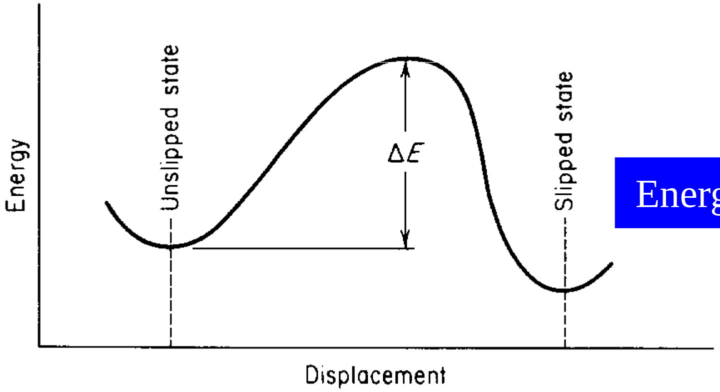
This sequence of events finally leads to deformed shape



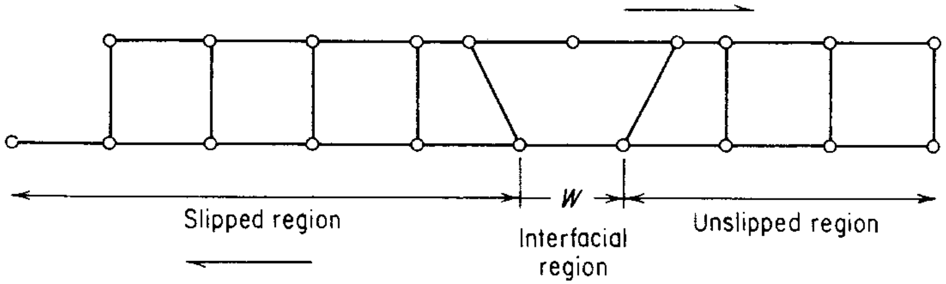
Net shape change

Stress to move a dislocation: Peierls – Nabarro (PN) stress

- At the fundamental level the motion of a dislocation involves the rearrangement of bonds which requires application of shear stress on the slip plane.
- Consider plastic deformation is the transition between unslipped to slipped state. As this process is opposed by an energy barrier ΔE, the materials cannot make the transition simultaneously.
- To minimize the energetic of the process the slipped material will grow at the expenses of the unslipped region by the advance of an interfacial region (width of the dislocation w)



Energy change from unslipped to slipped state



Stages in the growth of slipped region

Stress to move a dislocation: Peierls – Nabarro (PN) stress

- ❑ The original model is due to Peierls & Nabarro (formula as below) and the ‘sufficient’ stress which needs to be applied is called Peierls-Nabarro stress (PN stress) or simply Peierls stress.

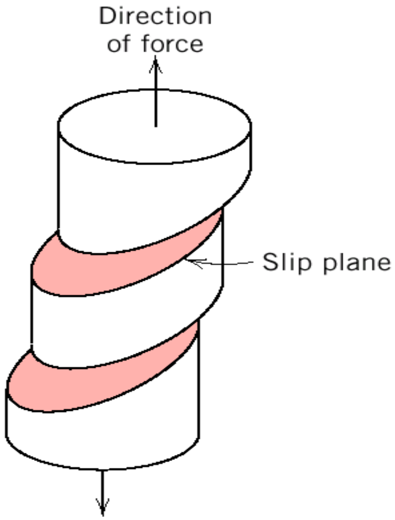
$$\tau_{PN} = G\, e^{-\left(\frac{2\pi w}{b}\right)}$$

- G → shear modulus of the crystal
- w → width of the dislocation !!!
- b → |**b**|

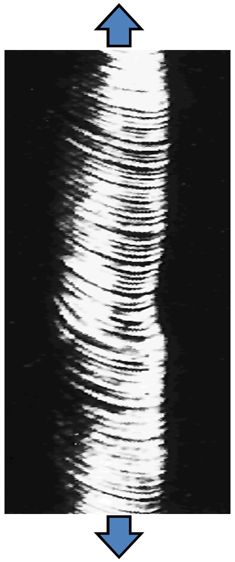
- ❑ Width of the dislocation is considered as a basis for the ease of motion of a dislocation in the model which is a function of the bonding in the material.
- ❑ Peierls equation shows that wide dislocations will require low stress to move the dislocations
- ❑ In ceramics the interfacial energy is high and the dislocation width is very narrow. Hence they are relatively immobile compared to ductile materials (dislocation width nearly 10 atomic spacings).
- ❑ Ceramics become ductile t high temperature as thermal activation help the dislocations to overcome the energy barrier

Slip in Single Crystal

- ☐ If a single crystal of a metal is stressed in tension beyond its elastic limit, it elongates slightly and a step appears on the surface due to the relative displacement of one part of the crystal with respect to the others and the elongation stops.
- ☐ Further increase in the load causes movement of another parallel plane, resulting in another step. Similarly number of small steps are formed on the surface of the single crystal that are parallel to one another and loop around the circumference of the specimen.
- ☐ Each step (shear band) results from the movement of a large number of dislocations and their propagation in the slip system.



Macroscopic slip in single crystal



Slip in a zinc single crystal

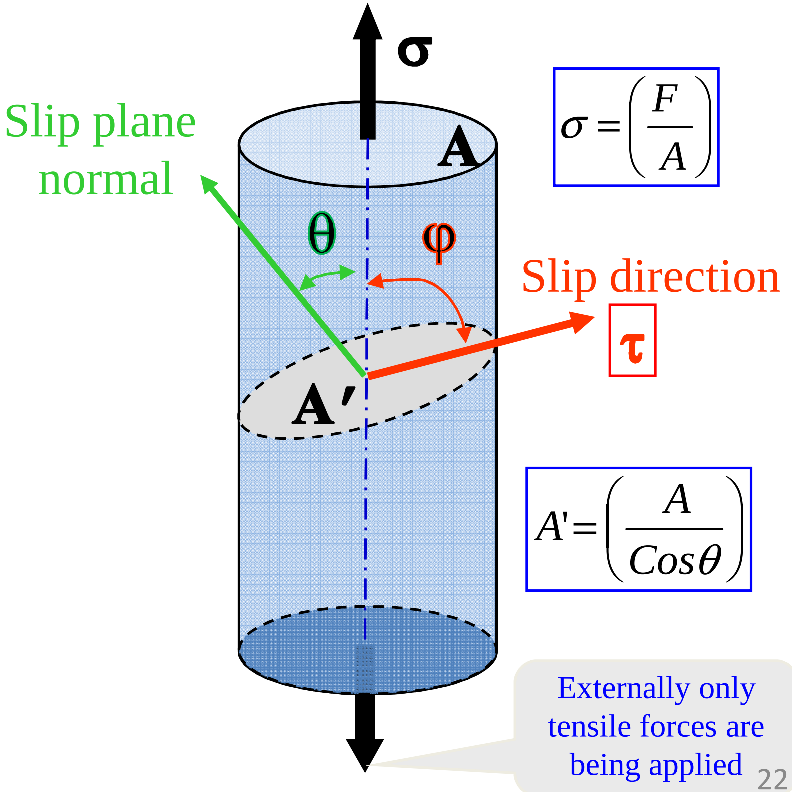
Critical Resolved Shear Stress (CRSS)

- ❑ Extent of slip in a single crystal depends on the magnitude of shearing stress produced by external loads, geometry of the crystal structure and the orientation of he active slip planes with respect to the shearing stress.
- ❑ Slip begins when the shearing stress on slip plane in the slip direction/Resolved Shear Stress (RSS) reaches a critical value called the Critical Resolved Shear Stress (CRSS) and plastic deformation starts *(The actual Schmid's law)*
- ❑ Even if we apply an tensile force on the specimen → the shear stress resolved onto the slip plane is responsible for slip.

$$Stress = \left(\frac{Force}{Area}\right)_{1D}$$

$$\tau = \left(\frac{F \ Cos \ \alpha}{A \ / \ Cos \ \theta}\right)$$

$$\boxed{\tau_{RSS} = \sigma \ \underbrace{Cos\theta \, Cos\varphi}_{\text{Schmid factor}}}$$



$$\sigma = \left(\frac{F}{A}\right)$$

$$A' = \left(\frac{A}{Cos\theta}\right)$$

Externally only tensile forces are being applied

Critical Resolved Shear Stress (CRSS)

- ❑ τ_{RSS} is maximum (P/2A) when $\phi = \lambda = 45^o$
- ❑ If the tension axis is normal to slip plane i.e. $\lambda = 90^o$ or if it is parallel to the slip plane i.e. $\phi = 90^o$ then $\tau_{RSS} = 0$ and slip will not occur as per Schmid's law.

Schmid's law

Slip is initiated when

$$\boxed{\tau_{RSS} \geq \tau_{CRSS}}$$

- ❑ τ_{CRSS} is a material parameter, which is determined from experiments

Yield strength of a single crystal

$$\boxed{\sigma_y = \frac{\tau_{CRSS}}{Cos\theta Cos\varphi}}$$

Solved Example

Consider a single crystal of BCC iron oriented such that a tensile stress is applied along a [010] direction.

(a) Compute the resolved shear stress along a (110) plane and in a [111] direction when a tensile stress of 52 MPa (7500 psi) is applied

(b) If slip occurs on a (110) plane and in a $[\bar{1}11]$ direction, and the critical resolved shear stress is 30 MPa (4350 psi), calculate the magnitude of the applied tensile stress necessary to initiate yielding.

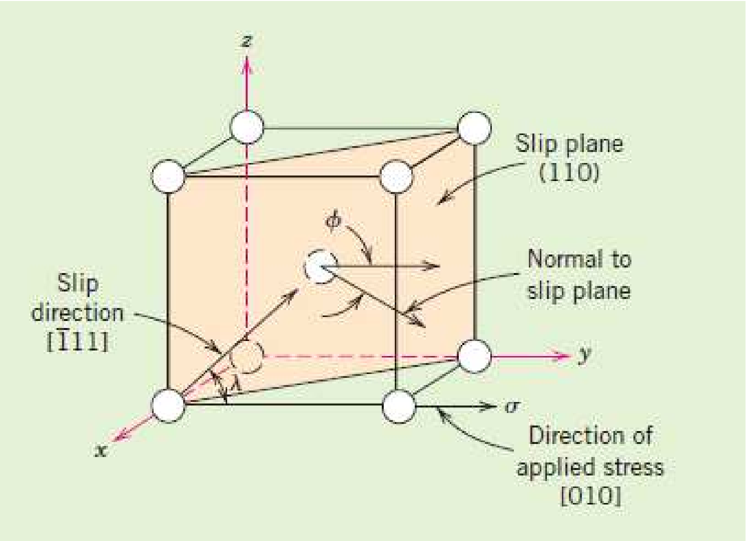
Solution

a. Determine the value of ,the angle between the normal to the (110) slip plane (i.e., the [110] direction) and the [010] direction using $[u_1v_1w_1] = [110]$, $[u_2v_2w_2] = [010]$ and the following equation.

$$\theta = \cos^{-1}\left(\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{(u_1^2 + v_1^2 + w_1^2)(u_2^2 + v_2^2 + w_2^2)}}\right)$$

$$\phi = \cos^{-1}\left(\frac{(1)(0) + (1)(1) + (0)(0)}{\sqrt{[(1)^2 + (1)^2 + (0)^2][(0)^2 + (1)^2 + (0)^2]}}\right)$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{2}}\right) = 45^o$$



Solved Example

- Similarly determine the value of λ, the angle between $[\bar{1}11]$ and [010] directions as follows:

$$\lambda = \cos^{-1}\left(\frac{(-1)(0)+(1)(1)+(1)(0)}{\sqrt{[(-1)^2+(1)^2+(1)^2][(0)^2+(1)^2+(0)^2]}}\right) = \cos^{-1}\left(\frac{1}{\sqrt{3}}\right) = 54.7^o$$

- Then calculate the value of τ_{RSS} using the following expression:

$$\begin{aligned} \tau_{RSS} &= \sigma \cos\phi \cos\lambda \\ &= (152\ Mpa)(\cos 45)(\cos 54.7) \\ &= 21.3\ Mpa \\ &= 13060\ psi \end{aligned}$$

- Yield Strength σ_Y

$$\sigma_y = \frac{30MPa}{(\cos 45)(\cos 54.7)} = 73.4Mpa$$

Solved Example 2

Determine the tensile stress that is applied along the $[1\bar{1}0]$ axis of a silver crystal to cause slip on the (111) $[011]$ system. The critical resolved shear stress is 6 MPa.

Solution:

- ❑ Determine the angle ϕ between the tensile axis $[1\bar{1}0]$ and normal to $(\bar{1}\bar{1}1)$ using the following equation.

$$\cos\theta = \left(\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{(u_1^2 + v_1^2 + w_1^2)(u_2^2 + v_2^2 + w_2^2)}}\right)$$

$$\cos\phi = \left(\frac{(1)(1) + (-1)(-1) + (0)(-1)}{\sqrt{[(1)^2 + (-1)^2 + (0)^2][(1)^2 + (-1)^2 + (-1)^2]}}\right) = \frac{1}{\sqrt{2}\sqrt{3}} = \frac{2}{\sqrt{6}}$$

- ❑ Determine the angle λ between tensile axis $[1\bar{1}0]$ and slip direction $[0\bar{1}1]$

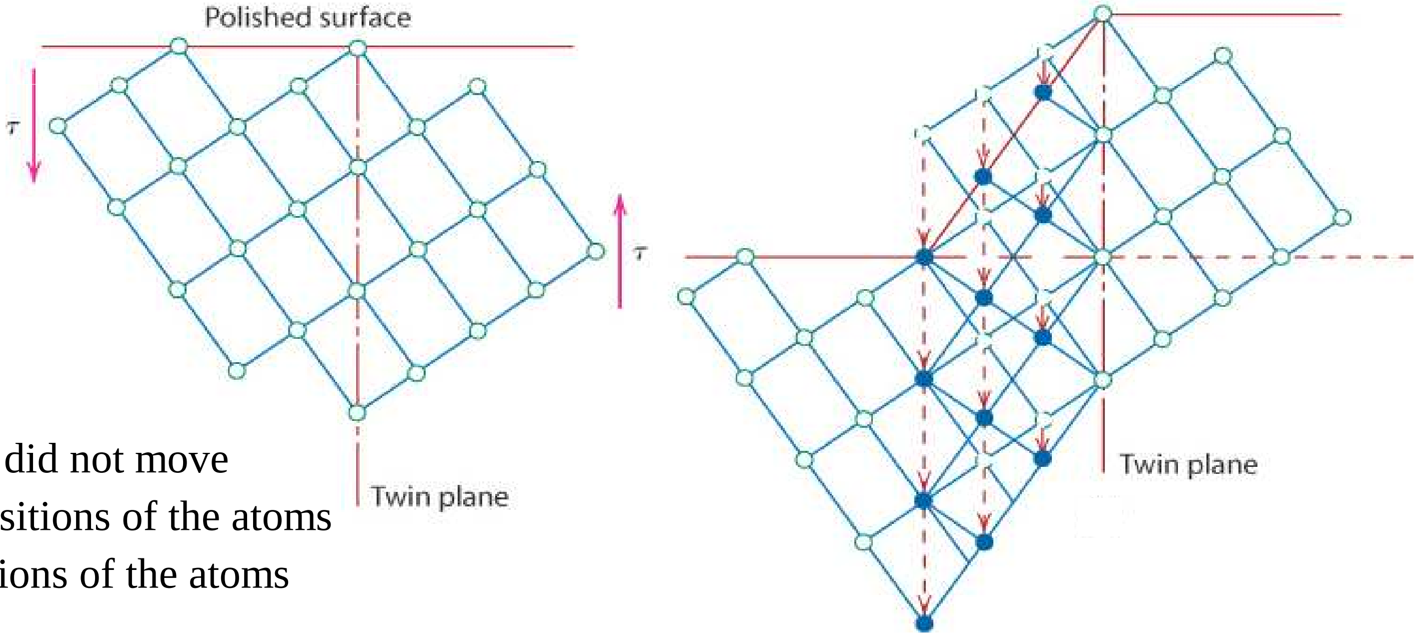
$$\cos\lambda = \left(\frac{(1)(0) + (-1)(-1) + (0)(-1)}{\sqrt{[(1)^2 + (-1)^2 + (0)^2][(0)^2 + (-1)^2 + (-1)^2]}}\right) = \frac{1}{\sqrt{2}\sqrt{2}} = \frac{1}{2}$$

- ❑ Then *calculate the Tensile Stress using the expression:*

$$\sigma = \frac{P}{A} = \frac{\tau_{RSS}}{\cos\phi\cos\lambda} = \frac{6MPa}{{}^{2}\!/_{\sqrt{6}} \times \frac{1}{2}} = 6\sqrt{6} = 14.7\,Mpa$$

Plastic deformation by Twin

- In addition to slip (dislocation movement), plastic deformation can also occur by twinning.
- Twinning results when a portion of the crystal takes up an orientation that is related to the orientation of the rest of the untwinned lattice in a definite, symmetrical way.
- Twinned portion of the crystal is a mirror image of the parent crystal and the plane of symmetry between the two portions is called twinning plane.
- Twinning may favorably reorient slip systems to promote dislocation movement.



○ - Atoms that did not move

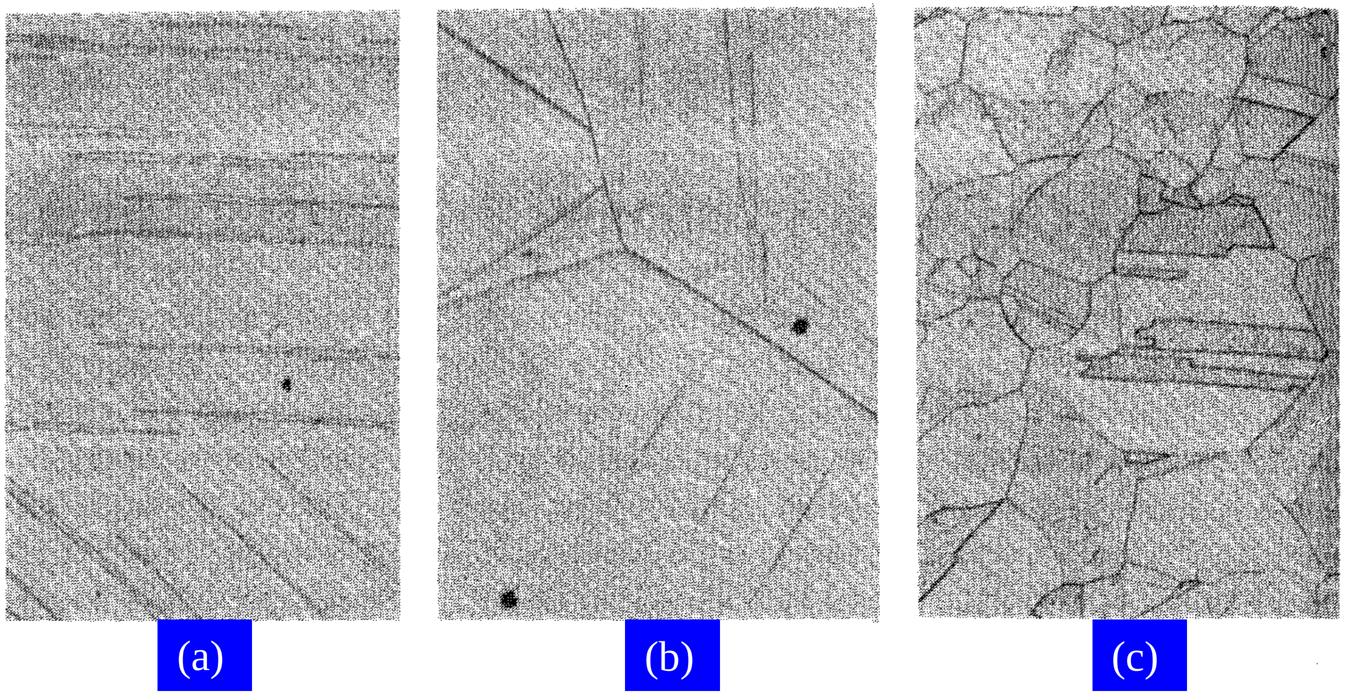
◌ - Original positions of the atoms

● - Final positions of the atoms

Schematic diagram showing how twinning results from an applied shear stress

Plastic deformation by Twin

- Twins are generally of two types: Mechanical Twins and Annealing twins
- Mechanical twins are generally seen in bcc or hcp metals and produced under conditions of rapid rate of loading and decreased temperature.
- Annealing twins are produced as the result of annealing. These twins are generally seen in fcc metals.
- Annealing twins are usually broader and with straighter sides than mechanical twins.



(a) Mechanical Twins (Neumann bands in iron), (b) Mechanical Twins in zinc produced by polishing (c) Annealing Twins in gold-silver alloy

Plastic deformation by Twin

- Twinning generally occurs when the slip systems are restricted or when the slip systems are restricted or when something increases the critical resolved shear stress so that the twinning stress is lower than the stress for slip.
- So, twinning generally occurs at low temperatures or high strain rates in bcc or fcc metals or in hcp metals.
- Twinning occurs on specific twinning planes and twinning directions.

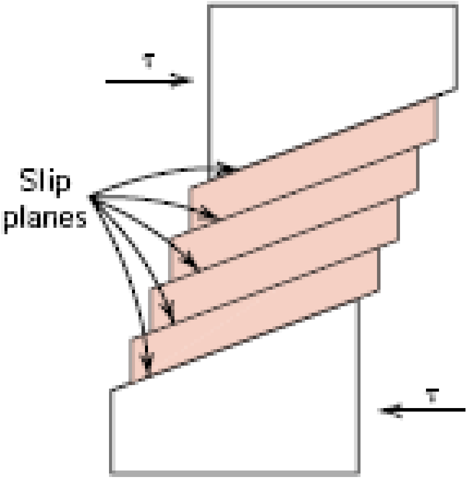
Twin planes and Twin directions

Crystal Structure	Typical Examples	Twin Plane	Twin Direction
BCC	α-Fe, Ta	(112)	[111]
HCP	Zn, Cd, Mg, Ti	$(10\bar{1}2)$	$[\bar{1}011]$
FCC	Ag, Au, Cu	(111)	[112]

Difference between Slip and Twin

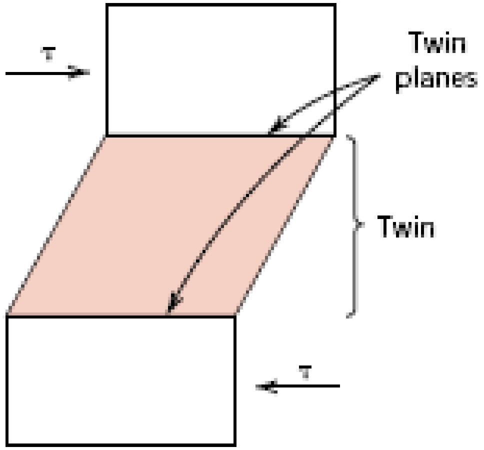
Slip

- The crystallographic orientation above and below the slip plane is the same both before and after the deformation
- Slip occurs in distinct atomic spacing multiples
- Slip Leaves a series of steps (lines)
- Normally slip results in relatively large deformations
- Mostly seen in FCC and BCC structure, as they have more slip systems



Twin

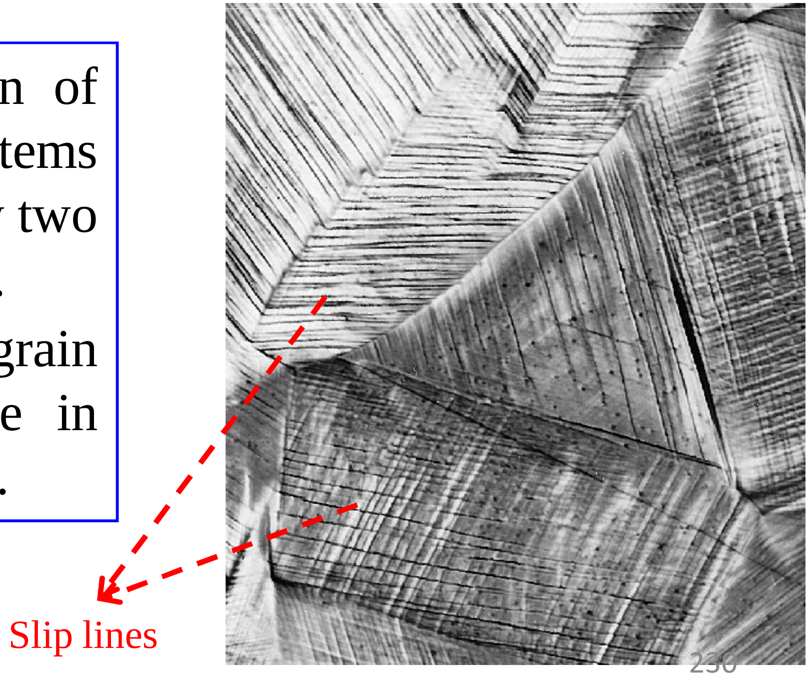
- Orientation difference is seen across the twin plane
- the atomic displacement for twinning is less than the inter-atomic separation
- Twinning leaves small but well defined regions of the crystal deformed
- Only small deformations result for twinning
- Is most important for HCP structure , because of its small number of slip system



Plastic deformation of Polycrystalline Materials

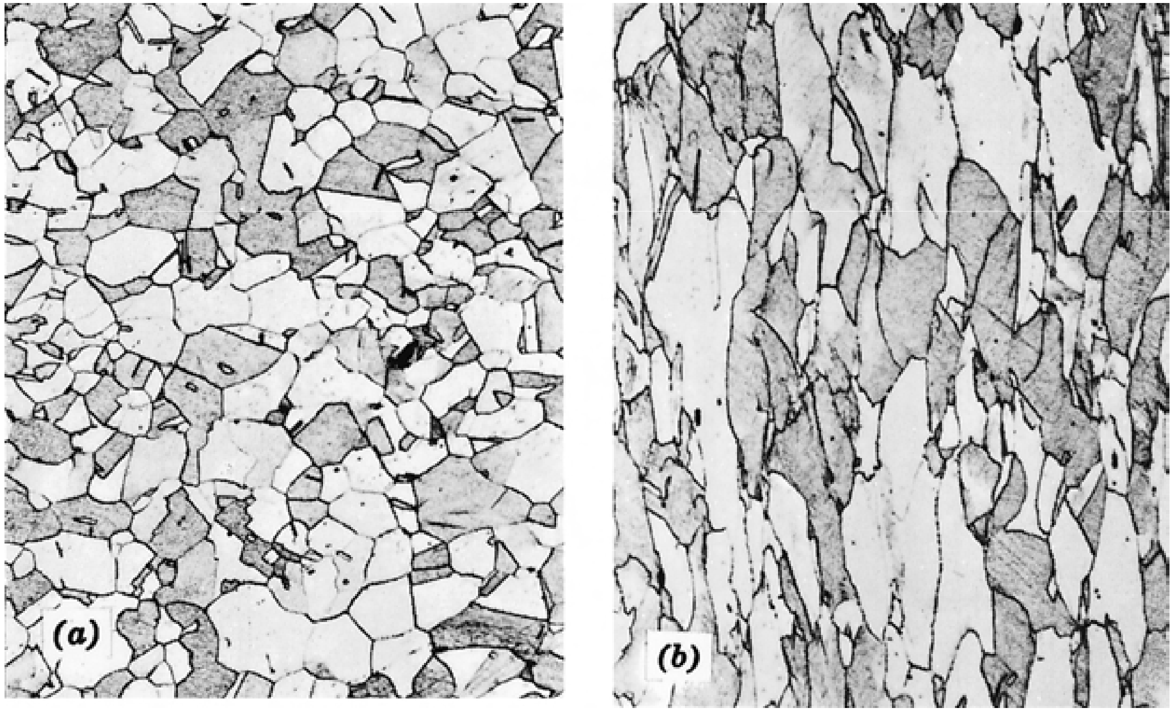
- ❑ Plastic deformation in polycrystalline materials is very complex than those in the single crystals due to the presence of grain boundaries, different orientation of neighboring crystals, presence of several phases etc.
- ❑ Due to random crystallographic orientations, the slip planes and slip direction varies from one grain to another
- ❑ As a result the resolved shear stress τ_{RSS} will vary from one crystal to another and the dislocations will move along the slip systems with favorable orientation (i.e. the highest resolved shear stress).

- ❑ When a polished polycrystalline specimen of copper is plastically deformed, two slip systems operate for most of the grains (evidenced by two sets of parallel yet intersecting sets of lines).
- ❑ Slip lines are visible, and the variation in grain orientation is indicated by the difference in alignment of the slip lines for several grains.



Plastic deformation of Polycrystalline Materials

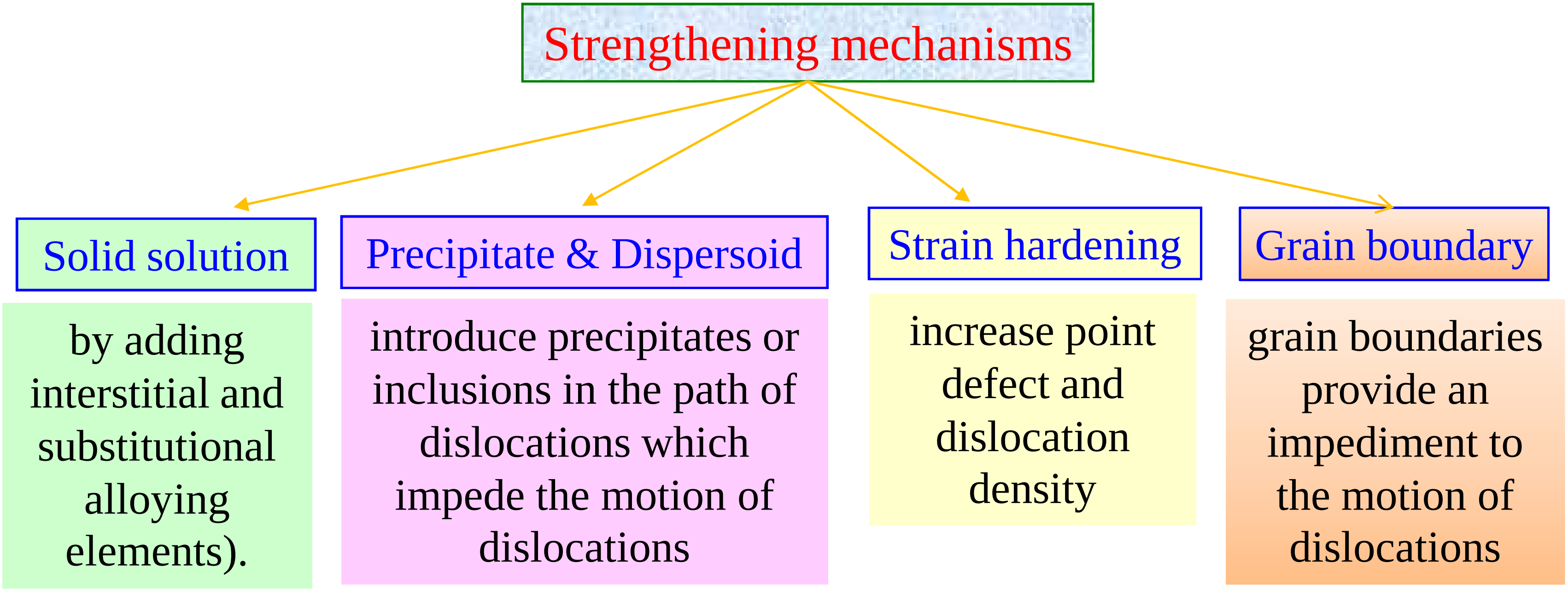
- During deformation, mechanical integrity and coherency are maintained along the grain boundaries; i.e. the grain boundaries usually do not come apart or open up.
- As a consequence, each individual grain is constrained, to some degree in the shape it may assume by its neighboring grains.



Alteration of the grain structure of a polycrystalline metal as a result of plastic deformation (a) Before deformation the grains are equiaxed. (b) After deformation elongated grains are produced

Strengthening Mechanisms

- The ability of a metal to deform depends on the ability of the dislocations to move and the slip of dislocations weakens the crystal. Hence we have two strategies to strengthen the crystal/material:
  - completely remove dislocations → difficult, but dislocation free whiskers have been produced *(however, this is not a good strategy as dislocations can nucleate during loading)*
  - *I*ncrease resistance to the motion of dislocations or put impediments to the motion of dislocations → this can be done in many ways as listed below.



Strengthening mechanisms

Solid solution

by adding interstitial and substitutional alloying elements).

Precipitate & Dispersoid

introduce precipitates or inclusions in the path of dislocations which impede the motion of dislocations

Strain hardening

increase point defect and dislocation density

Grain boundary

grain boundaries provide an impediment to the motion of dislocations

Solid Solution Strengthening

- The introduction of solute atoms into solid solution in the solvent-atom lattice invariably produces an alloy which is stronger than the pure metal
- Two types of solid solutions:
  - ⇨ Substitutional solid solutions → Solute atoms occupy lattice points in the solvent lattice (Hume Rothery's rules are to be satisfied)
  - ⇨ Interstitial solid solutions → Solute atoms occupy interstitial positions in the solvent lattice (Carbon, Nitrogen, Boron, Oxygen, Hydrogen are the common interstitial solutes)
- The stress fields around solute atoms interact with the stress fields around the dislocation.
- This interaction provides frictional resistance to dislocations motion and static locking of dislocations
- The factors playing an important role on strengthening effect:
  - ⇨ Size of the solute
  - ⇨ Concentration of solute
  - ⇨ Elastic modulus of the solute *(higher the elastic modulus of the solute greater the strengthening effect)*
  - ⇨ Nature of distortion produced by solute atoms (*Spherical or Non-spherical*)

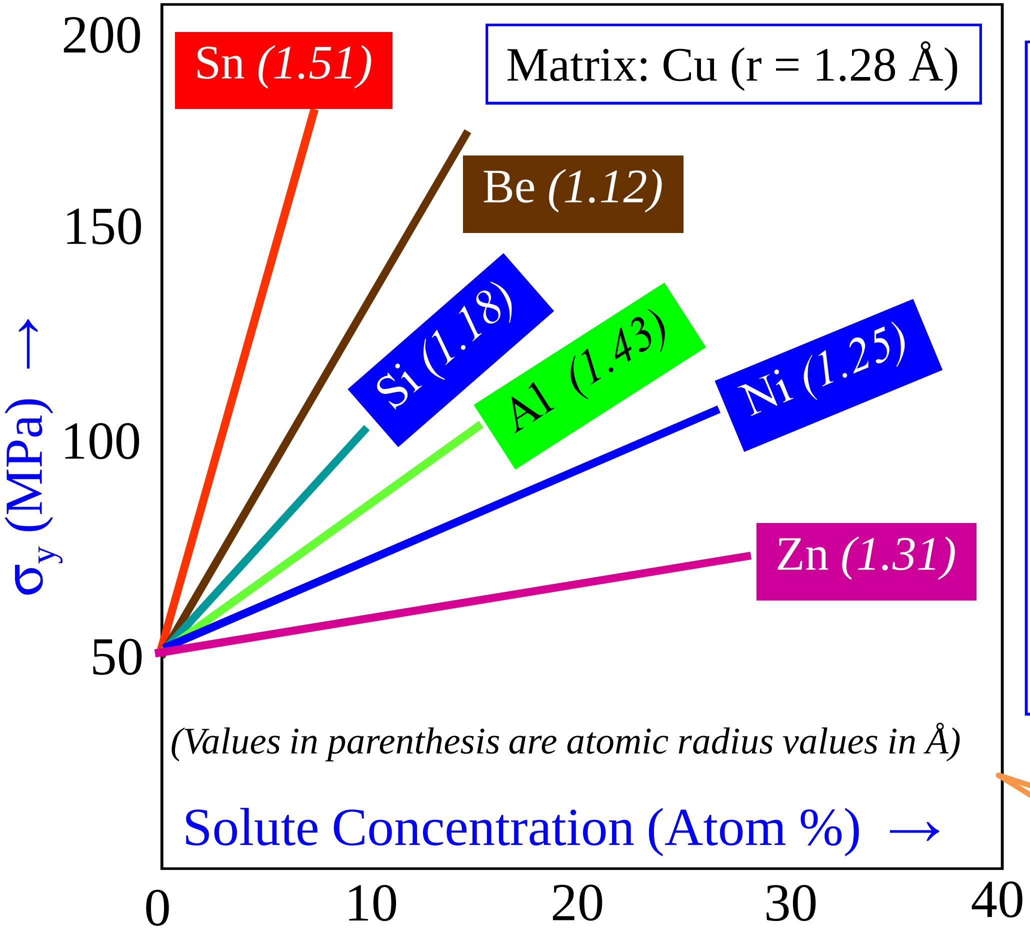
Effect of Size and Concentration of Solute

Size effect depends on:

- Size difference
- Concentration of the solute *(c)*

For the same size difference the smaller atom gives a greater strengthening effect

$$\sigma_y \overset{\sim}{\propto} c$$



Solute strengthening of Cu crystal by solutes of different sizes

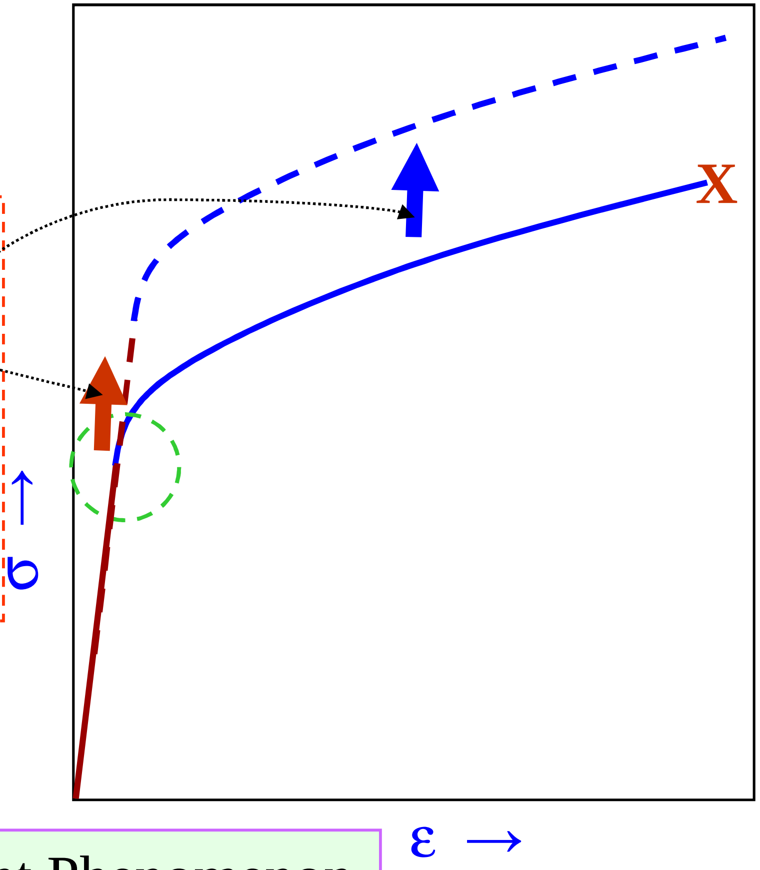
- ❑ More the size difference, more the intensity of stress field around solute atoms and more is the hardening effect.
- ❑ Large the concentration difference, more obstacles to dislocations motion and strength increases (Increase in σ_Y is proportional to concentration of the solute).

Solute atoms

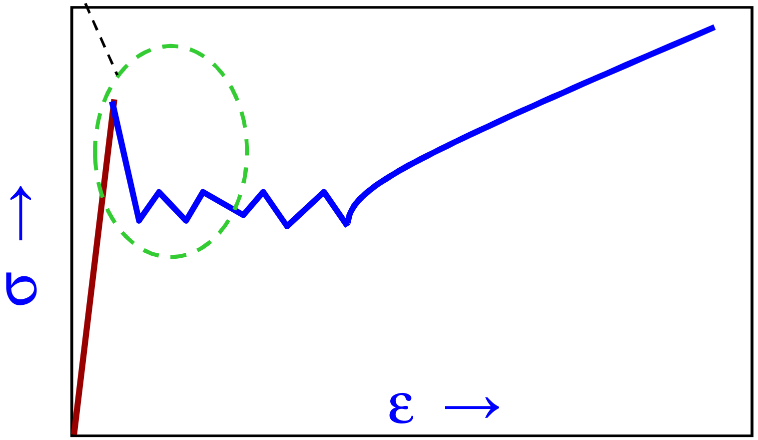
↑ σ_y

↑ level of σ - ε curve

By ↑ σ_i *(lattice friction)*

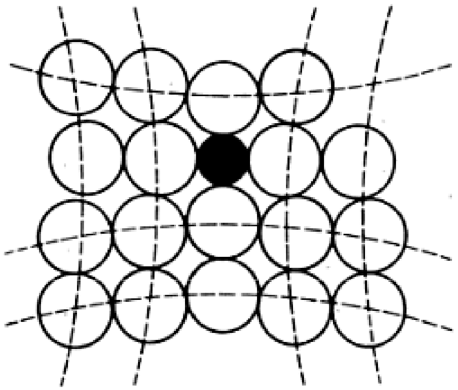


Often produce Yield Point Phenomenon

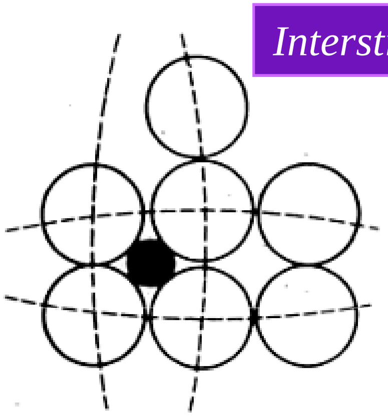


Relative strengthening effect of Interstitial and Substitutional atoms

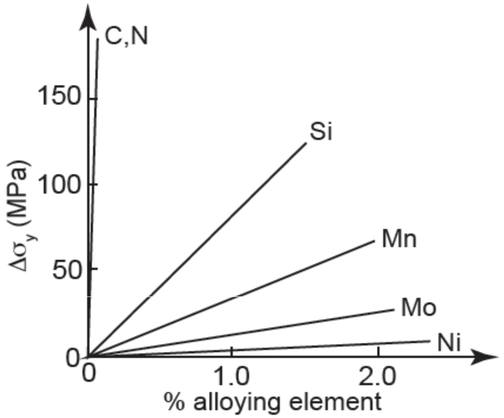
- Interstitial solute atoms have a non-spherical distortion field and can elastically interact with both edge and screw dislocations. Hence they give a higher hardening effect (per unit concentration) as compared to substitutional atoms which have (approximately) a spherical distortion field.

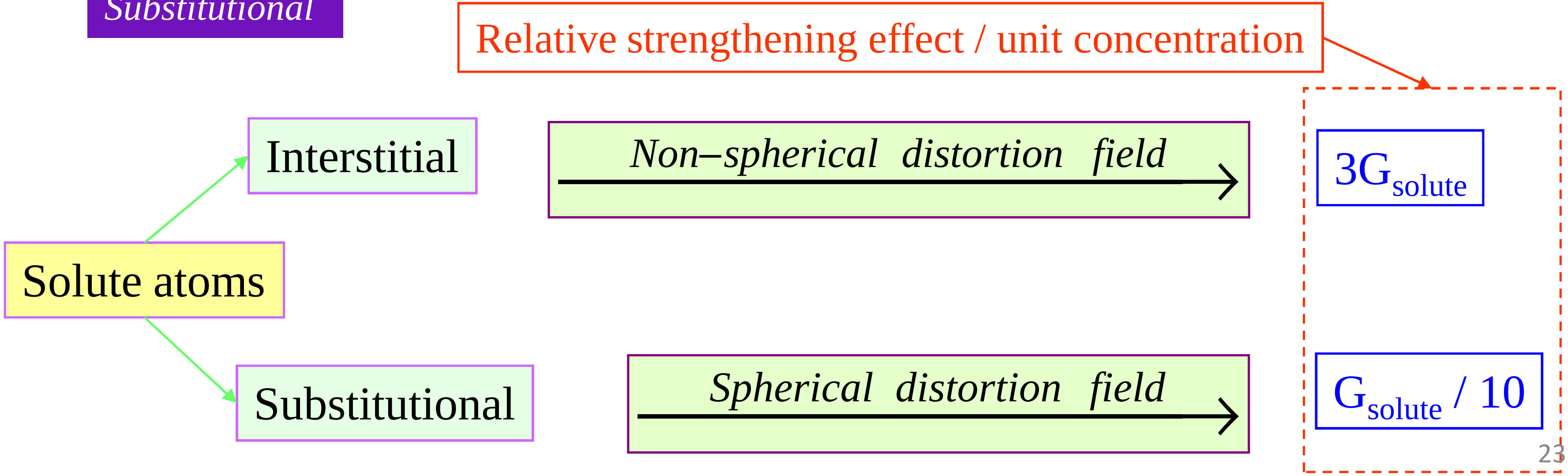


Substitutional



Interstitial





Relative strengthening effect / unit concentration

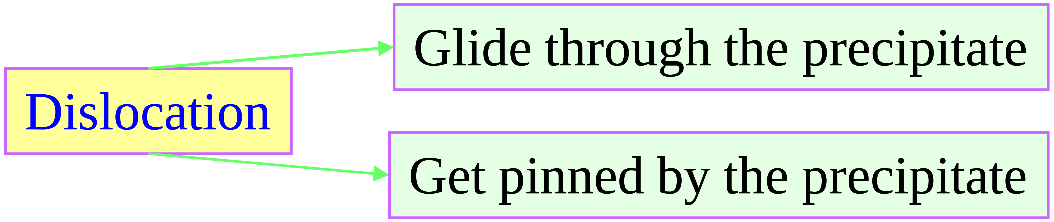
Solute atoms

Interstitial — *Non–spherical distortion field* → $3G_{solute}$

Substitutional — *Spherical distortion field* → $G_{solute} / 10$

Hardening of Precipitates

- ☐ Precipitates may be coherent, semi-coherent or incoherent. Coherent (& semi-coherent) precipitates are associated with coherency stresses.
- ☐ Dislocations cannot glide through incoherent precipitates.
- ☐ Inclusions behave similar to incoherent precipitates in this regard (precipitates are part of the system, whilst inclusions are external to the alloy system).
- ☐ A pinned dislocation (at a precipitate) has to either climb over it (which becomes favourable at high temperatures) or has to bow around it.



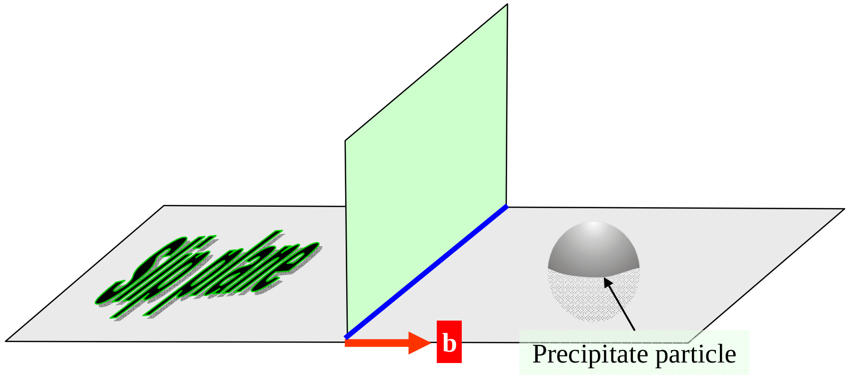
Dislocation

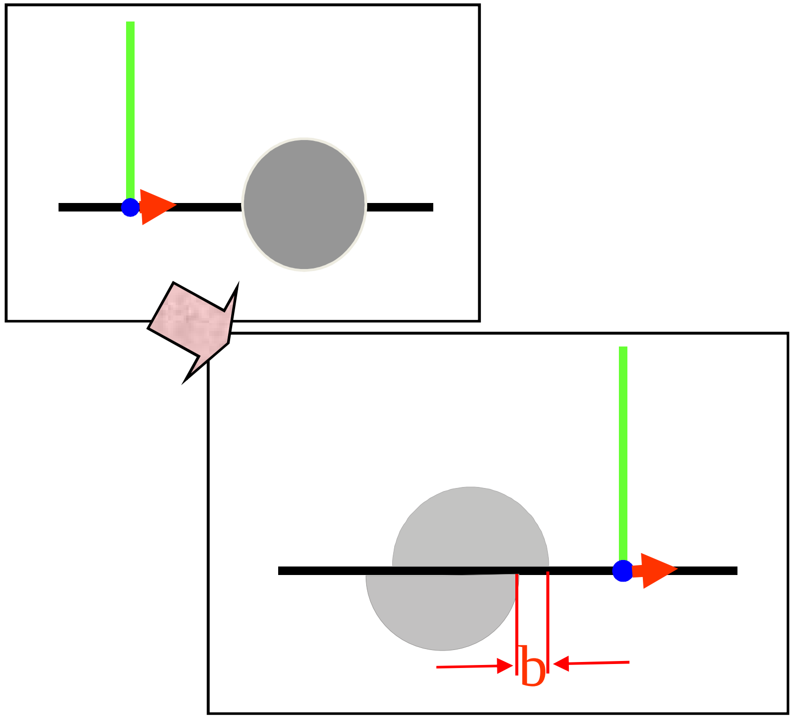
Glide through the precipitate → If the precipitate is coherent with the matrix

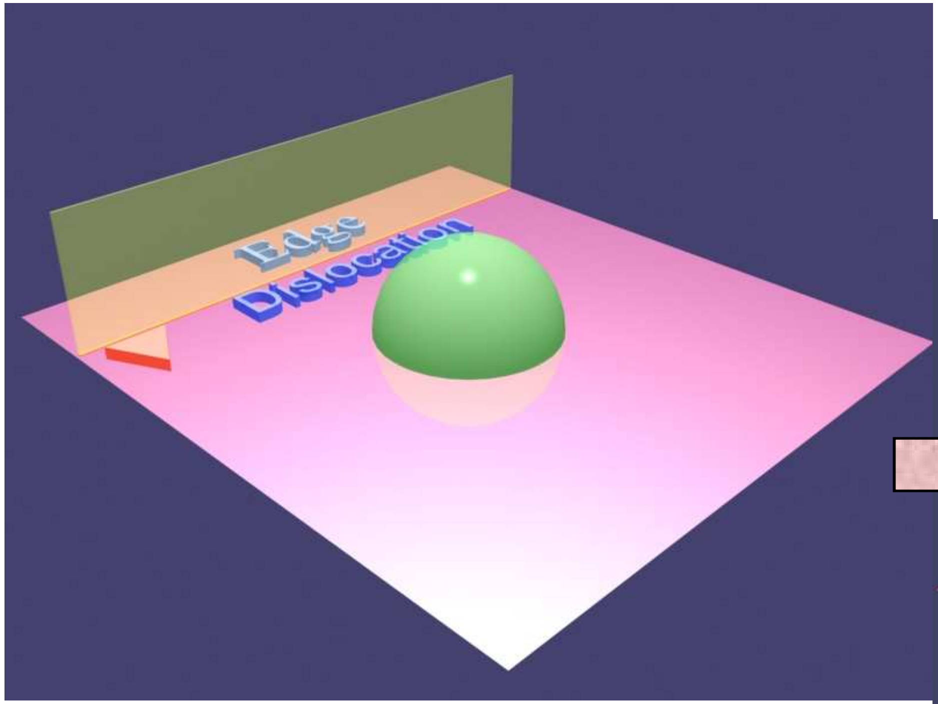
Get pinned by the precipitate

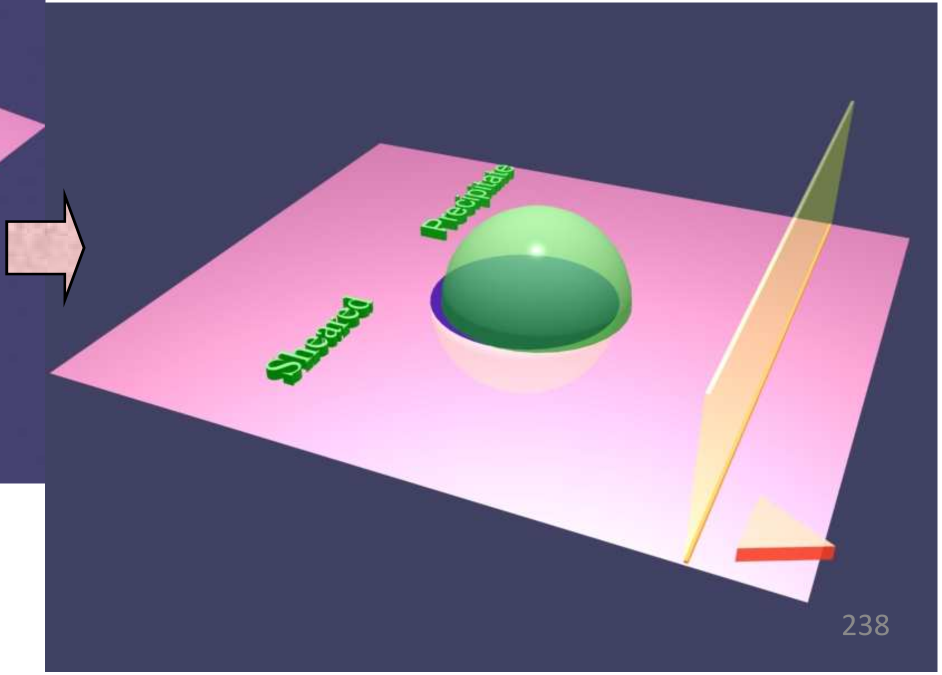
- Only if slip plane is continuous from the matrix through the precipitate ⇒ precipitate is *coherent* with the matrix.
- Stress to move the dislocation through the precipitate is ~ that to move it in the matrix (though it is usually higher as precipitates can be intermetallic compounds).
- Usually during precipitation the precipitate is coherent only when it is small and becomes incoherent on growth.
- $$\overset{\textbf{Small}}{\textit{Coherent}} \xrightarrow{\textit{Growth}} \textit{Partially}\quad \textit{coherent} \xrightarrow{\textit{Growth}} \overset{\textbf{Large}}{\textit{Incoherent}}$$
- Glide of the dislocation causes a displacement of the upper part of the precipitate w.r.t the lower part by **b** → ~ *cutting of the precipitate.*

Schematic views
→ edge dislocation glide through a coherent precipitate









If the particle is sheared, then how does the hardening effect come about?

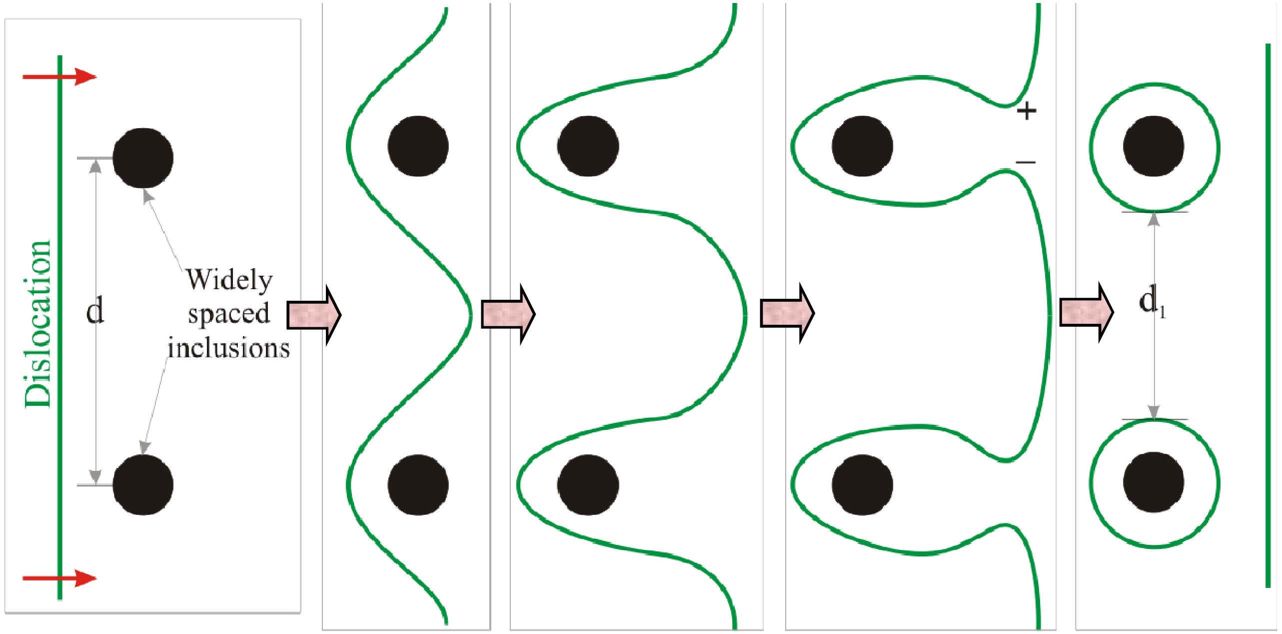
- We have seen that as the dislocation glides through the precipitate it is sheared.
- If the precipitate is sheared, then how does it offer any resistance to the motion of the dislocation? I.e. how can this lead to a hardening effect?
- The hardening effect due to a precipitate comes about due to many factors (many of which are system specific). The important ones are listed in the tree below.

- Dislocation
  - Glide through the precipitate → If the precipitate is coherent with the matrix
  - Get pinned by the precipitate

- Hardening effect
  - Increase in surface area due to particle shearing
  - Part of the dislocation line segment *(inside the precipitate)* could face a higher PN stress

Orowan bowing mechanism : Pinning effect

- Dislocations can bow around widely separated inclusions. In this process they leave dislocation loops around the inclusions, thus leading to an increase in dislocation density. This is known as the Orowan bowing mechanism as shown in the figure below. (*This is in 'some sense' similar to the Frank-Read mechanism*).
- The next dislocation arriving (similar to the first one), feels a repulsion from the dislocation loop and hence the stress required to drive further dislocations increases. Additionally, the effective separation distance (through which the dislocation has to bow) reduces from 'd' to 'd_1'.



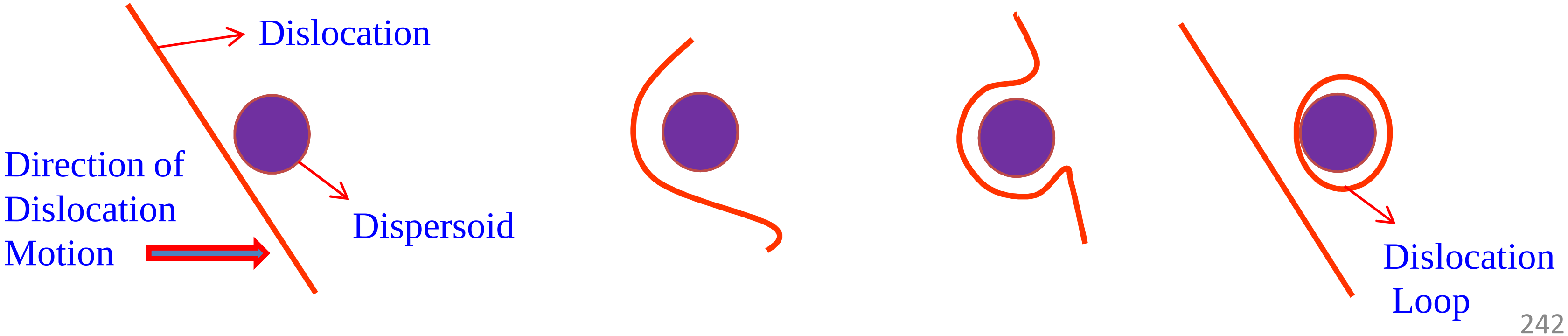
Precipitate Hardening effect

The hardening effect of precipitates can arise in many ways as below:

- ☐ Lattice Resistance: the dislocation may face an increased lattice friction stress in the precipitate.
- ☐ Chemical Strengthening: arises from additional interface created on shearing
- ☐ Stacking-fault Strengthening: due to difference between stacking-fault energy between particle and matrix when these are both FCC or HCP (when dislocations are split into partials)
- ☐ Modulus Hardening: due to difference in elastic moduli of the matrix and particle
- ☐ Coherency Strengthening: due to elastic coherency strains surrounding the particle
- ☐ Order Strengthening: due to additional work required to create an APB in case of dislocations passing through precipitates which have an ordered lattice

Strengthening by Dispersoids

- ☐ In dispersion hardening, the hard particles are mixed with matrix powder and consolidated and processed by powder metallurgy techniques.
- ☐ Example: *Thoria dispersed Nickel* → Fine particles of Thoria are dispersed in the nickel matrix and the inter particle distance is enough to hinder the dislocation movement thereby increasing the strength up to 0.9 times T_m (T_m in ^{0}C).
- ☐ In dispersion hardening, dispersoids are incoherent with the matrix and dislocations cannot glide through these dispersoids and gets pinned.
- ☐ A pinned dislocation (at a precipitate) has to either climb over it (which becomes favorable at high temperatures) or has to bow around it (Orowan's Mechanism of Dispersion Hardening)
- ☐ Dislocation loop exert a back stress on dislocation which needs to be overcome for additional slip to take place and this causes hardening.



Strain Hardening : Forest Dislocations

What causes Strain hardening? → multiplication of dislocations

Strain hardening

Annealed material $\xrightarrow{Cold\ work}$ *Stronger material*

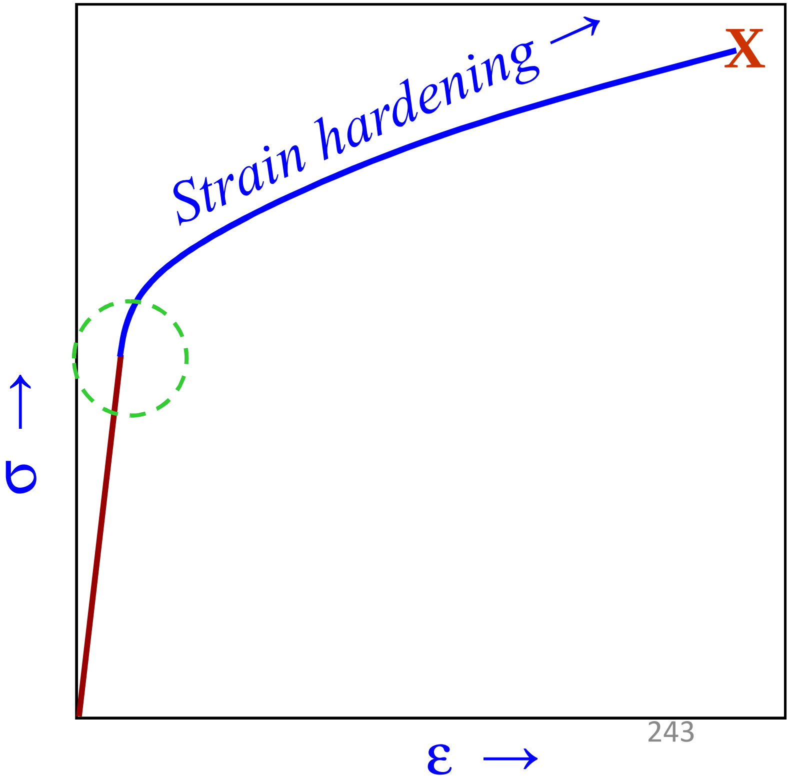
$$\rho_{dislocation} \sim (10^{6} - 10^{9}) \xrightarrow{Cold\ work} \rho_{dislocation} \sim (10^{12} - 10^{14})$$

- Why increase in dislocation density ?
- Why strain hardening ?

If dislocations were to leave the surface of the crystal by slip / glide then the dislocation density should decrease on plastic deformation →

but observation is contrary to this

This implies some sources of dislocation multiplication / creation should exist



Some specific sources/methods of formation/multiplication of dislocations include

- ☐ It is difficult to obtain crystals without dislocations (under special conditions whiskers have been grown without dislocations).
- ☐ Dislocation can arise by/form:
  - Solidification (errors in the formation of a perfect crystal lattice)
  - Plastic deformation (nucleation and multiplication)
  - Irradiation
- ☐ High stresses
  - ▶ Heterogeneous nucleation at second phase particles
  - ▶ During phase transformation
- ☐ Frank-Read source
- ☐ Orowan bowing mechanism

Strain hardening

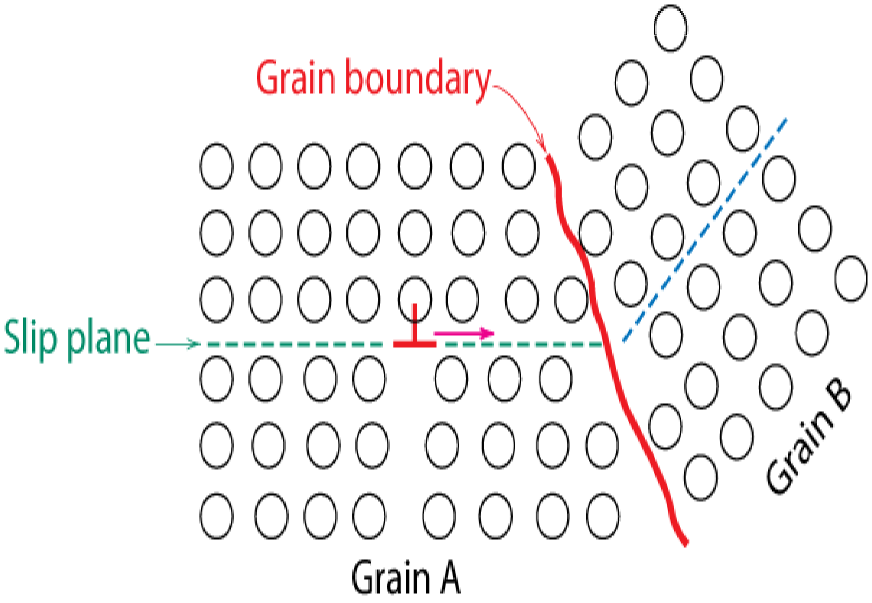
- ☐ We had noted that stress to cause further plastic deformation (flow stress) increases with strain → strain hardening. This happens at
- ☐ Dislocations moving in non-parallel slip planes can intersect with each other → results in an increase in stress required to cause further plastic deformation ⇒ *Strain Hardening / work hardening*
- ☐ One such mechanism by which the dislocation is immobilized is the Lomer-Cottrell barrier.

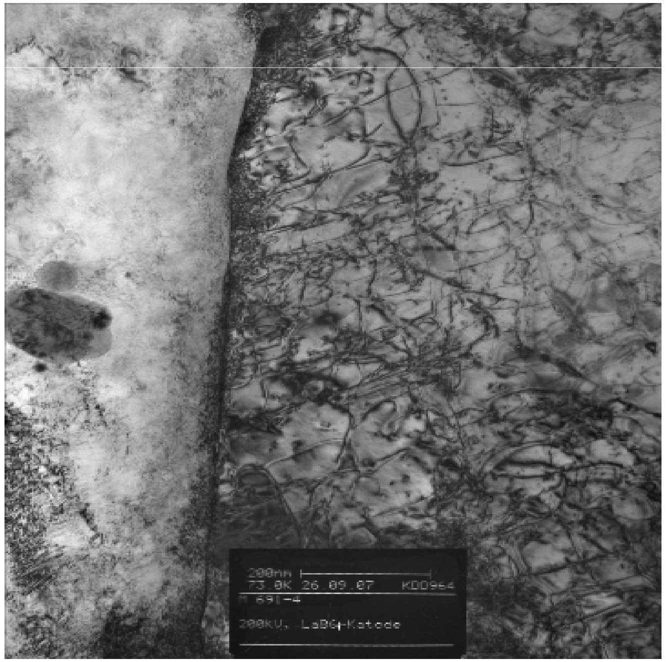
Strengthening by Grain Boundary

- ❑ Grain boundary is the boundary between two grains in a polycrystalline aggregate and this is the region of a disturbed lattice which is of few atomic diameters distance.
- ❑ There are two important ways in which grain boundary acts as a barrier to the dislocation

  ⇨ Difficulty for a dislocation to pass through two different grain orientations (need to change the direction)

  ⇨ The atomic disorder within a grain boundary region contributes to a discontinuity of slip planes from one grain to other.





Dislocation pile-up at grain boundaries

Hall – Petch Relation

- ❑ A fine grained material is harder and stronger than one that is coarse grained since greater amounts of grain boundaries in the fine grained materials impede dislocation motion.
- ❑ The general relationship between yield stress (tensile strength) and grain size was proposed by Hall and Petch, which is known as Hall-Petch relation.

$$\sigma_{Yield} = \sigma_o + k_y d^{-\frac{1}{2}}$$

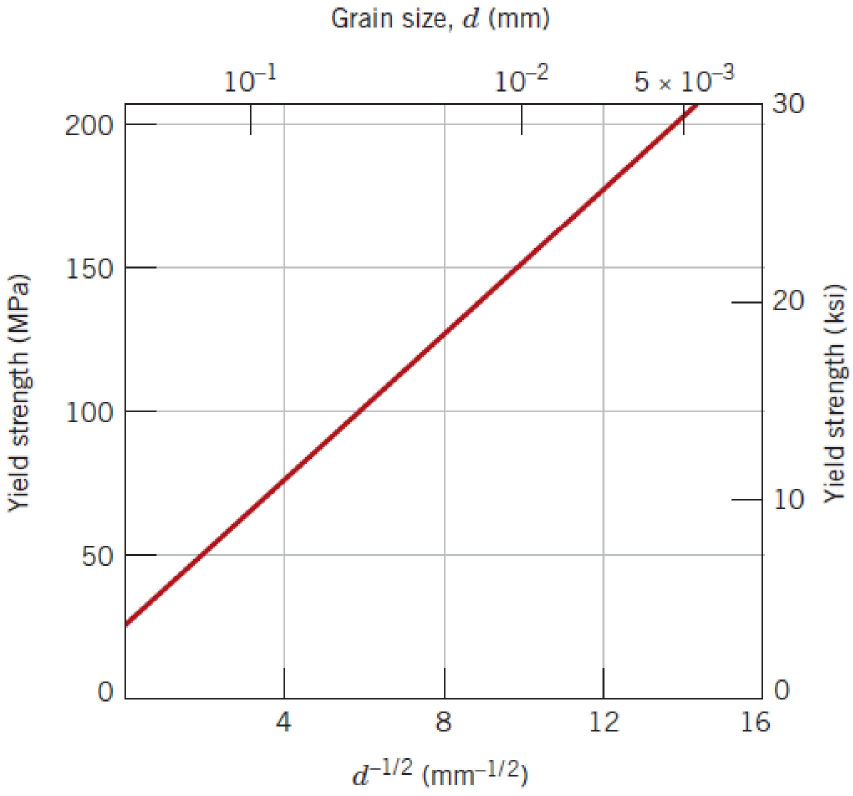
Where,

σ_{yield} = *Yield stress*

σ_o = *Friction stress or resistance to dislocation motion*

k_y = *Locking parameter or the hardening contribution from the grain boundary*

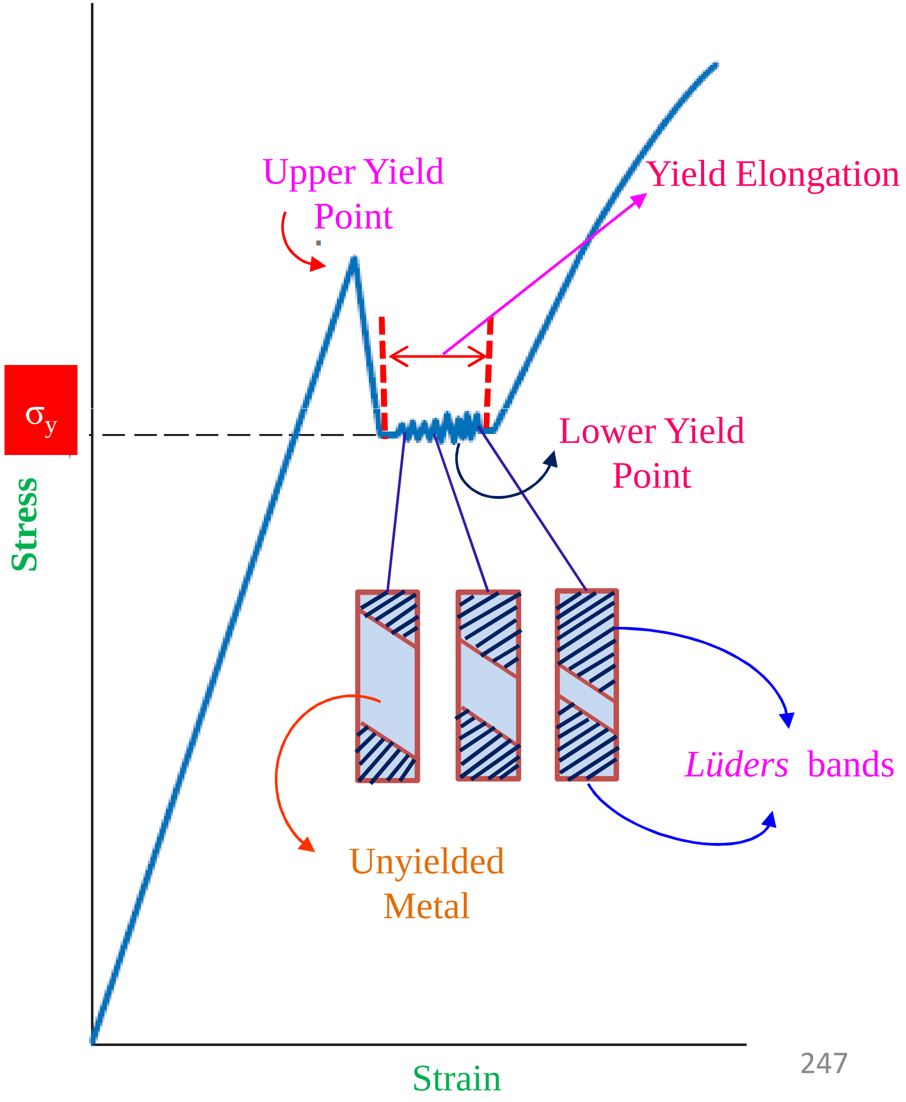
d = *Grain diameter*



Influence of grain size on yield strength of 70Cu-30Zn Brass

Yield-Point Phenomenon

- ❑ Many metals, particularly low carbon steel, show a localized, heterogeneous type of transition from elastic to plastic deformation which produces a yield point in the stress-strain curve.
- ❑ For these metals, load increases steadily with elastic strain, drops suddenly, fluctuates around a certain value (Plateau region) and then rises with further strain.
- ❑ The load at which sudden drop occurs corresponds to the upper yield point, the constant load is called the lower yield point, and the elongation that occurs at constant load is called the yield-point elongation.
- ❑ At the upper yield point, plastic deformation is initiated forming a discrete band of deformed metal, known as *Lüders band*/Hartmann lines or stretcher strains
- ❑ Then these bands propagate to cover the entire length of the specimen.

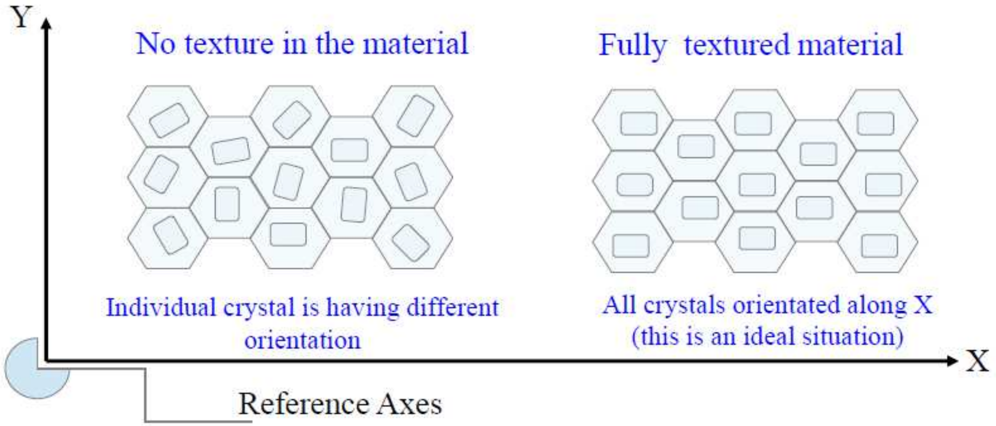


Explanation of Yield-Point Phenomenon in terms of Dislocation Behavior

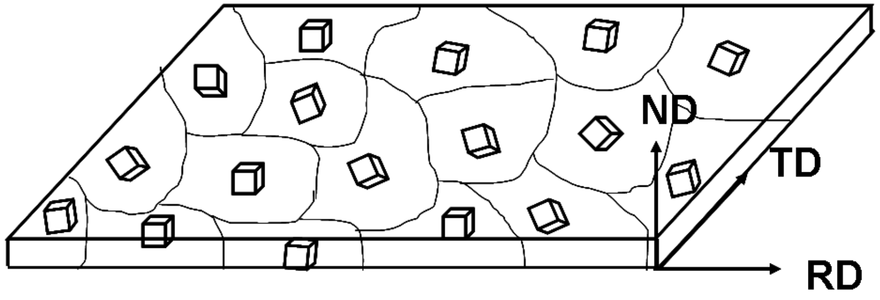
- Solute atoms in a solution (Carbon or Nitrogen atoms in iron) readily diffuse into the minimum energy positions (distorted regions near the dislocations line) while the material is stress-free.
- The interaction between the solute atoms and the dislocation line is very strong and some breakaway stress is needed to pull a dislocation line away from the line of solute atoms.
- When external stress is applied, the dislocations ‘tears off’ its pinning points and the stress required for this defines the upper yield strength.
- After the dislocation has left its pinning points, it is more mobile than before, and the yield strength reduces (lower yield strength).
- The dislocations released into the slip planes pile up at the grain boundaries and produces a stress concentration at its tip which in turn increases the stress in the neighboring grain, allowing dislocations there to become mobile as well.
- This results in the formation of narrow bands of localized deformation, so-called Lüders bands within the material.
- This alternation between local hardening by dislocation pile-up and removal of this deformation obstacle by tearing off dislocations in the neighboring grain causes a strongly serrated flow curve (yield point elongation).
- Only after the Lüders bands have spread throughout the material and all dislocations are removed from their pinning points, the yield strength increases beyond the lower yield strength by work hardening.

Preferred Orientation (Texture)

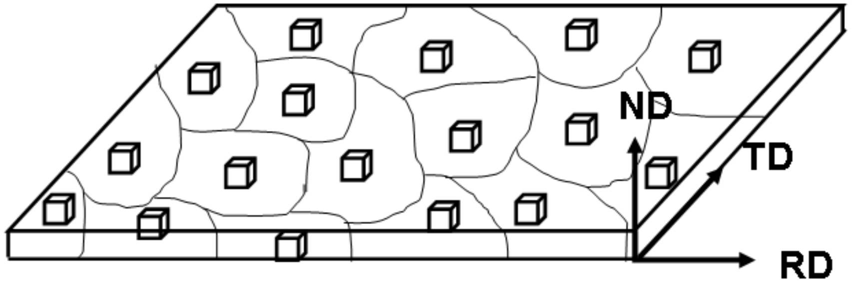
- In Latin, textor means weaver and in materials science, texture is the way in which a polycrystalline material is woven.



- Polycrystalline material is constituted from a large number of small crystallites (limited volume of material in which periodicity of crystal lattice is present). Each of these crystallites has a specific orientation of the crystal lattice .



A texture-less sheet
(Configuration like a powder aggregate)



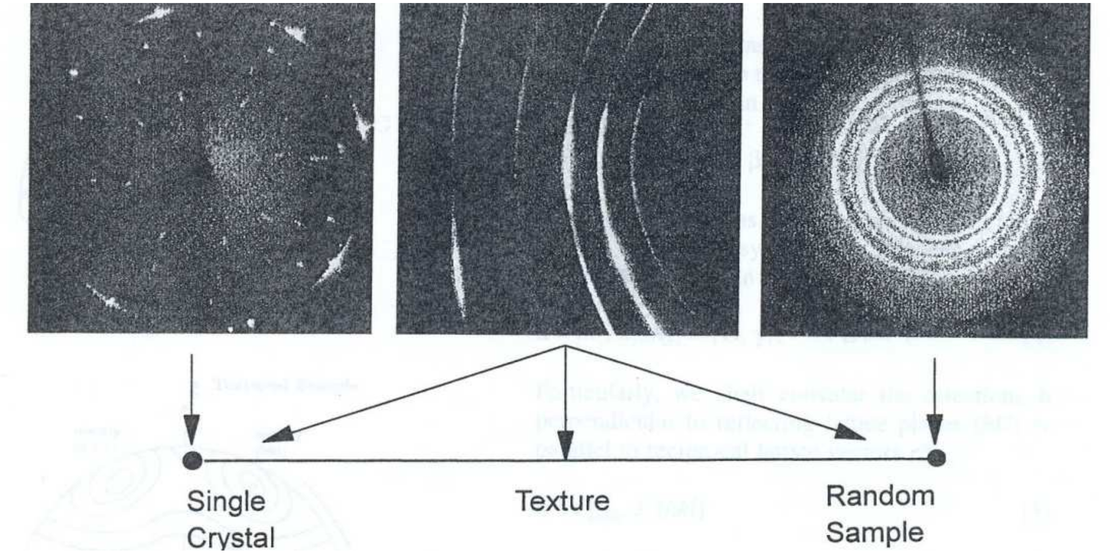
A fully textured sheet
The cube texture
(001) ‖ ND (Sheet Normal Direction)
[100] ‖ RD (Sheet Rolling Direction)

Preferred Orientation (Texture)

- When a metal undergoes a severe amount of deformation, its crystallographic planes tend to orient themselves in a preferred manner with respect to the direction of maximum strain; in which case the material is said to have a "texture".
- The type of preferred orientation which is developed depends mainly on number and type of slip systems available, principal strains, temperature of deformation and type of texture present prior to deformation.
- For uniaxial deformation or other processes, texture is expressed in terms of miller indices of directions [uvw] aligned along the specimen axis, also called Fiber texture.
- Fiber texture is symmetrical to the wire axis. BCC metals have a fiber texture with <110> direction parallel to the wire axis. FCC metals have double fiber texture with both <111> and <100> directions parallel to the fiber axis.
- Texture develops or changes due to: (i) Crystallization/ solidification (from a non-crystalline / liquid state) (ii) Plastic deformation (by slip and twinning) (iii) Annealing (from the same phase) (iv) Phase transformation (from a different phase)
- Texture resulting from plastic deformation is strongly dependent on available slip and twinning systems but is not affected by processing variables like die angle, roll diameter, speed etc. Thus, same texture is produced whether a rod is made by rolling or drawing.
- Recrystallization of a cold worked metal produces a texture which is different from and stronger than that existing in the deformed metal. This is called an annealing or Recrystallization texture.

Preferred Orientation (Texture)

- Preferred Orientations are determined by X-Ray Methods.
- Diffraction patterns from a single crystal is in the form of isolated spots, while for a randomly oriented polycrystalline material, the diffraction pattern is in the form of concentric rings (Debye-Scherrer rings) corresponding to different planes and the intensity of rings will be uniform for all angles.
- Textured polycrystalline materials are somewhat in-between. Here the diffraction pattern consists of Debye-Scherrer rings, but the intensity distribution is non-uniform along the circumference of the rings.



Diffraction pattern from the crystals of materials

Hot Working

- Plastic deformation which is carried out under conditions of temperature and strain rate such that recovery processes occur substantially so that large strains can be achieved with essentially no strain hardening.
- Normally performed at temperature $>0.6T_m$ & at high strain rates in the range of 0.5-500 s^{-1}

Advantages of Hot Working

- Larger deformation can be accomplished and more rapidly by hot working since the metal is in plastic state.
- Porosity of the metal is considerably minimized.
- Concentrated impurities, if any in the metal are disintegrated and distributed throughout the metal.
- Grain structure of the metal is refined and physical properties is improved.
- No residual stresses in the material

Disadvantages of Hot Working

- Poor surface finish and loss of metal due to rapid oxidation or scale formation on the metal surface
- Close tolerances cannot be maintained.
- It involves excessive expenditure on account of high cost of tooling. This, however, is compensated by the high production rate and better quality of products.

Warm Working

- Warm working is the plastic deformation of a meta at temperature below the temperature range of recrystallization and above the room temperature i.e. intermediate to hot and cold working.

Advantages compared to Cold Working

- Combines the advantages of both hot and cold working into one operation.
- Fewer number of annealing operation (because of less strain hardening)
- Lesser loads on tooling and equipment
- Greater metal ductility

Advantages compared to Hot Working

- Improved dimensional control,
- Lower energy costs.
- Better precision of components
- Lesser scaling and decarburization on parts
- Better surface finish
- Lesser thermal shock on tooling
- Lesser thermal fatigue to tooling, and so greater life of tooling.

Cold Working

- Plastic deformation which is carried out in a temperature region and over a time interval such that the strain hardening is not relieved is called cold work.
- Normally performed at room temperature but in general < $0.3T_m$, where recovery is limited and recrystallization does not occur.

Advantages of Cold Working

- Due to work hardening Strength and hardness of the metal are increased.
- It is an ideal method for increasing hardness of those metals which do not respond to the heat treatment.
- Better dimensional control is possible because the reduction in size is not much.
- Provide fine grain size and good surface finish (No oxidation takes place).
- Handling is easier because of low operating temperature.
- Directional properties can be imparted.

Disadvantages of Cold Working

- Only ductile metals can be shaped through cold working.
- Over-working of metal results in brittleness and it has to be annealed to remove the same.
- Subsequent heat treatment is mostly needed to remove the residual stresses set up during cold working.
- Higher forces and heavier and more powerful equipment are required for deformation.

Recovery, Recrystallization & Grain Growth

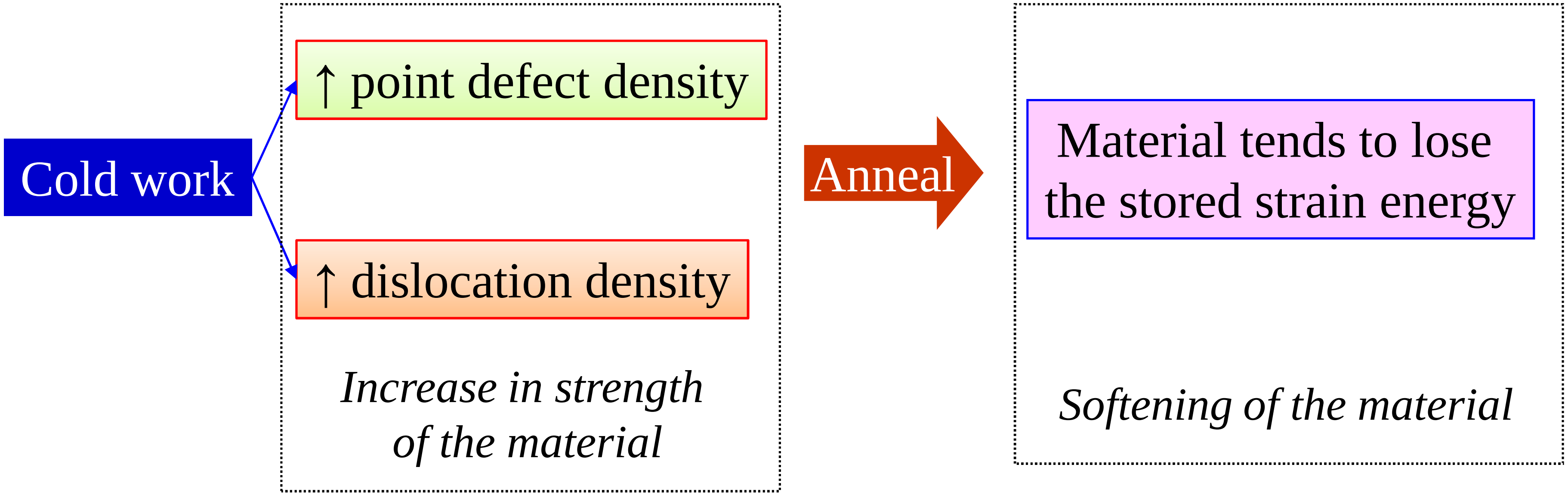
Introduction

Plastic deformation in the temperature range (0.3 – 0.5) T_m → COLD WORK

- Point defects and dislocations have strain energy associated with them
- (1 -10) % of the energy expended in plastic deformation is stored in the form of strain energy (in these defects) → *The material becomes battery of energy..!*
- The cold worked material is in a micro structurally metastable state.
- Depending on the severity of the cold work the dislocation density can increase 4-6 orders of magnitude more. The material becomes stronger, but less ductile.
- The cold worked material is stronger (harder), but is brittle.
- Heating the material (typically below $0.5T_m$) is and holding for sufficient time is a heat treatment process called annealing.
- Depending on the temperature of annealing processes like Recovery at lower temperatures) or Recrystallization (at higher temperatures) may take place. During these processes the material tends to go from a micro structurally metastable state to a lower energy state (towards a stable state).
- Further 'annealing' of the recrystallized material can lead to grain growth.

$$\begin{array}{ccc} \textit{Annealed material} & & \textit{Stronger material} \\ \rho_{\text{dislocation}} \sim (10^6 - 10^9) & \xrightarrow{\textit{Cold work}} & \rho_{\text{dislocation}} \sim (10^{12} - 10^{14}) \end{array}$$

Introduction



Cold work

↑ point defect density

↑ dislocation density

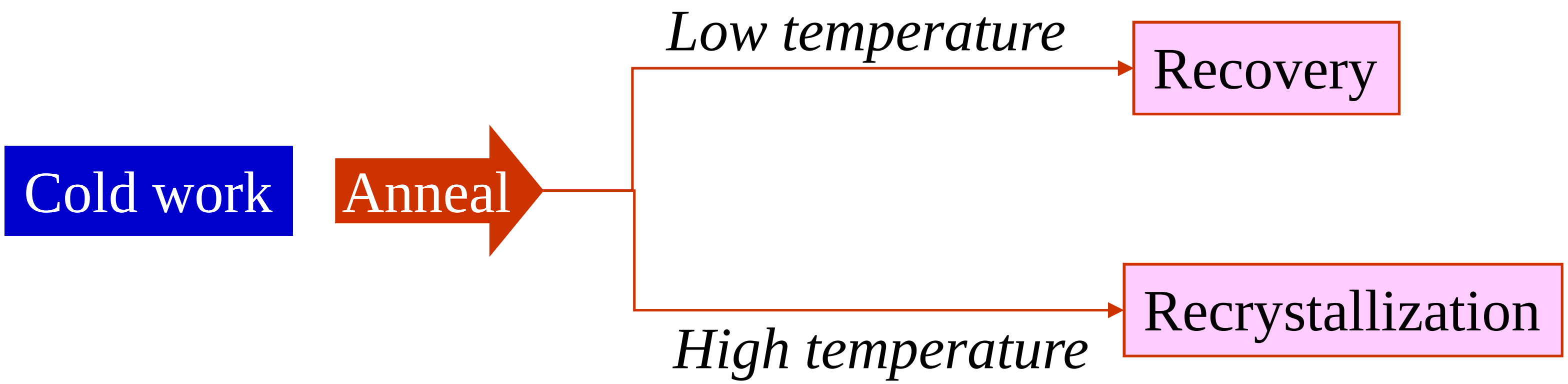
Increase in strength of the material

Anneal

Material tends to lose the stored strain energy

Softening of the material

- During cold work the point defect density (vacancies, self interstitials…) and dislocation density increase. Typical cold working techniques are rolling, forging, extrusion etc.
- Cold working is typically done on ductile metals (e.g. Al, Cu, Ni)



Cold work

Anneal

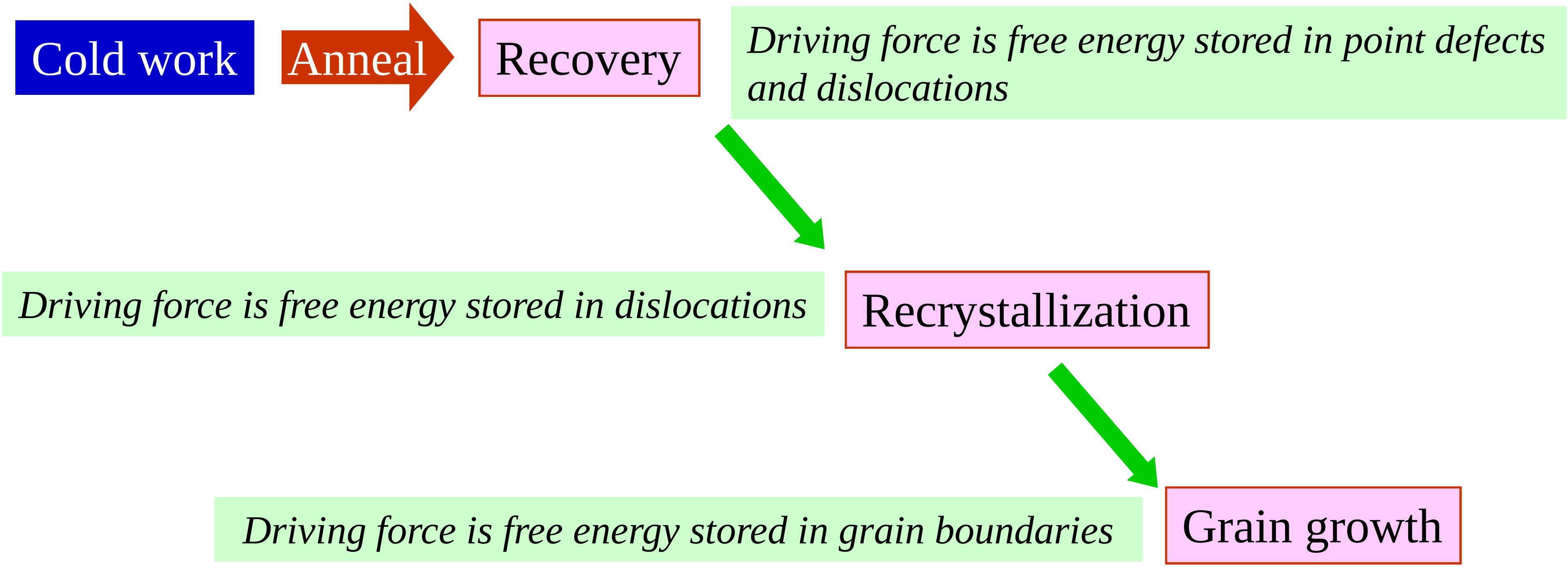
Low temperature

Recovery

High temperature

Recrystallization

Overview of processes taking place during annealing of cold worked material and the driving force for these processes



Cold work

Anneal

Recovery

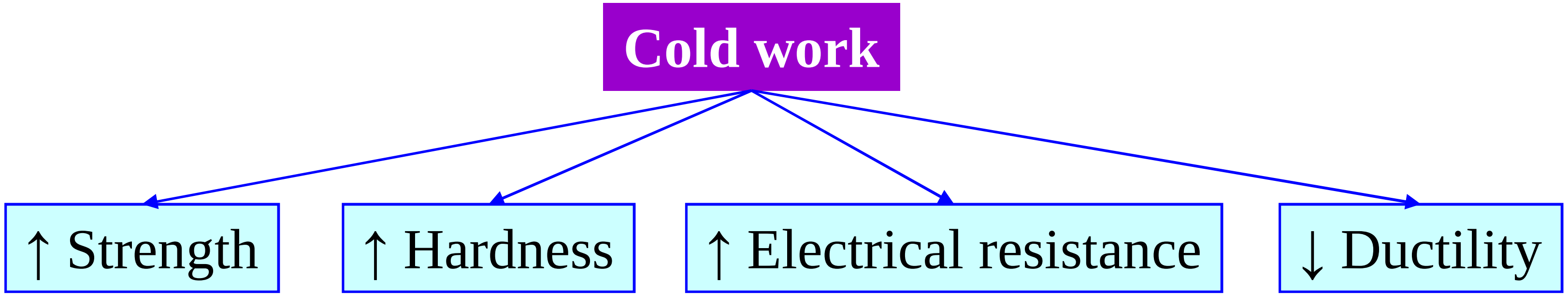
Driving force is free energy stored in point defects and dislocations

Recrystallization

Driving force is free energy stored in dislocations

Grain growth

Driving force is free energy stored in grain boundaries



Cold work

↑ Strength

↑ Hardness

↑ Electrical resistance

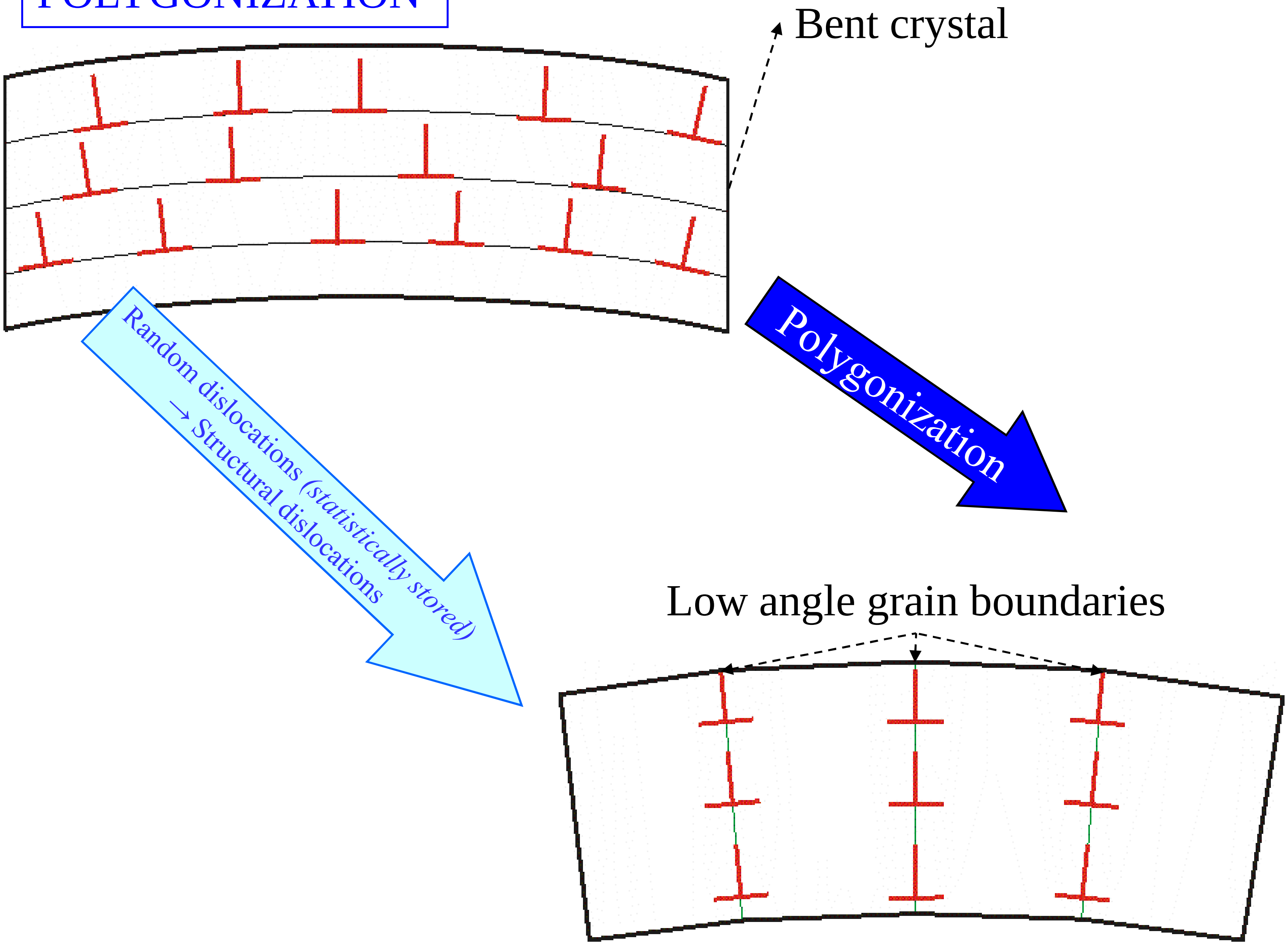
↓ Ductility

Changes occur to almost all physical and mechanical properties

RECOVERY

- ☐ Recovery takes place at low temperatures of annealing
- ☐ "Apparently no change in microstructure"
- ☐ Excess point defects created during Cold work are absorbed:
  - ▶ at surface or grain boundaries
  - ▶ by dislocation climb
- ☐ Random dislocations of opposite sign come together and annihilate each other
- ☐ Dislocations of same sign arrange into low energy configurations:
  - ▶ Edge → Tilt boundaries
  - ▶ Screw → Twist boundaries
    - ➔ POLYGONIZATION
- ☐ Overall reduction in dislocation density is small
- ☐ At the early stage of annealing of cold formed metals, external thermal energy permits the dislocations to move and form the boundaries of a polygonized subgrain structure while the dislocation density stays almost unchanged. This process also removes the residual stresses formed due to cold working significant. The recovering of physical and mechanical properties varies with the temperature and time.

POLYGONIZATION



Bent crystal

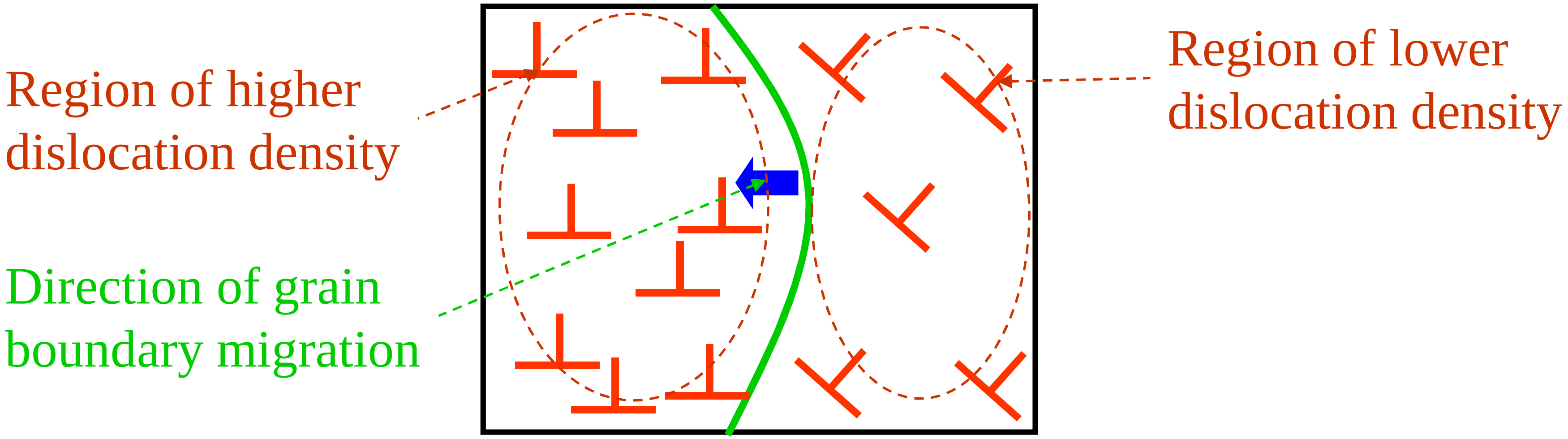
Random dislocations (*statistically stored*)
→ Structural dislocations

Polygonization

Low angle grain boundaries

RECRYSTALLIZATION

- ☐ $T_{recrystallization} \in (0.3 - 0.5)\, T_m$
- ☐ "Nucleation" and growth of new, strain free crystals
- ☐ Nucleation of new grains in the usual sense may not be present and grain boundary migrates into a region of higher dislocation density
- ☐ *ΔG (recrystallization) = G (deformed material) – G (undeformed material)*
- ☐ $T_{Recrystallization}$ is the temperature at which 50 % of the material recrystallizes in 1 hour



Region of higher dislocation density

Direction of grain boundary migration

Region of lower dislocation density

RECRYSTALLIZATION

- ❑ Deformation ↑ ⇒ recrystallization temperature ($T_{recrystallization}$) ↓
- ❑ Initial grain size ↓ ⇒ recrystallization temperature ↓
- ❑ High cold work + low initial grain size ⇒ finer recrystallized grains
- ❑ ↑ cold work temperature ⇒ lower strain energy stored
  ⇒ ↑ recrystallization temperature
- ❑ Rate of recrystallization = exponential function of temperature
- ❑ $T_{recrystallization}$ = strong function of the purity of the material
  $T_{recrystallization}$ (very pure materials) ~ 0.3 T_m
  $T_{recrystallization}$ (impure) ~ (0.5 – 0.6) T_m

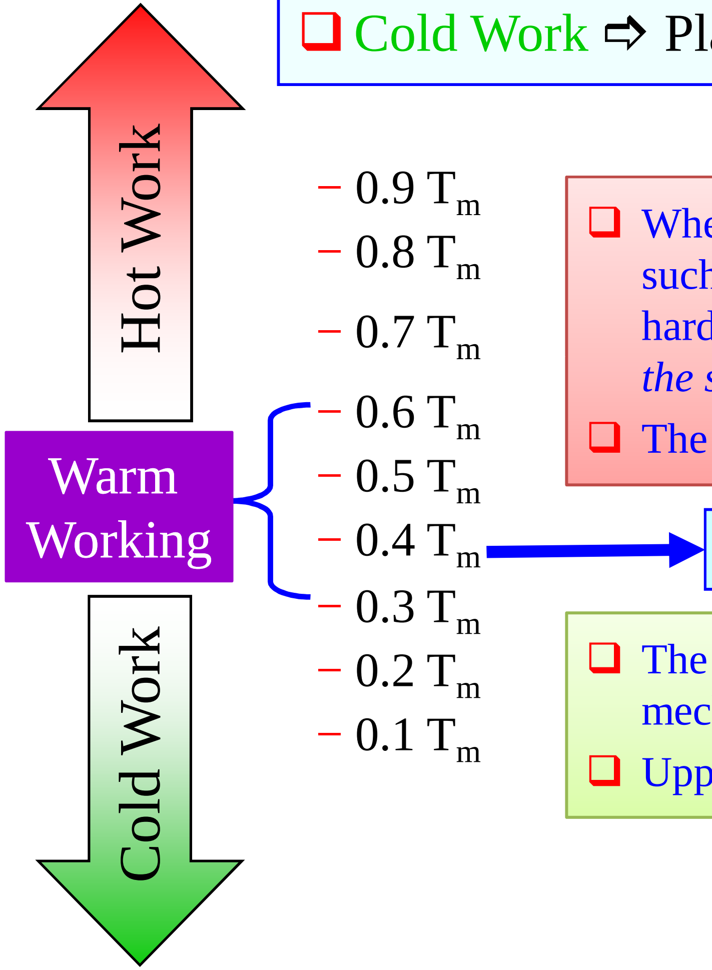
► $T_{recrystallization}$ (99.999% pure Al) ~ 75°C
$T_{recrystallization}$ (commercial purity) ~ 275°C

- ❑ The impurity atoms segregate to the grain boundary and retard their motion → *Solute drag* (can be used to retain strength of materials at high temperatures)
- ❑ Second phase particles also pin down the grain boundary during its migration

Hot Work and Cold Work

Often the range is further subdivided into Hot, Cold and Warm working as in the figure

- Hot Work ⇨ Plastic deformation above $T_{\text{Recrystallization}}$
- Cold Work ⇨ Plastic deformation below $T_{\text{Recrystallization}}$



Hot Work

– $0.9\ T_m$

– $0.8\ T_m$

– $0.7\ T_m$

– $0.6\ T_m$

– $0.5\ T_m$

– $0.4\ T_m$

– $0.3\ T_m$

– $0.2\ T_m$

– $0.1\ T_m$

Warm Working

Cold Work

- When a metal is hot worked. The conditions of deformation are such that the sample is soft and ductile. The effects of strain hardening are negated by dynamic and static processes (*which keep the sample ductile)*
- The lower limit of temperature for hot working is taken as $0.6\ T_m$

Recrystallization temperature ($\sim 0.4\ T_m$)

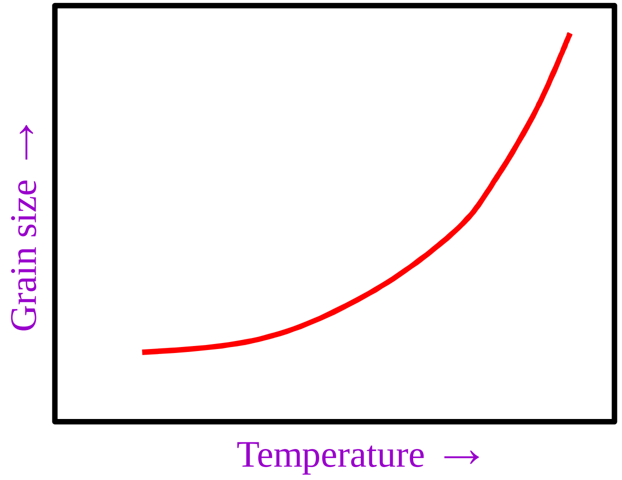
- The effects of strain hardening is not negated. Recovery mechanisms involve mainly motion of point defects.
- Upper limit ►$0.3\ T_m$

GRAIN GROWTH

- ☐ Large grains have lower free energy than small grains. This is associated with the reduction of the amount of grain boundary.
- ☐ Therefore, under ideal conditions, the lower energy state for a metal would be as a single crystal. This is driving force for grain growth.
- ☐ Opposing this force is the rigidity of the lattice. As the temperature increases, the rigidity of the lattice decreases and the rate of grain growth is more rapid.
- ☐ At any given temperature there is a maximum grain size at which these two effects are in equilibrium

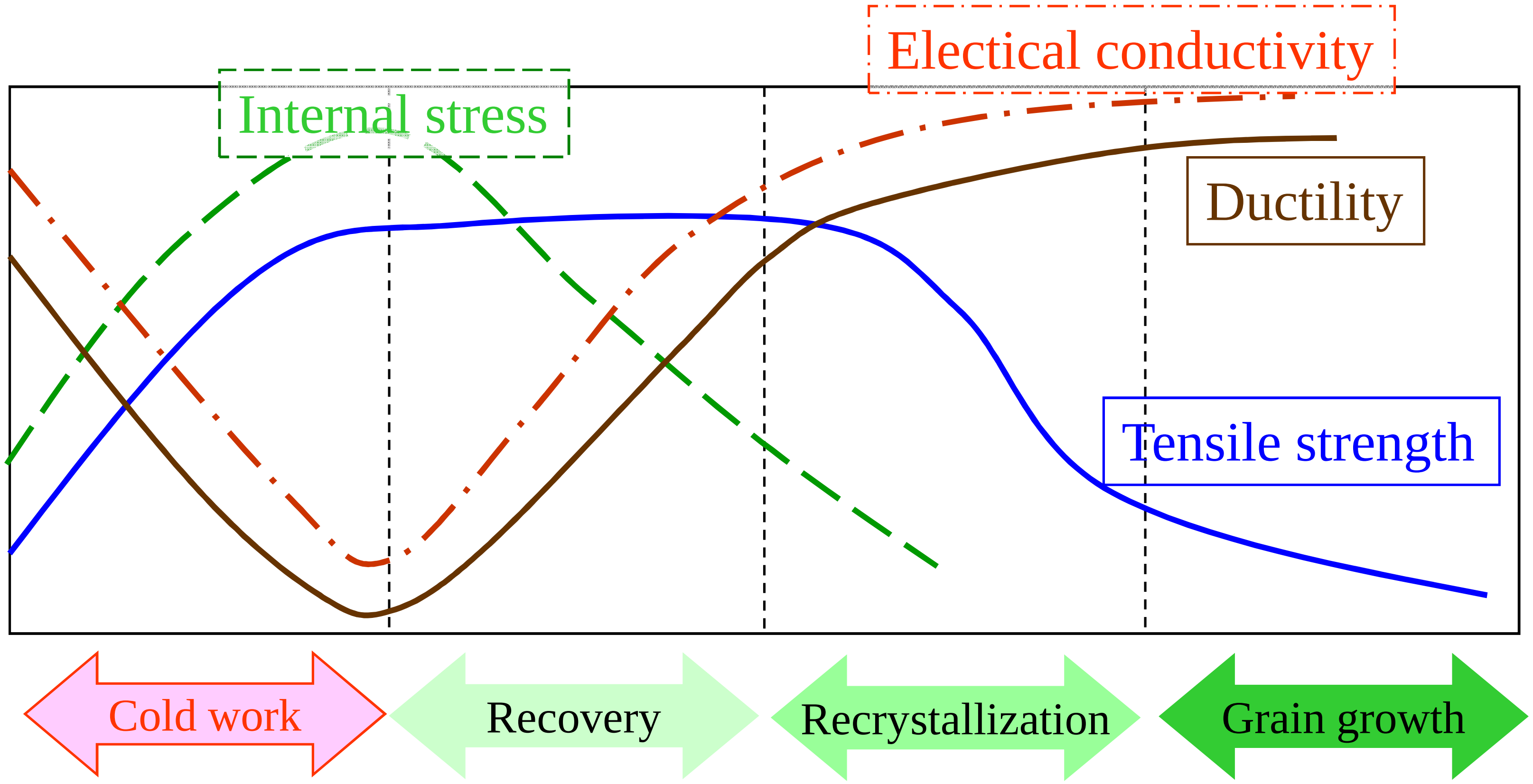
Grain growth

- ↓ Heating Time↓
- ↓ Degree of prior deformation ↑
- ↓ Time at temperature↑
- ↓ Annealing temperature↓
- ↓ Insoluble impurities↑

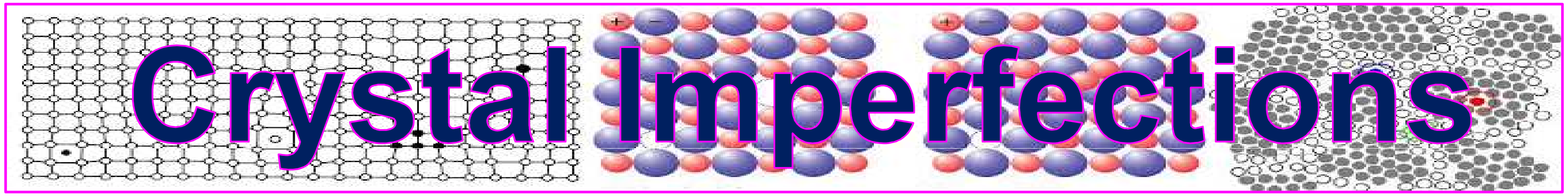


Effect of temperature on recrystallized grain size

Summary


Electical conductivity
Internal stress
Ductility
Tensile strength
Cold work
Recovery
Recrystallization
Grain growth

Crystal Imperfections



Introduction

- ❑ *You have been introduced to the lattice structures and types of bonding in crystalline solids in earlier lectures.*
- ❑ You know that the behavior of electrons determine the way the atoms interact- the type of bonding (metallic, ionic, covalent and vanderwaals), that holds atoms in a solid together.
  - ✓ But is the knowledge of bonding and crystal structure is sufficient to predict the macroscopic properties of materials?
- ❑ So far in our study of crystalline solids, we have assumed a correspondence between the abstract three-dimensional lattice and the actual structure of solids. This implies that crystals are perfect.
- ❑ Perfect Crystal : A crystal, in which all the atoms are at rest on their correct lattice position in the crystal.
- ❑ Such perfect crystals could only exist at absolute zero, and thermal vibrations can be treated as a form of defect in crystal structures.
  - ✓ For T > 0K, defects always exist in the structure.

REAL CRYSTALS ARE NEVER PERFECT, THERE ARE ALWAYS DEFECTS

Introduction

- ☐ *For example :* If a bulk metal (i.e., steel) were a single perfect crystal, it would have a strength far exceeding the strongest steel ever produced from metallurgical research. May be this is one of the limitation, in the strength of a metal comes from the number and type of defect, rather than from the nature of the ideal crystal lattice.
- ☐ *Many other important properties of materials are due to the imperfections caused by crystal defects (may be…!)*
- ☐ In this topic we will discuss different types of imperfections or defects in the ideal arrangement of atoms in a crystal.
- ☐ For example : When/If you buy a diamond ring, it is mostly the number and type of defects in the diamond crystal that define the amount of money you pay for a given crystal size.
- ☐ Another example : Forging a metal tool introduces defects ….! and increases strength and elasticity of the tool. Note, that in the case the required properties are achieved without changes in composition of the material, but just by manipulating the crystal defects.

> "Crystals are like people, it is the defects in them which tend to make them interesting"

> - Colin Humphreys

Thermodynamic cause of crystal imperfections

- Crystal defects are thermodynamically-controlled phenomena.
  - ✓ To understand how defects come about, consider the effect of probability on entropy in the following two examples.
- A typical single crystal of a large gemstone contains about 1 mole of atoms. Now compare the effect of adding a single additional defect to
- An ideal crystal → 1 defect
  - Probability for defect location is 10^{23}
  - There is large increase in the system's entropy
- A lattice which already has 10% defects → 10% + 1 defect
  - Probability for defect location is 10
  - There is only a small increase in total entropy
- This kind of entropy is called configurational entropy. It is given by the equation

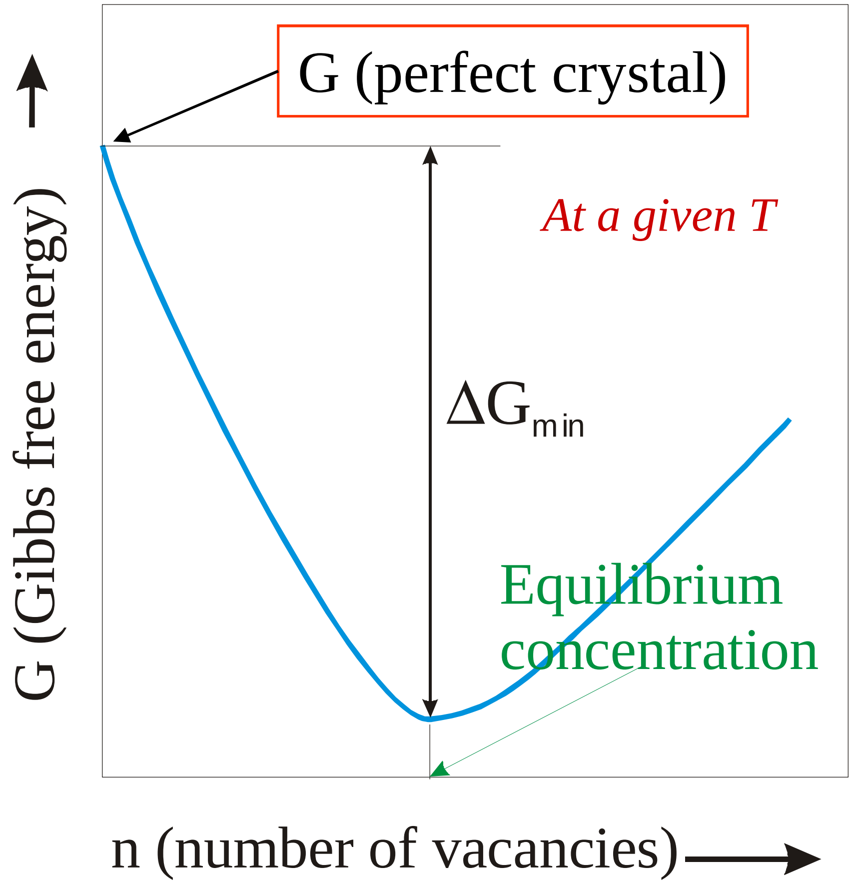
$$S = K \ln(\omega)$$

K = Boltzmann constant

ω = Probability

- So far the effect of entropy; however, the creation of any kind of defect costs energy, since the total lattice energy will be reduced. The competing effects of the energy required to disturb the lattice and the initial large gain in entropy causes a minimum in the free energy.

Thermodynamic cause of crystal imperfections



T (ºC)	n/N
500	1×10^{-10}
1000	1×10^{-5}
1500	5×10^{-4}
2000	3×10^{-3}

ΔH_f = 1 eV/vacancy

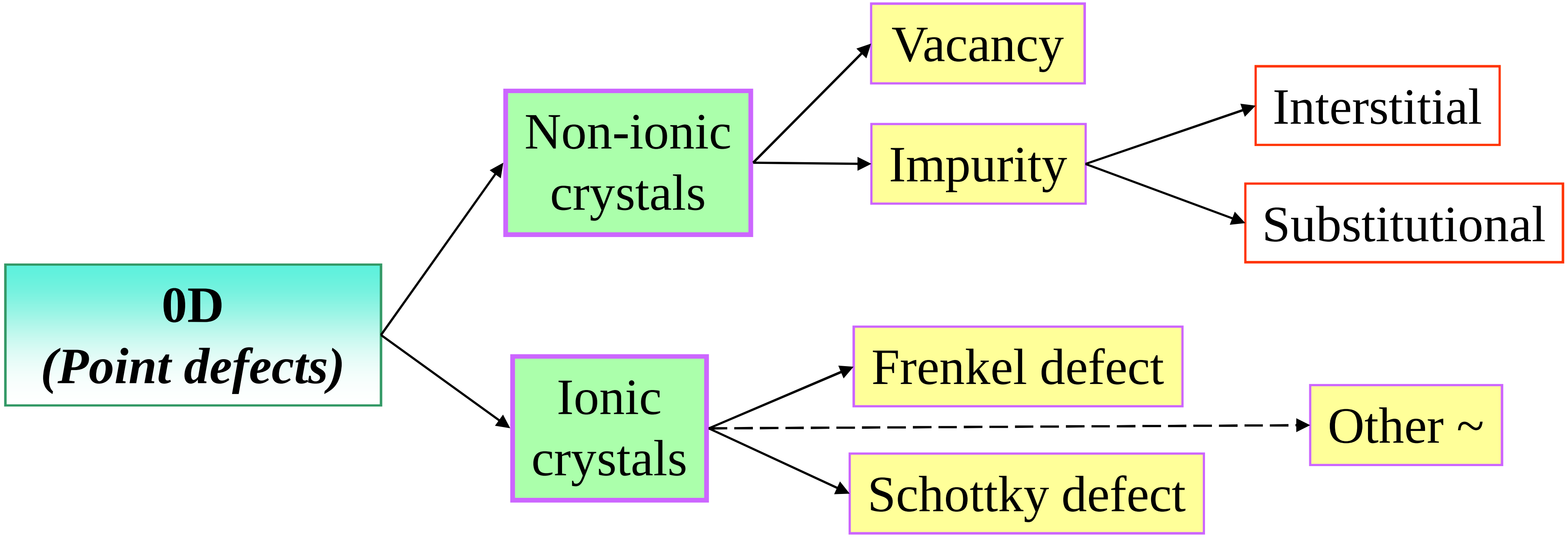
= 0.16×10^{-18} J/vacancy

- ❑ Certain equilibrium number of vacancies are preferred at T > 0K

CLASSIFICATION OF DEFECTS BASED ON DIMENSIONALITY

- **0D** ***(Point defects)***
  - Vacancy
  - Impurity
  - Frenkel defect
  - Schottky defect
- **1D** ***(Line defects)***
  - Dislocation
  - Disclination
  - Dispiration
- ***2D*** ***(Surface / Interface)***
  - Surface
  - Interphase boundary
  - Grain boundary
  - Twin boundary
  - Stacking faults
- ***3D*** ***(Volume defects)***
  - Twins
  - Precipitate
  - Faulted region
  - Voids / Cracks
  - *Thermal vibration*

Point Defects



0D

(Point defects)

Non-ionic crystals

Vacancy

Impurity

Interstitial

Substitutional

Ionic crystals

Frenkel defect

Other ~

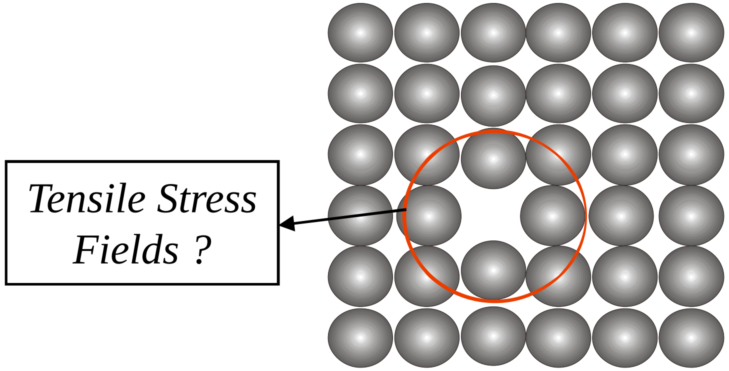
Schottky defect

- ☐ Imperfect point-like regions in the crystal about the size of 1-2 atomic diameters

Point Defects : Non-ionic crystals

Vacancy

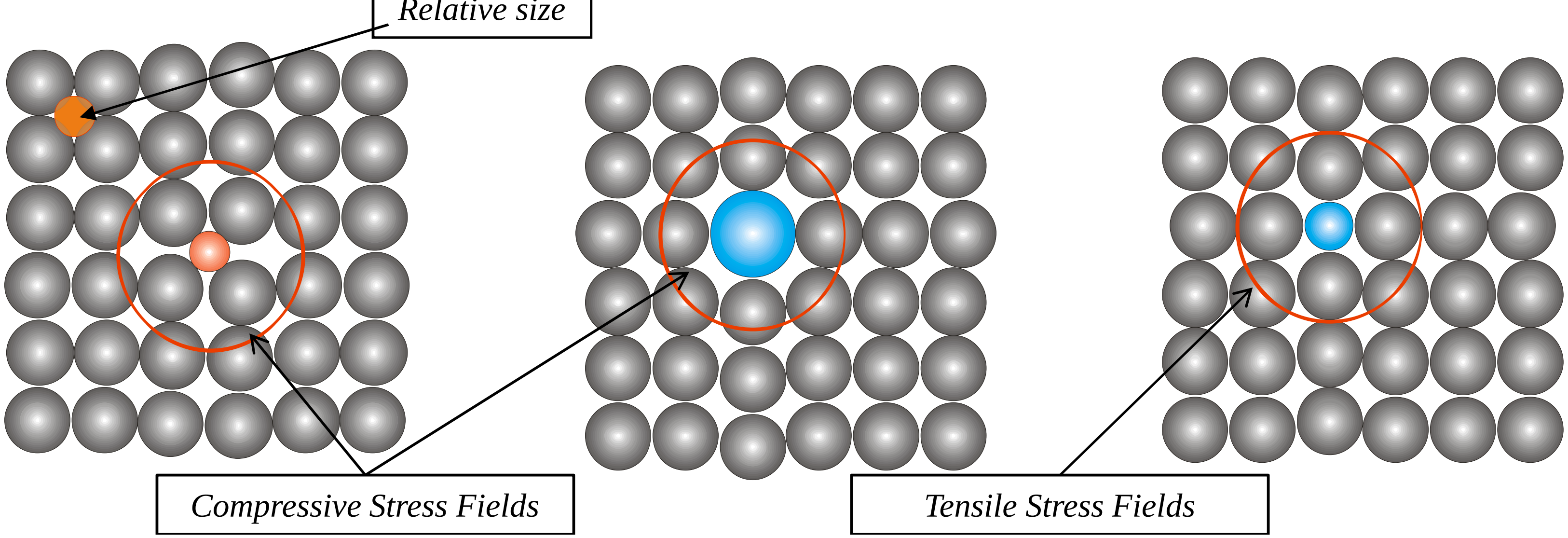
- ❑ Missing atom from an atomic site
- ❑ Atoms around the vacancy displaced
- ❑ Tensile stress field produced in the vicinity



Impurity → Interstitial

Impurity → Substitutional

- ❑ Substitutional Impurity
  - Foreign atom replacing the parent atom in the crystal
  - E.g. **Cu** sitting in the lattice site of FCC-**Ni**
- ❑ Interstitial Impurity
  - Foreign atom sitting in the void of a crystal
  - E.g. **C** sitting in the octahedral void in HT FCC-**Fe**



Interstitial **C** sitting in the octahedral void in HT FCC-**Fe**

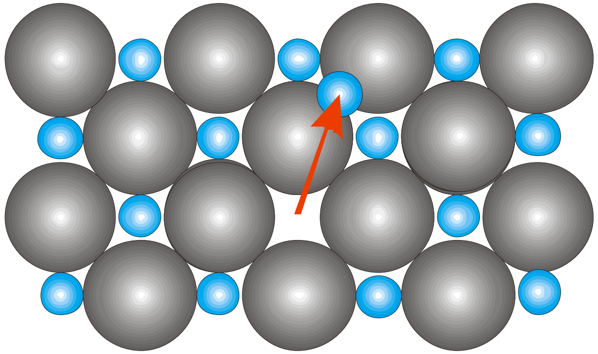
- $r_{\text{Octahedral void}} / r_{\text{FCC atom}} = 0.414$
- $r_{\text{Fe-FCC}} = 1.29$ Å ⇒ $r_{\text{Octahedral void}} = 0.414 \times 1.29 = 0.53$ Å
- $r_{\text{C}} = 0.71$ Å
- ⇒ Compressive strains around the C atom
- Solubility limited to 2 wt% (9.3 at%)

Interstitial **C** sitting in the octahedral void in LT BCC-**Fe**

- $r_{\text{Tetrahedral void}} / r_{\text{BCC atom}} = 0.29$ • $r_{\text{C}} = 0.71$ Å
- $r_{\text{Fe-BCC}} = 1.258$ Å ⇒ $r_{\text{Tetrahedral void}} = 0.29 \times 1.258 = 0.364$ Å
- ► But C sits in smaller octahedral void- displaces fewer atoms
- ⇒ Severe compressive strains around the C atom
- Solubility limited to 0.008 wt% (0.037 at%)

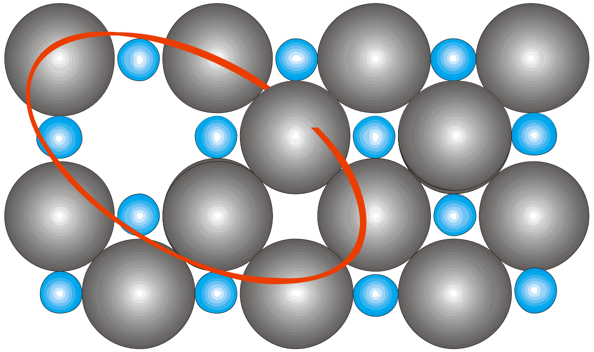
Point Defects : Ionic crystals

❑ *Overall electrical neutrality has to be maintained*



Frenkel defect

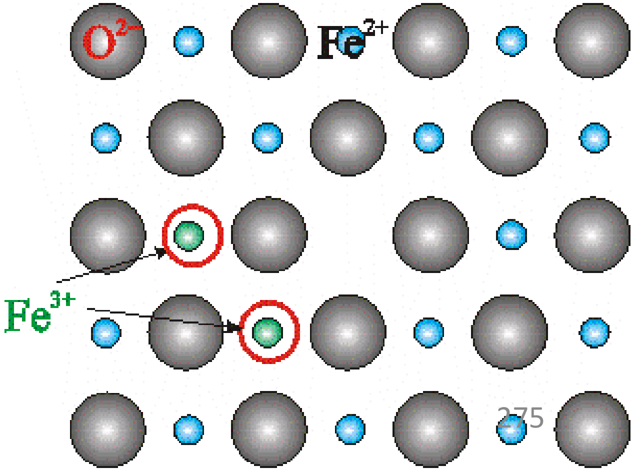
- Cation (being smaller get displaced to interstitial voids
- E.g. AgI, CaF_2



Schottky defect

- Pair of anion and cation vacancies
- E.g. Alkali halides

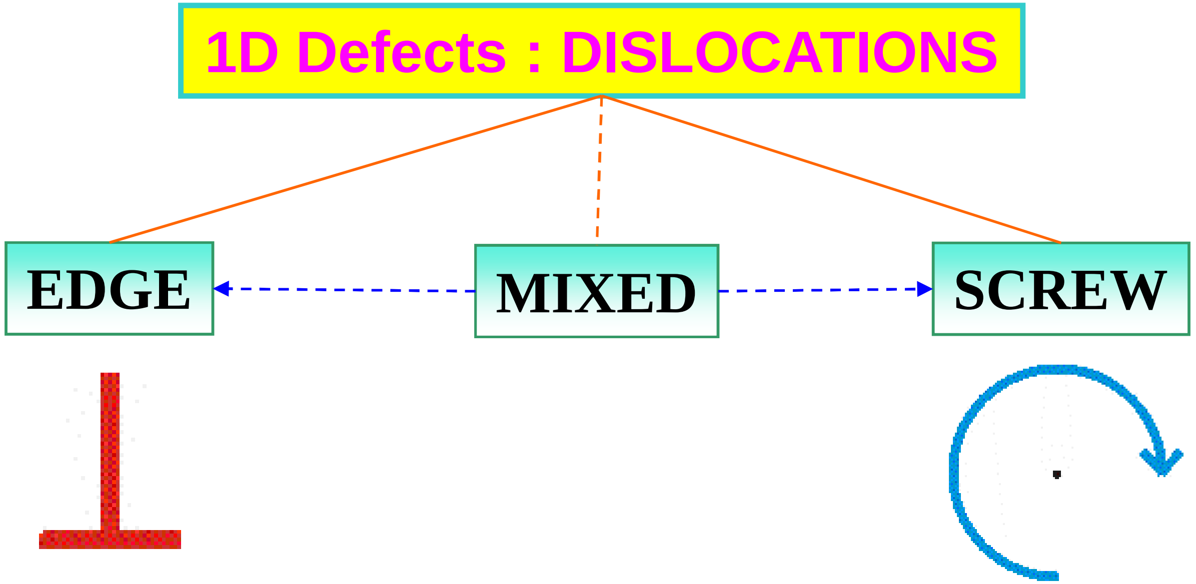
Other defects due to charge balance



- ❑ FeO heated in oxygen atmosphere → Fe_xO *($x < 1$)*
- ❑ Vacant cation sites are present
- ❑ Charge is compensated by conversion of ferrous to ferric ion:

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

- ❑ For every vacancy (of Fe cation) two ferrous ions are converted to ferric ions → provides the 2 electrons required by excess oxygen



1D Defects : DISLOCATIONS

EDGE

MIXED

SCREW

- Usually dislocations have a mixed character and *Edge* and *Screw* dislocations are the ideal extremes

DISLOCATIONS

Random

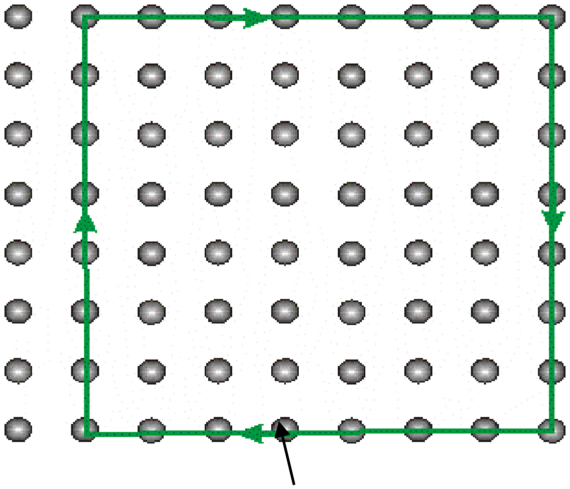
Structural

- Geometrically necessary dislocations

Introduction

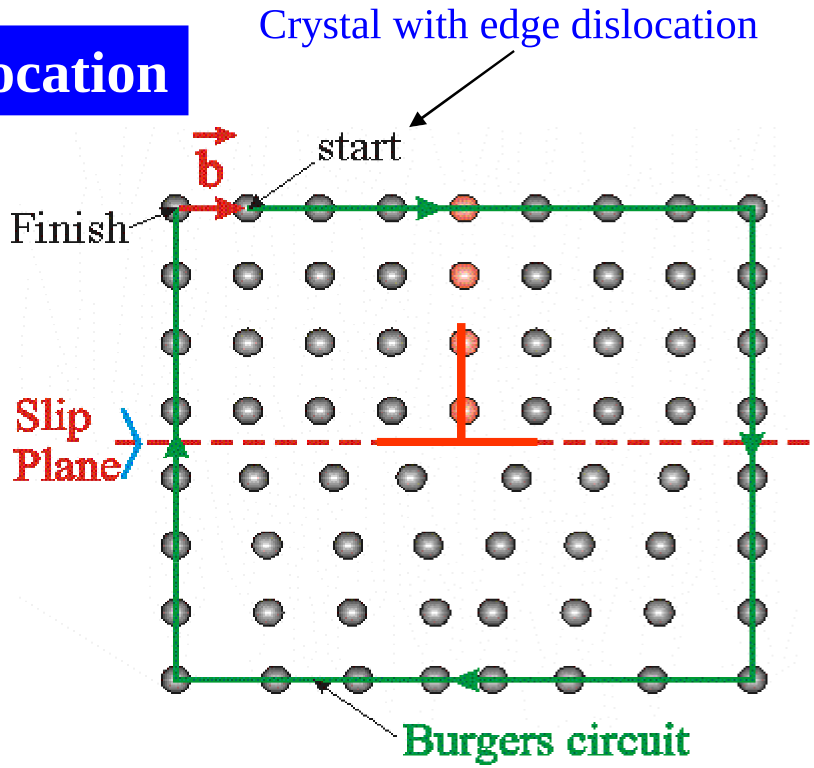
- Dislocation is a boundary between the slipped and the unslipped parts of the crystal lying over a slip plane
- The intersection of the extra half-plane of atoms with the slip plane defines the dislocation line *(for an edge dislocation)*
- Direction and magnitude of slip is characterized by the Burgers vector of the dislocation *(A dislocation is born with a Burgers vector and expresses it even in its death!)*
- The Burgers vector is determined by the Burgers Circuit
- Right hand screw (finish to start) convention is used for determining the direction of the Burgers vector
- As the periodic force field of a crystal requires that atoms must move from one equilibrium position to another ⇒ **b** must connect one lattice position to another *(for a full dislocation)*
- Dislocations tend to have as small a Burgers vector as possible
- The edge dislocation has compressive stress field above and tensile stress field below the slip plane.
- Dislocations are non-equilibrium defects and would leave the crystal if given an opportunity

Burgers Vector

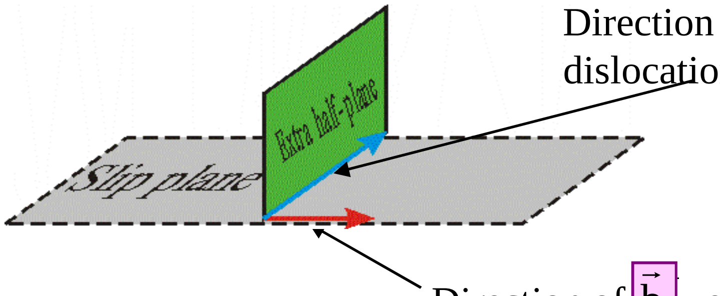


Perfect crystal

Edge dislocation

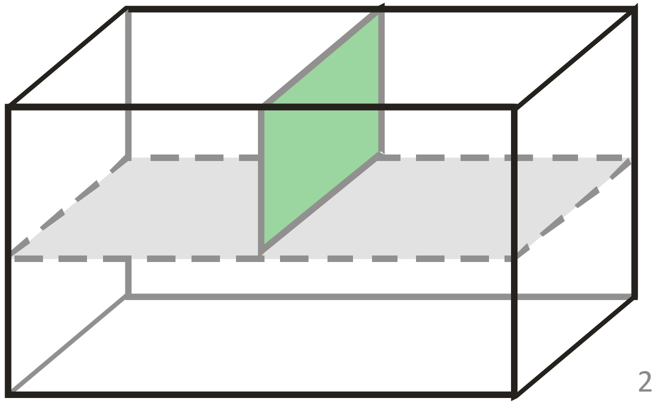


RHFS:
Right Hand Finish to Start convention



Direction of $\boxed{\vec{t}}$ vector
dislocation line vector

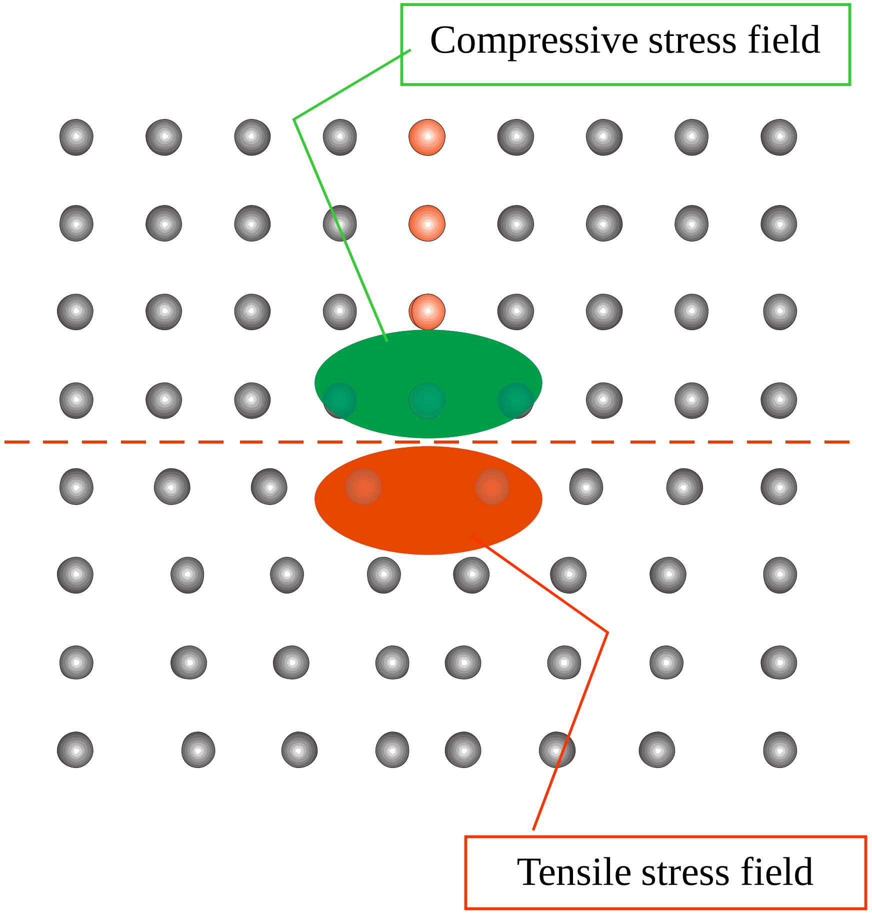
Direction of $\boxed{\vec{b}}$ vector



A dislocation has associated with it two vectors:

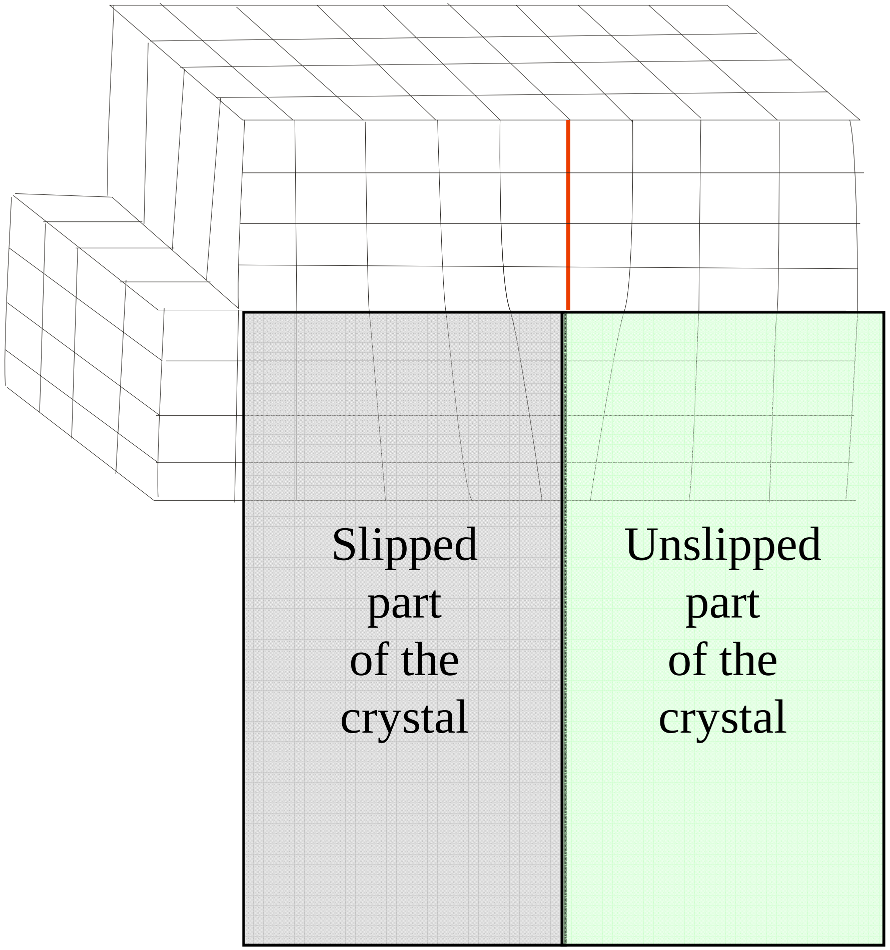
$\vec{t} \rightarrow$ A unit tangent vector along the dislocation line

$\vec{b} \rightarrow$ The Burgers vector



Compressive stress field

Tensile stress field

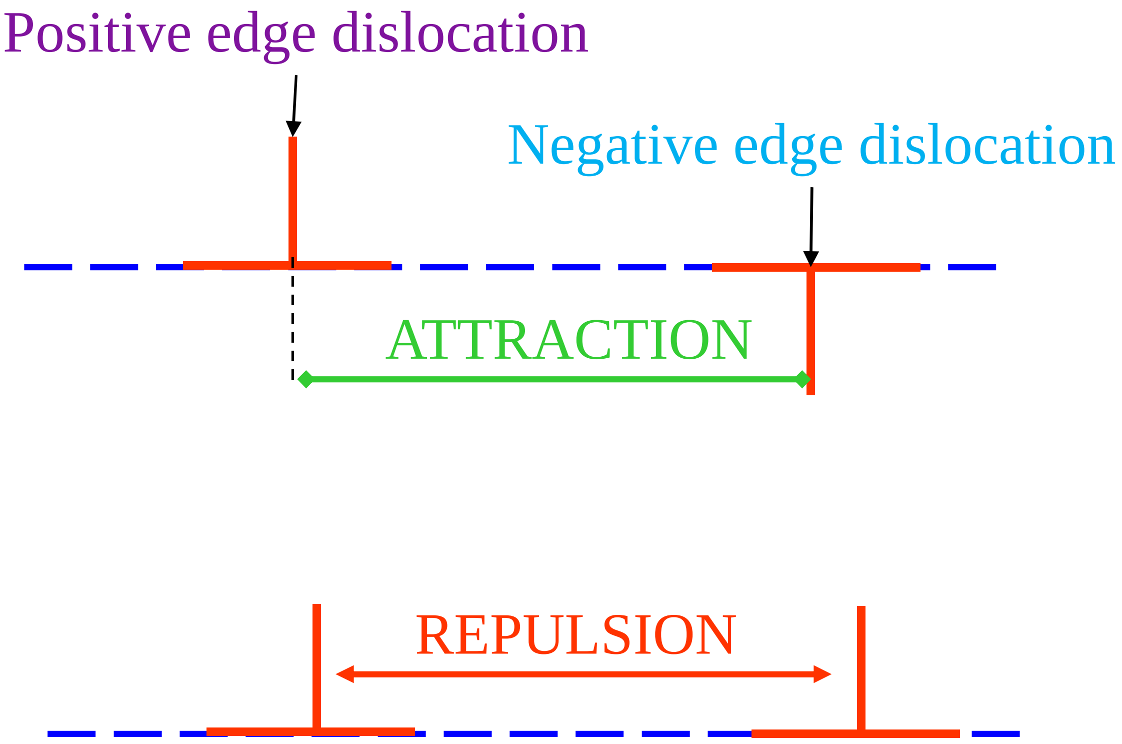


Slipped part of the crystal

Unslipped part of the crystal

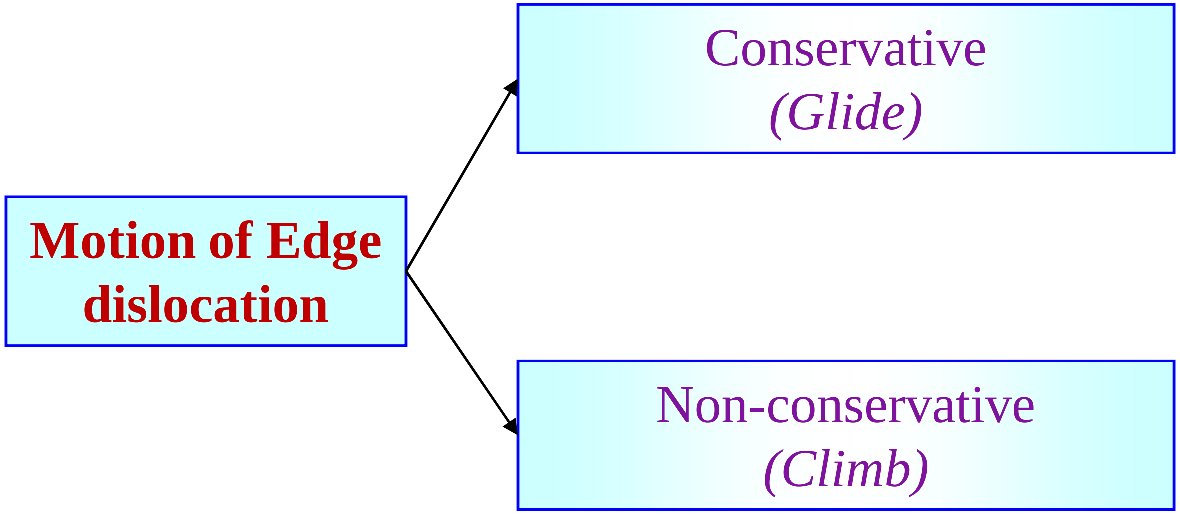
Dislocation is a boundary between the slipped and the unslipped parts of the crystal lying over a slip plane

+ve & -ve edge dislocations



Can come together and cancel one another

Motion of dislocations



Motion of Edge dislocation

Conservative
(Glide)

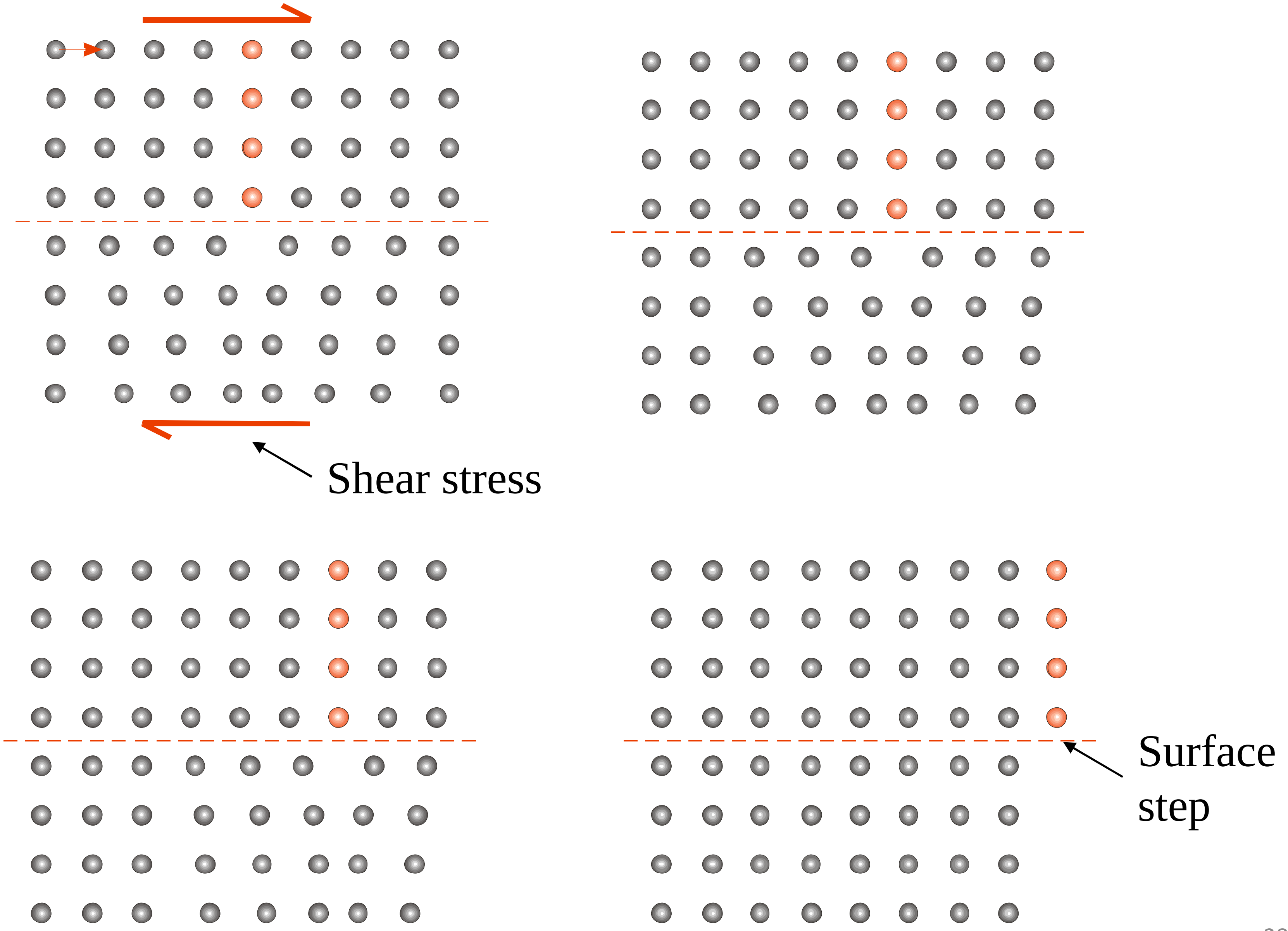
Motion of dislocations
On the slip plane

Non-conservative
(Climb)

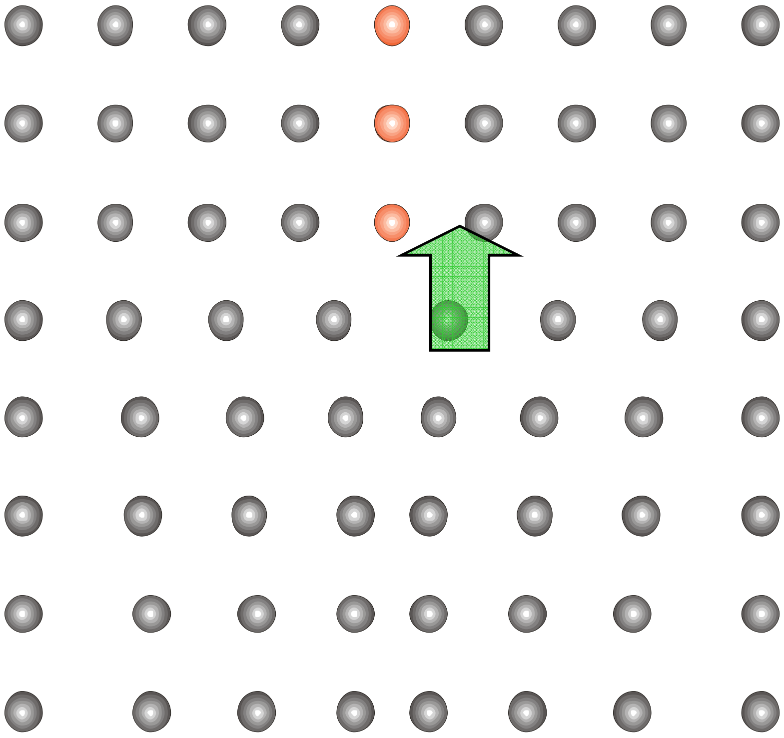
Motion of dislocation
⊥ to the slip plane

- For edge dislocation: as **b** ⊥ **t** → they define a plane → *the slip plane*
- Climb involves addition or subtraction of a row of atoms below the half plane
  - +ve climb = climb up → removal of a plane of atoms
  - –ve climb = climb down → addition of a plane of atoms

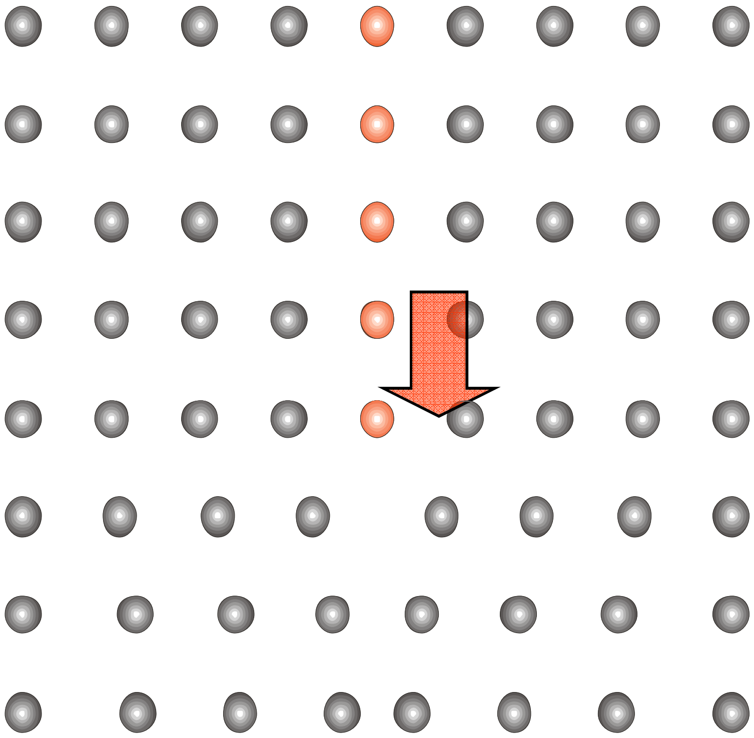
Edge Dislocation Glide



Edge Climb

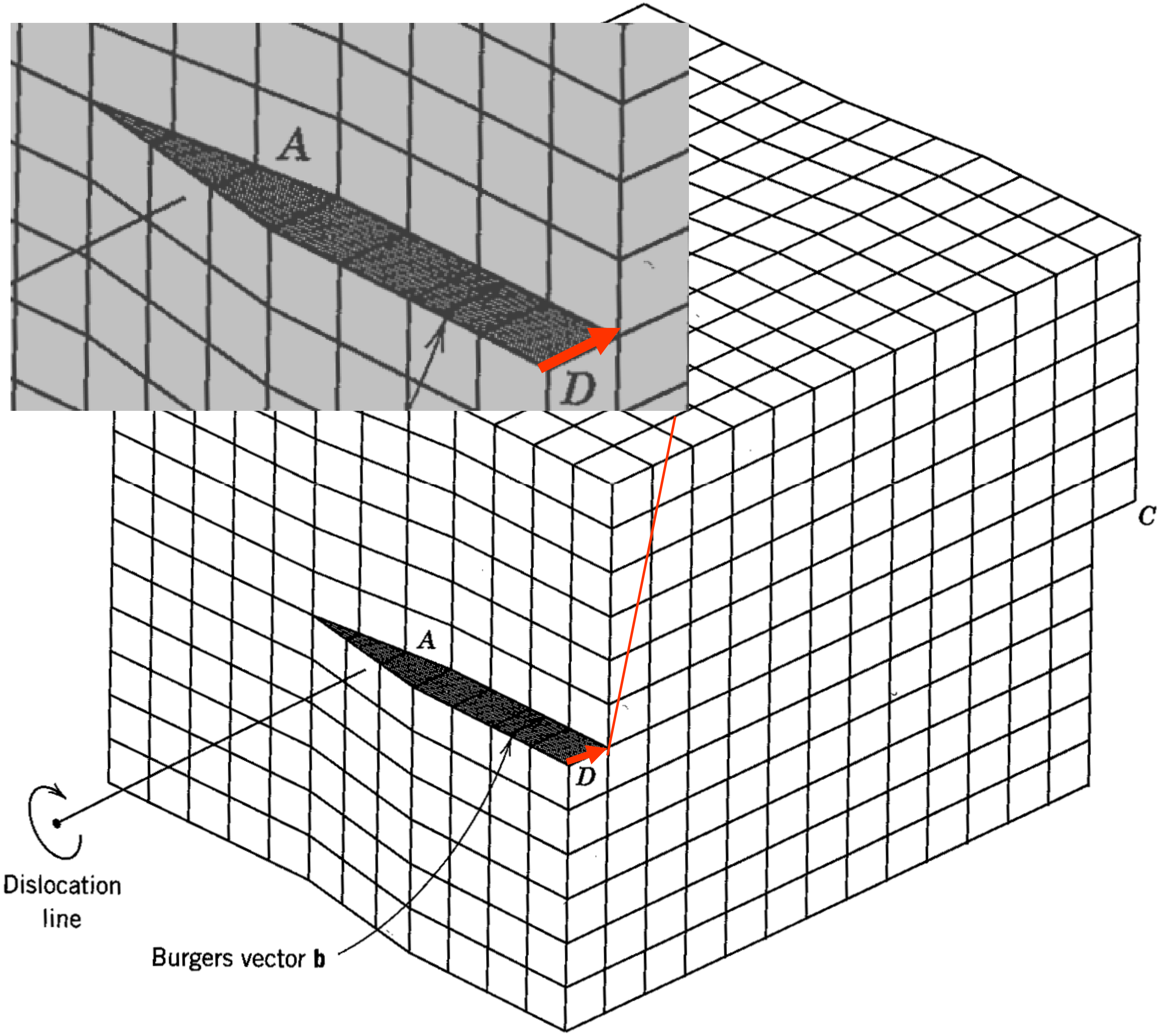


Positive climb
Removal of a row of atoms

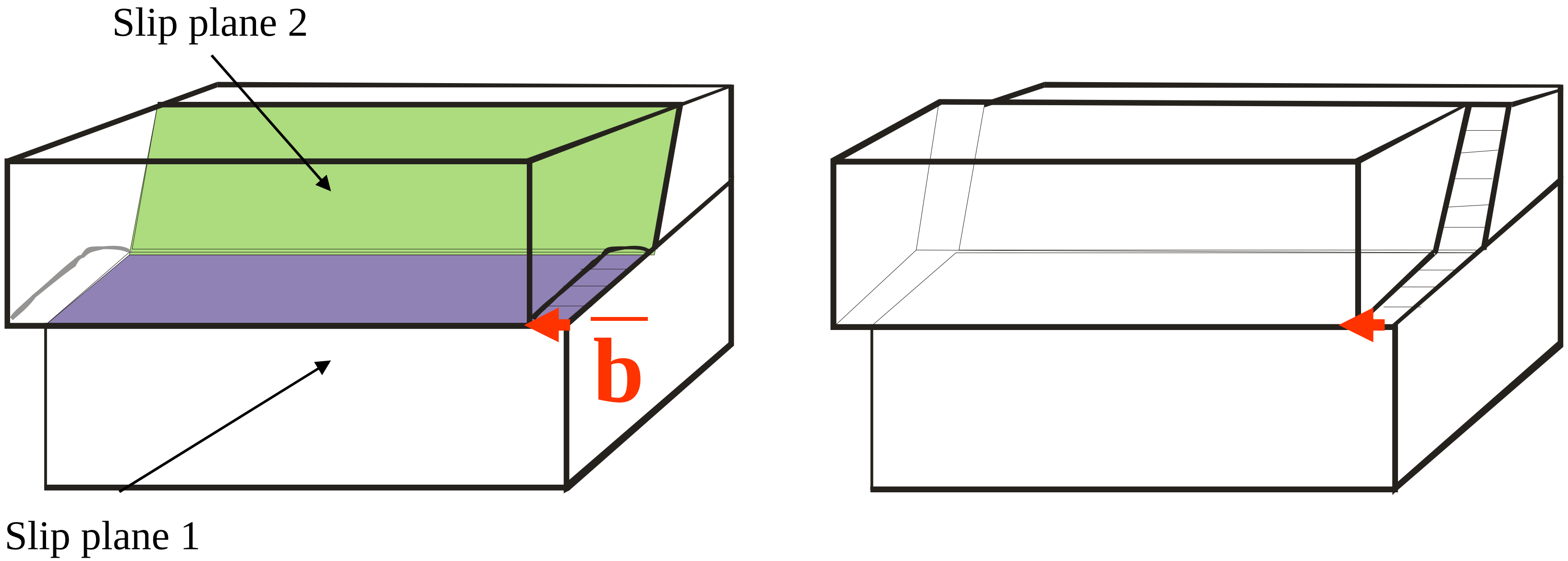


Negative climb
Addition of a row of atoms

Screw dislocation



Screw dislocation cross-slip



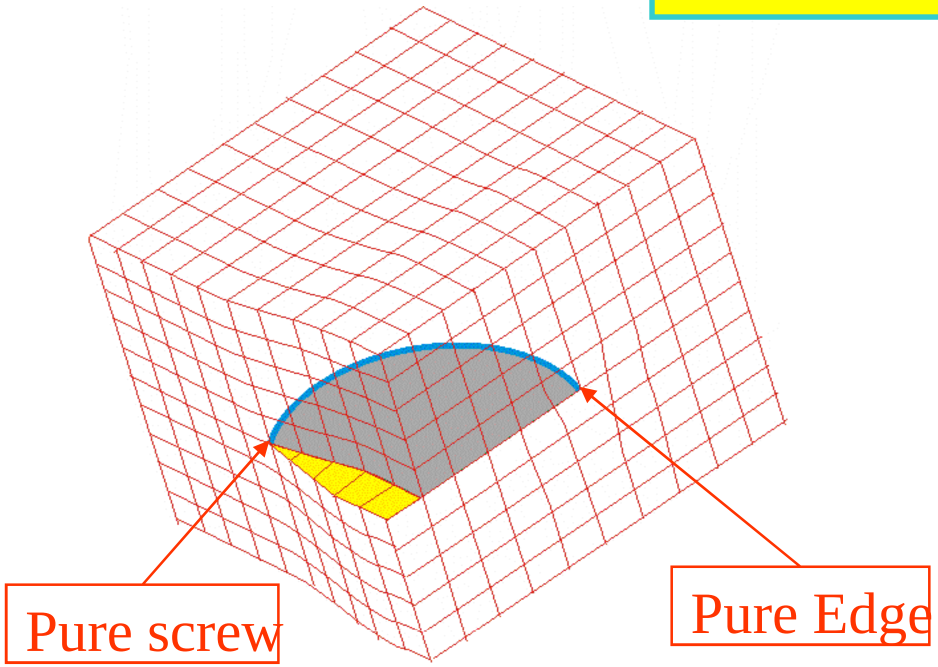
The dislocation is shown cross-slipping from the blue plane to the green plane

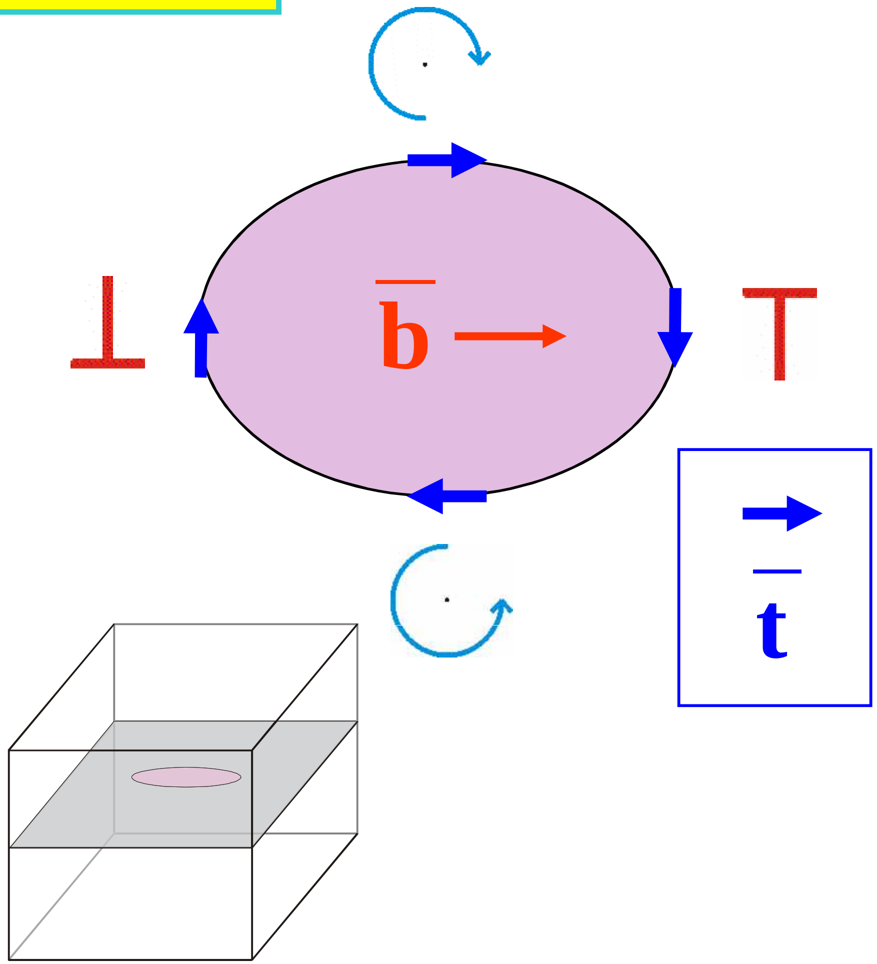
- ☐ The dislocation line ends on
  - ✓ The free surface of the crystal
  - ✓ Internal surface or interface
  - ✓ Closes on itself to form a loop
  - ✓ Ends in a node
- ☐ A node is the intersection point of more than two dislocations
- ☐ The vectoral sum of the Burgers vectors of dislocations meeting at a node = 0

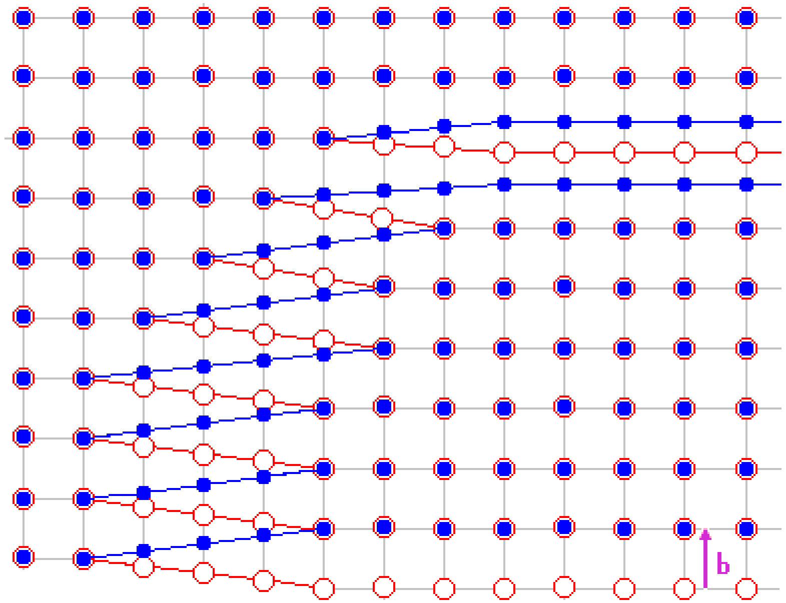
Geometric properties of dislocations

Dislocation Property	**Type of dislocation**	
	Edge	**Screw**
Relation between dislocation line (**t**) and **b**	⊥	||
Slip direction	|| to **b**	|| to **b**
Direction of dislocation line movement relative to **b**	||	⊥
Process by which dislocation may leave slip plane	climb	Cross-slip

Mixed dislocations







We are looking at the plane of the cut (sort of a semicircle centered in the lower left corner). Blue circles denote atoms just below, red circles atoms just above the cut. Up on the right the dislocation is a pure edge dislocation on the lower left it is pure screw. In between it is mixed. In the link this dislocation is shown moving in an animated illustration.

Energy of dislocations

- ☐ Dislocations have distortion energy associated with them
- ☐ E per unit length
- ☐ Edge → Compressive and tensile stress fields
  Screw → Shear strains

Energy of dislocation
- Elastic — E
- Non-elastic *(Core)* — ~E/10

Energy of a dislocation / unit length →

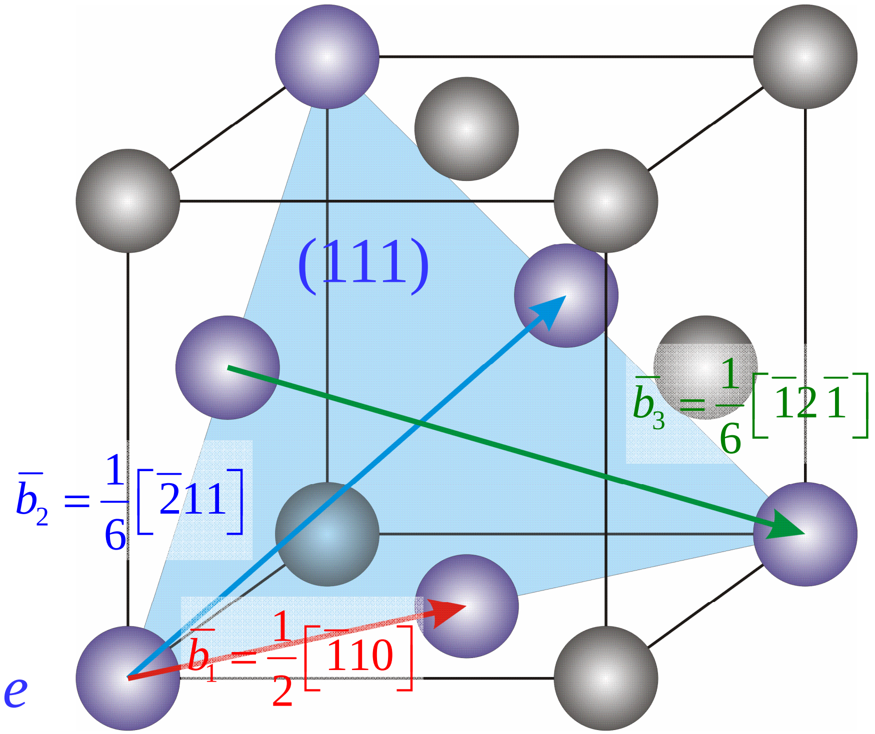
$$E \cong \frac{1}{2} G b^2$$

G → (μ) shear modulus
b → |**b**|

Dislocations will have as small **b** as possible

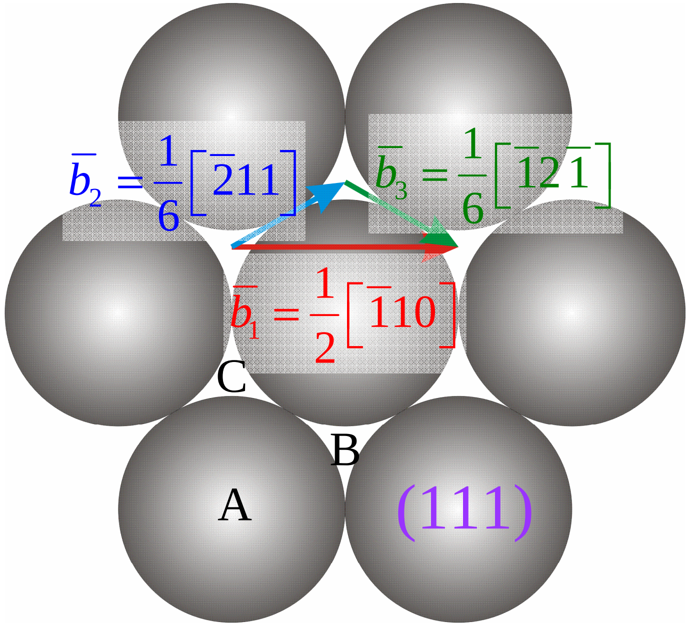
Dislocations
(in terms of lattice translation)
- Full — **b** → Full lattice translation
- Partial — **b** → Fraction of lattice translation

Dissociation of dislocations : FCC



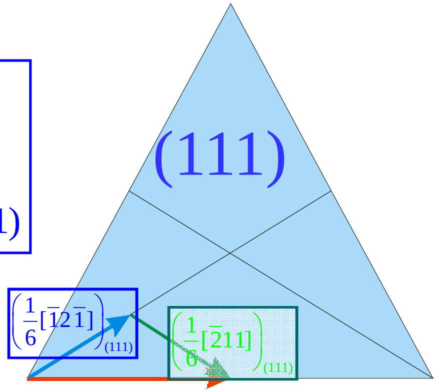
(111)
Slip plane

Some of the atoms are omitted for clarity



$$\boxed{\left(\frac{1}{2}[\bar{1}10]\right)_{(111)}} \rightarrow \boxed{\left(\frac{1}{6}[\bar{1}2\bar{1}]\right)_{(111)}} + \boxed{\left(\frac{1}{6}[\bar{2}11]\right)_{(111)}}$$

Shockley Partials

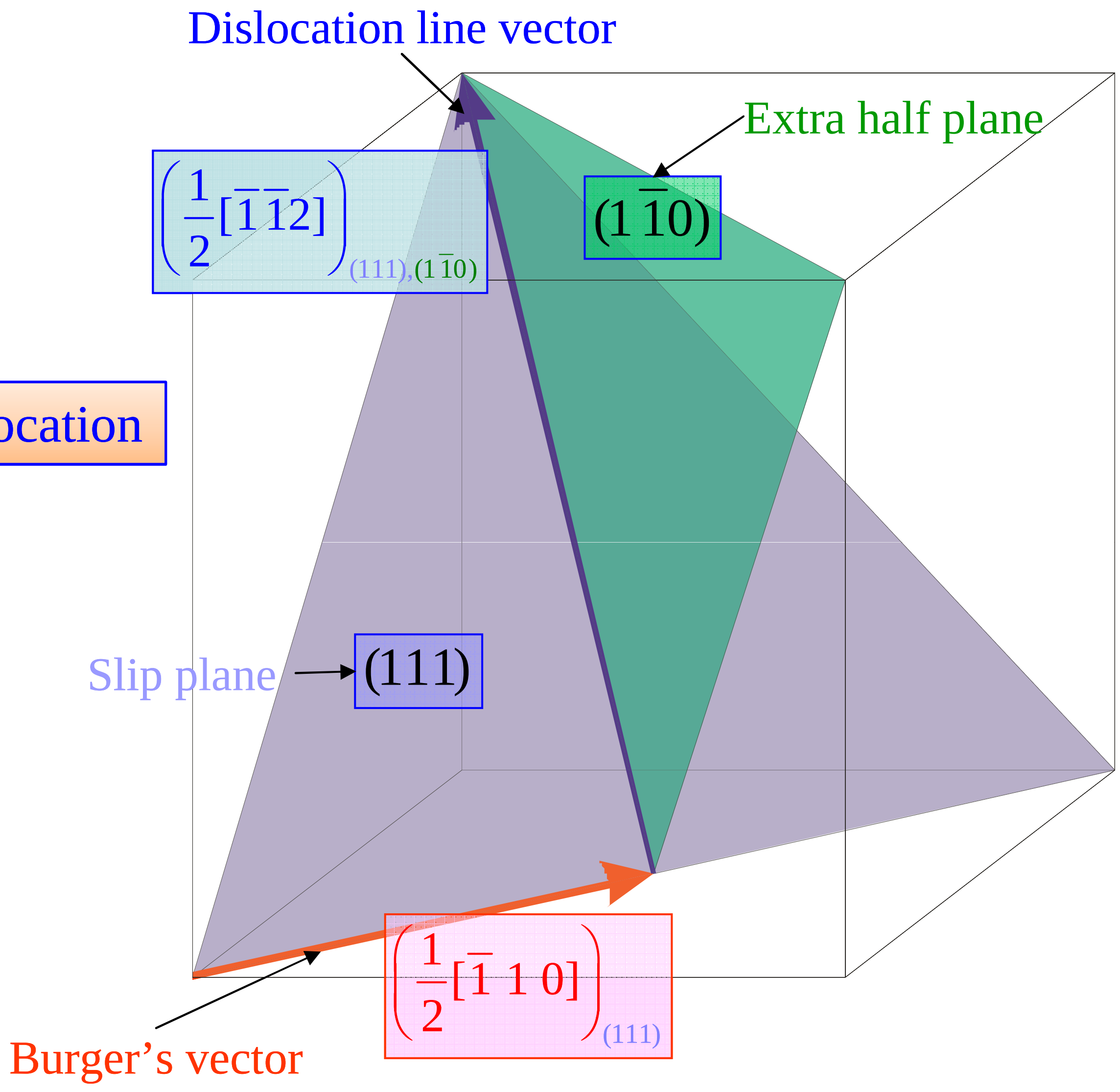


$$b_1^2 > (b_2^2 + b_3^2)$$

½ > ⅓

Dissociation of dislocations : FCC

Pure edge dislocation



Dislocation line vector

$\left(\frac{1}{2}[\bar{1}\bar{1}2]\right)_{(111),(1\bar{1}0)}$

Extra half plane

$(1\bar{1}0)$

Slip plane

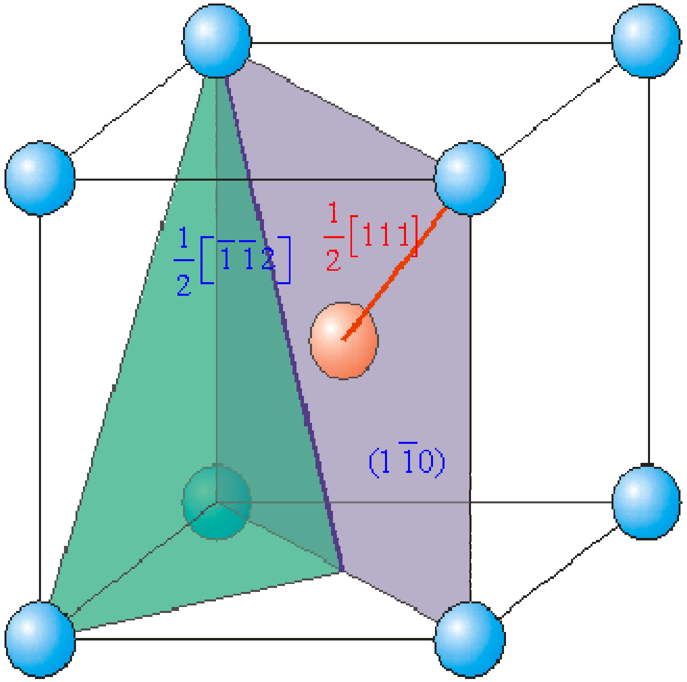
(111)

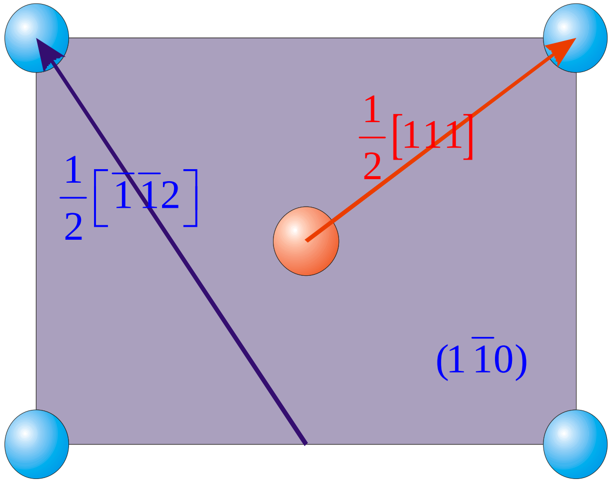
Burger's vector

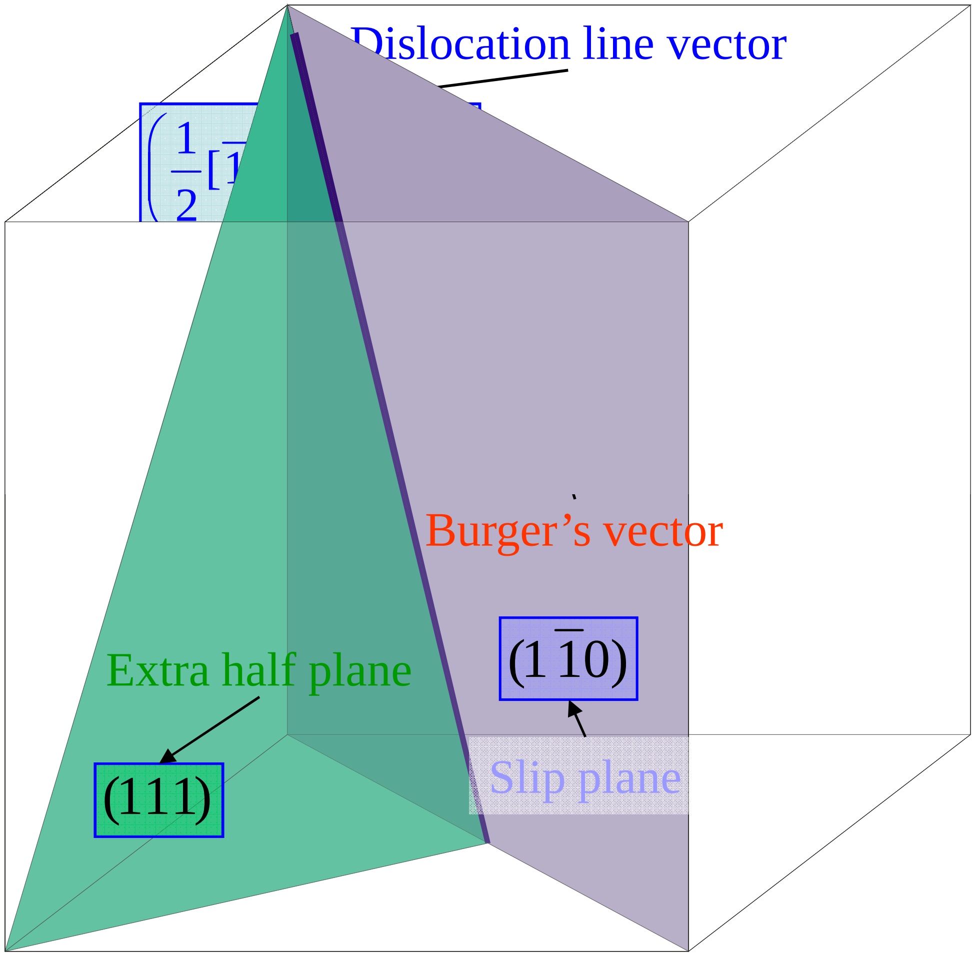
$\left(\frac{1}{2}[\bar{1}\,1\,0]\right)_{(111)}$

The extra- "half plane" consists of two 'planes' of atoms

Dissociation of dislocations : BCC





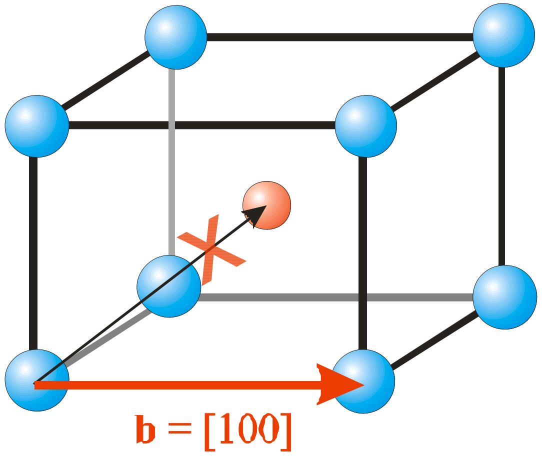


Pure edge dislocation

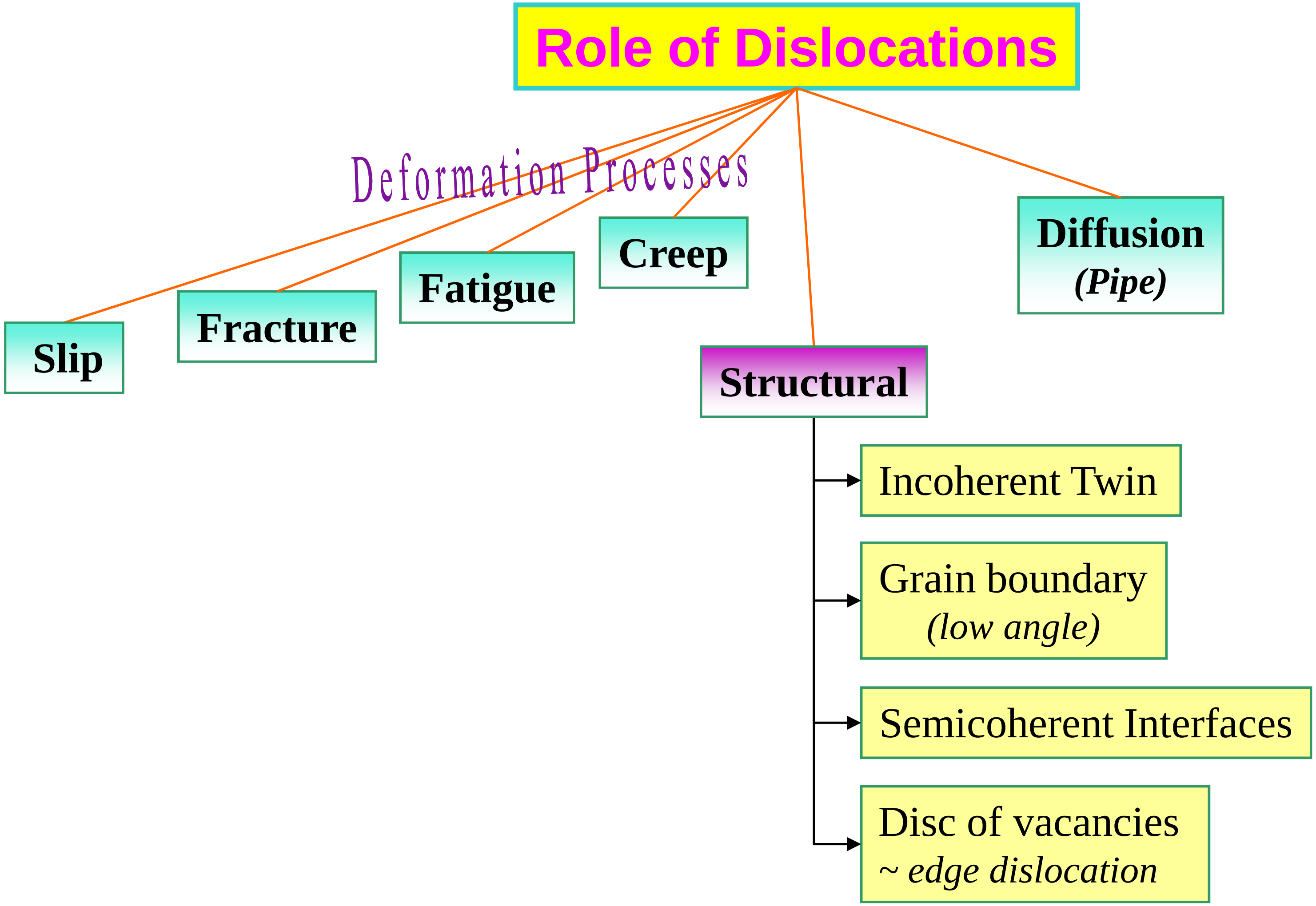
Dislocations in Ionic crystals

- ☐ In ionic crystals if there is an extra half-plane of atoms contained only atoms of one type then the charge neutrality condition would be violated ⇒ unstable condition
- ☐ Burgers vector has to be a full lattice translation
  CsCl → **b = <100>** *Cannot be ½<111>*
  NaCl → **b = ½ <110>** *Cannot be ½<100>*
- ☐ This makes Burgers vector large in ionic crystals
  Cu → |**b**| = 2.55 Å
  NaCl → |**b**| = 3.95 Å

CsCl



Role of Dislocations



Deformation Processes

Slip

Fracture

Fatigue

Creep

Structural

- Incoherent Twin
- Grain boundary *(low angle)*
- Semicoherent Interfaces
- Disc of vacancies ~ *edge dislocation*

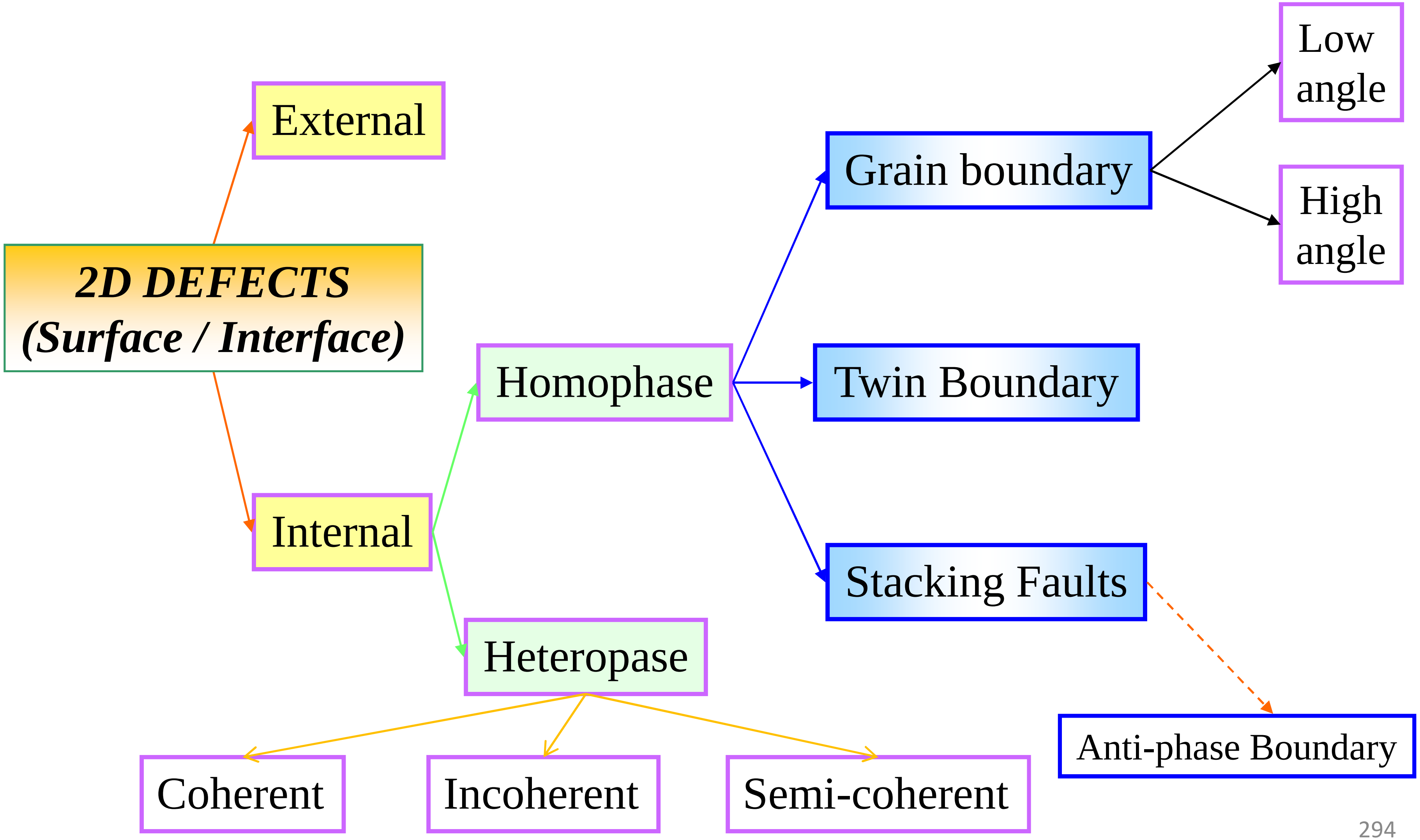
Diffusion ***(Pipe)***

Formation of dislocations (in the bulk of the crystal)

- ☐ Due to accidents in crystal growth from the melt
- ☐ Mechanical deformation of the crystal

2D Defects : Surface defects

- ☐ 2D in a mathematical sense
- ☐ The region of distortion is ~ few atomic diameters in thickness



2D DEFECTS (Surface / Interface)

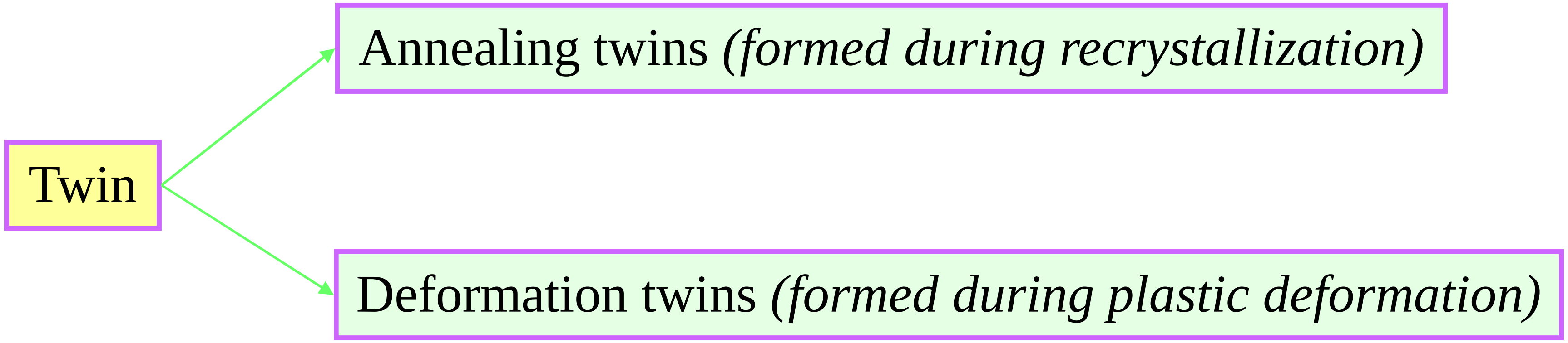
- External
- Internal
  - Homophase
    - Grain boundary
      - Low angle
      - High angle
    - Twin Boundary
    - Stacking Faults
      - Anti-phase Boundary
  - Heteropase
    - Coherent
    - Incoherent
    - Semi-coherent

Grain Boundary

- The grain boundary region may be distorted with atoms belonging to neither crystal
- The thickness may be of the order of few atomic diameters
- The crystal orientation changes abruptly at the grain boundary
- In an low angle boundary the orientation difference is $< 10^o$
- In the low angle boundary the distortion is not so drastic as the high-angle boundary → can be described as an array of dislocations
- Grain boundary energy is responsible for grain growth on heating ~ ($>0.5T_m$)
- Large grains grow at the expense of smaller ones
- The average no. of nearest neighbours for an atom in the grain boundary of a close packed crystal is 11

Twin Boundary

- The atomic arrangement on one side of the twin boundary is related to the other side by a symmetry operation (usually a mirror)
- Twin boundaries usually occur in pairs such that the orientation difference introduced by one is restored by the other
- The region between the regions is called the twinned region



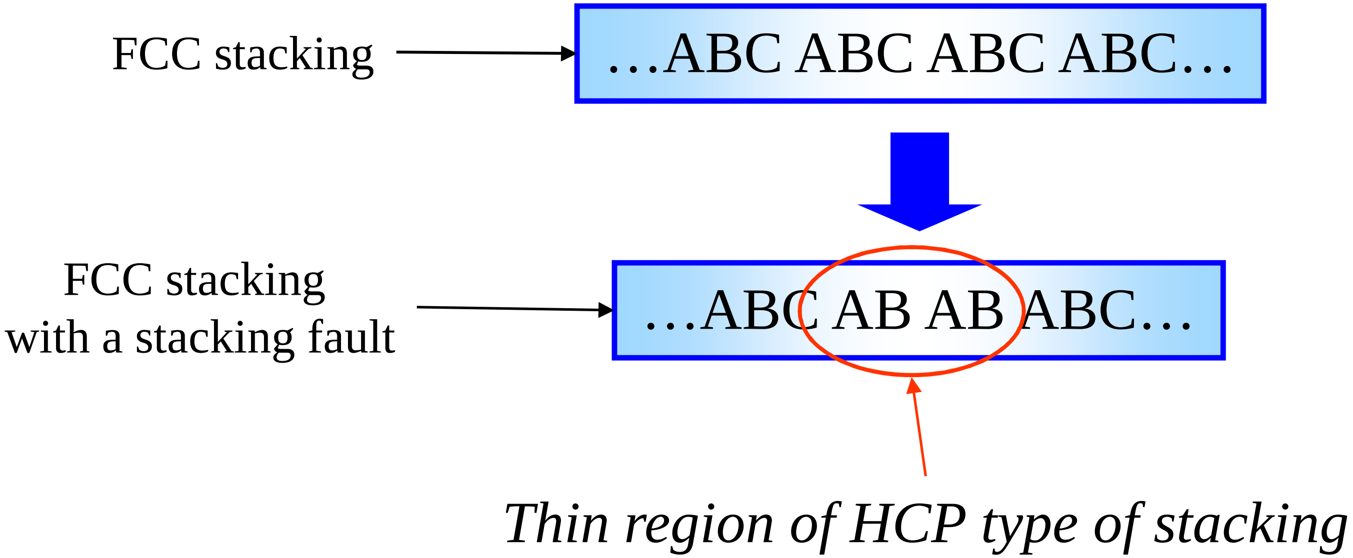
Twin

Annealing twins *(formed during recrystallization)*

Deformation twins *(formed during plastic deformation)*

Stacking Fault

- Error in the sequence of stacking atomic planes → Stacking fault
- Defined by a shift vector



FCC stacking → …ABC ABC ABC ABC…

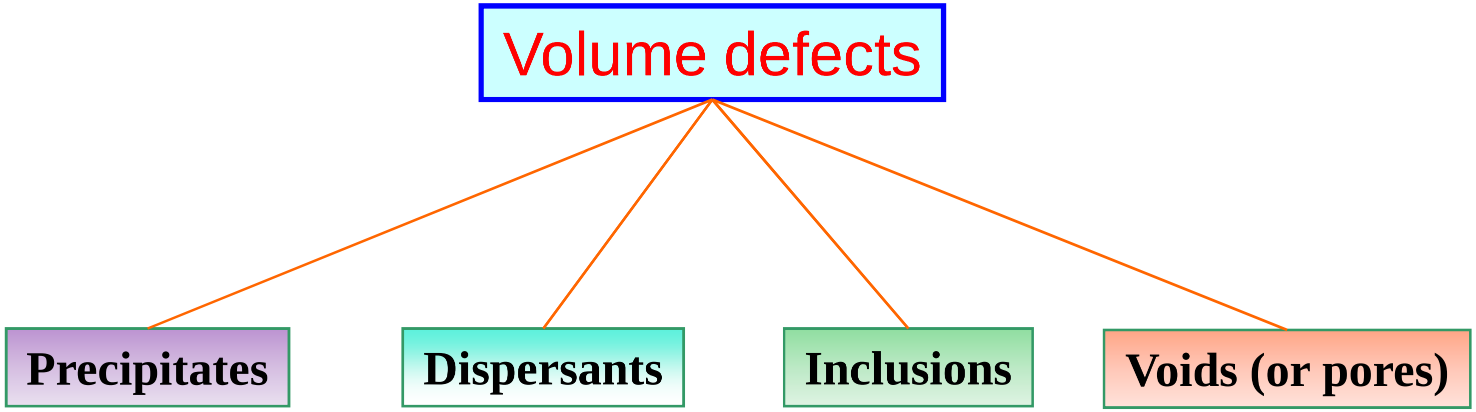
FCC stacking
with a stacking fault → …ABC AB AB ABC…

Thin region of HCP type of stacking

- In above the number of nearest neighbours remains the same
  but next-nearest neighbours are different than that in FCC
- Stacking fault energy ~ 0.01 – 0.05 J/m^2
- Stacking fault in HCP can lead to thin region of FCC kind of stacking

3D Defects : volume defects

Volume defects in crystals are three dimensional aggregates of atoms or vacancies


Volume defects

Precipitates

Dispersants

Inclusions

Voids (or pores)

PRECIPITATES

Precipitates are small particles that are introduced into the matrix by solid state reactions. While precipitates are used for several purposes, their most common purpose is to increase the strength of structural alloys by acting as obstacles to the motion of dislocations. Their efficiency in doing this depends on their size, their internal properties, and their distribution through the lattice. However, their role in the microstructure is to modify the behavior of the matrix rather than to act as separate phases in their own right.

3D Defects : volume defects

DISPERSANTS

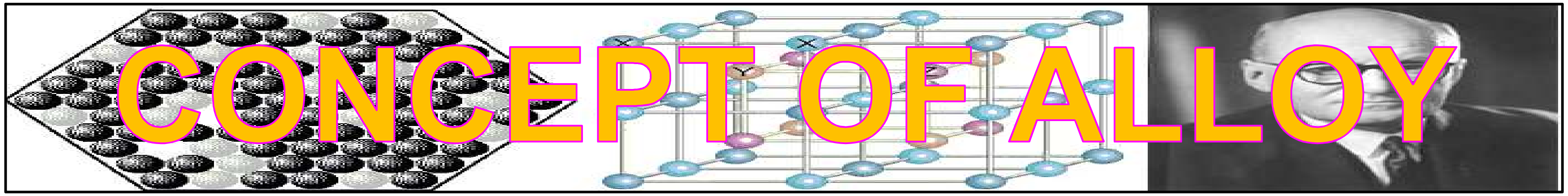
Dispersants are larger particles that behave as a second phase as well as influencing the behavior of the primary phase. They may be large precipitates, grains, or polygranular particles distributed through the microstructure. When a microstructure contains dispersants such properties as mechanical strength and electrical conductivity are some average of the properties of the dispersant phase and the parent.

INCLUSIONS

Inclusions are foreign particles or large precipitate particles. They are usually undesirable constituents in the microstructure. For example, inclusions have a deleterious effect on the useful strength of structural alloys since they are preferential sites for failure. They are also often harmful in microelectronic devices since they disturb the geometry of the device by interfering in manufacturing, or alter its electrical properties by introducing undesirable properties of their own.

VOIDS (OR PORES)

Voids (or pores) are caused by gases that are trapped during solidification or by vacancy condensation in the solid state. They are almost always undesirable defects. Their principal effect is to decrease mechanical strength and promote fracture at small loads.



CONCEPT OF ALLOY

Avala Lava Kumar* : Suneeti Purohit : Gautam Behera

Department of Metallurgical & Materials Engineering (MME)

Veer Surendra Sai University of Technology (VSSUT), Burla -768018

**E-mail : lavakumar.vssut@gmail.com*

Introduction

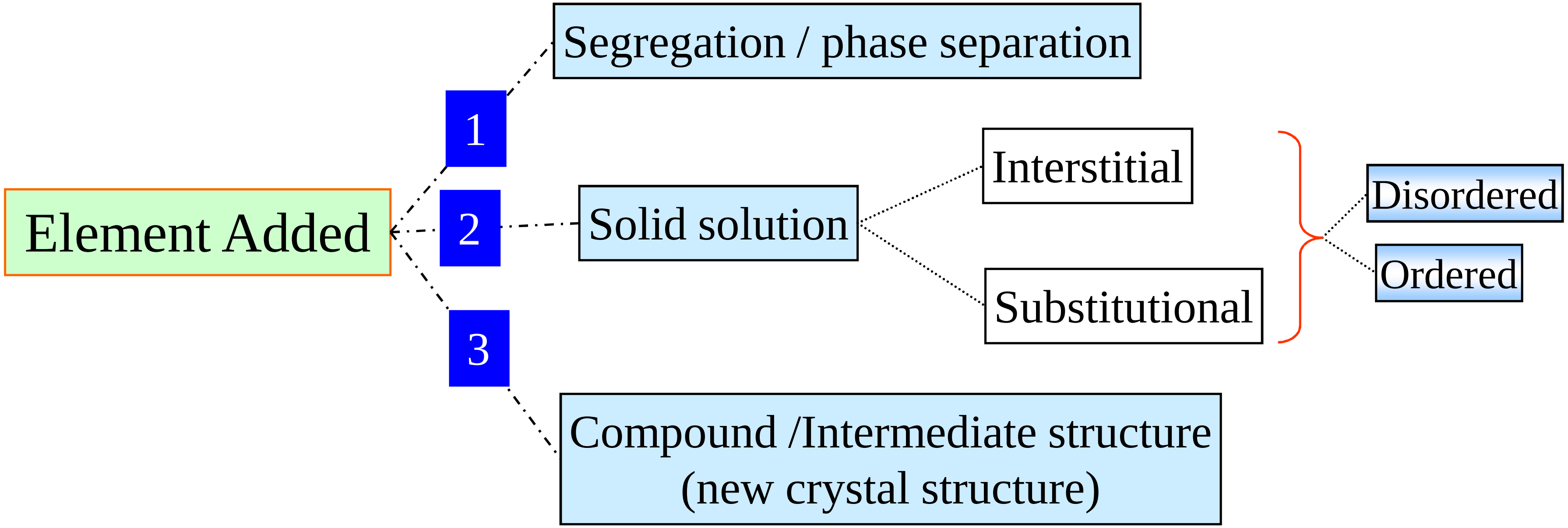
- An alloy is a substance that has metallic properties and is composed of two or more chemical elements, of which at least one is a metal.
- An alloy system contains all the alloys that can be formed by several elements combined in all possible proportions. If the system is made up of two elements, it is called a *binary alloy system*; three elements, a *ternary alloy system*; etc.
- Taking only 45 of the most common metals, any combination of two gives 990 binary systems. Combinations of three give over 14,000 ternary systems.
- However, in each system, a large number of different alloys are possible. If the composition is varied by 1 percent, each binary system will yield 100 different alloys.
- *Since commercial alloys often contain many elements, it is apparent that the number of possible alloys is almost infinite.*
- Alloys may be homogeneous (uniform) or mixtures. If the alloy is homogeneous it will consist of a single phase, and if it is a mixture it will be a combination of several phases.
- The uniformity of an alloy phase is not determined on an atomic scale, such as the composition of each unit lattice cell, but rather on a much larger scale.

Phase

- A phase is anything which is homogeneous and physically distinct.
- Any structure which is visible as physically distinct microscopically may be considered as a phase
- For most pure elements the term *phase* is synonymous with state. There is, therefore, for pure elements, a gaseous, liquid, and solid phase.
- Some metals are allotropic in the solid state and will have different solid phases. When the metal undergoes a change in crystal structure, it undergoes a phase change since each type of crystal structure is physically distinct.
- In a pure material when other elements are added intentionally they are called alloying elements*
- Alloying elements are added to improve certain properties of the pure element
- The alloying element can be accommodated in one of the three possibilities as shown in the figure below

* When added small quantity it is often called doping
‘In Principle’ there is no difference between an ‘*impurity*’ and ‘*alloying*’

Classification of alloys



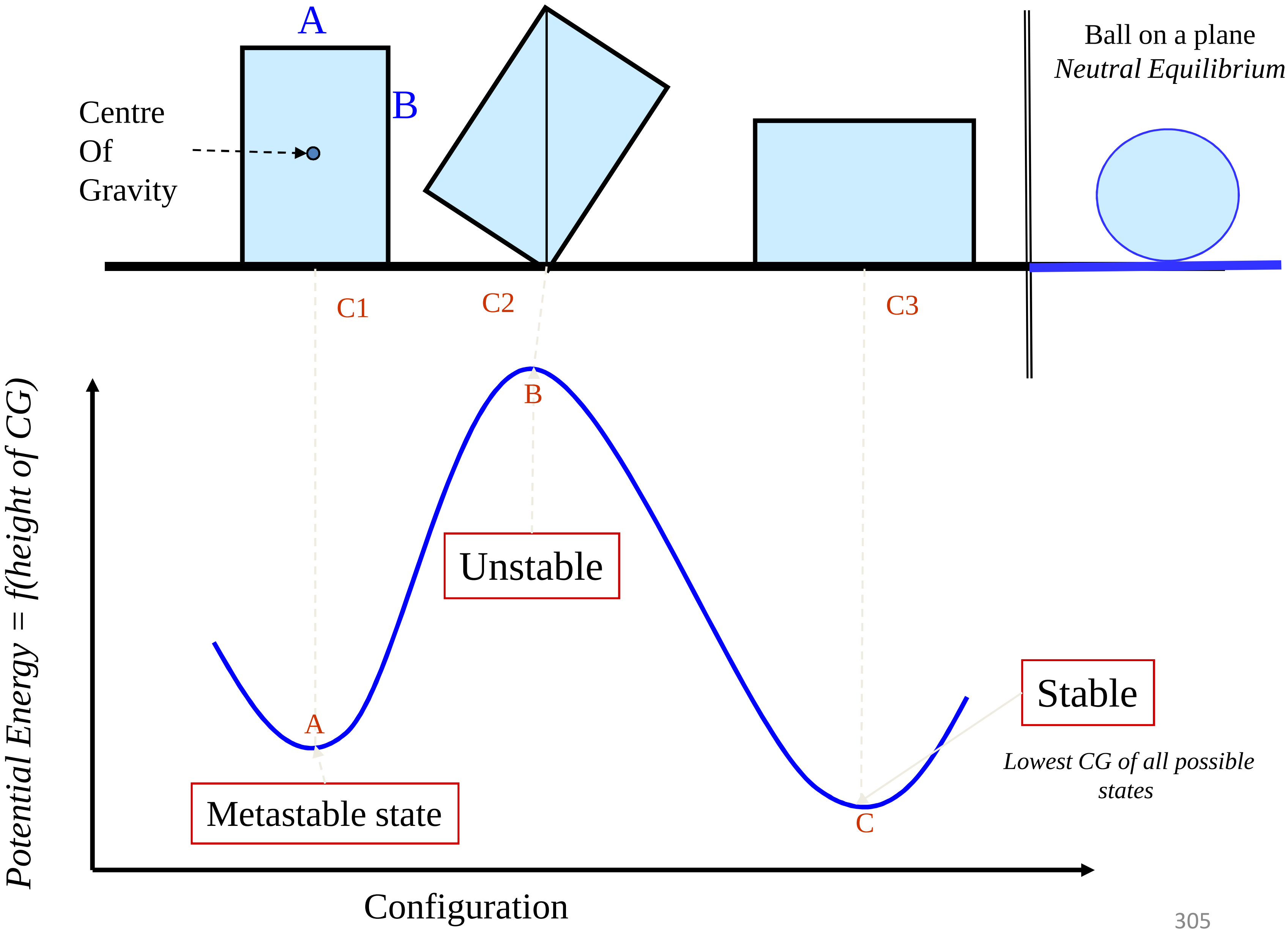
1 Segregation / phase separation

- ❑ The added element does not dissolve* in the parent/matrix phase →
  - ➢ in may form a separate phase**
  - ➢ in a polycrystal it may go to the grain boundary
  - ➢ in may segregate to other defects like dislocation cores etc.
- ❑ The solubility in the case of a substitutional solid solution is given by Hume-Rothery rules (considered soon)

Solid Solutions

- Any solution is composed of two parts: a solute and a solvent. The solute is the minor part of the solution or the material which is dissolved, while the solvent constituents the major portion of the solution.
- *The most common solutions involve water as the solvent, such as sugar or salt dissolved in water.*
- There are three possible conditions for a solution: unsaturated, saturated, and supersaturated.
- If the solvent is dissolving less of the solute than it could dissolve at a given temperature and pressure, it is said to be unsaturated.
- If it is dissolving the limiting amount of solute, it is saturated.
- If it is dissolving more of the solute than it should, under equilibrium conditions, the solution is supersaturated.
- The supersaturated condition is an unstable one, and given enough time or a little energy, the solution tends to become stable or saturated by rejecting or precipitating the excess solute.
- ***A solid solution is simply a solution in the solid state and consists of two kinds of atoms combined in one type of space lattice.***

Mechanical Equilibrium of a Rectangular Block



Substitutional Solid Solutions

2 Solid solution

- Substitutional
- Interstitial

- In this type of solution, the atoms of the solute substitute for atoms of the solvent in the lattice structure of the solvent.
- Several factors are now known, largely through the work of *Hume-Rothery*, that control the range of solubility in alloy systems.

Empirical rules for the formation of substitutional solid solution

- The solute and solvent atoms do not differ by more than 15% in diameter
- The electro-negativity difference between the elements is small
- The valency and crystal structure of the elements is same

Additional rule

- Element with higher valency is dissolved more in an element of lower valency rather than vice-versa

HUME ROTHERY RULES

HUME ROTHERY RULES

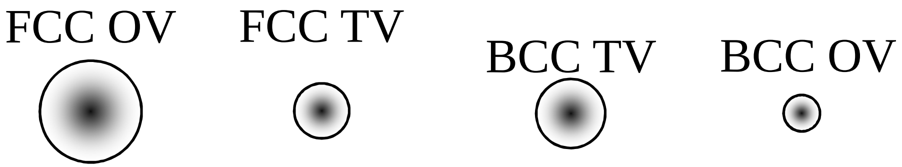
Examples of pairs of elements satisfying Hume Rothery rules and forming complete solid solution in all proportions

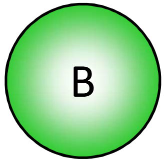
System		**Crystal structure**	**Radius of atoms (Å)**	**Valency**	**Electronegativity**
Ag-Au	Ag	FCC	1.44	1	1.9
	Au	FCC	1.44	1	2.4
Cu-Ni	Cu	FCC	1.28	1	1.9
	Ni	FCC	1.25	2	1.8
Ge-Si	Ge	DC	1.22	4	1.8
	Si	DC	1.18	4	1.8

A continuous series of solid solutions may not form even if the above conditions are satisfied *e.g.* *Cu-γFe*

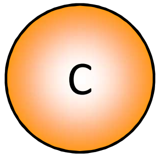
Interstitial Solid Solutions

- ❑ The second species added goes into the voids of the parent lattice
- ❑ E.g. Octahedral and tetrahedral voids in CCP, HCP (& BCC) crystals (E.g. of solvents: Fe, Mo, Cr etc.)
- ❑ E.g. C (r = 0.77 Å), N (r = 0.71 Å), O (r = 0.66 Å), H (r = 0.46 Å)
- ❑ If the solute atom has a diameter < 0.59 r_{host} then extensive solubility is expected *(may or may not happen!)*
- ❑ Solubility for interstitial atoms is more in transition elements (Fe, Ti, V, Zr, Ni, W, U, Mn, Cr) → due to electronic structure *(incomplete inner shell)*
- ❑ C is especially insoluble in most non-transition elements

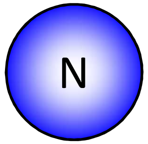




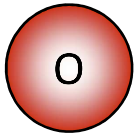
$r^B = 0.81\ \overset{\circ}{A}$



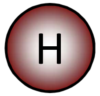
$r^C = 0.77\ \overset{\circ}{A}$



$r^N = 0.71\ \overset{\circ}{A}$



$r^O = 0.66\ \overset{\circ}{A}$



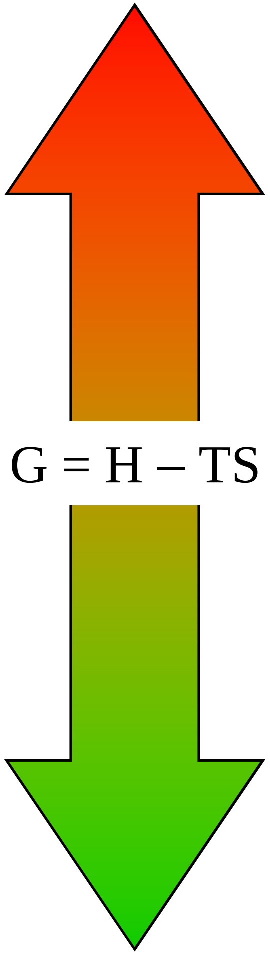
$r^H = 0.46\ \overset{\circ}{A}$

Order-Disorder Transformations

- ❑ On interesting class of alloys are those which show order-disorder transformations
- ❑ Typically the high temperature phase is dis-ordered while the low temperature phase is ordered (e.g. CuZn system→ next slide)
- ❑ The order can be positional or orientational
- ❑ In case of positionally ordered structures:
  - ▪ The ordered structure can be considered as a superlattice
  - ▪ The 'superlattice' consists of two or more interpenetrating 'sub-lattices' → with each sublattice being occupied by a specific elements

    (further complications include: SL-1 being occupied by A-atoms and SL-2 being occupied by B & C atoms- with probabilistic occupation of B & C atoms in SL-2, which is disordered)
- ❑ Order and disorder can be with respect to a physical property like magnetization. E.g. in the Ferromagnetic phase of Fe, the magnetic moments (spins) are aligned within a domain. On heating Fe above the Curie temperature the magnetic moments become randomly oriented, giving rise to the paramagnetic phase.

Positional Order

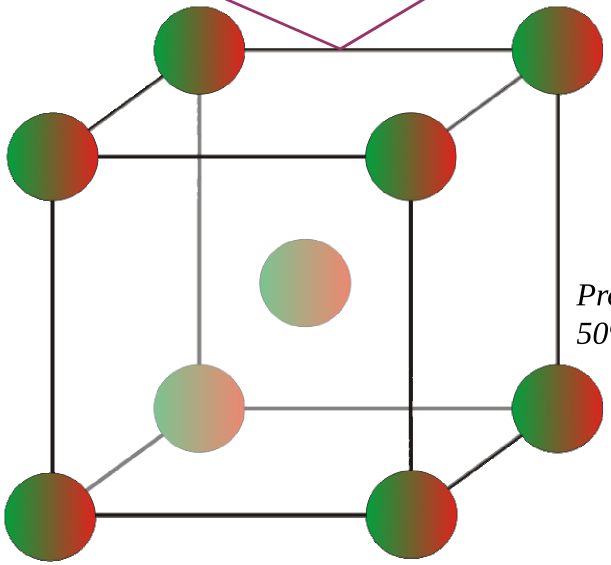


High T disordered

G = H – TS

Low T ordered

In a strict sense this is not a crystal !! (i.e. it is amorphous)



BCC

50% Cu

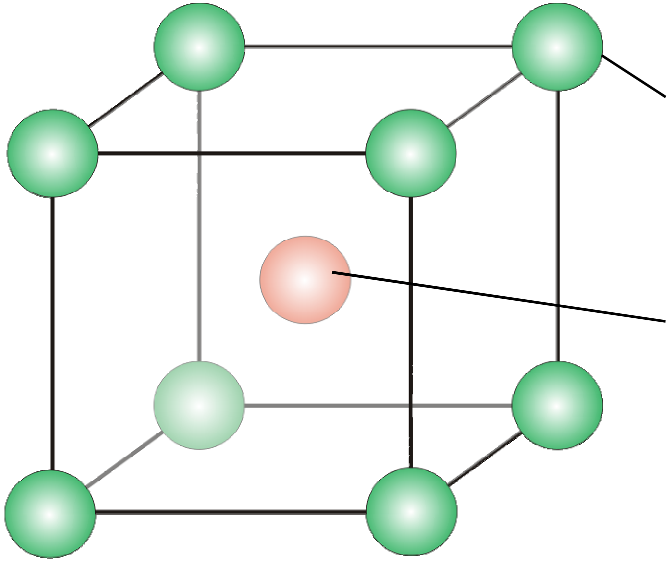
Probabilistic occupation

50% Zn

Probabilistic occupation of each BCC lattice site:
50% by Cu, 50% by Zn

470ºC

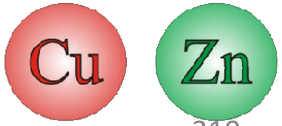
being a second order transition this temperature is not 'sharp'



Sublattice-1 (SL-1)

Sublattice-2 (SL-2)

SC



SL-1 occupied by Cu and SL-2 occupied by Zn. Origin of SL-2 at (½, ½, ½)

ORDERING

- ❑ A-B bonds are preferred to AA or BB bonds

  e.g. Cu-Zn bonds are preferred compared to Cu-Cu or Zn-Zn bonds
- ❑ The ordered alloy in the Cu-Zn alloys is an example of an INTERMEDIATE STRUCTURE that forms in the system with limited solid solubility
- ❑ The structure of the ordered alloy is different from that of both the component elements (Cu-FCC, Zn-HCP)
- ❑ The formation of the ordered structure is accompanied by change in properties. *E.g. in Permalloy ordering leads to → reduction in magnetic permeability, increase in hardness etc.* [~Compound]
- ❑ Complete solid solutions are formed when the ratios of the components of the alloy (atomic) are whole no.s → 1:1, 1:2, 1:3 etc. [CuAu, Cu_3Au..]
- ❑ Ordered solid solutions are *(in some sense)* in-between solid solutions and chemical compounds
- ❑ Degree of order decreases on heating and vanishes on reaching disordering temperature [≠ compound]
- ❑ Off stoichiometry in the ordered structure is accommodated by:
  - ◘ Vacancies in one of the sublattices *(structural vacancies)*

    NiAl with B2 structure Al rich compositions result from vacant Ni sites
  - ◘ Replacement of atom in one sublattice with atoms from other sublattice

    NiAl with B2 structure Ni rich compositions result from antisite defects

ORDERING

$$\Delta G = \Delta H - T\Delta S$$

↑ T ⇒ Disordered

↓ T ⇒ Ordered

Long Range Order (LRO) parameter (L)

$$L = \frac{r_A - X_A}{1 - X_A}$$

- r_A → probability that A sublattice is occupied with the right atom
- X_A → mole fraction of A in the alloy
- L → Long Range Order

- E.g.: In a $A_{50}B_{50}$alloy say 90% of the A atoms are sitting on A sublattice (right position), then: $r_A = 0.9$

$$L = \frac{0.9 - 0.5}{1 - 0.5} = \frac{0.4}{0.5} = 0.8$$

For complete order: $r_A = 1$ ⇒

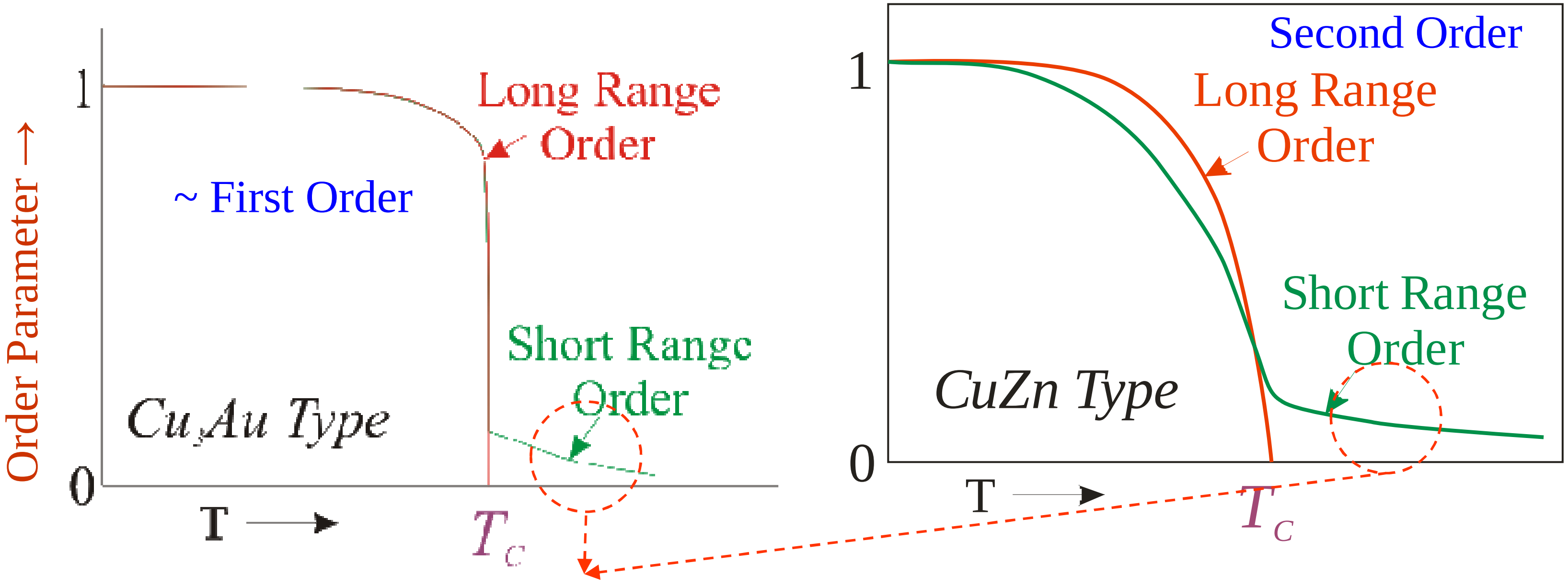
$$L = \frac{1.0 - 0.5}{1 - 0.5} = \frac{0.5}{0.5} = 1.0$$

❑ Solid solutions which have a negative enthalpy of mixing ($\Delta H_{mix} < 0$) prefer unlike nearest neighbours → show tendency for ordering

For complete disorder L =0

Long Range Order (LRO) versus Short Range Order (SRO)

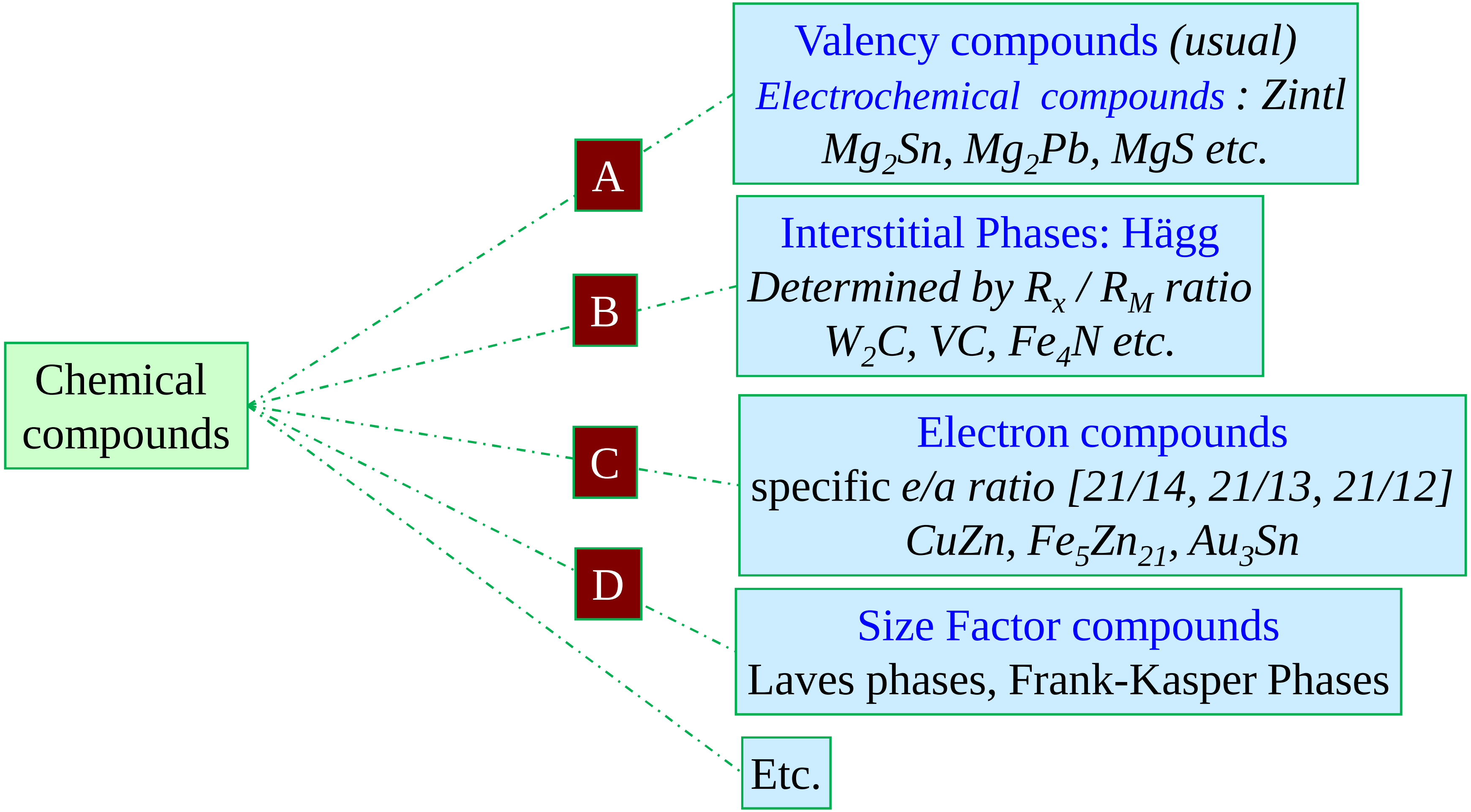
- Similar to long range order (LRO) we can define Short Range Order (SRO)
- Even after long range order has been destroyed short range order can persist
- In the example below the LRO parameter and the SRO parameter have been plotted for two alloys [Cu_3Au (structure considered next) & CuZn]
- Above T_c *(the disordering temperature)* LRO has been destroyed *(order parameter goes to zero)* but SRO persists
- Note that the disordering takes place over a range of temperatures *(i.e. is not abrupt)*



Persistence of SRO after LRO has been destroyed

3 Compound /Intermediate structure

- Intermetallic compounds can be very different from the normal chemical compounds (e.g. H_2O)



Chemical compounds

A

Valency compounds *(usual)*
Electrochemical compounds : Zintl
Mg_2Sn, Mg_2Pb, MgS *etc.*

B

Interstitial Phases: Hägg
Determined by R_x / R_M *ratio*
W_2C, VC, Fe_4N *etc.*

C

Electron compounds
specific *e/a ratio [21/14, 21/13, 21/12]*
$CuZn$, Fe_5Zn_{21}, Au_3Sn

D

Size Factor compounds
Laves phases, Frank-Kasper Phases

Etc.

A

Valency compounds (*Zintl Phases, Electrochemical compounds)*

The following includes features distinguishing them from solid solutions

- Different crystal lattice as compared to the components
- Most chemical compounds have complex crystal structures
- Each component has a specific location in the lattice
- Composition can be specified by a simple formula → A_nB_m (Mg_2Sn, Mg_2Pb, MgS) (m,n are small whole numbers)
- Different properties than the components
- Constant melting point and dissociation temperature
- Accompanied by substantial thermal effect
- Typically formed by elements with very different electronic and crystal structures
- The bonding in intermetallic compounds is usually metallic
- The bonding between a metal and a non-metal could also be metallic
- A large number of intermetallic compounds do not obey valency rules or have a constant composition *(thus distinguishing them from usual chemical compounds)*

In some sense the tendency to form compounds is opposite of that to form solid solutions!

B Interstitial Phases: Hägg Phases

- ❑ Transition metals form compounds with elements with small atomic size (H, C, N, B)
- ❑ Formulae:

  $M_4X \rightarrow Fe_4N, Mn_4N$
  $M_2X \rightarrow W_2C, Mo_2C, Fe_2N$
  $MX \rightarrow WC, VC, TiC, NbC, TiN$
- ❑ The crystal structure depends on R_x / R_M ratio

  If ➢ $R_x / R_M < 0.59 \rightarrow$ Simple crystal lattices (Cubic, Hexagonal)
  Non-metal occupies specific interstitial sites in the cubic or hexagonal crystal
  If ➢ $R_x / R_M > 0.59 \rightarrow$ Complex crystal structures (e.g. Fe_3C)
- ❑ Apart from size factor valency of the interstitial atom also seems to play some role
- ❑ Typically interstitial phases have a variable composition *(the chemical formula indicates the maximum amount of non-metal in the structure)*
- ❑ Properties include:
  - ➢ High electrical conductivity (with decreasing conductivity with increasing temperature as for a metal)
  - ➢ Metallic lustre
  - ➢ Many of the interstitial phases are hard (e.g. WC, VC)
  - ➢ The carbides have high melting point
  - ➢ Some covalent character to the bonding in some of these phases

Interstitial solid solutions on the other hand have much lower content of the interstitial atoms and the crystal structure of the parent is retained

C Electron Compounds

- ❑ These compounds are formed usually in:
  - ➢ Monovalent metals (Cu, Ag, Au, Li, Na)
  - ➢ Transition metals (Fe, Co, Mn)
  - ➢ Other metals with a valency values between 2-5
- ❑ Alloys of Cu, Ag, Au frequently form electron compounds
- ❑ These compounds have specific ratios for: number of valence electrons/atoms →
  - ➢ 21/14 → (=3/2=1.5) → BCC, Complex cubic, Hexagonal
Called β compounds *(E.g. CuBe, CuZn,* Cu_3Al*, NiAl)*
  - ➢ 21/13 → (=1.62) → Complex crystals
Called γ compounds *(E.g.* Cu_5Zn_8, Cu_5Cd_8, Fe_5Zn_{21}, Co_5Zn_{21}*)*
  - ➢ 21/12 → (=7/4=1.75) → Hexagonal crystals
Called ε phase *(*$CuZn_3$, $CuCd_3$, Cu_3Si, Au_3Sn*)*
- ❑ These compounds can form over a wide range of compositions
- ❑ Many of these ordered compounds get disordered on heating

D Size Factor compounds: (i) Laves phases (ii) Frank-Kasper Phases

D(i) Laves Phases

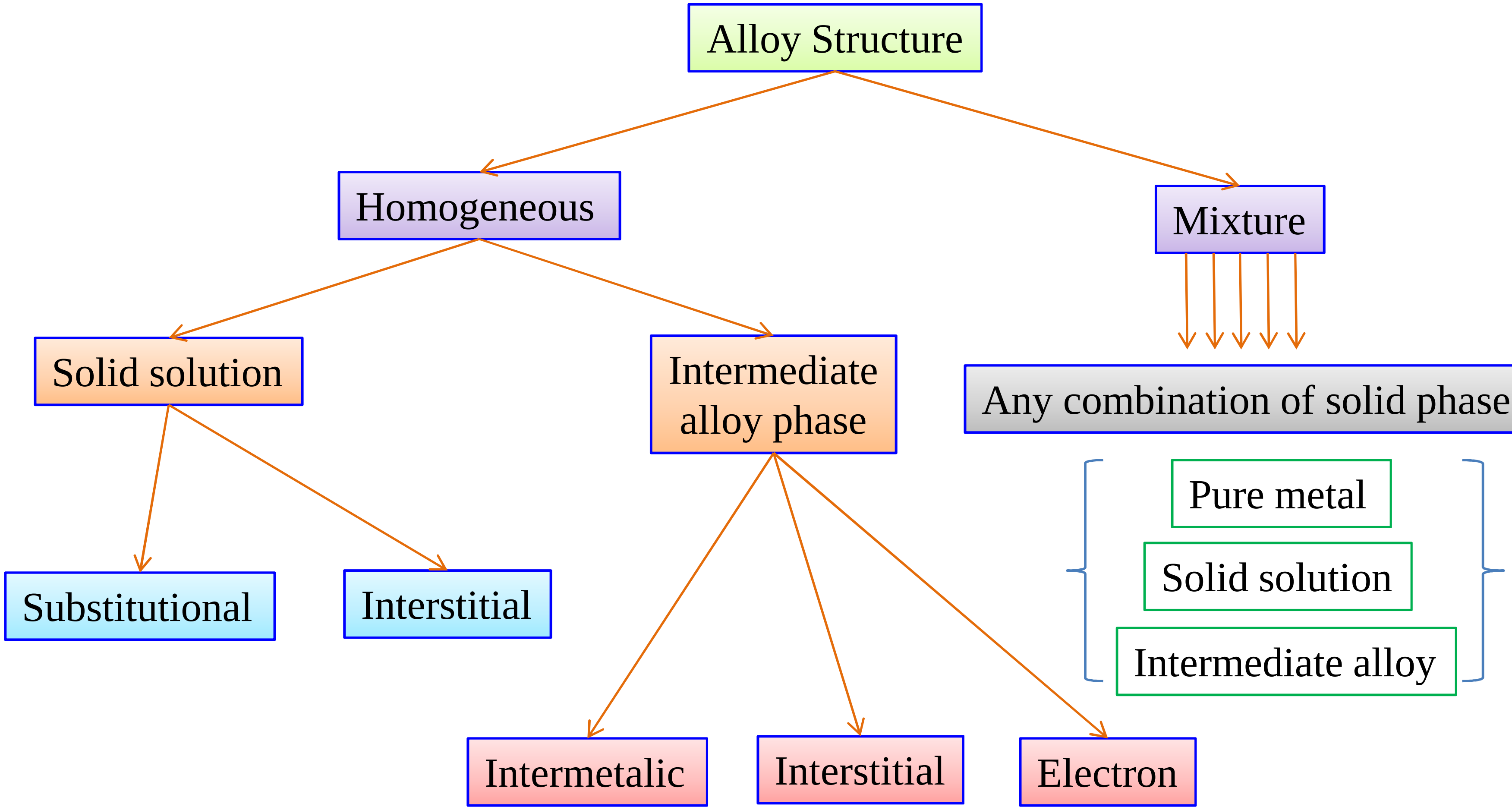
(1/1.225) = 0.816

- ❑ These phases have a formula: AB_2
- ❑ Laves phases can be regarded as tetrahedrally close packed (TCP) structures with an ideal ratio of the radii $(r_A/r_B) = (3/2)^{1/2} \sim 1.225$ *[or usually $r_A/r_B \in (1.1, 1.6)$]*
- ❑ If $r_A/r_B = 1.225$ then a high packing density is achieved with the chemical formula AB_2 with a average coordination number of 13.3
- ❑ Crystal structures:
  - ➢ Hexagonal → $MgZn_2$ (C15), $MgNi_2$ (C36)
  - ➢ FCC → $MgCu_2$ (C14)
- ❑ There are more than 1400 members belonging to the 'Laves family'
- ❑ Many ternary and multinary representatives of the Laves phases have been reported with excess of A or B elements. Some ternary Laves phases are known in systems with no corresponding binary Laves phases.
- ❑ The range of existence of the three phases (C15, C36, C14) in ternary Laves phases is influenced by the e/a ratio *(partial Hume-Rothery character).*

D(ii) Frank-Kasper

- ❑ Have coordination numbers (CN): CN =12, CN = 14, CN = 15, CN = 16

Summary



Alloy Structure

Homogeneous

Mixture

Solid solution

Intermediate alloy phase

Any combination of solid phases

Pure metal

Solid solution

Intermediate alloy

Substitutional

Interstitial

Intermetalic

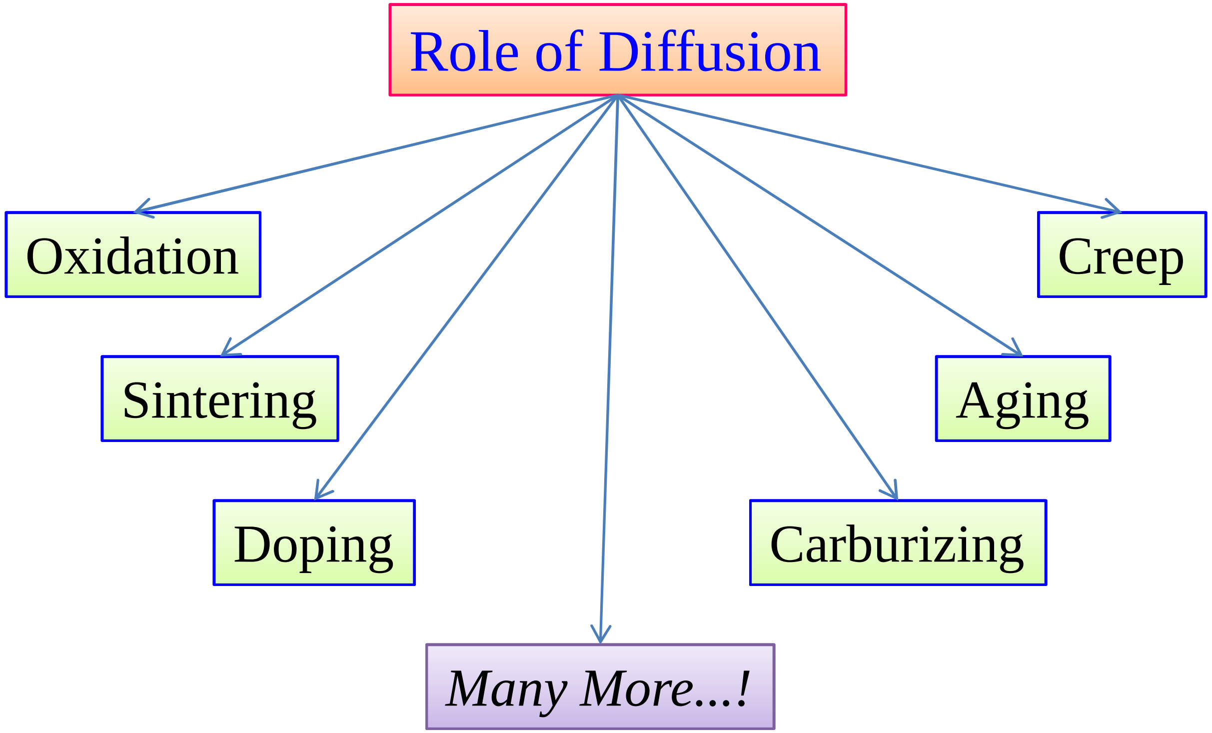
Interstitial

Electron

DIFFUSION

Introduction

- Diffusion is defined as, random movement of atoms/ molecules in solid, liquid and gas. For example dissolution of ink in water and smoke in air
- It can also defined as, Diffusion is a process of mass transport by atomic movement under the influence of thermal energy and a concentration gradient.
- To comprehend many materials related phenomenon one must understand diffusion.



Role of Diffusion

Oxidation

Creep

Sintering

Aging

Doping

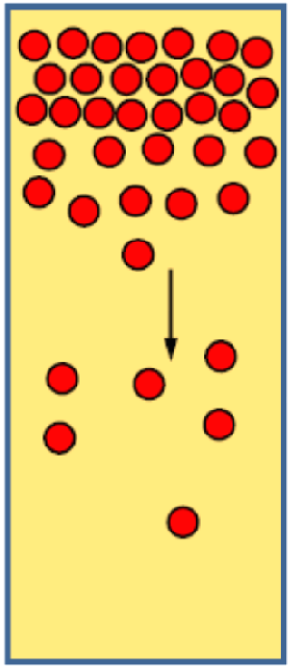
Carburizing

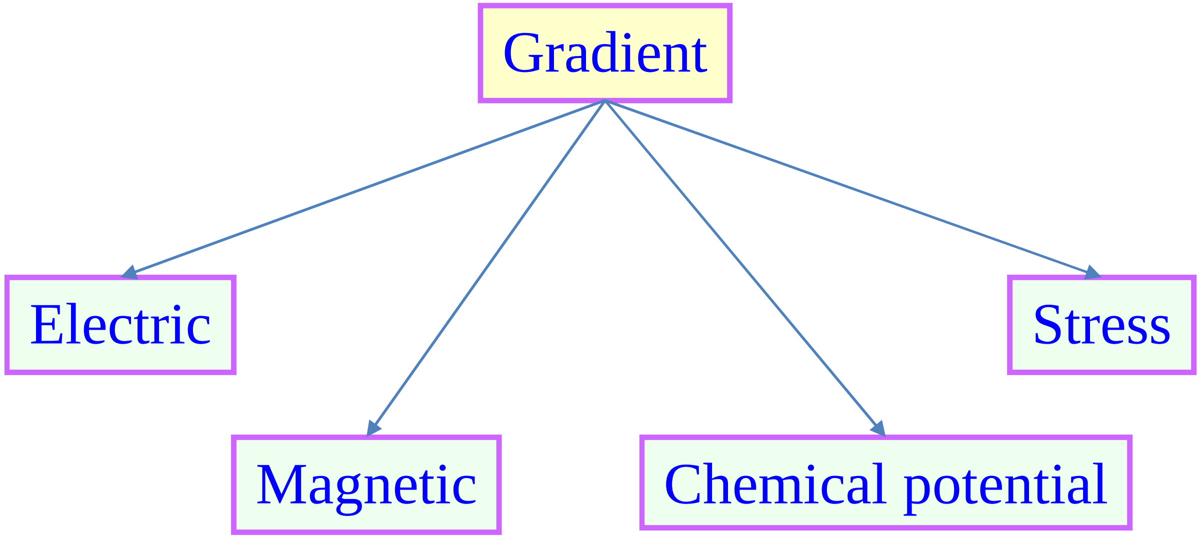
Many More...!

Materials Joining : Diffusion Bonding

Diffusion Phenomena

- Mass flow process by which species change their position relative to their neighbors.
- Driven by *thermal energy* and a *gradient*
- Thermal energy → thermal vibrations → Atomic jumps
- Atoms move from higher to lower concentration region. If this movement is from one element to another e.g. Cu to Ni, then it is termed as *Inter-diffusion.* If the movement is within similar atoms as in pure metals, it is termed *self-diffusion.*





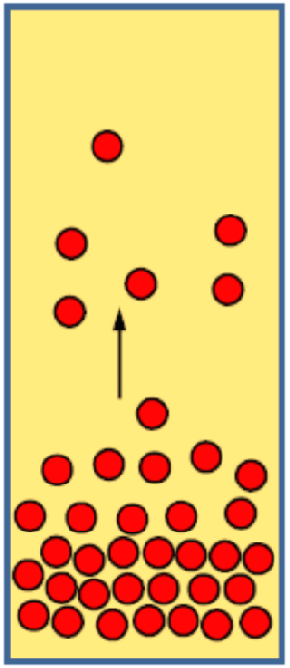
Gradient

Electric

Magnetic

Chemical potential

Stress

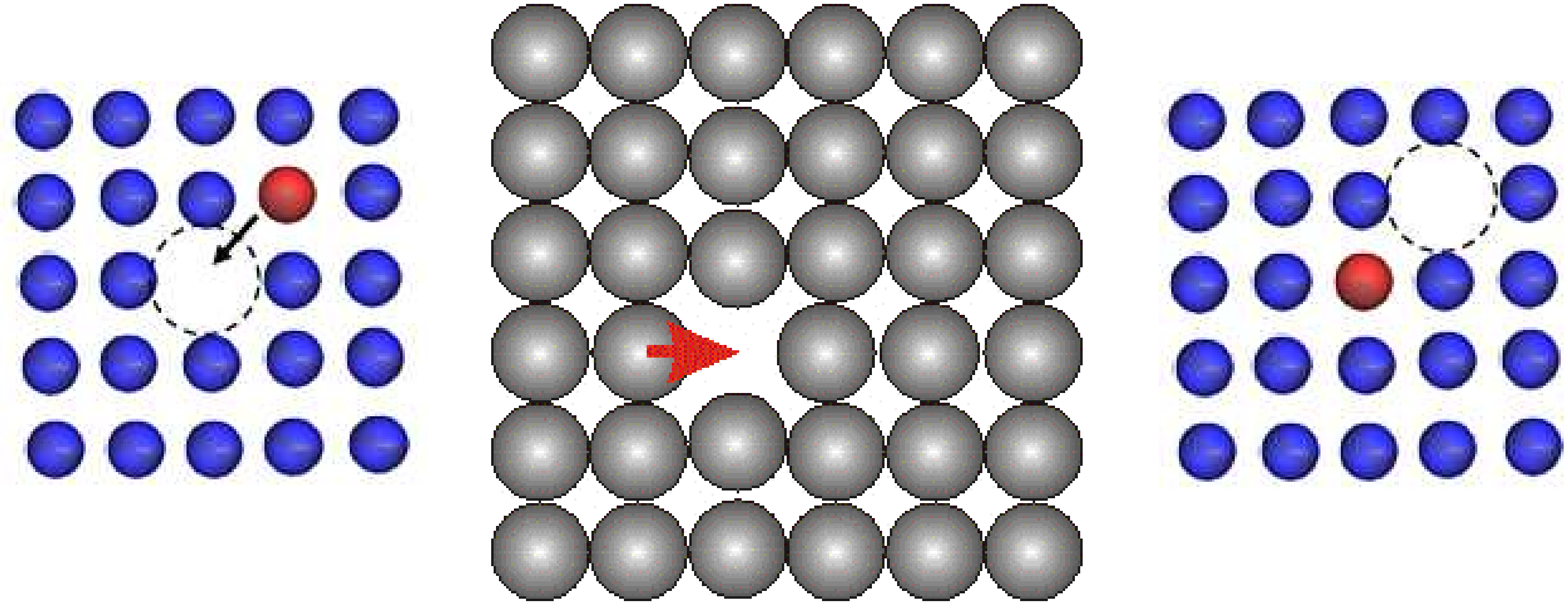


Diffusion Mechanism

- Diffusion of atoms involves movement in steps from one lattice site to the another. An empty adjacent site and breaking of bonds with the neighbor atoms are the two necessary conditions for this.

Vacancy Mechanism

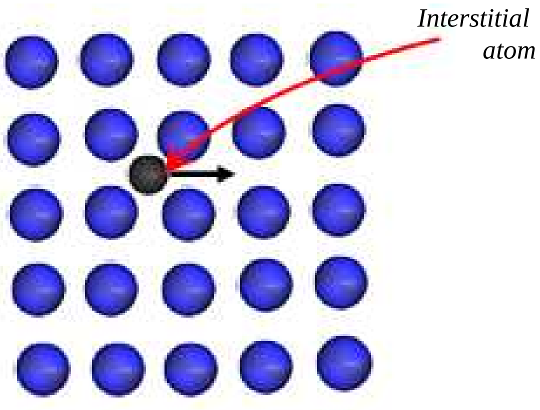
- This mechanism involves movement of atoms (we are interested in substitutional atoms) from a regular lattice site to an adjacent vacancy. Since vacancy and atoms exchange position, the vacancy flux is in the opposite direction.

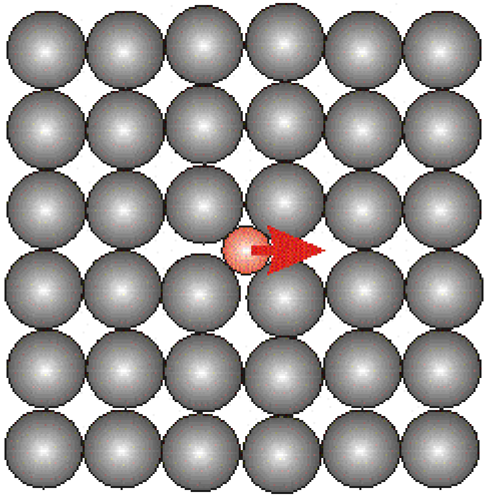


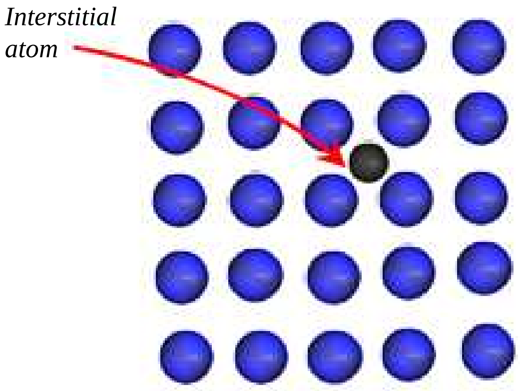
Diffusion Mechanism

Interstitial Mechanism

- This mechanism Involves migration of atoms from one interstitial site to a neighboring empty interstitial site.
- Usually the solubility of interstitial atoms (e.g. carbon in steel) is small. This implies that most of the interstitial sites are vacant. Hence, if an interstitial species wants to jump, ‘most likely’ the neighboring site will be vacant and jump of the atomic species can take place.
- This mechanism is more prevalent for impurity such a hydrogen, carbon, nitrogen, oxygen which are small enough to fit into an interstitial position.



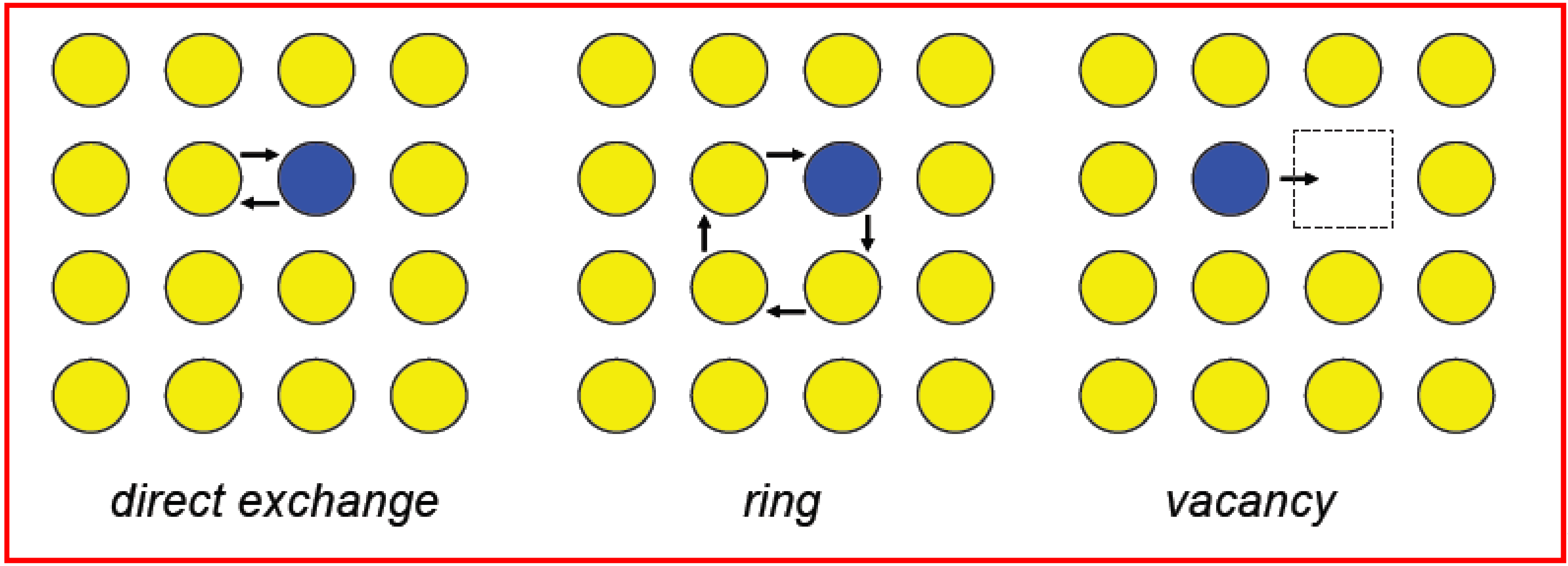




Diffusion Mechanism

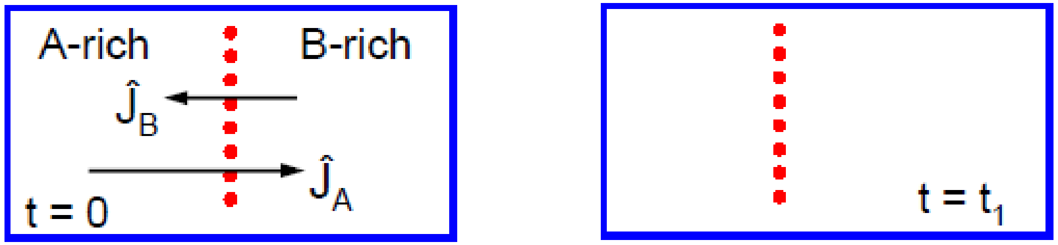
Atom Interchange Mechanism

- It is possible for movement to take place by a direct interchange between two adjacent atoms or by a four –atom ring interchange.
- However, these would probably occur only under special conditions, since the physical problem of squeezing between closely packed neighboring atoms would increase the barrier for diffusion.
- Note: The rate of diffusion is much greater in a rapidly cooled alloy than in the same alloy slow cooled. The difference is due to the larger number of vacancies retained in the alloy by fast cooling.



Kirkendall effect

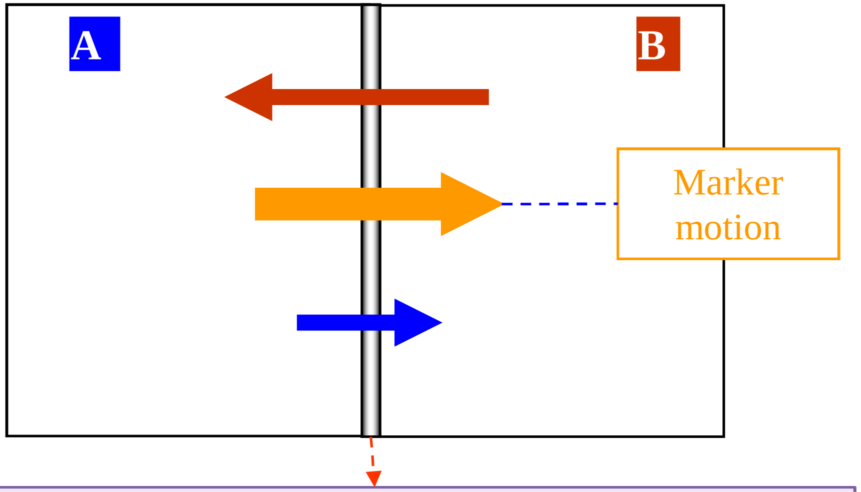
- If the diffusion rates of two metals A and B into each other are different, the boundary between them shifts and moves towards the faster diffusing metal.



Diffusion rate
$\hat{J}_A > \hat{J}_B$
t = time

- This is known as kirkendall effect. Named after the inventor Ernest Kirkendall (1914-2005). It can be demonstrated experimentally by placing an inert marker at the interface

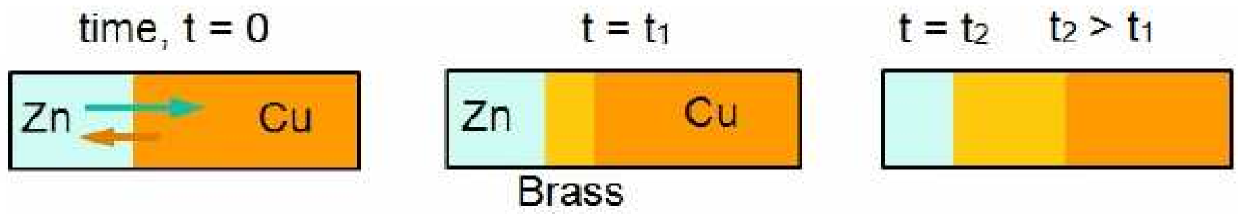
✓ Materials A and B welded together with inert marker and given a diffusion anneal
✓ Usually the lower melting component diffuses faster (say B)



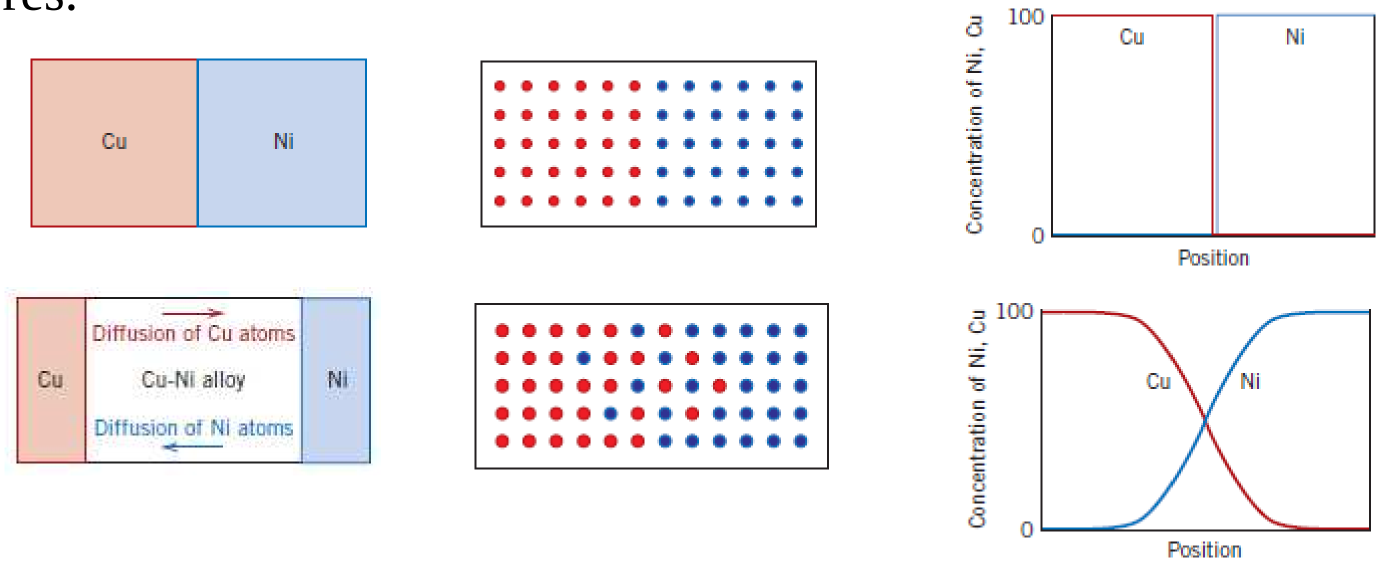
***Inert Marker** – thin rod of a high melting material which is basically insoluble in A & B*

Kirkendall effect

- Zn diffuses faster into Cu than Cu in Zn. A diffusion couple of Cu and Zn will lead to formation of a growing layer of Cu-Zn alloy (*Brass*).



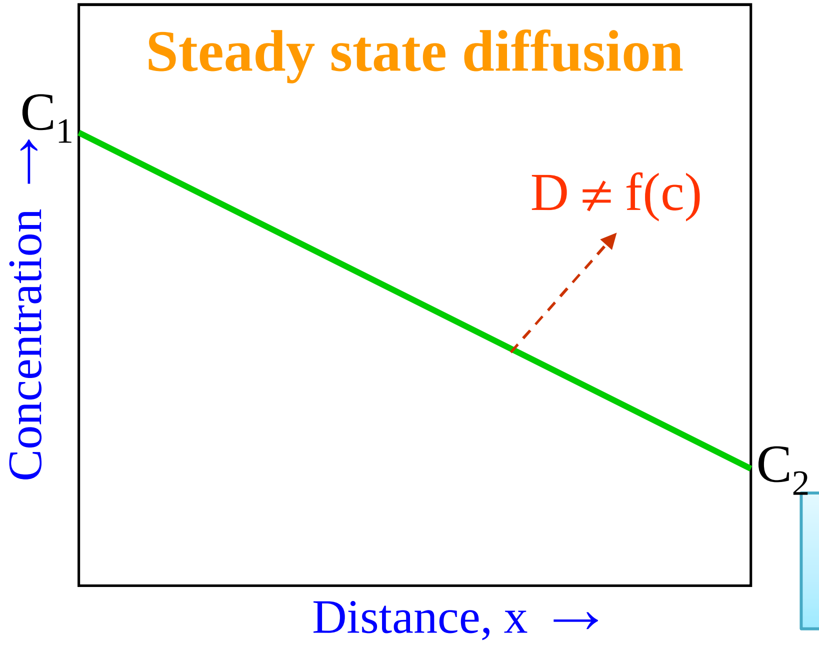
- Same will happen in a Cu-Ni couple as copper diffuses faster in nickel than nickel in copper.
- Since this takes place by vacancy mechanism, pores will form in cu (of the Cu-Ni couple as the vacancy flux in the opposite direction (towards Cu) will condense to form pores.



steady and non-steady state diffusion

- Diffusional processes can be either steady-state or non-steady-state. These two types of diffusion processes are distinguished by use of a parameter called flux.
- It is defined as net number of atoms crossing a unit area perpendicular to a given direction per unit time. For steady-state diffusion, flux is constant with time, whereas for non-steady-state diffusion, flux varies with time.
- A schematic view of concentration gradient with distance for both steady-state and non-steady-state diffusion processes are shown below.

- Flux (J) *(restricted definition)* → Flow / area / time [Atoms / m^2 / s]

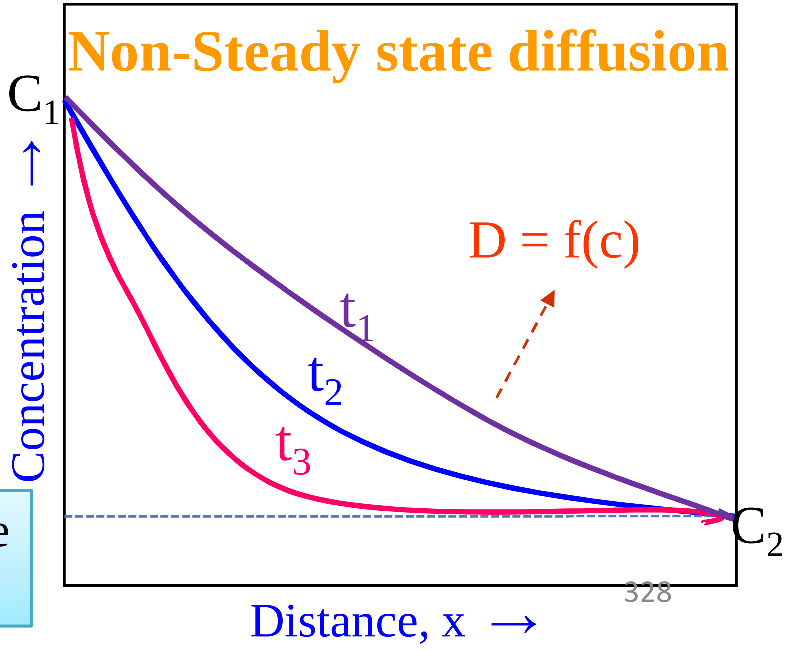


Steady state

$J \neq f(x,t)$

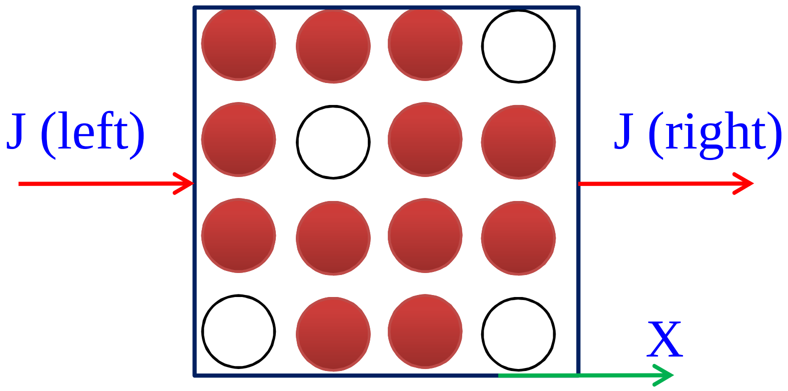
Non-steady state

$J = f(x,t)$



steady and non-steady state diffusion

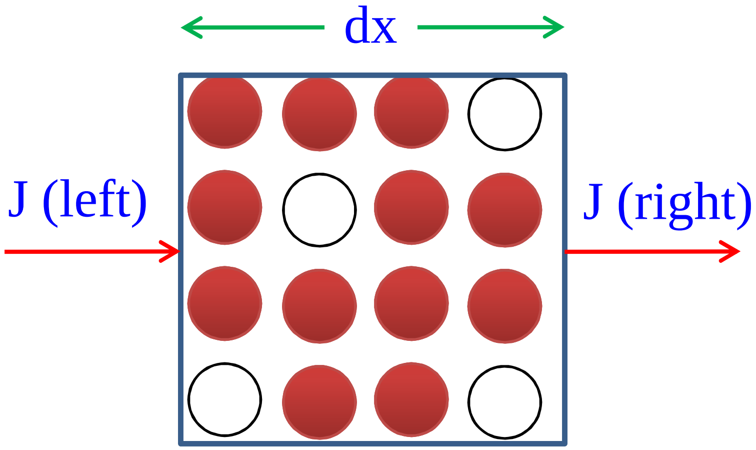
Steady State : Concentration profile not changing with time.



Concentration 'C' in the box doesn't change with time

Steady State
J(x) Left = J(x) Right

Non-Steady State : Concentration profile changes with time.



Concentration accumulating in the box

Non-Steady State
J(x) Left ≠J(x) Right

Fick's I law

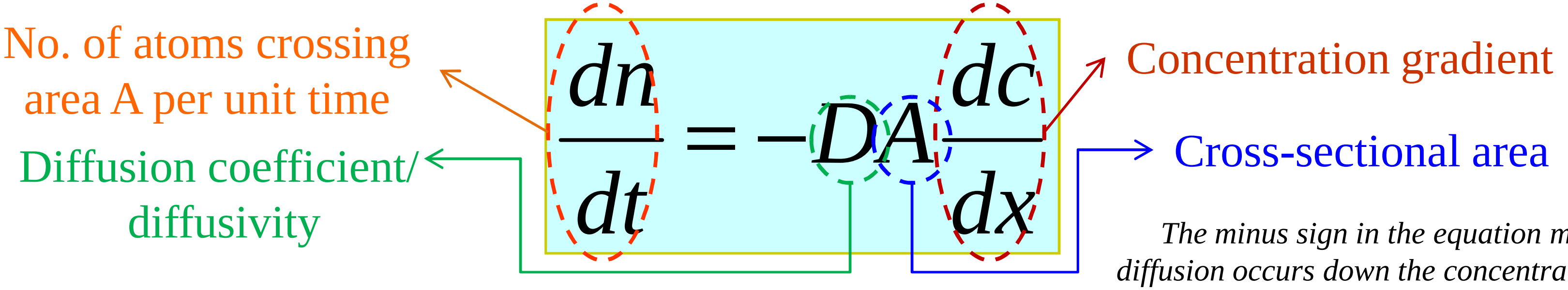
- ❑ Steady-state diffusion is described by Fick's first law which states that flux, J, is proportional to the concentration gradient.
- ❑ The constant of proportionality is called diffusion coefficient (diffusivity), D (cm^2/sec). diffusivity is characteristic of the system and depends on the nature of the diffusing species, the matrix in which it is diffusing, and the temperature at which diffusion occurs.
- ❑ Thus under steady-state flow, the flux is independent of time and remains the same at any cross-sectional plane along the diffusion direction. for the one-dimensional case, Fick's first law is given by

$$\boxed{J \equiv atoms/area/time \propto concentration\ gradient}$$

$$\boxed{J \propto \frac{dc}{dx}} \longrightarrow \boxed{J = -D\frac{dc}{dx}} \longrightarrow \boxed{J = \frac{1}{A}\frac{dn}{dt} = -D\frac{dc}{dx}}$$

Steady state

$J \neq f(x,t)$



$$\frac{dn}{dt} = -DA\frac{dc}{dx}$$

No. of atoms crossing area A per unit time

Diffusion coefficient/ diffusivity

Concentration gradient

Cross-sectional area

The minus sign in the equation means that diffusion occurs down the concentration gradient

Solved Example -1

The steady-state diffusion is found in the purification of hydrogen gas. Compute the number of kilograms of hydrogen that pass per hour through a 6-mm-thick sheet of palladium having an area of 0.25 m^2 at 600°C. Assume a diffusion coefficient of 1.7×10^{-8} m^2 / s, that the concentrations at the high- and low-pressure sides of the plate are 2.0 and 0.4 kg of hydrogen per cubic meter of palladium, and that steady-state conditions have been attained.

This Problem calls for the mass of hydrogen, per hour, that diffuses through a pd sheet.

From the Fick’s I law:

$$\boxed{M = JAt = -DAt\frac{\Delta c}{\Delta x}}$$

$$\boxed{= -(1.7\times10^{-8} m^2/s)(0.25 m^2)(3600 s/h)\left[\frac{0.4-2.0 kg/m^3}{6\times10^{-3} s}\right]}$$

$$\boxed{= 4.1\times10^{-3} kg/h}$$

Solved Example -2

A sheet of BCC iron 2 mm thick was exposed to a carburizing gas atmosphere on one side and a decarburizing atmosphere on the other side at *675ºC*. After having reached steady state, the iron was quickly cooled to room temperature. The carbon concentrations at the two surfaces of the sheet were determined to be 0.015 and 0.0068 wt%. Compute the diffusion coefficient if the diffusion flux is 7.36×10^{-9} kg/m^2-s *(Hint : convert the concentrations from weight percent to kilograms of carbon per cubic meter of iron.*

This problem calls for computation of the diffusion coefficient for a steady-state diffusion situation. Let us first convert the carbon concentrations from weight percent to kilograms carbon per meter cubed using below equation.

For 0.015 wt% C

$$C'_C = \left[\frac{C_C}{\frac{C_C}{\rho_C} + \frac{C_C}{\rho_{Fe}}} \times 10^3 \right]$$

$$C'_C = \left[\frac{0.015}{\frac{0.015}{2.25} + \frac{99.985}{7.87}} \times 10^3 \right]$$

$$= 1.18 kgC/m^3$$

Similarly, for 0.0068 wt% C

$$C''_C = \left[\frac{0.0068}{\frac{0.0068}{2.25} + \frac{99.9932}{7.87}} \times 10^3 \right]$$

$$= 0.535 kgC/m^3$$

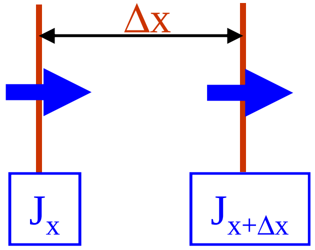
$$D = -J \frac{X_A - X_B}{C_A - C_B}$$

$$= -(7.36 \times 10^{-9} Kg/m^2 - s)\left[\frac{-2 \times 10^{-3} m}{1.18 Kg/m^3 - 0.535 Kg/m^3} \right]$$

$$= 2.3 \times 10^{-11} m^2/s$$

Fick’s II law

- Most interesting cases of diffusion are non-steady-state processes since the concentration at a given position changes with time, and thus the flux changes with time.
- This is the case when the diffusion flux depends on time, which means that a type of atoms accumulates in a region or depleted from a region (which may cause them to accumulate in another region). *Fick’s second law characterizes these processes, which is expressed as:*



$$Accumulation = J_x - J_{x+\Delta x}$$

$$Accumulation = J_x - \left\{ J_x + \frac{\partial J}{\partial x}\Delta x \right\}$$

$$\left(\frac{\partial c}{\partial t}\right)\Delta x = J_x - \left\{ J_x + \frac{\partial J}{\partial x}\Delta x \right\}$$

$$\left[\left(\frac{Atoms}{m^3}\frac{1}{s}\right).m\right] = \left[\frac{Atoms}{m^2 s}\right] \equiv [J]$$

$$\left(\frac{\partial c}{\partial t}\right)\Delta x = -\frac{\partial J}{\partial x}\Delta x$$

$$\left(\frac{\partial c}{\partial t}\right) = -\frac{\partial}{\partial x}\left(-D\frac{\partial c}{\partial x}\right)$$

$$\left(\frac{\partial c}{\partial t}\right) = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right)$$

$$\left(\frac{\partial c}{\partial t}\right) = D\frac{\partial^2 c}{\partial x^2}$$

Fick’s II law

Non-steady state

$J = f(x,t)$

Solutions to Fick's II law

$$\left(\frac{\partial c}{\partial t}\right) = D\frac{\partial^2 c}{\partial x^2}$$

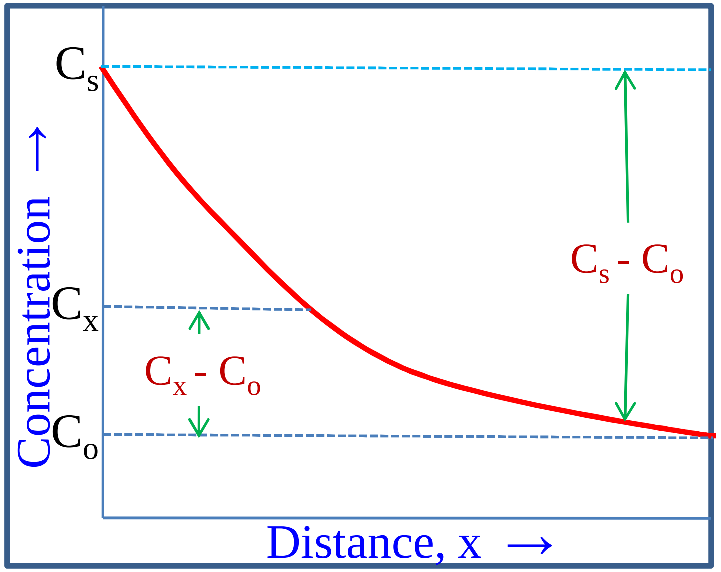
- ☐ Solution to the above expression is possible when meaningful boundary conditions are specified. One common set of boundary conditions can be written as:

For t = 0, $C = C_o$ at $0 \le x \le \infty$

For t > 0, $C = C_s$ at $x = 0$

$C = C_o$ at $x = \infty$

$$\frac{C(x,t) - C_o}{C_s - C_o} = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$



Where C_x represents the concentration at depth x after time t. The term erf stands for Gaussian error function. Corresponding error function values for a variable are usually found from standard mathematical tables. The above equation demonstrates the relationship between concentration, position, and time. Thus the equation can be used to explain many practical industrial problems like corrosion resistance of duralumin, carburization and decarburization of steel, doping of semi conductors etc.

Solved Example - 3

An FCC iron–carbon alloy initially containing 0.55 wt% C is exposed to an oxygen-rich and virtually carbon-free atmosphere at 1325 K (1052ºC). Under these circumstances the carbon diffuses from the alloy and reacts at the surface with the oxygen in the atmosphere; that is, the carbon concentration at the surface position is maintained essentially at 0 wt% C. (This process of carbon depletion is termed *decarburization.) At what position will the* carbon concentration be 0.25 wt% after a 10-h treatment? The value of *D at 1325 K is* 4.3×10^{-11} m^2/s.

This problem asks that we determine the position at which the carbon concentration is 0.25 wt% after a 10-h heat treatment at 1325 K when C_o = 0.55 wt% C.

$$\frac{C_x - C_o}{C_s - C_o} = \frac{0.25 - 0.55}{0 - 0.55} = 0.5455 = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 0.4545$$

Z	Erf (Z)
0.40	0.4284
Z	0.4545
0.45	0.4755

Using tabulation of error function values and linear interpretation

$$\frac{Z - 0.40}{0.45 - 0.40} = \frac{0.4545 - 0.4284}{0.4755 - 0.4284}$$

$$Z = 0.4277$$

$$\left(\frac{x}{2\sqrt{Dt}}\right) = 0.4277$$

$$x = 2(0.4277)\sqrt{Dt} = (0.8554)\sqrt{(3.6 \times 10^4\, s)(4.3 \times 10^{-11}\, m^2/s)}$$

$$= 1.06 \times 10^{-3}\, m = 1.06 mm$$

Solved Example - 4

Nitrogen from a gaseous phase is to be diffused into pure iron at 675ºC. If the surface concentration is maintained at 0.2 wt% N, what will be the concentration 2 mm from the surface after 25 h? The diffusion coefficient for nitrogen in iron at 675ºC is 1.9×10^{-11} m^2/s .

This problem asks us to compute the nitrogen concentration C_x at the 2 mm position after a 25 h diffusion time, when diffusion is non steady-state.

$$\frac{C_x - C_o}{C_s - C_o} = \frac{C_x - 0}{0.2 - 0} = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$= 1 - \mathrm{erf}\left(\frac{2\times 10^{-3} m}{2\sqrt{(1.9\times 10^{-11} m^2/s)(25h)(3600s/h)}}\right)$$

$$= 1 - erf(0.765)$$

Using tabulation of error function values and linear interpretation

Z	Erf (Z)
0.750	0.7112
0.765	y
0.800	0.7421

$$\frac{0.765 - 0.750}{0.800 - 0.750} = \frac{y - 0.7112}{0.7421 - 0.7112}$$

$$y = erf(0.765) = 0.7205$$

$$\frac{C_x - 0}{0.2 - 0} = 1.0 - 0.7205$$

$$C_x = 0.056 wt\% N$$

Factors affecting Diffusion

Ease of a diffusion process is characterized by the parameter *D*, *diffusivity*. The value of diffusivity for a particular system depends on many factors as many mechanisms could be operative.

Diffusing species

If the diffusing species is able to occupy interstitial sites, then it can easily diffuse through the parent matrix. On the other hand if the size of substitutional species is almost equal to that of parent atomic size, substitutional diffusion would be easier. Thus size of diffusing species will have great influence on diffusivity of the system.

Lattice structure

Diffusion is faster in open lattices or in open directions than in closed directions.

Presence of defects

As mentioned in earlier section, defects like dislocations, grain boundaries act as short-circuit paths for diffusing species, where the activation energy is diffusion is less. Thus the presence of defects enhances the diffusivity of diffusing species.

Factors affecting Diffusion

Temperature

- ☐ Temperature has a most profound influence on the diffusivity and diffusion rates. It is known that there is a barrier to diffusion created by neighboring atoms those need to move to let the diffusing atom pass. Thus, atomic vibrations created by temperature assist diffusion.
- ☐ Empirical analysis of the system resulted in an Arrhenius type of relationship between diffusivity and temperature.

$$D = D_0 \, e^{\left(-\frac{Q}{kT}\right)}$$

- ☐ Where D_0 is a pre-exponential constant, Q is the activation energy for diffusion, R is gas constant (Boltzmann's constant) and T is absolute temperature.
- ☐ From the above equation it can be inferred that large activation energy means relatively small diffusion coefficient. It can also be observed that there exists a linear proportional relation between (lnD) and (1/T). Thus by plotting and considering the intercepts, values of Q and D_0 can be found experimentally (*see in next slide for clear understanding*).

Diffusion paths with lesser resistance

Experimentally determined activation energies for diffusion…!

$$Q_{surface} < Q_{grain\ boundary} < Q_{pipe} < Q_{lattice}$$

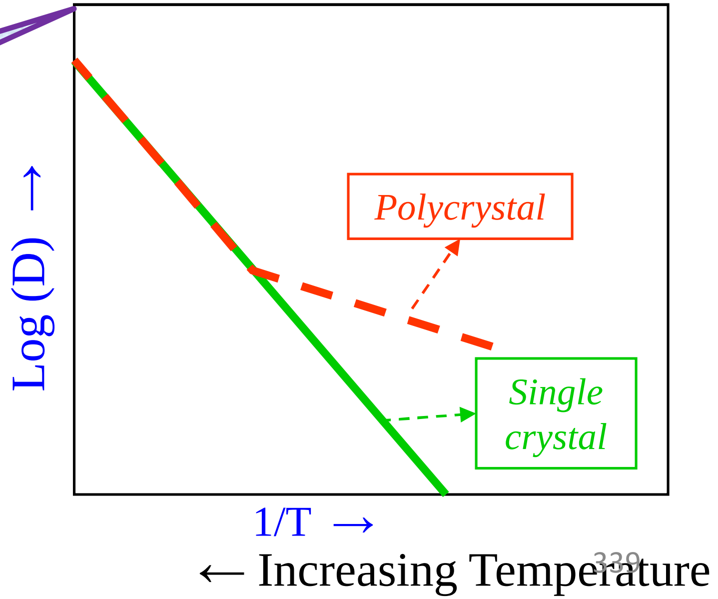
Lower activation energy automatically implies higher diffusivity

Core of dislocation lines offer paths of lower resistance PIPE DIFFUSION

Diffusivity for a given path along with the available cross-section for the path will determine the diffusion rate for that path

Comparison of Diffusivity for self-diffusion of Ag → Single crystal vs. polycrystal

- $Q_{grain\ boundary}$ = *110 kJ /mole*
- $Q_{Lattice}$ = *192 kJ /mole*



Solved Example - 5

Using the following diffusion data, compute the value of D for the diffusion of magnesium in aluminum at 400ºC.

$D_{o(\text{Mg in Al})} = 1.2 \times 10^{-4}\ m^2/s$ $Q_d = 131$ KJ/mol

This problem asks us to compute the magnitude of D for the diffusion of Mg in Al at 400ºC (673K).

$$\boxed{D = (1.2\times10^{-4}\, m^2/s)\exp\left[-\frac{131{,}000\, J/mol}{(8.31 J/mol-k)(673k)}\right]}$$

$$\boxed{= 8.1\times10^{-15}\, m^2/s}$$

Solved Example - 6

At what temperature will the difusion coefficient for the diffusion of zinc in copper have a value of 2.6×10^{-16} m²/s

$D_o = 2.4 \times 10^{-5}$ m²/s $Q_d = 189$ KJ/mol

We are asked to calculate the temperature at which the diffusion coefficient for the diffusion of Zn in Cu has a value of 2.6×10^{-16} m²/s. Solving for T from below equation

$$T = -\frac{Q_d}{R(\ln D_o - \ln D)}$$

By using the given data we can get

$$T = \left[-\frac{189{,}000\,J/mol}{(8.31\,J/mol-k)[\ln(2.6\times10^{-16}\,m^2/s) - \ln(2.4\times10^{-5}\,m^2/s)} \right]$$

$$= 901K = 628^0 C$$

Solved Example - 7

The diffusion coefficients for nickel in iron are given at two temperatures:

At 1473K 2.2×10^{-15} m^2/s

At 1673K 4.8×10^{-14} m^2/s

a) Determine the values of D_o and the activation energy Q_d.

b) What is the magnitude of D at 1300°C (1573K)

$$T = -\frac{Q_d}{R(\ln D_o - \ln D)}$$

From this equation we can compute two simultaneous equations they are

$$\ln D_1 = \ln D_0 - \frac{Q_d}{R}\{\frac{1}{T_1}\}$$

$$\ln D_2 = \ln D_0 - \frac{Q_d}{R}\{\frac{1}{T_2}\}$$

⇨

$$Q_d = -R\frac{\ln D_1 - \ln D_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$

$$Q_d = -(8.314 J/mol-K)\frac{[\ln(2.2\times10^{-15}) - \ln(4.8\times10^{-14})}{\frac{1}{1473K} - \frac{1}{1673K}}$$

$$\boxed{= 315{,}700 J/mol}$$

Now we can solve D_o from this equation

$$D_0 = D_1\, e^{\left(-\frac{Q_d}{RT_1}\right)}$$

$$= (2.2\times10^{-15} m^2/s)\exp\left[\frac{315{,}700 J/mol}{(8.31 J/mol-k)(1473k)}\right]$$

$$= 3.5\times10^{-4} m^2/s$$

(b) Using these values of D_o and $Q_{d,}$ D_{at} 1573K is just

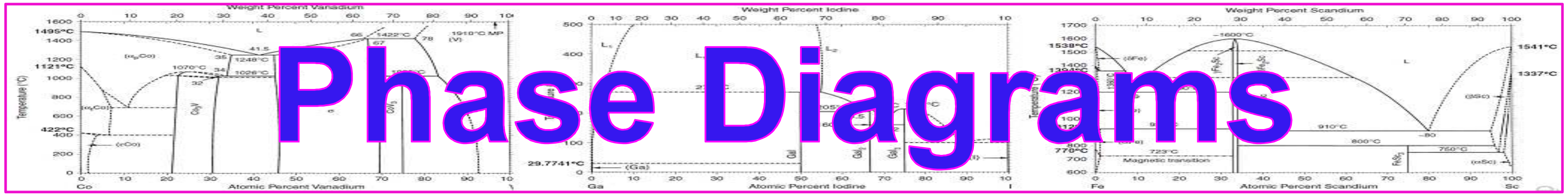
$$D = (3.5\times10^{-4} m^2/s)\exp\left[-\frac{315{,}700 J/mol}{(8.31 J/mol-k)(1573k)}\right]$$

$$= 1.1\times10^{-14} m^2/s$$

Summary

Diffusion Faster for	Diffusion Slower for
Open crystal structures	Close packed structures
Lower melting temperature materials.	Higher melting temperature materials
Smaller diffusing atoms	Larger diffusing atoms
Cations	Anions
Materials with secondary bonding	Materials with covalent bonding
Lower density materials	Higher density materials

Phase Diagrams



Avala Lava Kumar* : Suneeti Purohit : Gautam Behera

Department of Metallurgical & Materials Engineering (MME)

Veer Surendra Sai University of Technology (VSSUT), Burla -768018

**E-mail : lavakumar.vssut@gmail.com*

Introduction

- ☐ Phase diagrams are an important tool in the armory of an materials scientist
- ☐ In the simplest sense a phase diagram demarcates regions of existence of various phases. (*Phase diagrams are maps)*
- ☐ Phase diagrams are also referred to as "equilibrium diagrams" or "constitutional diagrams". This usage requires special attention: through the term used is "equilibrium", in practical terms the equilibrium is *not global equilibrium but Microstructural level equilibrium.*
- ☐ Broadly two kinds of phase diagrams can be differentiated*→ those involving time and those which do not involve time.
- ☐ In this chapter we shall deal with the phase diagrams not involving time.

  This type can be further sub classified into:
  - ✓ Those with composition as a variable (e.g. T vs. %Composition)
  - ✓ Those without composition as a variable (e.g. P vs. T)
- ☐ Time-Temperature-Transformation (TTT) diagrams and Continuous-Cooling-Transformation (CCT) diagrams involve time. These diagrams will be considered in the chapter on Heat treatment.

**This is form a convenience in understanding point of view*

Definitions

Components of a system

- ☐ Independent chemical species which comprise the system. These could be Elements, Ions, Compounds

  Example: Au-Cu system : Components →Au, Cu (elements)

  Ice-water system : Component→H_2O (compound)

  Al_2O_3-Cr_2O_3 system : Components→Al_2O_3, Cr_2O_3

Phase

- ☐ A physically homogeneous and distinct portion of a material system (e.g. gas, crystal, amorphous…)
- ☐ Gases : Gaseous state always a single phase → mixed at atomic or molecule level.
- ☐ Liquids: Liquid solution is a single phase → e.g. Nacl in H_2O and Liquid mixtures consists of two or more phases → e.g. Oil in water (*no mixing at the atomic level)*
- ☐ Solids: In general due to several compositions and crystals structures many phases are possible.
  - ✓ For the same composition different crystal structures represent different phases. E.g. *Fe (BCC) and Fe (FCC)* are different phases

Definitions

What kinds of phases exist?

- ☐ Based on state → Gas, Liquid, Solid
- ☐ Based on atomic order → Amorphous, Quasi-crystalline, Crystalline
- ☐ Based on band structure → Insulating, Semi-conducting, Semi-metallic, Metallic
- ☐ Based on Property → Para-electric, Ferromagnetic, Superconducting
- ☐ Based on stability → Stable, Metastable, Unstable
- ☐ Also sometimes- Based on size/geometry of an entity → Nanocrystalline, mesoporous, layered.

Phase transformation

- ☐ Phase transformation is the change of one phase into another. For example
  - ✓ Water → Ice and α-Fe (BCC) → γ-Fe (FCC)

Grain

- ☐ The single crystalline part of polycrystalline metal separated by similar entities by a grain boundary

Definitions

Solute

- ❑ The component of either a liquid or solid solution that is present to a lesser or minor extent; the component that is dissolved in the solvent.

Solvent

- ❑ The component of either a liquid or solid solution that is present to a greater or major extent; the component that dissolves the solute.

System

- ❑ System, has two meanings. First, ‘‘system’’ may refer to a specific body of material or object. Or, it may relate to the series of possible alloys consisting of the same components, but without regard to alloy composition

Solubility Limit

- ❑ For many alloy systems and at some specific temperature, there is a maximum concentration of solute atoms that may dissolve in the solvent to form a solid solution; this is called a Solubility Limit.

Definitions

Microstructure

- ☐ (Phases + defects + residual stress) & their distributions
- ☐ Structures requiring magnifications in the region of 100 to 1000 times. (or) The distribution of phases and defects in a material.

Phase diagram

- ☐ Map that gives relationship between phases in equilibrium in a system as a function of T, P and composition. *Map demarcating regions of stability of various phases*

Variables/Axis of phase diagrams

- ☐ The axes can be:
  - ✓ Thermodynamic (T, P, V)
  - ✓ Kinetic (t) or Composition variables (C, %X)
- ☐ In single component systems (unary systems) the usual variables are T & P
- ☐ In phase diagrams used in materials science the usual variable are T & %X
- ☐ In the study of phase transformation kinetics TTT diagrams or CCT diagrams are also used where the axis are T & t

Definitions

System Components

Phase diagrams and the systems they describe are often classified and named for the number (in Latin) of components in the system:

Number of components	Name of system or diagram
One	Unary
Two	Binary
Three	Ternary
Four	Quaternary
Five	Quinary
Six	Sexinary
Seven	Septenary
Eight	Octanary
Nine	Nonary
Ten	Decinary

Coordinates of Phase Diagrams

- Phase diagrams are usually plotted with temperature, in degrees centigrade or Fahrenheit, as the ordinate and the alloy composition in weight percentage as the abscissa.
- The weight % of component A:

$$W_A = \frac{weight of component A}{\Sigma Weight of all components} \times 100$$

- The atom (or mol)% of component A

$$X_A = \frac{number of atoms (or mols) of component A}{\Sigma number of atoms (or mols) of all components} \times 100$$

- The Conversion from weight percentage to atomic percentage may be made by the following formulas:

$$Atomic percent of A = \frac{X}{X + Y\left(\frac{M}{N}\right)} \times 100$$

$$Atomic percent of B = \frac{Y\left(\frac{M}{N}\right)}{X + Y\left(\frac{M}{N}\right)} \times 100$$

M = atomic weight of metal A & N = atomic weight of metal B

X = weight percentage of metal A & Y = weight percentage of metal B

Experimental Methods

Thermal Analysis

A plot is made of temperature vs. time, at constant composition, the resulting cooling curve will show a change in slope when a phase change occurs because of the evolution of heat by the phase change. This method seems to be best for determining the initial and final temperature of solidification. Phase changes occurring solely in the solid state generally involve only small heat changes, and other methods give more accurate results.

Metallographic Methods

This method consists in heating samples of an alloy to different temperatures, waiting for equilibrium to be established, and then quickly cooling to retain their high temperature structure. The samples are then examined microscopically. This method is difficulty to apply to metals at high temperatures because the rapidly cooled samples do not always retain their high temperature structure, and considerable skill is then required to interpret the observed microstructure correctly.

X-ray diffraction

Since this method measures lattice dimensions, it will indicate the appearance of a new phase either by the change in lattice dimension or by the appearance of a new crystal structure. This method is simple, precise, and very useful in determining the changes in solid solubility with temperature

Gibbs Phase Rule

- The phase rule connects the Degrees of Freedom, the number of components in a system and the number of phases present in a system via a simple equation.
- To understand the phase rule one must understand the variables in the system along with the degrees of freedom.
- We start with a general definition of the phrase “degrees of freedom”.

Degrees of Freedom

The degree of freedom, F, are those externally controllable conditions of temperature, pressure, and composition, which are independently variable and which must be specified in order to completely define the equilibrium state of the system.

For a system in equilibrium

$$F = C - P + 2$$

or

$$F - C + P = 2$$

F – Degrees of Freedom
C – Number of Components
P – Number of Phases

The degrees of freedom cannot be less than zero so that we have an upper limit to the number of phases that can exist in equilibrium for a given system.

Gibbs Phase Rule

Variables in a phase diagram

- C – No. of components
- P – No. of phases
- F – No. of degrees of freedom
- Variables in the system = Composition variables + Thermodynamic variables
- Composition of a phase specified by (C – 1) variables (*If the composition is expressed in %ages then the total is 100% → there is one equation connecting the composition variables and we need to specify only (C - 1) composition variables)*
- No. of variables required to specify the composition of all phases: P(C – 1) (*as there are P phases and each phase needs the specification of (C – 1) variables*)
- Thermodynamic variables = P + T (usually considered) = 2 (*at constant pressure (e.g. atmospheric pressure) the thermodynamic variable becomes 1)*
- Total no. of variables in the system = P (C – 1) + 2
- F < no. of variables → F < P (C – 1) + 2

Gibbs Phase Rule

- For a system in equilibrium the chemical potential of each species is same in all the phases
    - If $\alpha, \beta, \gamma \ldots$ are phases, then: $\mu_A(\alpha) = \mu_A(\beta) = \mu_A(\gamma) \ldots\ldots$
    - *Suppose there are 2 phases (α and β phases) and 3 components (A, B, C) in each phase then :* $\mu_A(\alpha) = \mu_A(\beta)$, $\mu_B(\alpha) = \mu_B(\beta)$, $\mu_C(\alpha) = \mu_C(\beta)$ → *i.e. there are three equations. For each component there are (P – 1) equations and for C components the total number of equations is C(P – 1). In the above example the number of equations is 3(2 – 1) = 3 equations.*
    - F = (Total number of variables) – (number of relations between variables)

      $$= [P(C-1)+2] - [C(P-1)] = C - P + 2$$

    - *In a single phase system F = Number of variables*

      $F = C - P + 2$

    - P↑ → F↓ (For a system with fixed number of components as the number phases increases the degrees of freedom decreases.

It is worthwhile to clarify a few terms at this stage:

- Components 'can' go on to make a phase (*of course one can have single component phases as well e.g. BCC iron phase)*
- Phases 'can' go on to make a microconstituent.
- Microconstituents 'can' go on to make a microstructure *(of course phases can also directly go on to make a microstructure)*

Gibbs Phase Rule

A way of understanding the Gibbs Phase Rule : $P + F = C + 2$

The degrees of freedom can be thought of as the difference between *what you (can) control and what the system controls*

$F = C+2 - P$

Degrees of freedom = What you can control - What the system controls

Can control the no. of components added and P&T

System decided how many phases to produce given the conditions

Variation of the number of degrees of freedom with number of components and number of phases

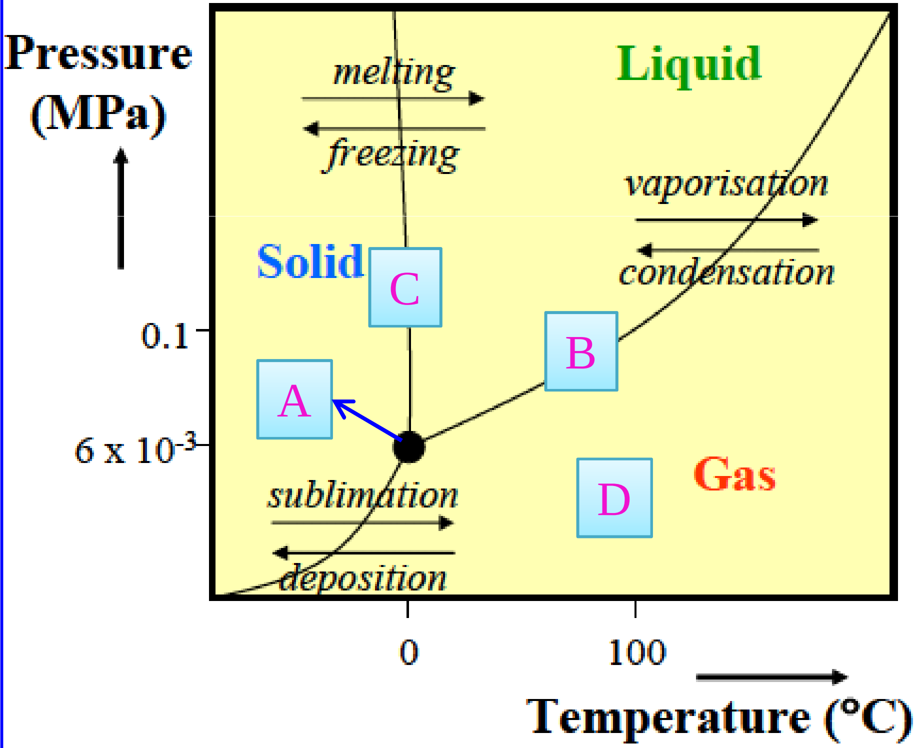
C = 2

No. of Phases	Total Variables $P(C-1)+2$	Degrees of freedom $C-P+2$	Degrees of freedom $C-P+1$
1	3	3	2
2	4	2	1
3	5	1	0
4	6	0	*Not possible*

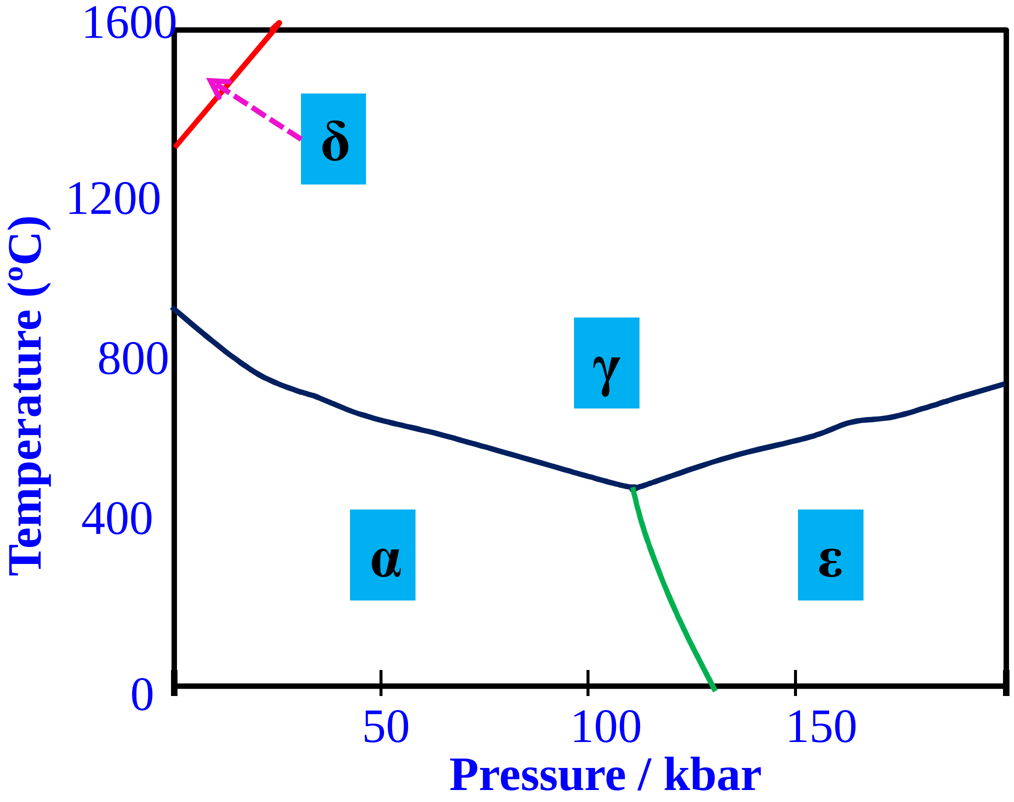
Unary Phase Diagram

- Let us start with the simplest system possible: the unary system wherein there is just one component.
- Though there are many possibilities even in unary phase diagram (in terms of the axis and phases), we shall only consider a T-P unary phase diagram.

- Let us consider the water (H_2O) unary phase diagram
- The Gibbs phase rule here is: F=C-P+2 (2 is for T&P) (no composition variables here)
- Along the 2 phase co-existence (at B & C) lines the degree of freedom (F) is 1 → i.e. we can chose either T or P and the other will be automatically fixed.
- The 3 phase co-existence points (at A) are invariant points with F=0. (Invariant point implies they are fixed for a given system).
- The single phase region at point D, T and P can both be varied while still being in the single phase region with F = 2.



Unary Phase Diagram



The above figure represents the phase diagram for pure iron. The triple point temperature and pressure are 490°C and 110 kbars, respectively. α, γ and ε refer to ferrite, austenite and ε-iron, respectively. δ is simply the higher temperature designation of α.

Binary Phase Diagram

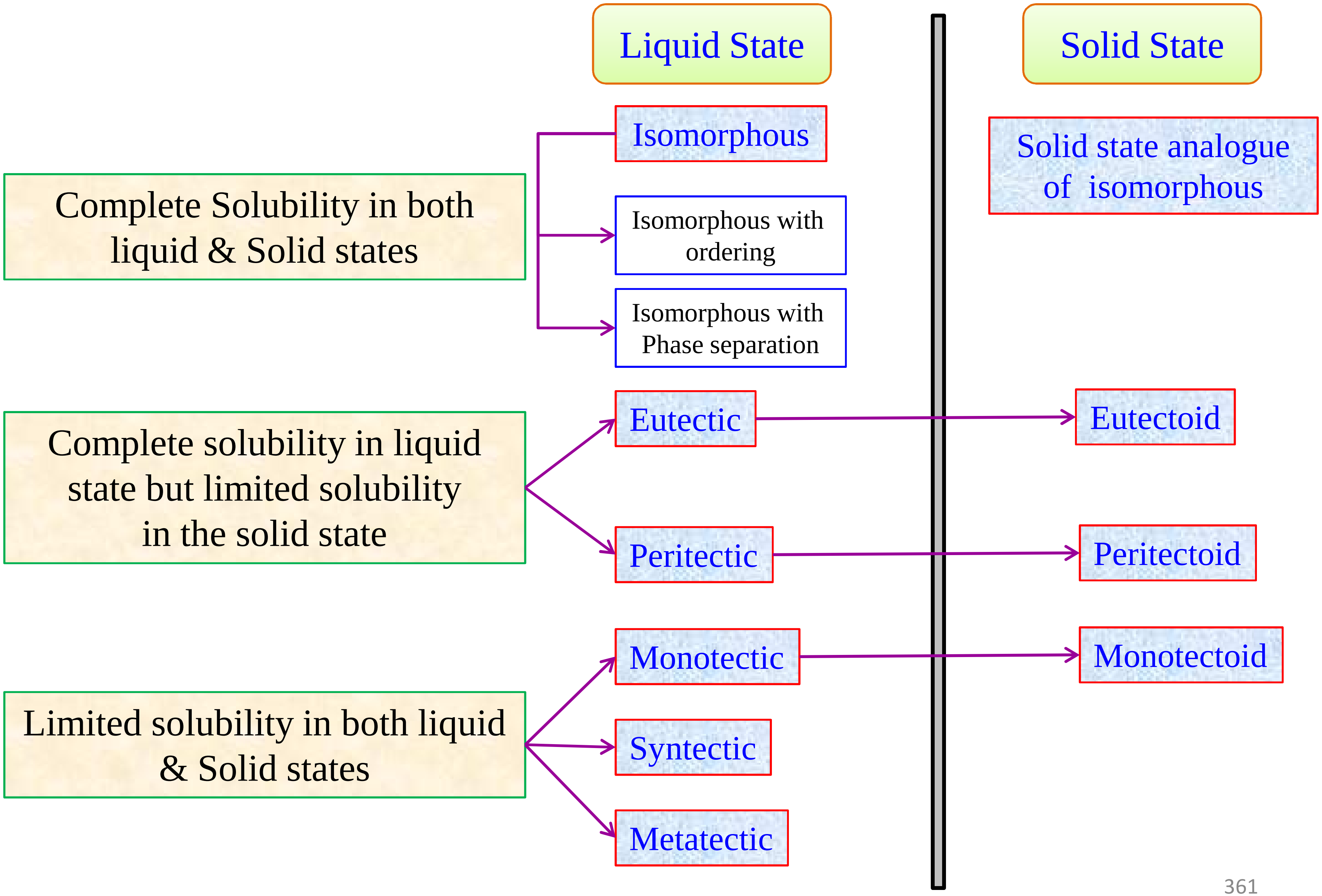
- Binary implies that there are two components.
- Pressure changes often have little effect on the equilibrium of solid phases (unless of course we apply 'huge' pressures).
- Hence, binary phase diagrams are usually drawn at 1 atmosphere pressure.
- The Gibbs phase rule is reduced to:
- Variables are reduced to : F = C – P + 1 *(1 is for T).*
- T & Composition (*these are the usual variables in materials phase diagrams)*

Phase rule for condensed phases $F = C - P + 1$

For T

- In the next page we consider the possible binary phase diagrams. These have been classified based on:
  - ✓ Complete solubility in both liquid & solid states
  - ✓ Complete solubility in both liquid state, but limited solubility in the solid state
  - ✓ Limited solubility in both liquid & solid states

Overview of possible Binary Phase Diagram



Liquid State

Solid State

Complete Solubility in both liquid & Solid states

- Isomorphous
- Isomorphous with ordering
- Isomorphous with Phase separation

Solid state analogue of isomorphous

Complete solubility in liquid state but limited solubility in the solid state

- Eutectic → Eutectoid
- Peritectic → Peritectoid

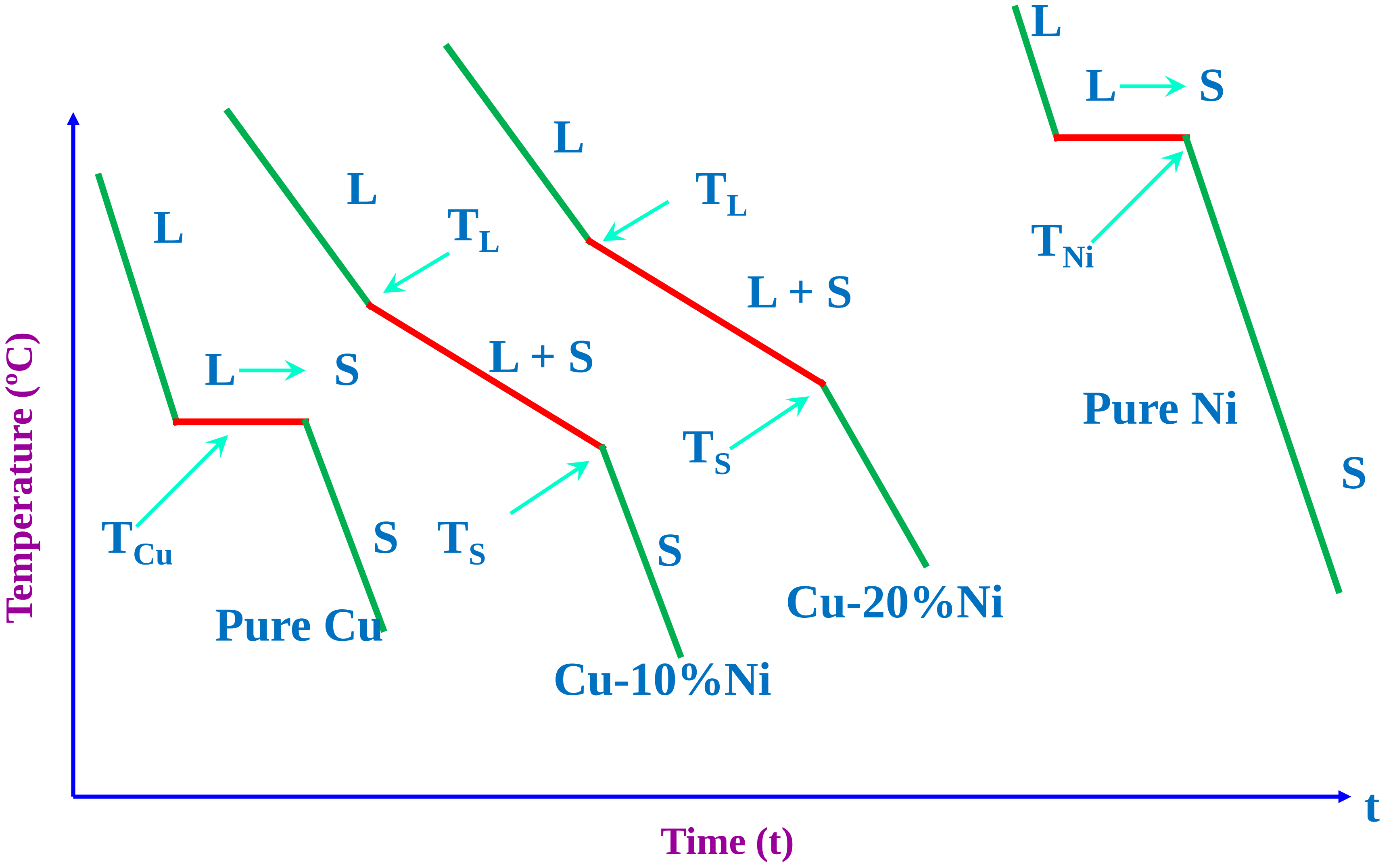
Limited solubility in both liquid & Solid states

- Monotectic → Monotectoid
- Syntectic
- Metatectic

Isomorphous Phase Diagram

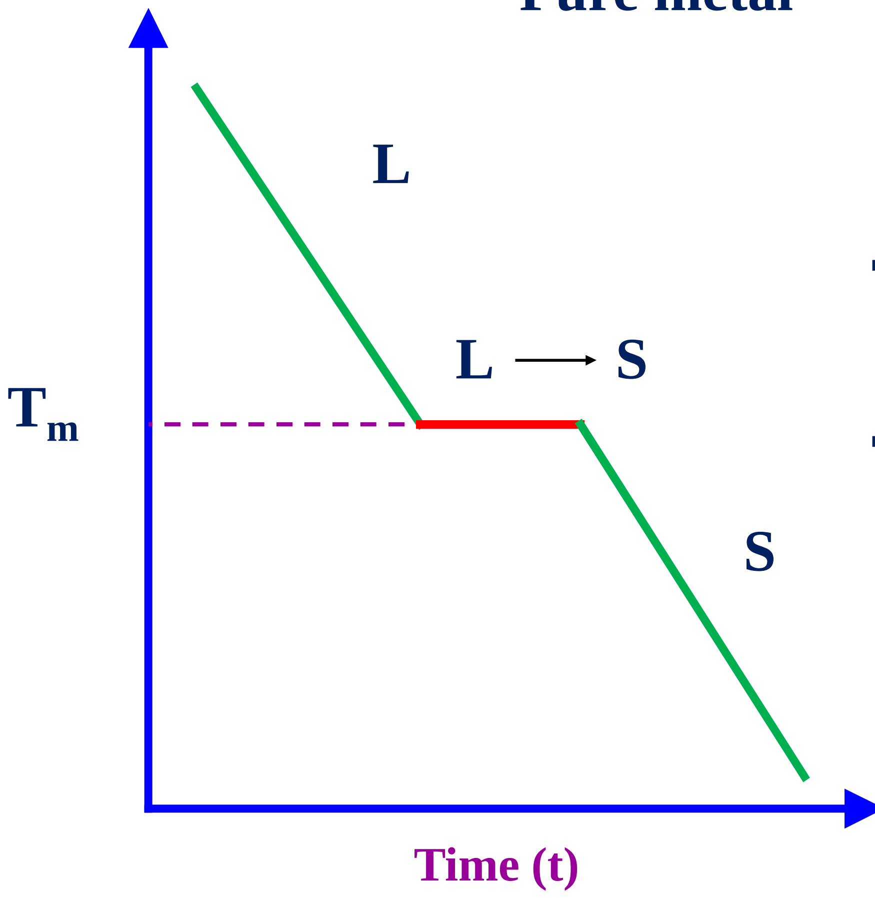
- ☐ Isomorphous phase diagrams form when there is complete solid and liquid solubility.
- ☐ Complete solid solubility implies that the crystal structure of the two components have to be same and Hume-Rothery rules to be followed.
- ☐ Examples of systems forming isomorphous systems: Cu-Ni, Ag-Au, Ge-Si, Al_2O_3-Cr_2O_3
- ☐ Both the liquid and solid contain the components A and B.
- ☐ In binary phase diagrams between two single phase regions there will be a two phase region → In the isomorphous diagram between the liquid and solid state there is the (Liquid + Solid) state.
- ☐ The Liquid + Solid state is NOT a semi-solid state → it is a solid of fixed composition and structure, in equilibrium with a liquid of fixed composition.
- ☐ In some systems (e.g. Au-Ni system) there might be phase separation in the solid state (i.e.,the complete solid solubility criterion may not be followed) → these will be considered as a variation of the isomorphous system (with complete solubility in the solid and the liquid state.

cooling curves : Isomorphous system

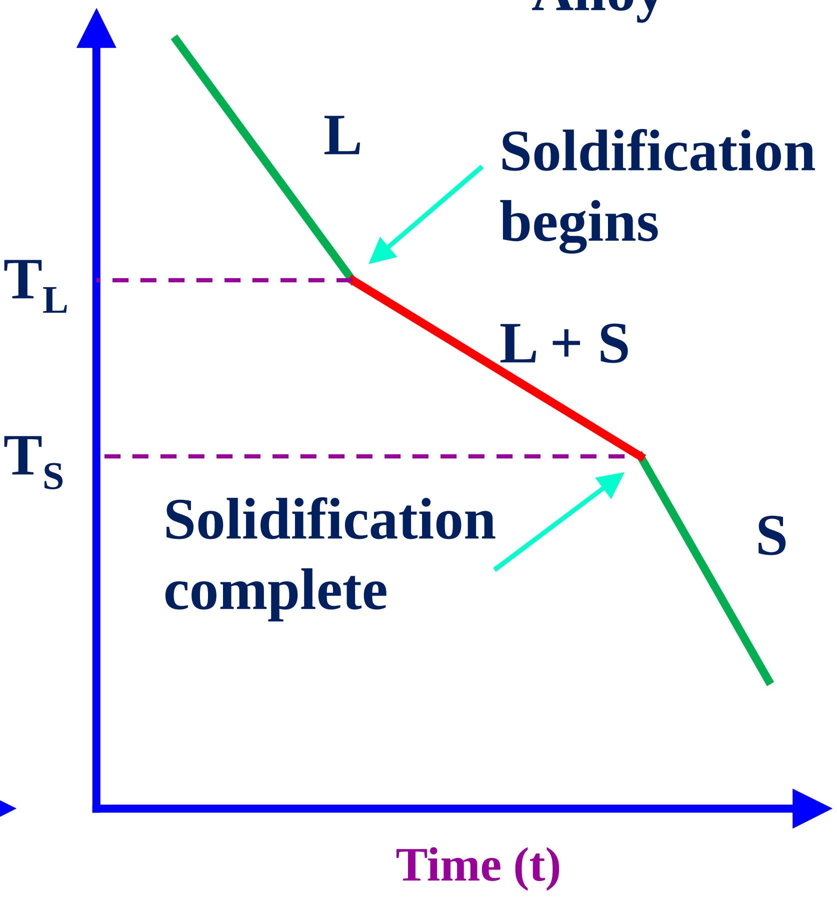


Revision : Solidification (cooling) curves

Pure metal

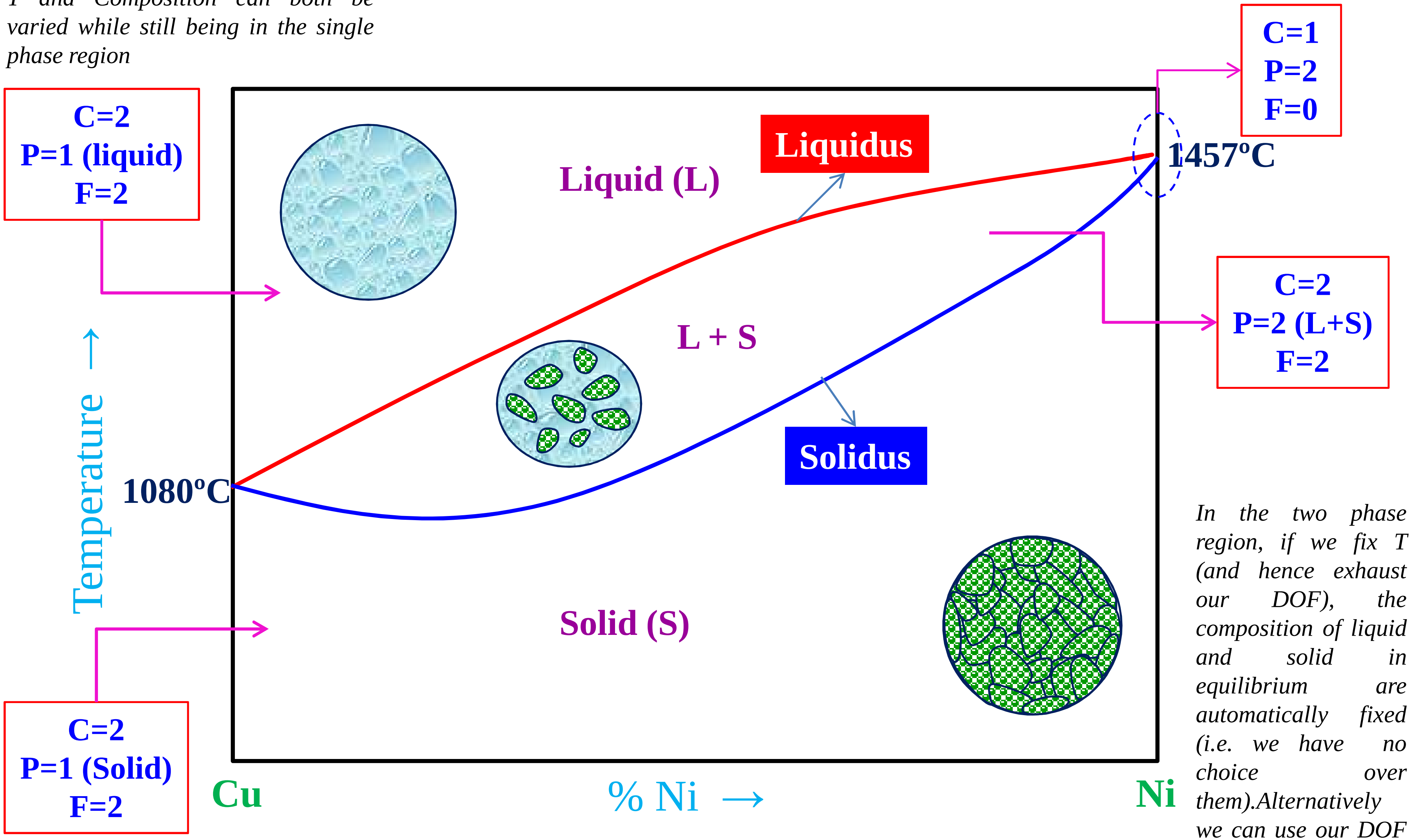


Alloy



Isomorphous Phase Diagram

T and Composition can both be varied while still being in the single phase region



C=2
P=1 (liquid)
F=2

C=1
P=2
F=0

C=2
P=2 (L+S)
F=2

C=2
P=1 (Solid)
F=2

T and Composition can both be varied while still being in the single phase region

In the two phase region, if we fix T (and hence exhaust our DOF), the composition of liquid and solid in equilibrium are automatically fixed (i.e. we have no choice over them).Alternatively we can use our DOF to chose C_L then T and C_s are automatically fixed.

Tie line and Lever rule

Chemical Composition of Phases

Tie Line Rule

- ❑ To determine the actual chemical composition of the phases of an alloy, in equilibrium at any specified temperature in a two phase region, draw a horizontal temperature line, called a *tie line*, to the boundaries of the field . These points of intersection are dropped to the base line, and the composition is read directly.

Relative Amounts of Each Phase

Lever Rule

- ❑ To determine the relative amounts of the two phases in equilibrium at any specified temperature in a two phase region , draw a vertical line representing the alloy and a horizontal temperature line to the boundaries of the field.
- ❑ The vertical line will divide the horizontal line into two parts whose lengths are inversely proportional to the amount of the phases present. This is also known as *Lever rule.*
- ❑ The point where the vertical line intersects the horizontal line may be considered as the *fulcrum* of a lever system.
- ❑ The relative lengths of the lever arms multiplied by the amounts of the phases present must balance.

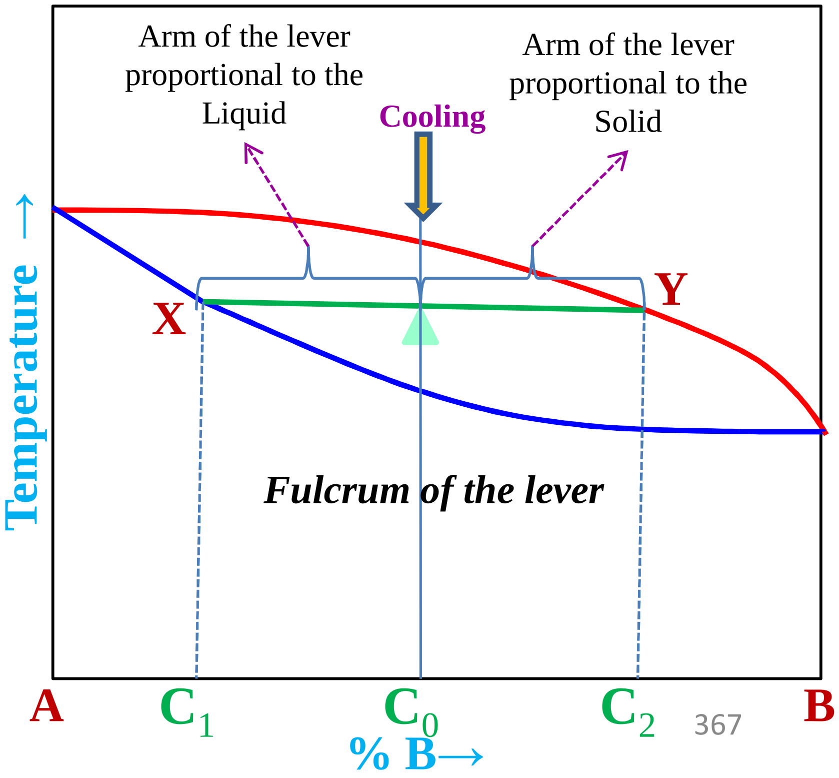
Tie line and Lever rule

- ❑ We draw a horizontal line (called the Tie Line)at the temperature of interest (say T_0). Let Tie line is XY.
- ❑ Solid (crystal) of composition **C_1** coexists with liquid of composition **C_2**
- ❑ Note that tie lines can be drawn only in the two phase coexistence regions (fields). Though they may be extended to mark the temperature.
- ❑ To find the fractions of solid and liquid we use the lever rule.

- ❑ The portion of the horizontal line in the two phase region is akin to 'lever' with the fulcrum at the nominal composition (**C_0**)
- ❑ The opposite arms of the lever are proportional to the fraction of the solid and liquid phase present (this is lever rule)

$$f_{liquid} = \frac{C_0 - C_1}{C_2 - C_1}$$

$$f_{Solid} = \frac{C_2 - C_0}{C_2 - C_1}$$



Tie line and Lever rule

Example

Cu – Ni System

At C_o = 35 wt% Ni

At T_A: Only Liquid (L)

W_{liquid} = 100 wt%, W_{solid} = 0

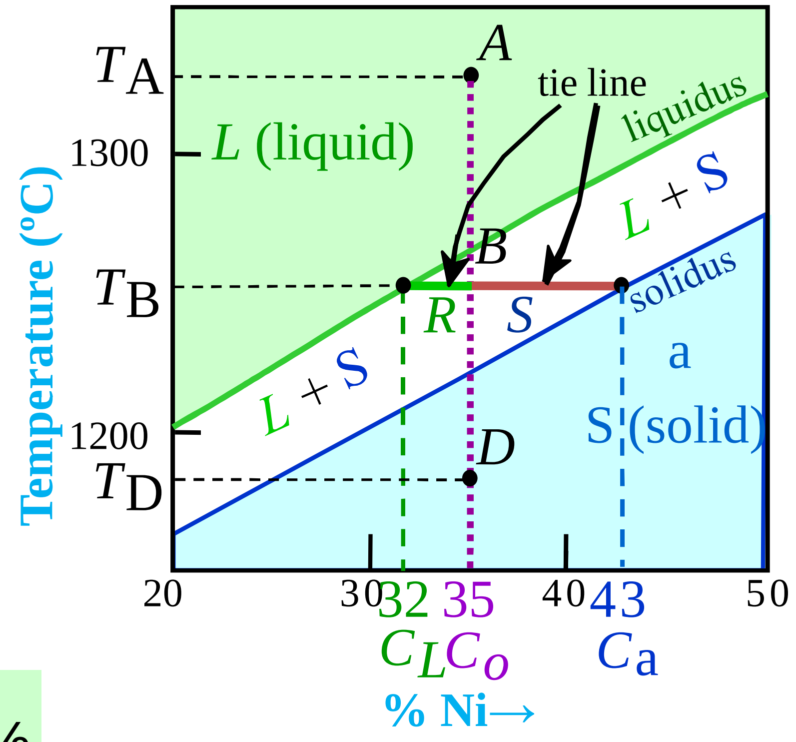
At T_D: Only Solid (S)

W_L = 0, W_{solid} = 100 wt%

At T_B: Both S and L

$$W_L = \frac{S}{R+S} = \frac{43-35}{43-32} = 73\,wt\%$$

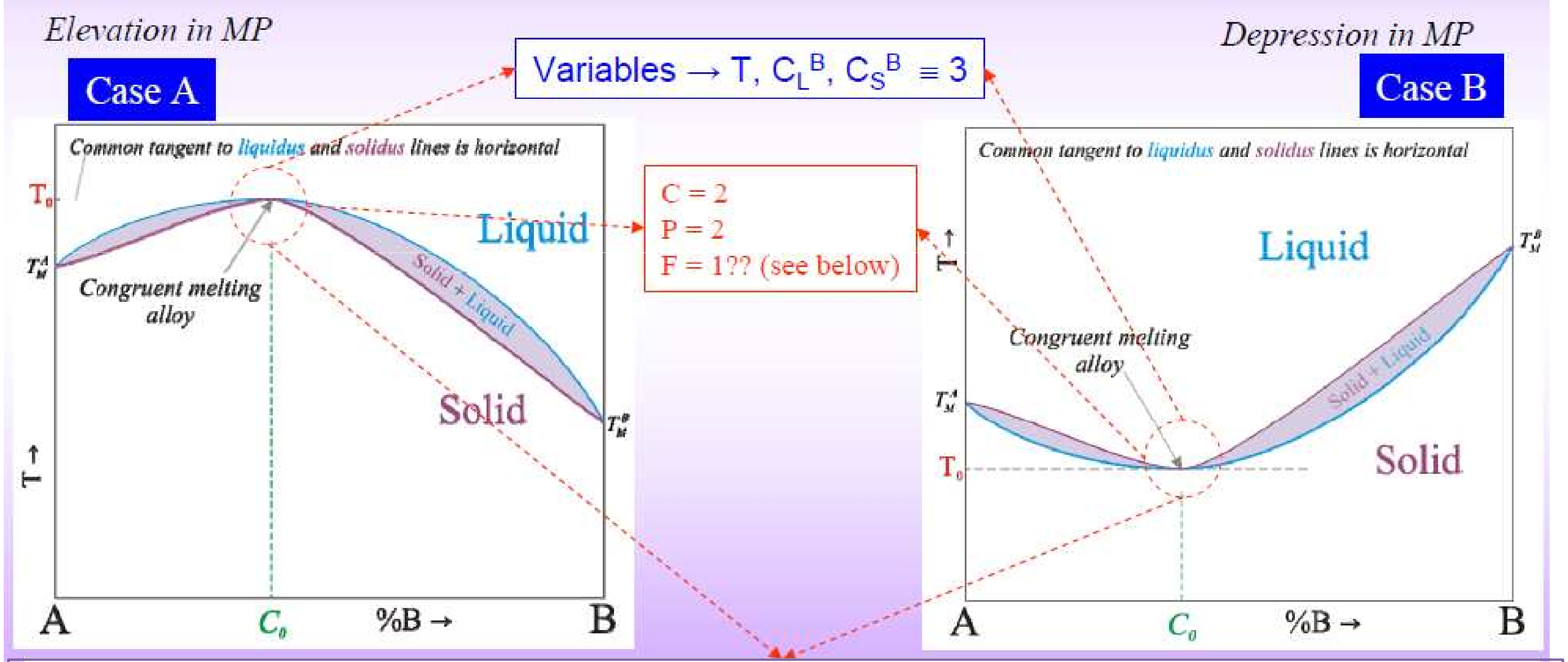
$$W_S = \frac{R}{R+S} = 27\text{ wt\%}$$



Notice: as in a lever "the opposite leg" controls with a balance (fulcrum) at the 'base composition' and R+S = tie line length = difference in composition limiting phase boundary, at the temp of interest

Variations of Isomorphous System

An alloy typically melts over a range of temperatures. However, there are special compositions which can melt at a single temperature like a pure metal. There is no difference in the liquid and solid composition. It begins and ends solidification at a constant temperature with no change in composition, and its cooling curve will show a horizontal line. Such alloys are known as a **congruent-melting alloys,** sometimes known as a **pseudo-eutectic alloy**. Ex: Cu-Au, Ni-Pd.



Variables → T, C_L^B, C_S^B ≡ 3

C = 2
P = 2
F = 1?? (see below)

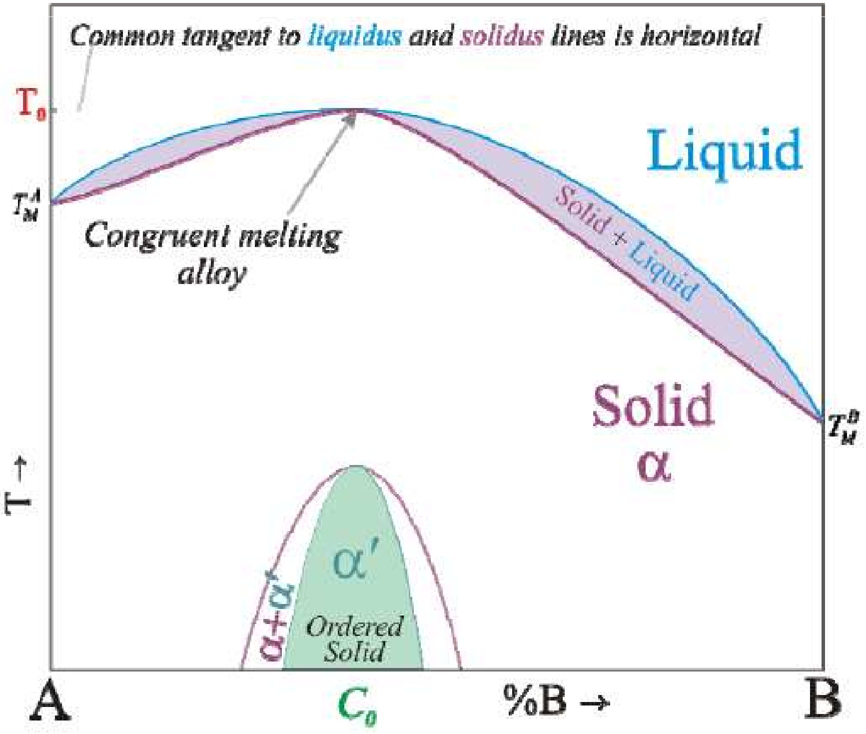
- Congruently melting alloys → just like a pure metal
- Is the DOF 1? No: in requiring that $\mathbf{C_L^B = C_S^B}$ we have exhausted the degree of freedom. Hence T is automatically fixed → DOF is actually Zero..!

Variations of Isomorphous System

- Elevation in the MP means that the solid state is 'more stable' (*crudely speaking the ordered state is more stable*) → ordering reaction is seen at low T.
- Depression in MP 'means' the liquid state (disordered) is more stable → phase separation is seen at low T. (*phase separation can be thought of as the opposite of ordering. Ordering (compound formation) occurs for –ve values for* ΔH_{mix}).

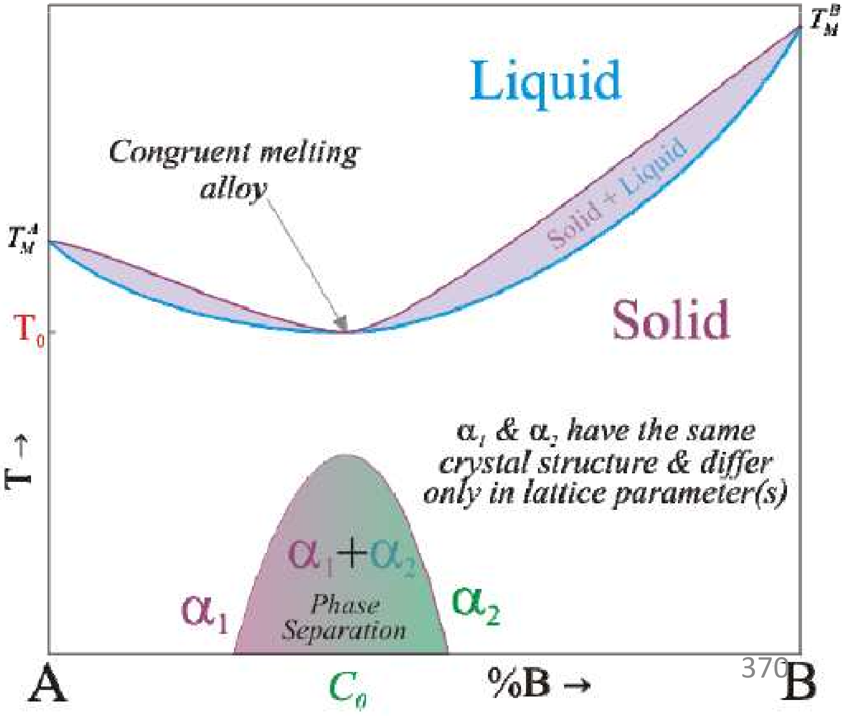
▪A – B bonds stronger than A – A and B – B bonds
▪Solid Stabilized → Ordered Solid Formation

Case 1

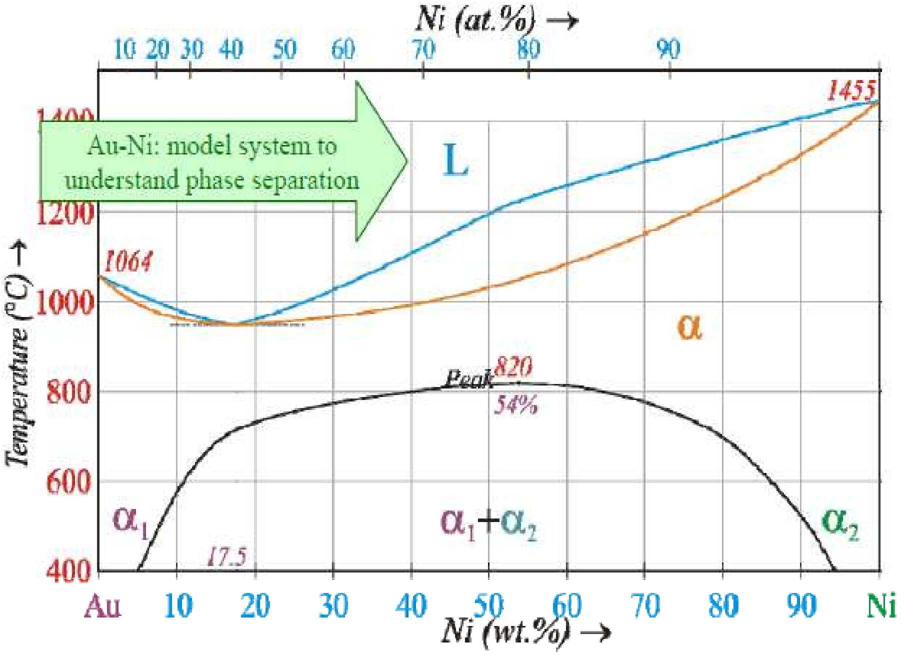

Common tangent to liquidus and solidus lines is horizontal

▪ A – A and B – B bonds stronger than A-B bonds
▪Liquid Stabilized → Phase separation in the solid

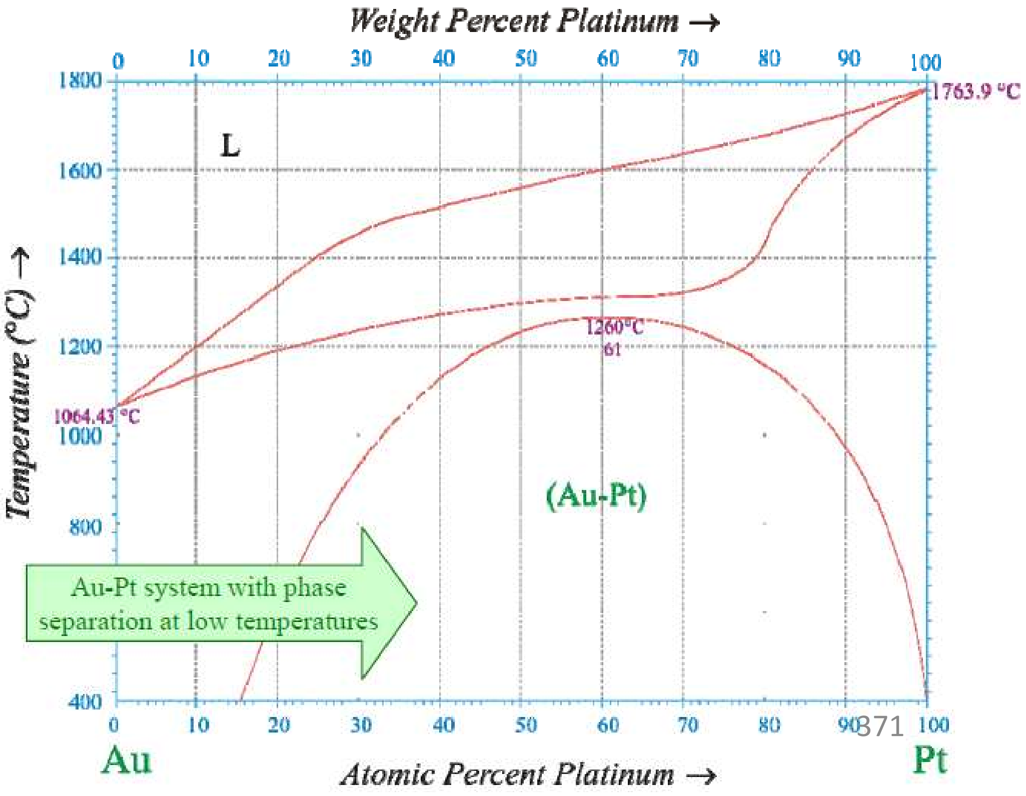
Case 2


α_1 & α_2 have the same crystal structure & differ only in lattice parameter(s)

Examples of Isomorphous System with phase separation



Au-Ni: model system to understand phase separation



Au-Pt system with phase separation at low temperatures

Equilibrium Cooling

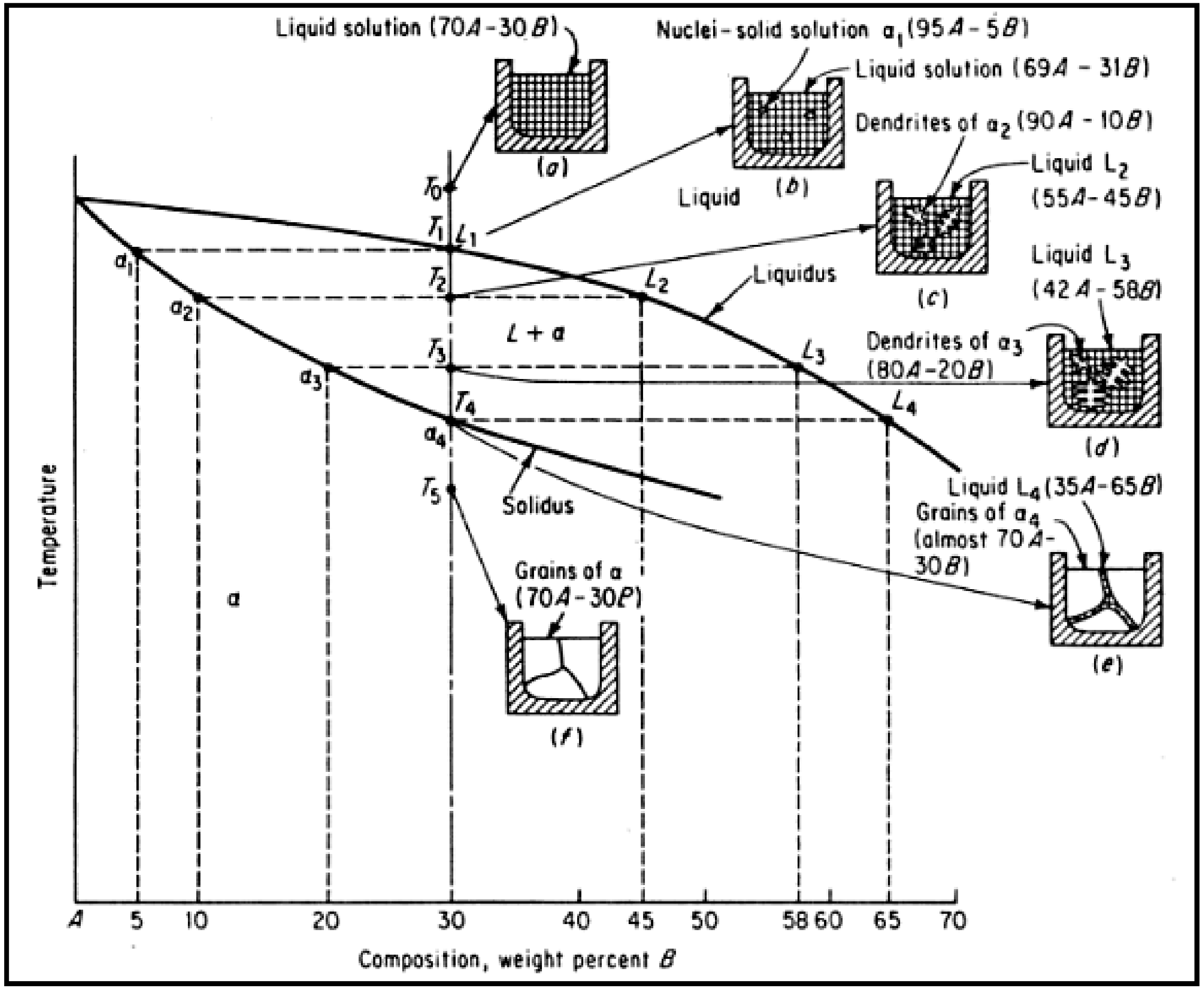
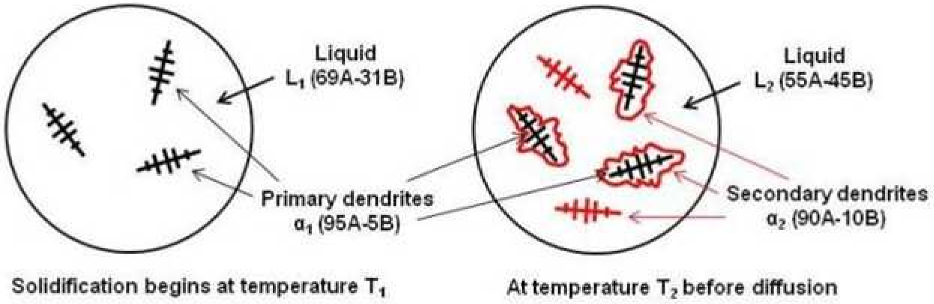


Figure: The above figure represents the very slow cooling , under equilibrium conditions, of a particular alloy 70A-30B will now be studied to observe the phase changes that occur .

Equilibrium Cooling

- ❑ This alloy at temperature T_0 is a homogeneous single-phase liquid solution (*a*) and remains so until temperature T_1 is reached. Since T_1 is on the liquidus line, freezing or solidification now begins.
- ❑ The first nuclei of solid solution to form α_1 will be very rich in the higher melting point metal A and will be composed of 95A-5B (*by tie line rule*). Since the solid solution in forming takes material very rich in A from the liquid, the liquid must get richer in B. Just after the start of solidification, the composition of the liquid is approximated as 69A-31B (b).
- ❑ When the lower temperature T_2 is reached, the liquid composition is at L_2. The only solid solution in equilibrium with L_2 and therefore the only solid solution forming at T_2 is α_2. Applying tie line rule, α_2 is composed of 10B. Hence, as the temperature is decreased, not only does the liquid composition become richer in B but also the solid solution.
- ❑ At T_2, crystals of α_2 are formed surrounding the α_1 composition cores and also separate dendrites of α_z (*see figure in below*).



Solidification begins at temperature T_1

At temperature T_2 before diffusion

Schematic Representation of the Alloy 70A-30B at Temperatures T_1 and T_2

Equilibrium Cooling

- ☐ In order for equilibrium to be established at $T_{2,}$ the entire solid phase must be a composition α_2. This requires diffusion of B atoms to the A-rich core not only from the solid just formed but also from the liquid. This is possible in crystal growth (c).
- ☐ The composition of the solid solution follows the solidus line while the composition of liquid follows the liquidus line, and both phases are becoming richer in B.
- ☐ At T_3 (d), the solid solution will make up approximately three-fourths of all the material present.
- ☐ Finally, the solidus line is reached at $T_{4,}$ and the last liquid $L_{4,}$ very rich in B, solidifies primarily at the grain boundaries (e).
- ☐ However, diffusion will take place and all the solid solution will be of uniform composition α(70A-30B), which is the overall composition of the alloy (f).
- ☐ There are only grains and grain boundaries. There is no evidence of any difference in chemical composition inside the grains, indicating that diffusion has made the grain homogeneous.

Equilibrium Cooling

- The very slow cooling , under equilibrium conditions, of particular alloy 65Cu - 35Ni will now be studied.

  A – Homogeneous single phase (Liquid)

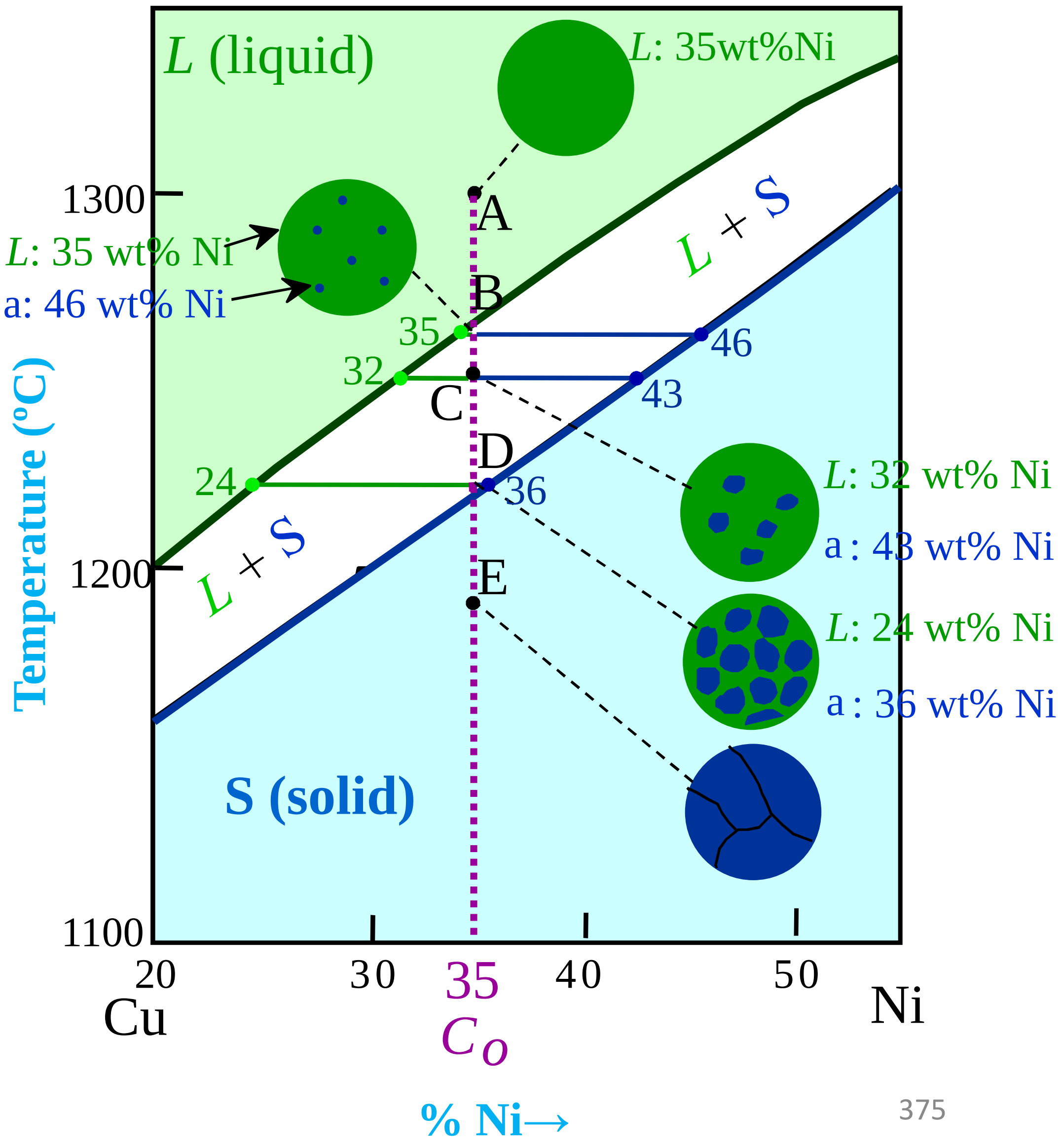
  B - 'B' is on the liquidus line, solidification now begins.

  C – Solid surrounded by liquid crystals.

  D – 'D' is on the solidus line, solidification now ends.

  E – Homogeneous single phase (Solid)

Cu-Ni Phase Diagram

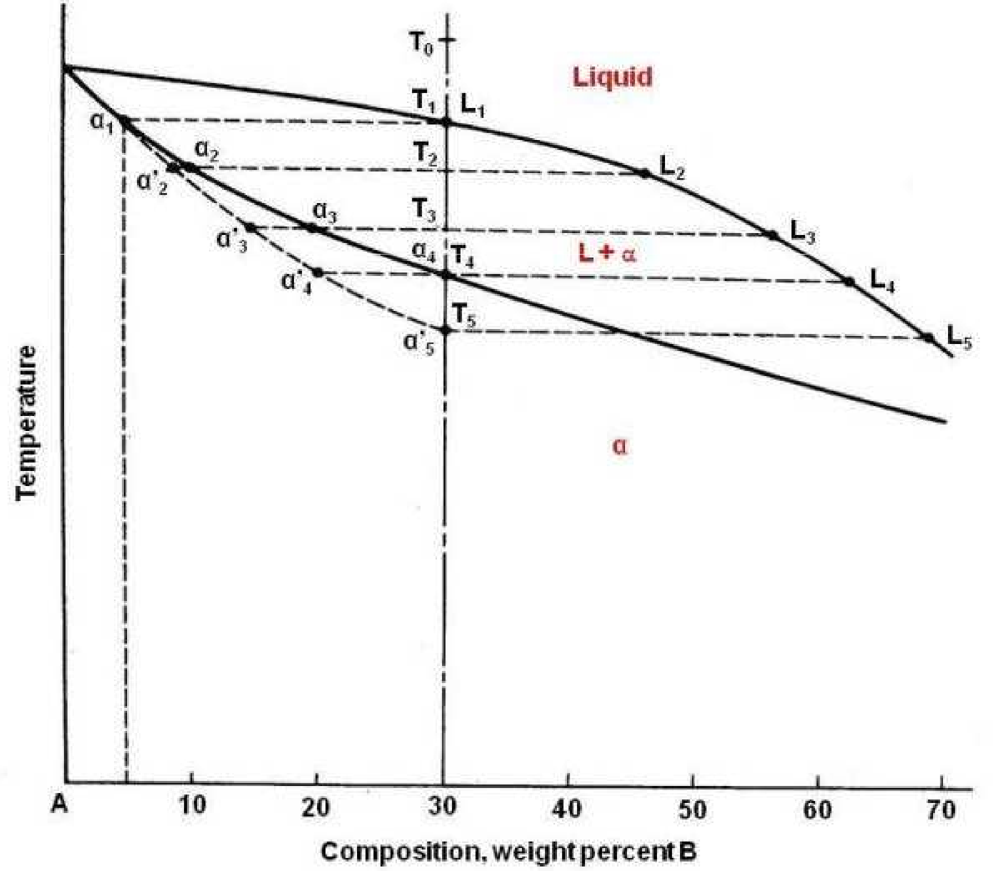


% Ni→

Non Equilibrium Cooling - Coring

- In actual practice it is extremely difficult to cool under equilibrium conditions. Since diffusion in the solid state takes place at a very slow rate, it is expected that with ordinary cooling rates there will be some difference in the conditions as indicated by the equilibrium diagram.

- Consider again 70A-30B alloy, solidification starts at T_1 forming a solid solution of composition α_1 .
- At T_2 the liquid is L_2 and the solid solution now forming is of composition α_2 . Since diffusion is too slow to keep pace with crystal growth, not enough time will be allowed to achieve uniformity in the solid, and the average composition will be between α_1 and α_2, say α'_2.



Nonequilibrium Cooling

Non Equilibrium Cooling - Coring

- As the temperature drops, the average composition of the solid solution will depart still further from equilibrium conditions. It seems that the composition of the solid solution is following a "nonequilibrium" solidus line α_1 to α'_5, shown dotted lines in figure.
- The liquid, on the other hand, has essentially the composition given by the liquidus line, since diffusion is relatively rapid in liquid. At T_3 the average solid solution will be of composition α'_3 instead of α_3.
- Under equilibrium cooling, solidification should be complete at T_4 ; however, since the average composition of the solid solution α'_4 has not reached the composition of the alloy, some liquid must still remain. Applying lever rule at T_4 gives $\alpha'_4 = 75\%$ and $L_4 = 25\%$.
- Therefore, solidification will continue until T_5 is reached. At this temperature the composition of the solid solution α'_5 coincides with the alloy composition, and solidification is complete. The last liquid to solidify, L_5, is richer in B than the last liquid to solidify under equilibrium conditions.

Non Equilibrium Cooling - Coring

- ❑ *The more rapidly the alloy is cooled the greater will be the composition range in the solidified alloy. Since the rate of chemical attack varies with composition, proper etching will reveal the dendritic structure microscopically (see below figure). The final solid consists of a "cored" structure with a higher-melting central portion surrounded by the lower-melting, last-to-solidify shell. The above condition is referred to as coring or dendritic segregation.*

- ❑ To summarize, nonequilibrium cooling results in an increased temperature range over which liquid and solid are present; Since diffusion has not kept pace with crystal growth, there will be a difference in chemical composition from the center to the outside of the grains. The faster the rate of cooling, the greater will be the above effects.

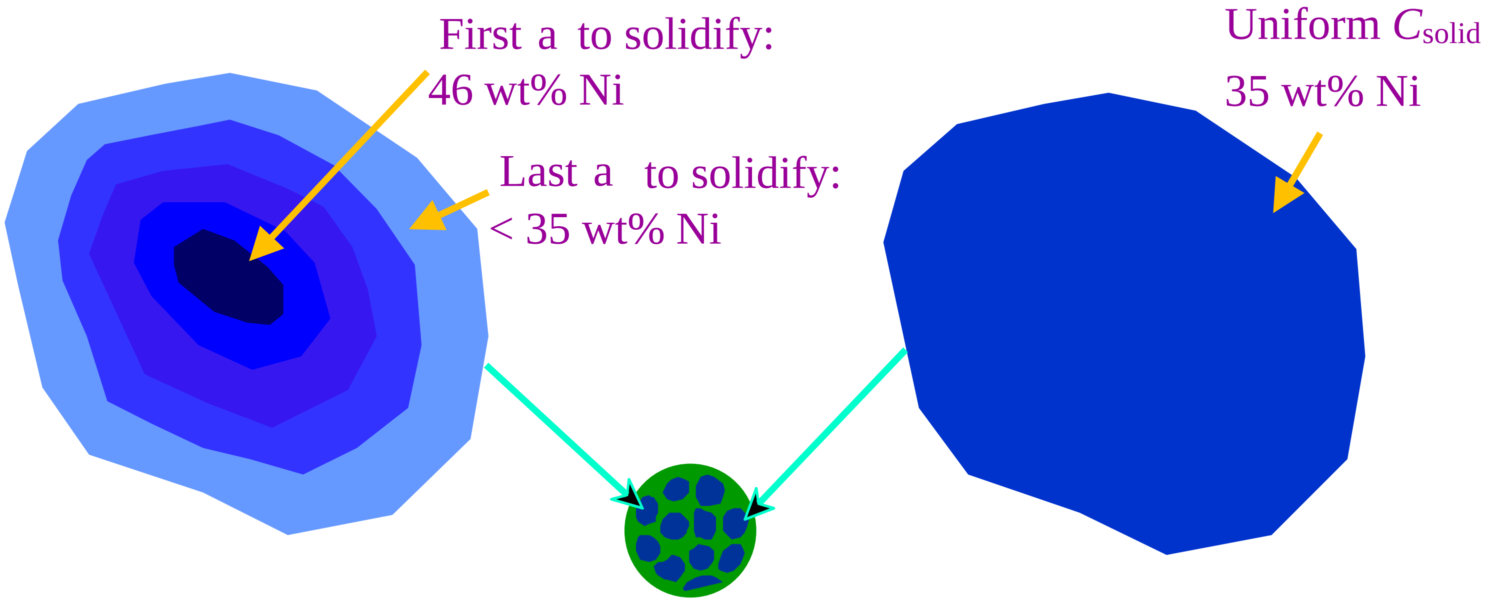
Cored *vs.* Equilibrium Phases

Consider Cu-Ni phase diagram case

First a to solidify has C_{solid} = 46 wt% Ni.
Last a to solidify has C_{solid} = 35 wt% Ni.

On Fast rate of cooling
Cored structure

On Slow rate of cooling
Equilibrium structure



First a to solidify:
46 wt% Ni

Last a to solidify:
< 35 wt% Ni

Uniform C_{solid}
35 wt% Ni

Homogenization

- Cored structures are most common in as-cast metals. From the earlier discussion of the origin of a cored structure, it is apparent that the last solid formed along the grain boundaries and in the inter-dendritic spaces is very rich in the lower-melting-point metal.

- Depending upon the properties of the lower-melting-point metal, the grain boundaries may act as a plane of weakness. It will also result in a serious lack of uniformity in mechanical and physical properties and, in some cases, increased susceptibility to intergranular corrosion because of preferential attack by corrosive medium. Therefore, for some applications a cored structure is objectionable.

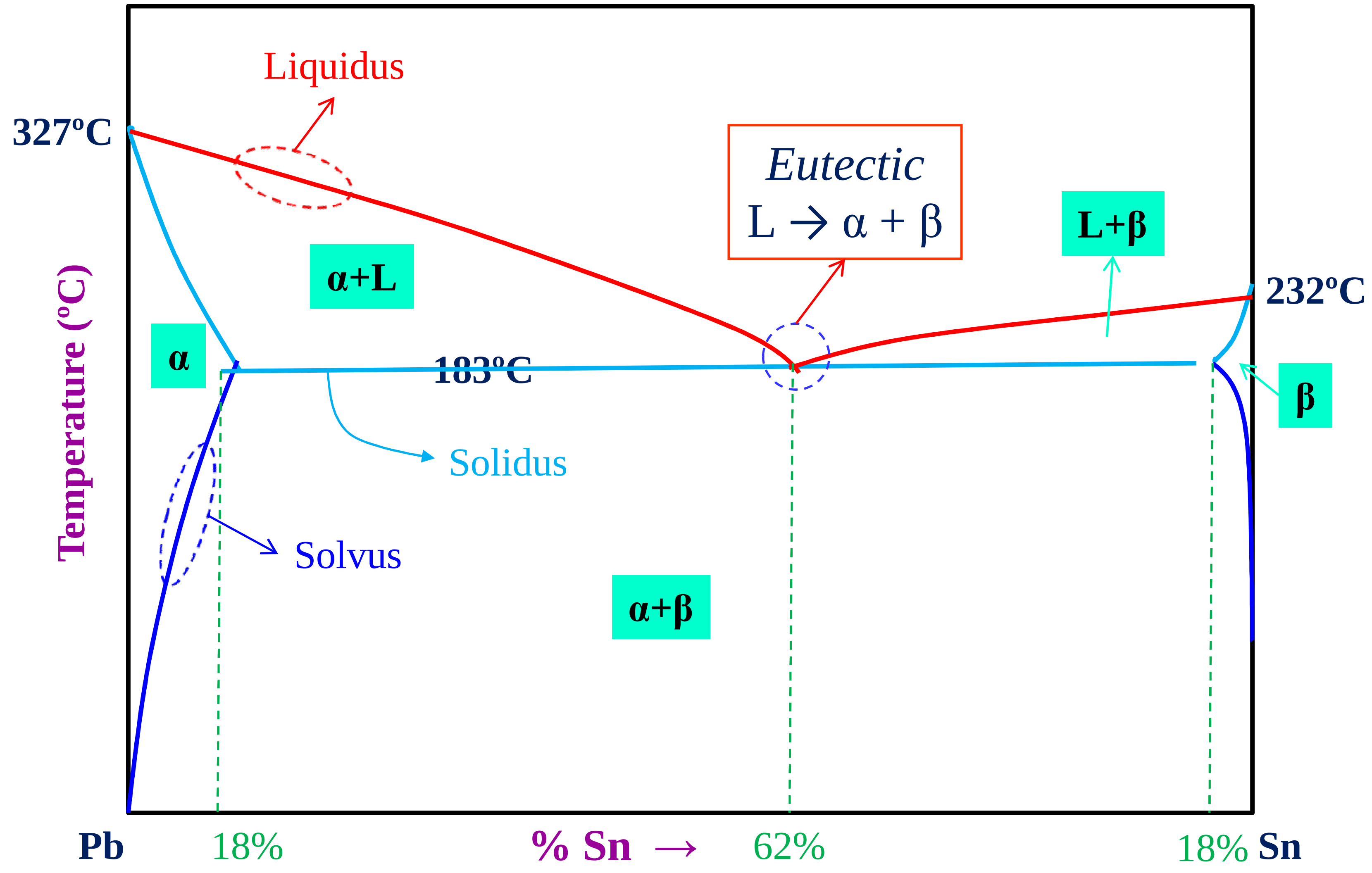
- There are two methods for solving the problem of coring. One is to prevent its formation by slow freezing from the liquid, but this result in large grain size and requires a very long time. The preferred method industrially is to achieve equalization of composition or homogenization of the cored structure by diffusion in the solid state.

- At room temperature, for most metals, the diffusion rate is very slow; but if the alloy is reheated to a temperature below the solidus line, diffusion will be more rapid and homogenization will occur in a relatively short time.

Eutectic Phase Diagram

- Very few systems exhibit an isomorphous phase diagram (usually the solid solubility of one component in another is limited).
- Often the solid solubility is severely limited – through the solid solubility is never zero (due to entropic reasons).
- In a Simple eutectic system (binary), there is one composition at which the liquid freezes at a single temperature. This is in some sense similar to a pure solid which freezes at a single temperature (unlike a pure substance the freezing produces a two solid phases both of which contain both the components).
- The term Eutectic means easy melting → The alloy of eutectic composition freezes at a lower temperature than the melting point s of the constituent components.
- *This has important implifications → e.g. the Pb-Sn eutectic alloy melts at 183 ºC, which is lower than the melting points of both Pb (327ºC) and Sn (232ºC) → Can be used for soldering purposes (as we want to input least amount of heat to solder two materials).*
- In the next page we consider the Pb-Sn eutectic phase diagram.

Eutectic Phase Diagram



Eutectic reaction at 183ºC

L → α + β

62%Sn → 18%Sn + 97%Sn

Example : Cu-Ag Eutectic System

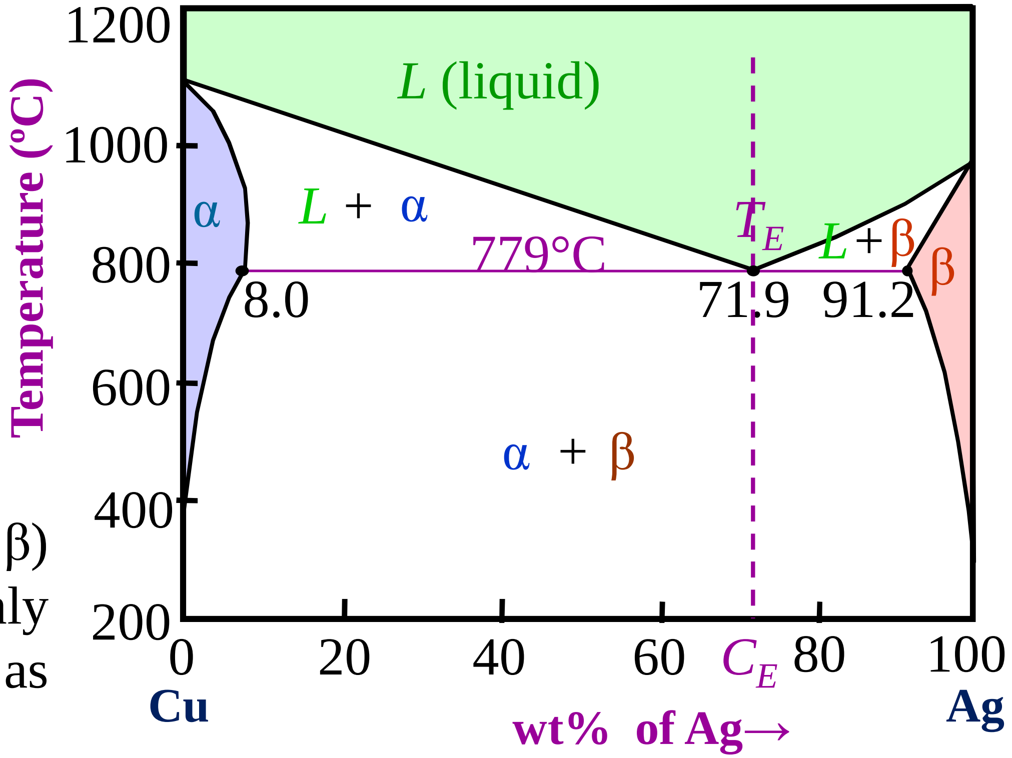
❑ Raoult's law states that the freezing point of a pure substance will be lowered by the addition of a second substance provided the latter is soluble in the pure substance when liquid and insoluble when solidified. The amount of lowering of the freezing point is proportional to the molecular weight of the solute.

- Limited solubility:

  α: mostly Cu

  β: mostly Ag

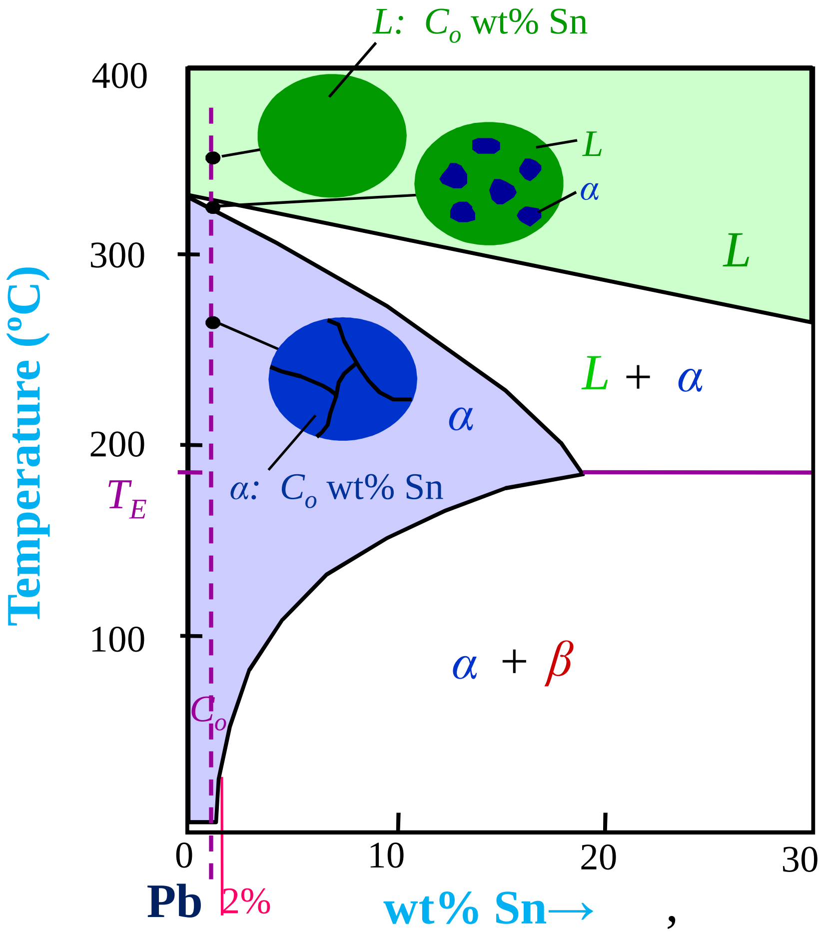
- T_E : No liquid below T_E
- C_E : Min. melting T_E



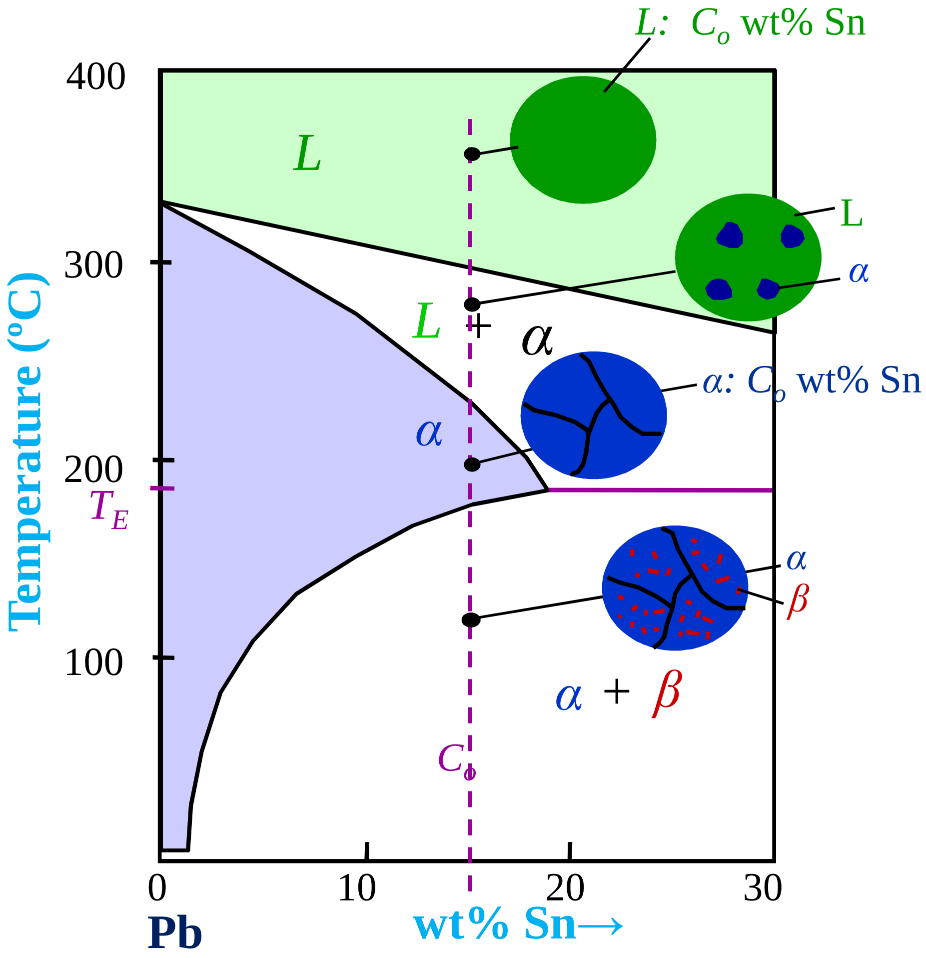
Three single phase regions – (L, α, β) exist at 71.9% Ag at 779°C commonly known as Eutectic. The reaction is as follows…!

$$L(C_E) \rightleftharpoons \alpha(C_{\alpha E}) + \beta(C_{\beta E})$$

Microstructural Characteristics of Eutectic System



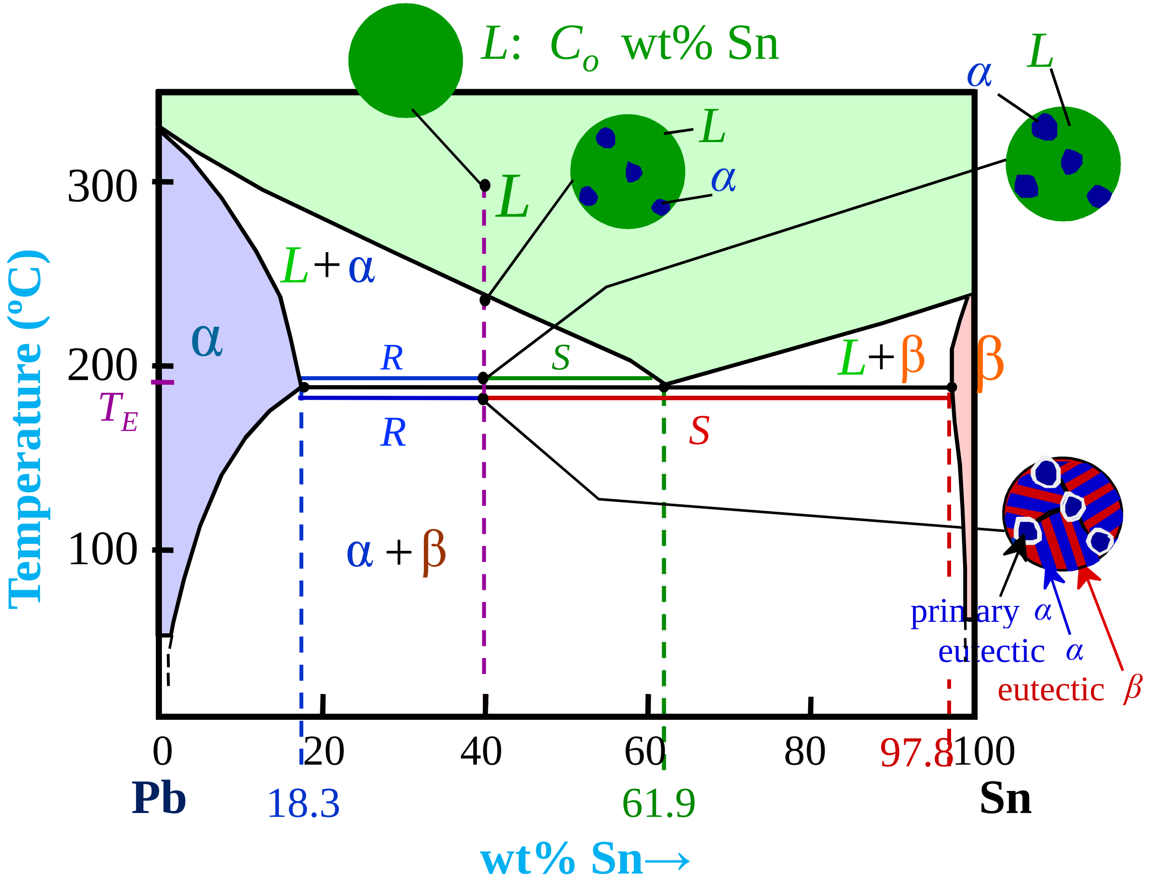
,



- ❑ To reiterate an important point: Phase diagram do not contain microstructural information (i.e. they cannot tell you what is the microstructures produced by cooling. Often microstructural information is overlaid on phase diagram for convenience. Hence, strictly cooling is not in the domain of phase diagram – but we can overlay such information keeping in view the assumptions involved.

Microstructural Characteristics of Eutectic System

- 18.3 wt% Sn < C_o < 61.9 wt% Sn
- Microstructure consists a crystals and a eutectic microstructure



→Just above T_E :

$C\alpha$ = 18.3 wt% Sn

C_L = 61.9 wt% Sn

$$W\alpha = \frac{S}{R+S} = 50 \text{ wt\%}$$

W_L = (1- $W\alpha$) = 50 wt%

→ Just below T_E :

$C\alpha$ = 18.3 wt% Sn

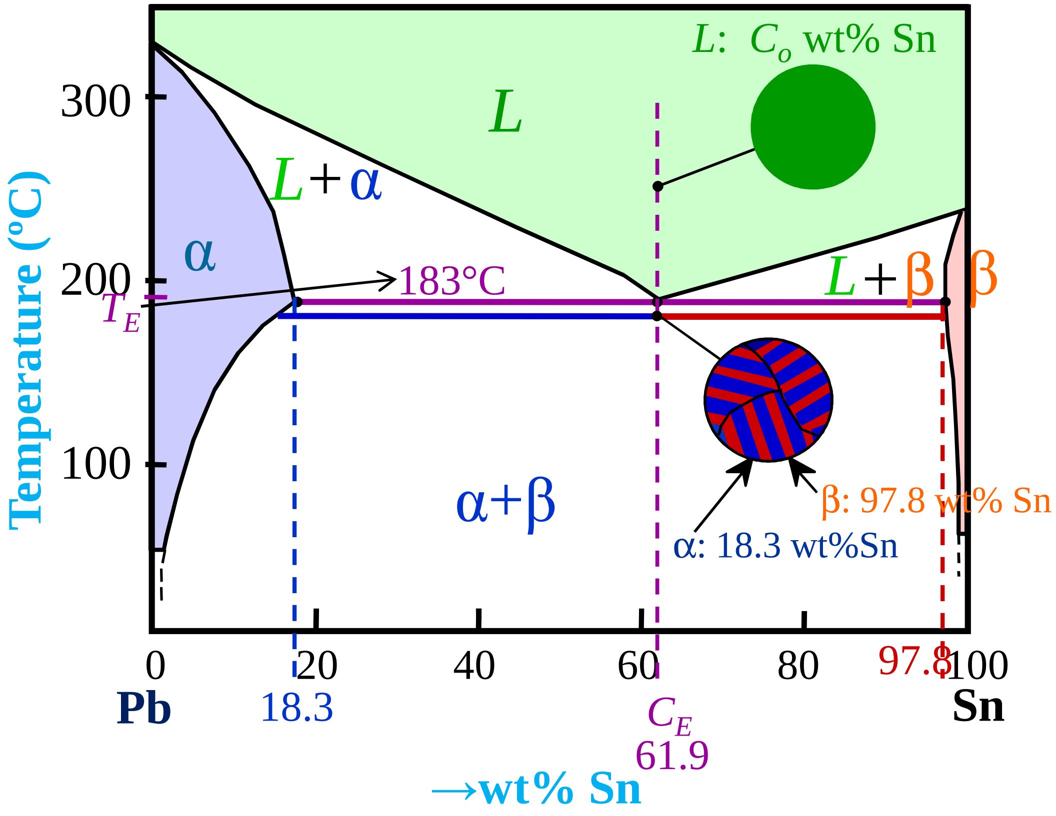
$C\beta$ = 97.8 wt% Sn

$$W\alpha = \frac{S}{R+S} = 72.6 \text{ wt\%}$$

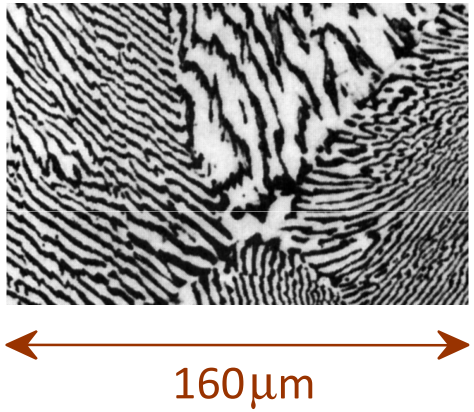
$W\beta$ = 27.4 wt%

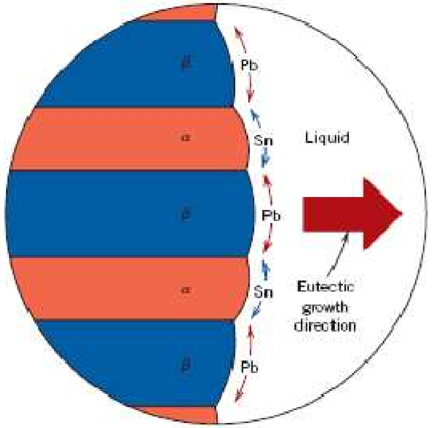
Microstructural Characteristics of Eutectic System

- ❑ $C_o = C_E$
- ❑ Microstructure represents Eutectic microstructure (lamellar structure) alternating layers (lamellae) of a and b crystals.



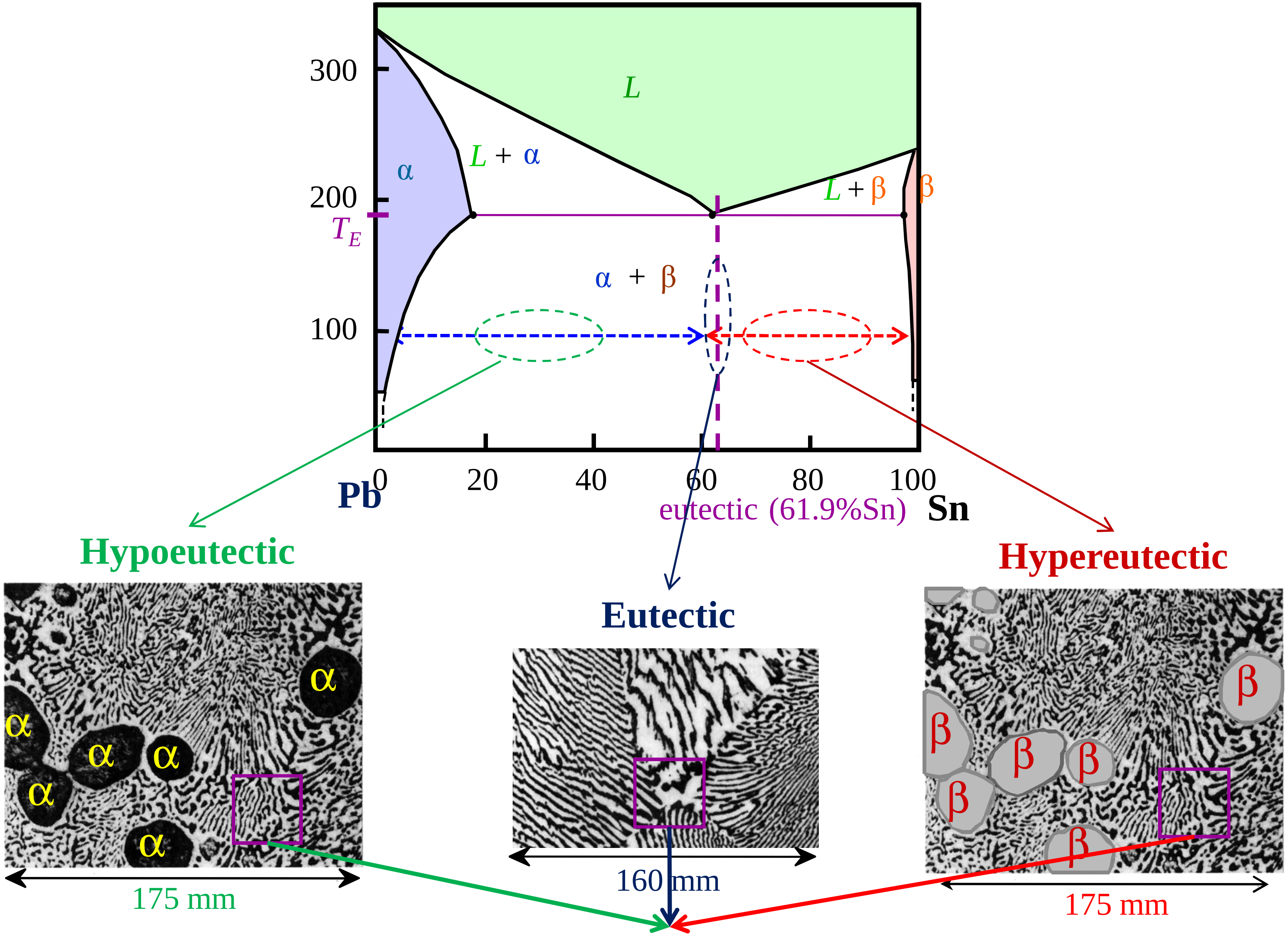
Pb-Sn Eutectic Microstructure





45.1% α and 54.8% β

Hypo Eutectic – Eutectic – Hyper Eutectic



eutectic (61.9%Sn)

Hypoeutectic

175 mm

Eutectic

160 mm

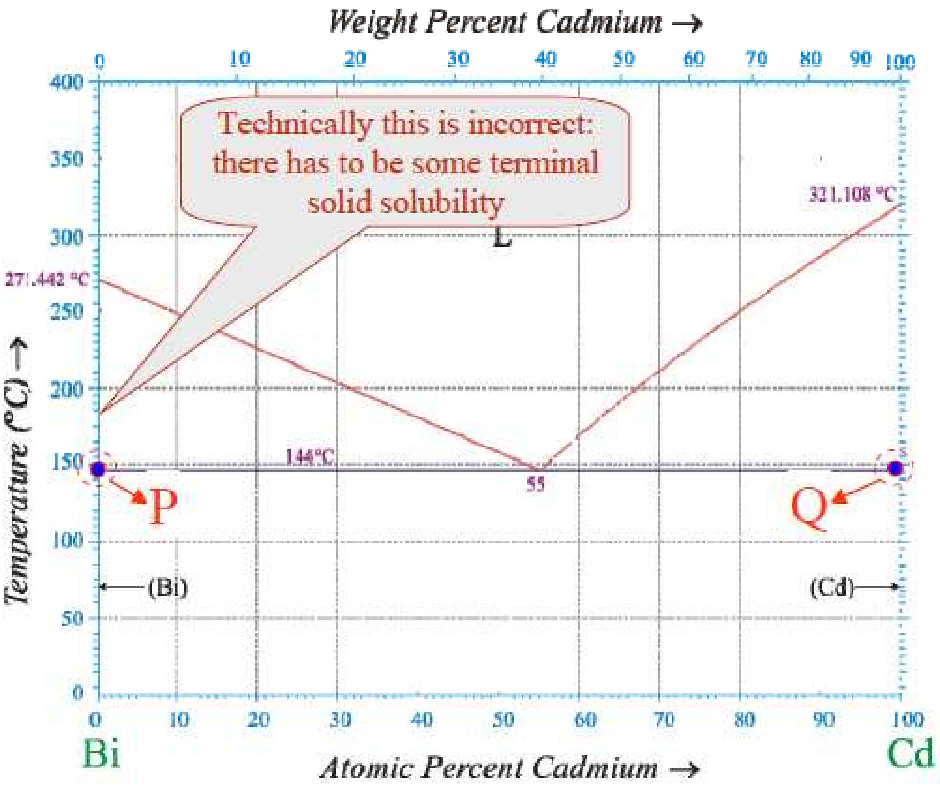
Hypereutectic

175 mm

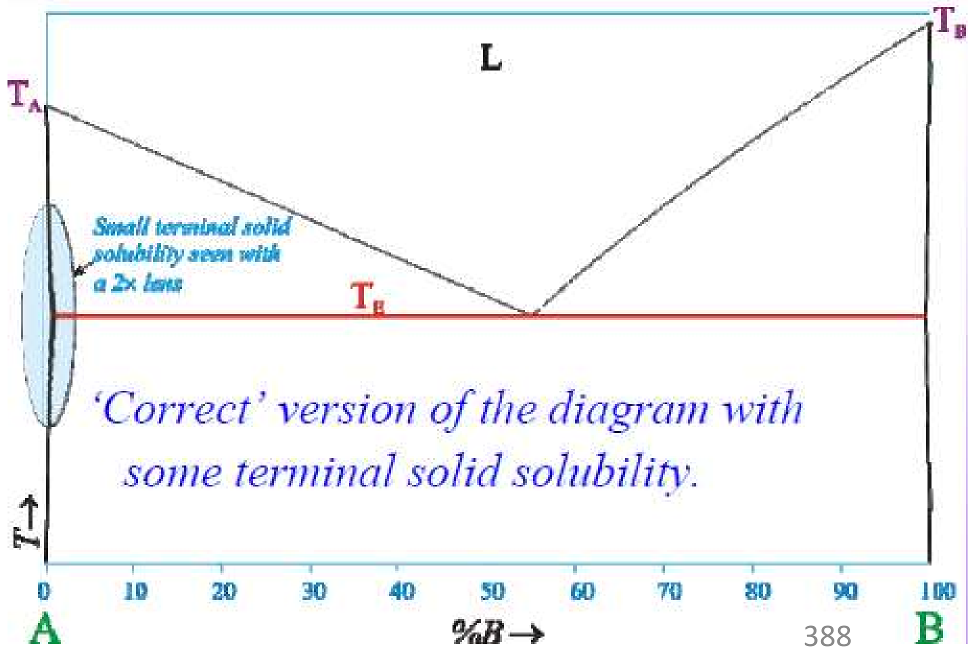
eutectic micro-constituent

Special Eutectic Systems

- Consider the eutectic system *without terminal solid solubility* : ***Bi-Cd***
- Technically it is incorrect to draw eutectic phase diagrams with zero solid solubility.
- This would imply that a pure component (say Bi in the example considered) melts over a range of temperatures (from ‘p’ to 271 ºC) → which is wrong.
- Also let us consider an example of a point ‘p’ (which lies on the ‘eutectic line’ PQ). At ‘p’ the phase rule becomes : F = C-P+1 = 1-3+1 = -1 !!!



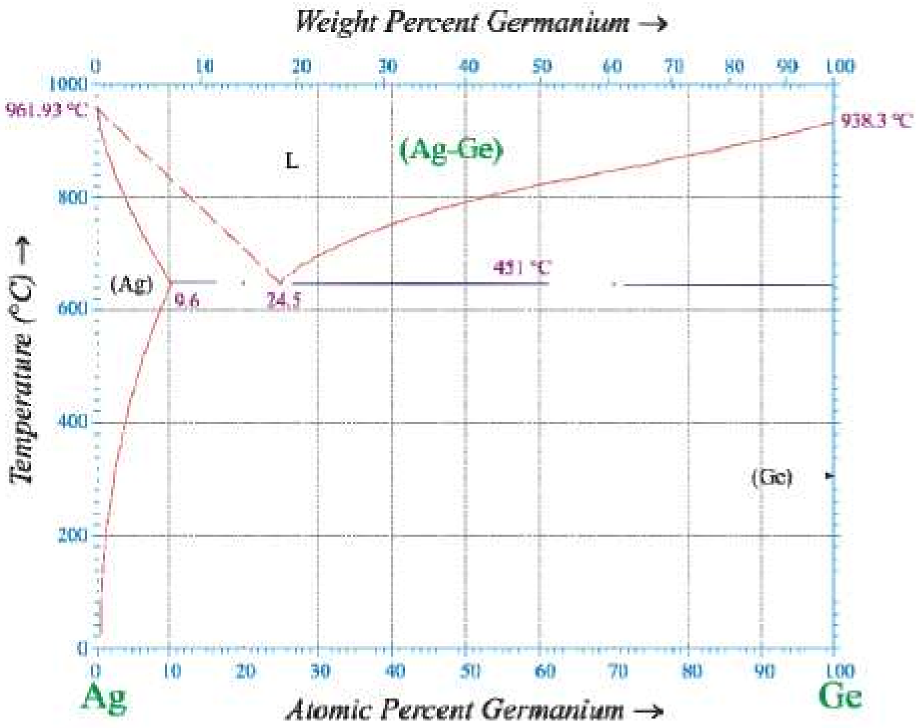
Technically this is incorrect: there has to be some terminal solid solubility

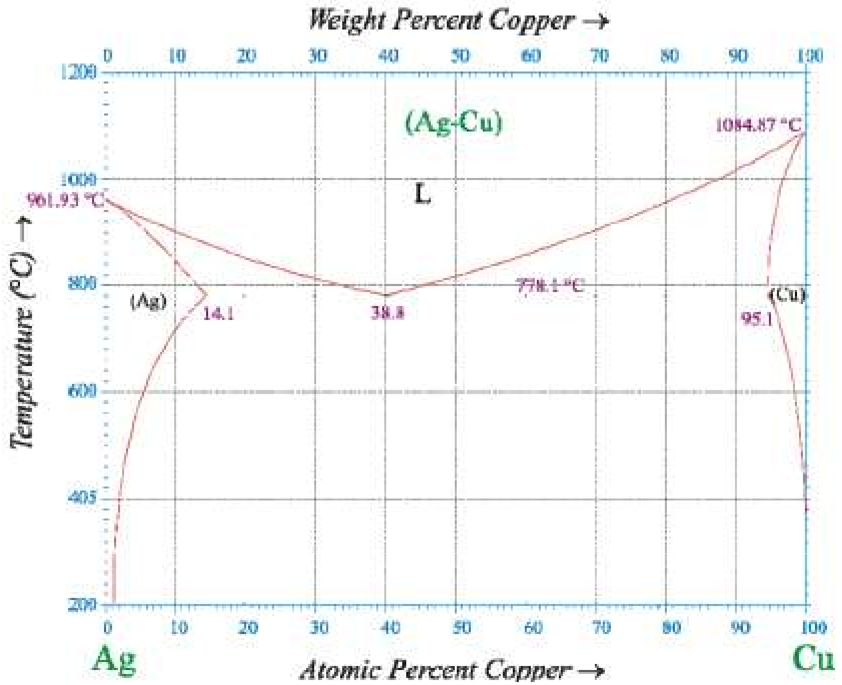


Small terminal solid solubility seen with a 2× lens

‘Correct’ version of the diagram with some terminal solid solubility.

Special Eutectic Systems





- Note that the above is an alternate way of arriving at the obvious contradiction that at ‘P’ on one hand we are saying that there is a pure component and on the other hand we are considering a three phase equilibrium (which can happen only for Bi-Cd alloys.
- In Eutectic systems, at Eutectic point E → 3 phases co-exist : L, α &β
- The number of components in a binary phase diagram is 2→ the number of DOF F=0
- This implies that the Eutectic point is an Invariant Point → For a given system it occurs at a fixed composition and temperature.

Application of Lever rule in Eutectic System

Solved Example

For a 40 wt% Sn-60 wt% Pb alloy at 150°C, find the phases present: α and β, Composition of phases

$C_O = 40$ wt% Sn
$C_a = 11$ wt% Sn
$C_b = 99$ wt% Sn

The relative amount of each phase by using lever rule

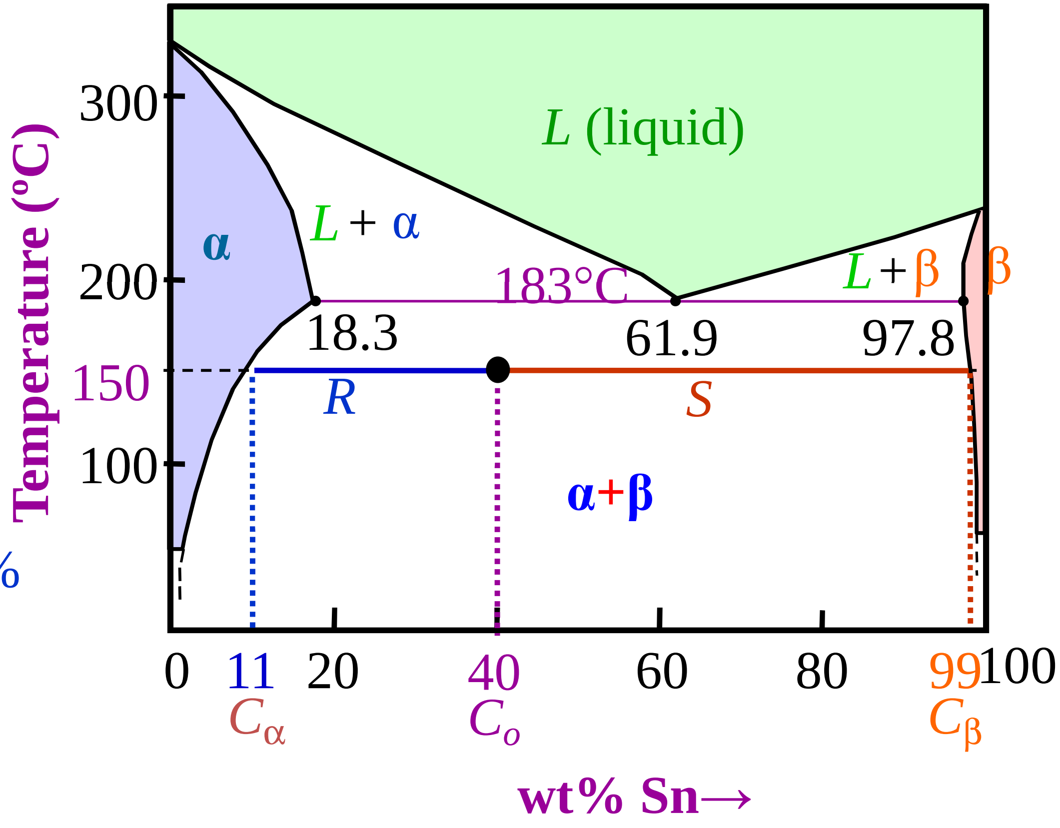
$$W_a = \frac{S}{R+S} = \frac{C_\beta - C_O}{C_\beta - C_\alpha}$$

$$= \frac{99 - 40}{99 - 11} = \frac{59}{88} = 67 \text{ wt\%}$$

$$W\beta = \frac{R}{R+S} = \frac{C_O - C_\alpha}{C_\beta - C_\alpha}$$

$$= \frac{40 - 11}{99 - 11} = \frac{29}{88} = 33 \text{ wt\%}$$

Pb-Sn Phase Diagram



Application of Lever rule in Eutectic System

Solved Example

For a 40 wt% Sn-60 wt% Pb alloy at 220°C, find the phases present: α and Liquid, Composition of phases

C_O = 40 wt% Sn
C_a = 17 wt% Sn
C_L = 46 wt% Sn

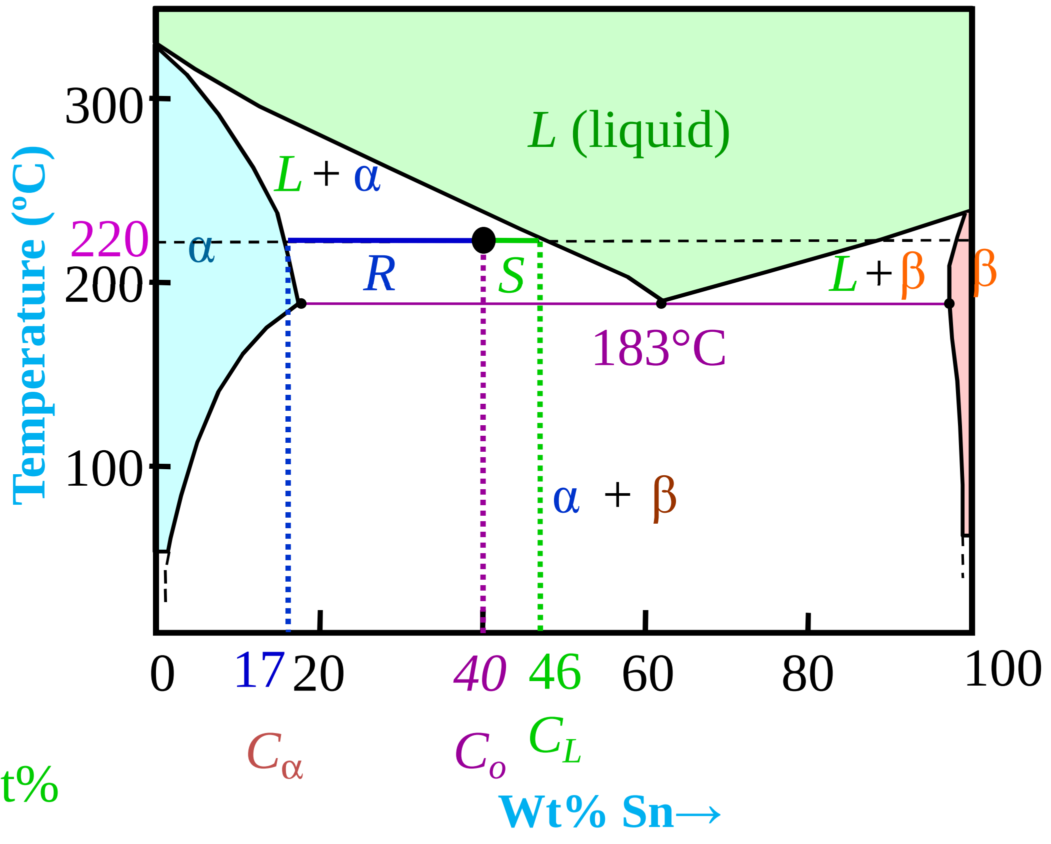
The relative amount of each phase by using lever rule

$$W_a = \frac{C_L - C_O}{C_L - C_\alpha} = \frac{46 - 40}{46 - 17}$$

$$= \frac{6}{29} = 21 \text{ wt\%}$$

$$W_L = \frac{C_O - C_\alpha}{C_L - C_\alpha} = \frac{23}{29} = 79 \text{ wt\%}$$

Pb-Sn Phase Diagram



Solved Example

During the solidification of a off eutectic (Pb-Sn) composition (C_0), 90 vol.% of the solid consisted of the eutectic mixture and 10vol.% of the proeutectic β phase. What is the value of C_0 ?

Density data for β and α

$\rho_\alpha = 10300\ Kg/\ \mathrm{m}^3$

$\rho_\beta = 7300\ Kg/\ \mathrm{m}^3$

Eutectic Data
183 ºC
62 wt% Sn

Let us start with some observations: ♦Pb is heavier than Sn and hence the density of α is more than that of β ♦Since the proeutectic phase is β → the composition is hypereutectic (towards the Sn side) ♦ The volume fraction (in %) are usually calculated by taking the area fractions by doing metallography (microstructure) and then converting it into volume fractions (usually volume fraction is assumed to be equal to area fraction

$$\underset{\mathbf{62\%Sn}}{\mathbf{L}} \rightleftharpoons \underset{\mathbf{18\%Sn}}{\boldsymbol{\alpha}} + \underset{\mathbf{97\%Sn}}{\boldsymbol{\beta}}$$

Using the fact that there is 10 Vol% β phase :

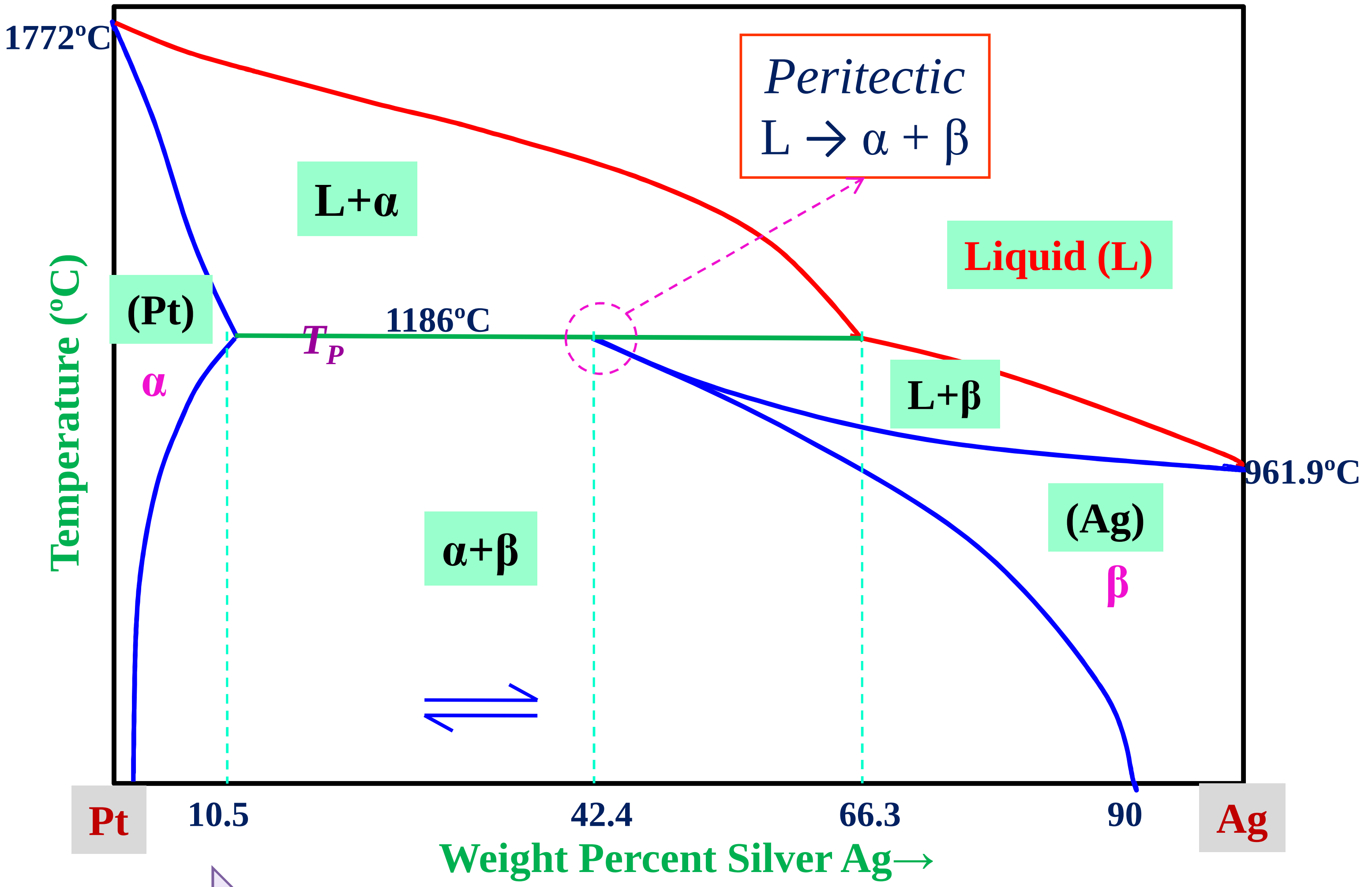
$$Wt.\,fraction of proeutectic \beta = \left[\frac{Wt. of \beta}{Wt. of the alloy}\right] = \frac{0.1\times 7300}{(0.1\times 7300)+(0.9\times \rho_{eutecticmix})}$$

$$Where,\ \rho_{eutecticmix} = 10300\left(\frac{97-62}{97-18}\right)+7300\left(\frac{62-18}{97-18}\right) = 4563+4066 = 8629\,Kg/m^3$$

Substituting in equation (1): Wt. fraction of proeutectic β = 0.086

$$U\sin g lever rule : 0.086 = \frac{C_0-0.62}{0.97-0.62},\ C_0 = 0.650 = 65.0\%$$

Peritectic Phase Diagram

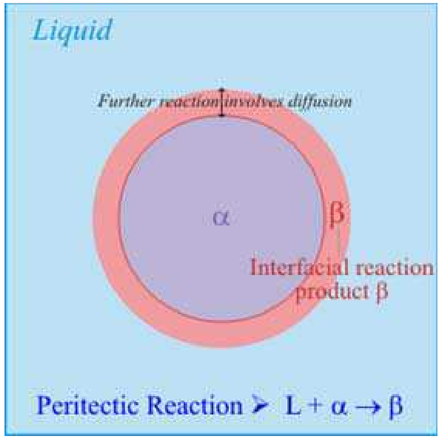


Peritectic Reaction

$$\underset{66.3\%Ag}{L} + \underset{10.5\%Ag}{\alpha} \xrightleftharpoons[1186^{\circ}C]{Cool} \underset{42.4\%Ag}{\beta}$$

Peritectic Phase Diagram

- ☐ Like the eutectic system, the Peritectic reaction is found in systems with complete liquid solubility but limited solid solubility.
- ☐ In the Peritectic reaction the liquid (L) reacts with one solid (α) to produce another solid (β). L+α → β
- ☐ Since the solid β forms at the interface between the L and the α, further reaction is dependent on solid state diffusion. Needless to say this becomes the rate limiting step and hence it is difficult to 'equilibrate' peritectic reactions (as compared to say eutectic reactions).

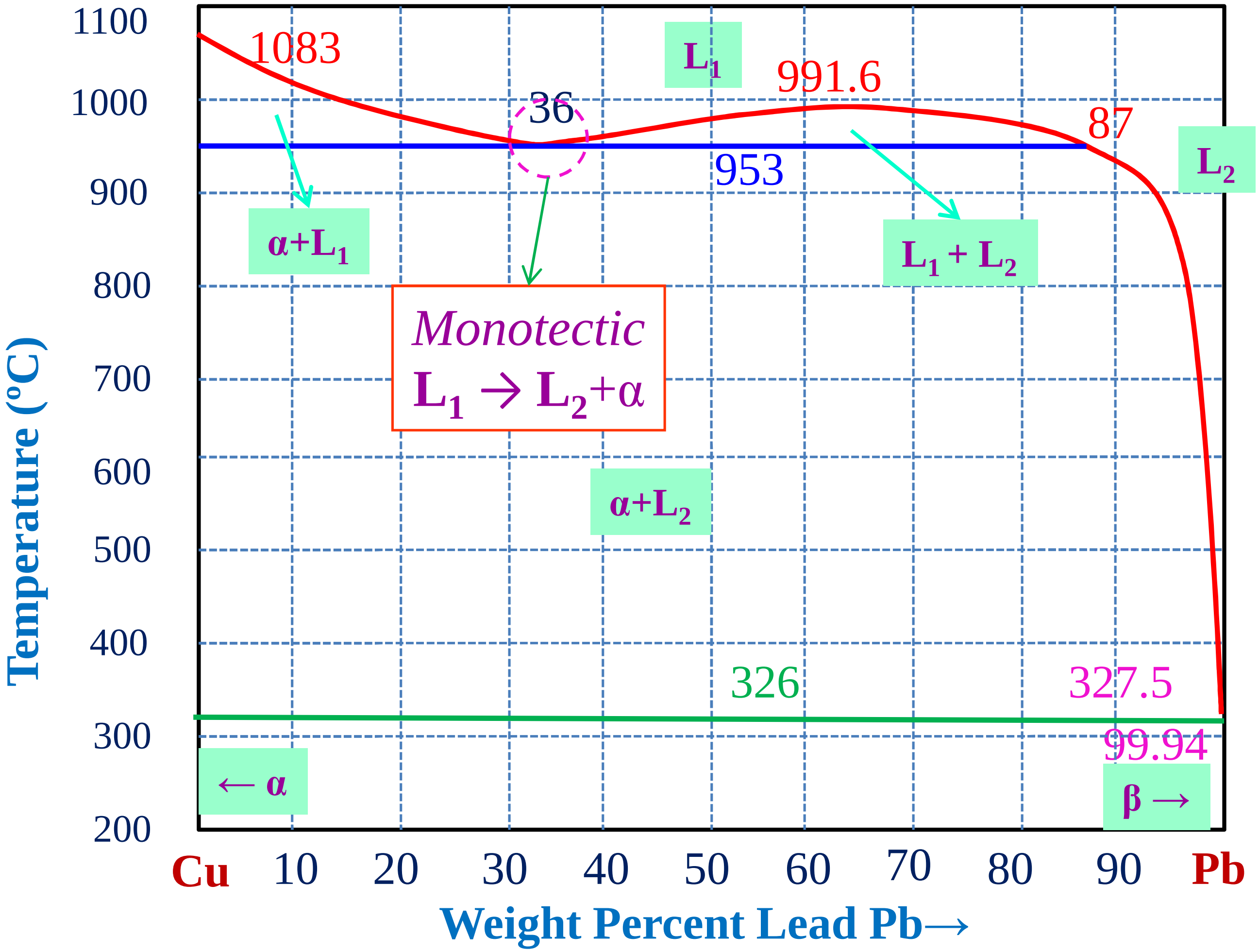


- ☐ In some Peritectic reactions (e.g. the Pt-Ag system – previous page). The (pure) β phase is not stable below the Peritectic temperature (T_P = *1186* ºC for Pt- Ag system) and splits into a mixture of (α+β) just below $T_{P.}$

Monotectic Phase Diagram

- In all the types discussed previously, it was assumed that there was complete solubility in the liquid state. It is quite possible, however, that over a certain composition range two liquid solutions are formed that are not soluble in each other.
- Another term for solubility is miscibility. Substances that are not soluble in each other, such as oil and water, are said to be immiscible. Substances that are partly soluble in each other are said to show a miscibility gap, and this is related to Monotectic Systems.
- When one liquid forms another liquid, plus a solid, on cooling, it is known as a *Monotectic Reaction.*
- It should be apparent that the Monotectic reaction resembles the eutectic reaction, the only difference being that one of the products is a liquid phase instead of a solid phase.
- *A*n example of an alloy system showing a Monotectic reaction is that between *copper and lead* given in next page. Notice that in this case the $L_1 + L_2$ is closed.
- Also, although the terminal solids are indicated as α and β, the solubility is actually so small that they are practically the pure metals, copper and lead.

Monotectic Phase Diagram



In Cu-Zn Phase diagram the eutectoid reaction occurs

At 560 ºC with 75% Zn

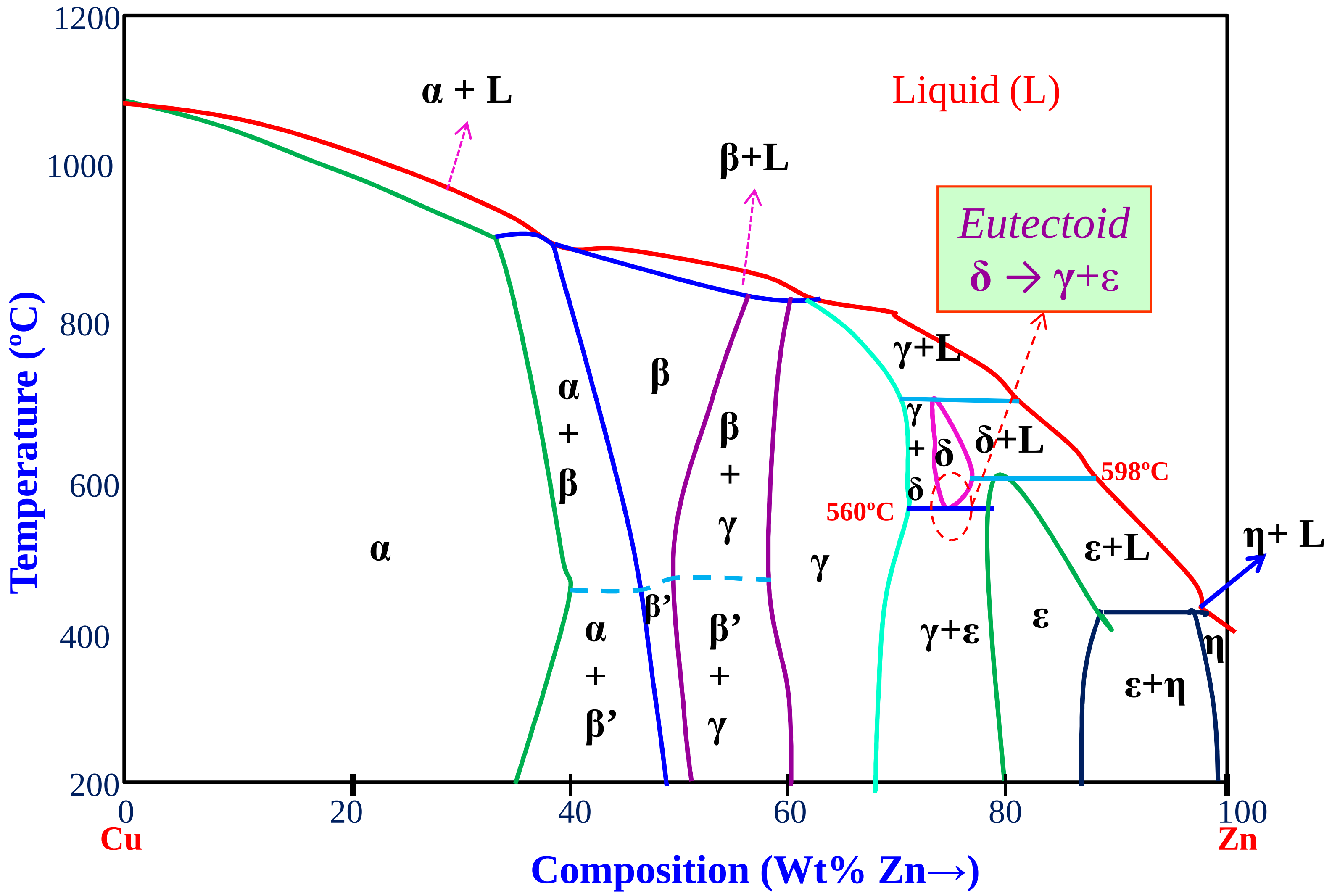
The Eutectoid Reaction

- This is a common reaction in the solid state. It is very similar to the eutectic reaction but does not involve the liquid . In this case, a solid phase transforms on cooling into two new solid phases. The general equation may be written as..!

$$Solid_1 \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftharpoons}} Solid_2 + Solid_3$$

- The resultant Eutectoid mixture is extremely fine, just like the eutectic mixture. Under the microscope both mixtures generally appear the same, and it is not possible to determine microscopically whether the mixture resulted from a eutectic reaction or eutectoid reaction.
- An equilibrium diagram of Cu-Zn, illustrating the eutectoid reaction is shown in figure (*see in next page).*
- In copper (Cu) – Zinc (Zn) system contains two terminal solid solutions i.e. these are extreme ends of phase diagram α and η, with four intermediate phases called β, γ, δ and ε. The β' phase is termed an ordered solid solution, one in which the copper and zinc atoms are situated in a specific and ordered arrangement within each unit cell.

Cu-Zn Phase Diagram - Eutectoid Reaction



Eutectoid
δ → γ+ε

Cu-Zn Phase Diagram - Eutectoid Reaction

- In the diagram, some phase boundary lines near the bottom are dashed to indicate that there positions have not been exactly determined. The reason for this is that at low temperatures, diffusion rates are very slow and inordinately long times are required for the attainment of equilibrium.
- Again only single- and two- phase regions are found on the diagram, and the same and we can utilize the lever rule for computing phase compositions and relative amounts.
- The commercial material brasses are copper-rich copper-zinc alloys: for example, cartridge brass has a composition of 70 wt% Cu-30 wt% Zn and a microstructure consisting of a single α phase.

In Cu-Zn Phase diagram the eutectoid reaction occurs at 560 °C with 75% Zn

$$\delta \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftharpoons}} \gamma + \varepsilon$$

Cu 70, Zn 30 (wt%), recrystallied annealing twins

The Peritectoid Reaction

- This is a fairly common reaction in the solid state and appears in many alloy systems. The peritectoid reaction may be written as

$$Solid_1 + Solid_2 \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftharpoons}} Solid_3$$

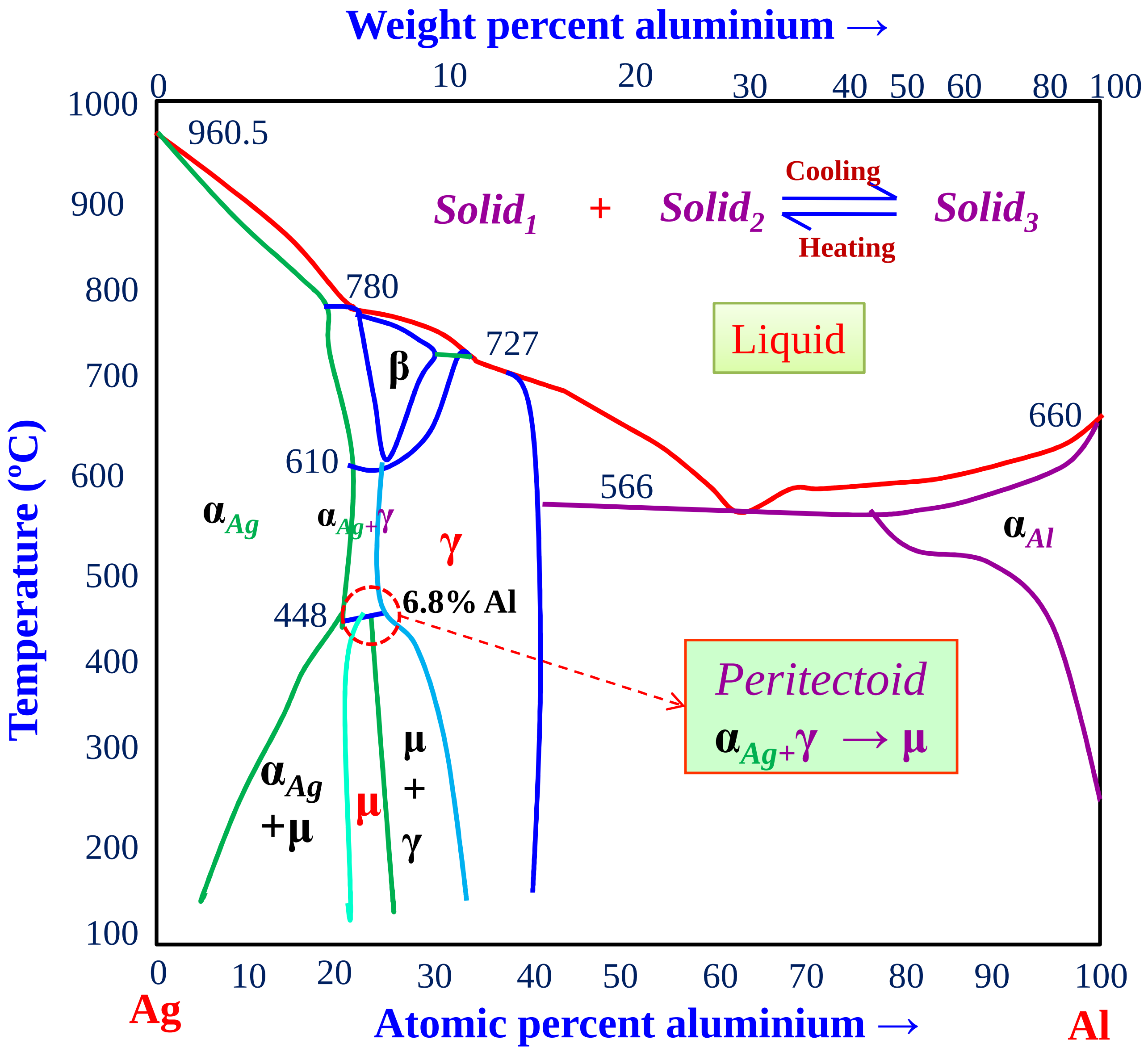
- The new solid phase is usually an intermediate alloy, but it may also be a solid solution .The peritectoid reaction has the same relationship to the peritectic reaction as the eutectoid has to the eutectic. Essentially, it is the replacement of a liquid by a solid.

- The peritectoid reaction occurs entirely in the solid state and usually at lower temperatures than the peritectic reaction, the diffusion rate will be slower and there is less likelihood that equilibrium structures will be reached.

- Consider Silver (Ag) – Aluminium (Al) phase diagram (*in next page*) containing a peritectoid reaction.

- If a 7% Al alloy is rapidly cooled from the two phase area just above the peritectoid temperature the two phases will be retained, and the microstructure will show a matrix of γ with just a few particles of α. When we cool at below the peritectoid temperature by holding we get single phase μ.

Peritectoid Reaction : Ag-Al Phase Diagram

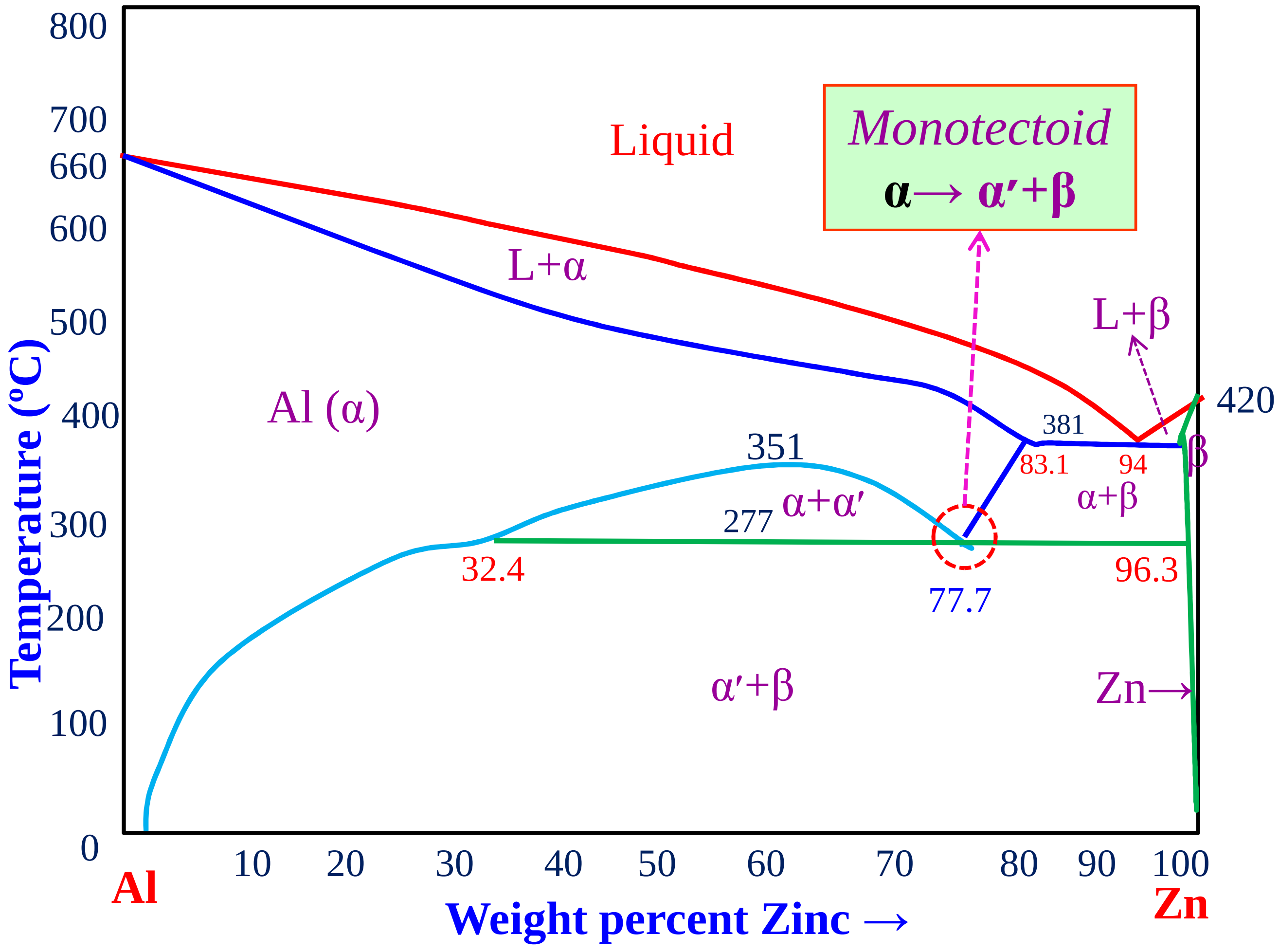


$\text{Solid}_1 + \text{Solid}_2 \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftharpoons}} \text{Solid}_3$

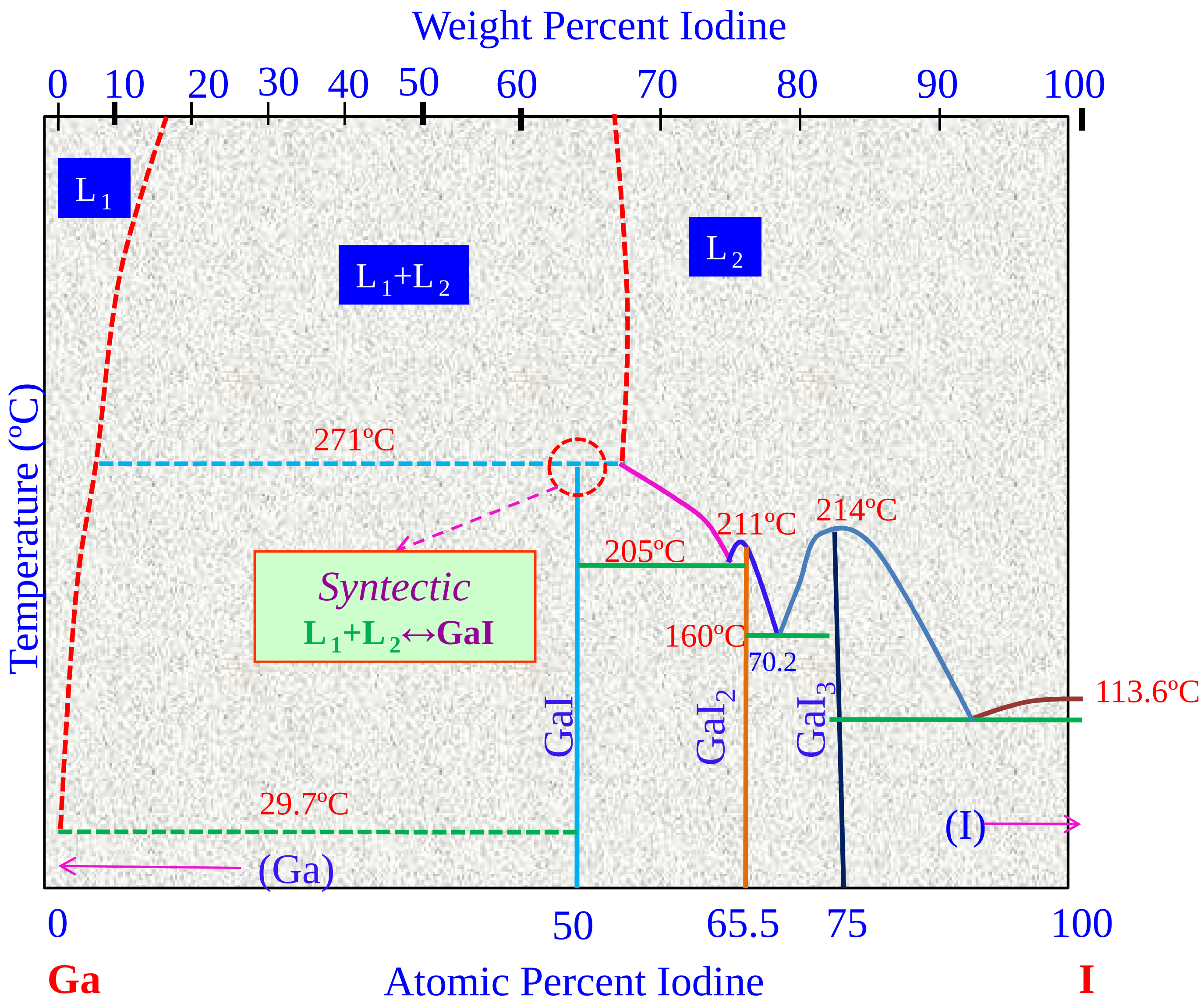
Peritectoid

$\alpha_{Ag} + \gamma \rightarrow \mu$

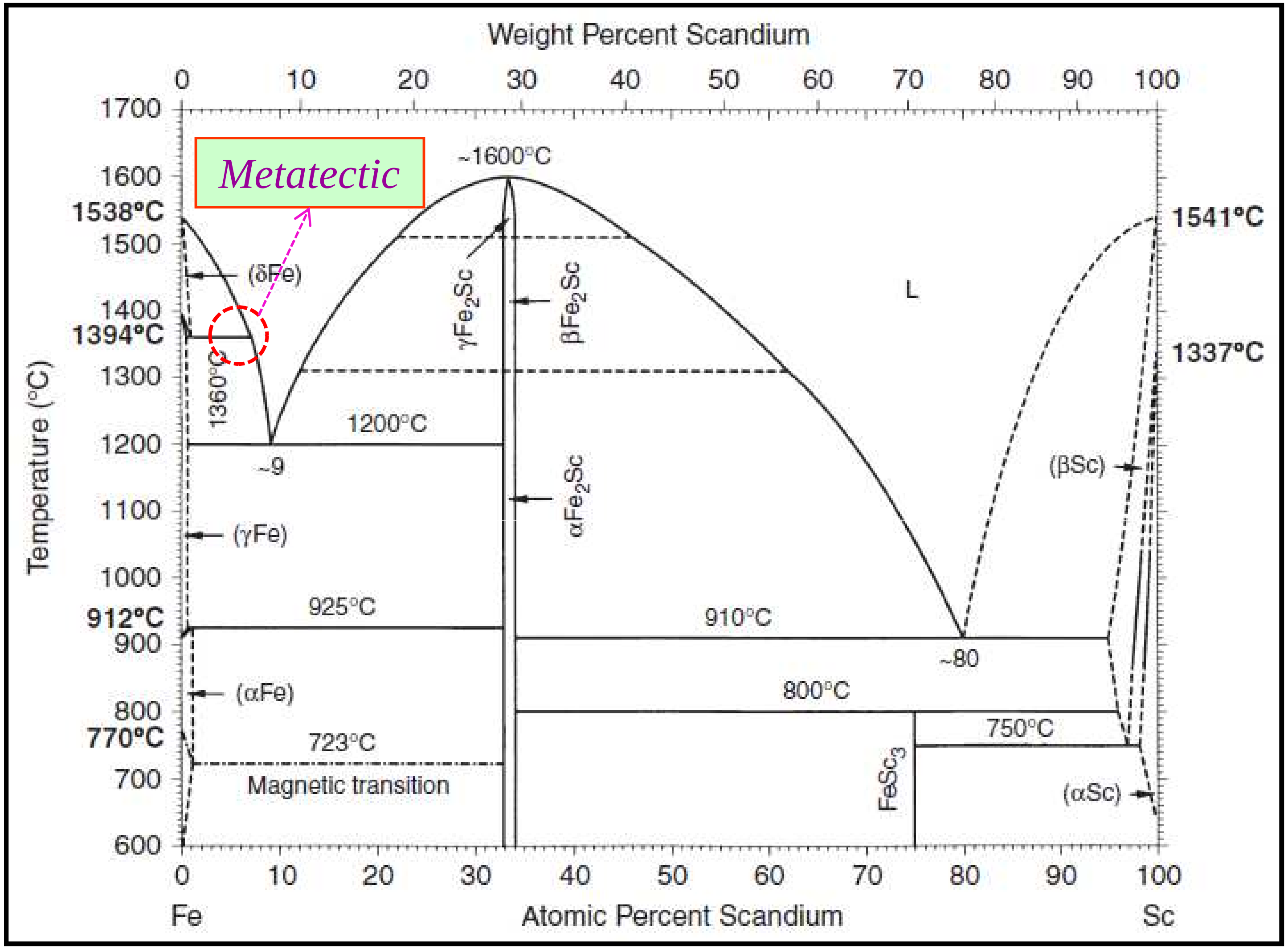
Monotectoid Reaction : Al-Zn Phase Diagram



Syntectic Reaction : Ga – I Phase Diagram



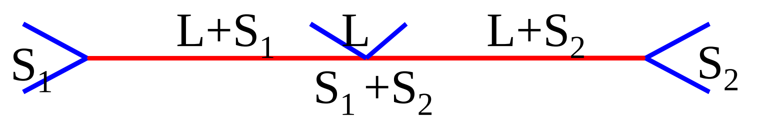
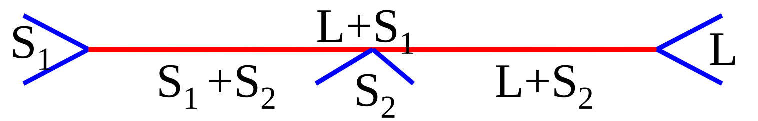
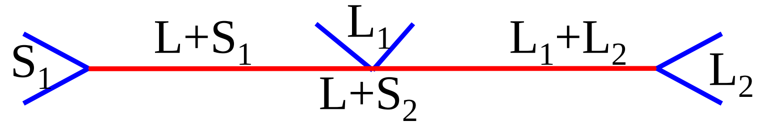
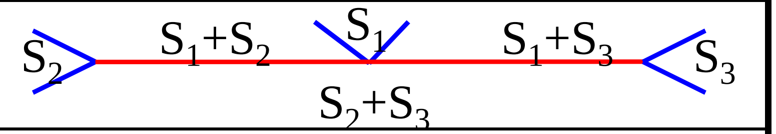
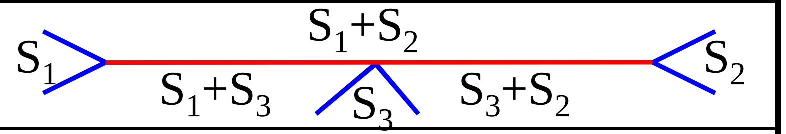
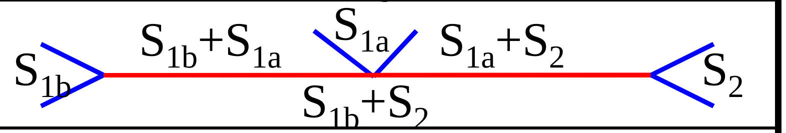
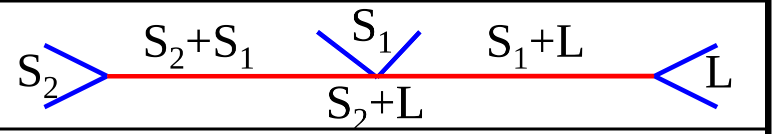
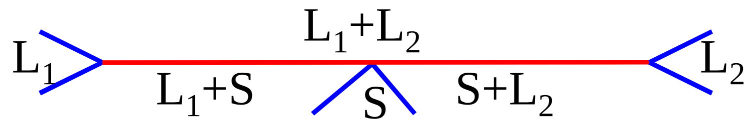
Metatectic Reaction : Fe - Sc Phase Diagram



- In the above Fe-Sc system represents a Metatectic reaction,

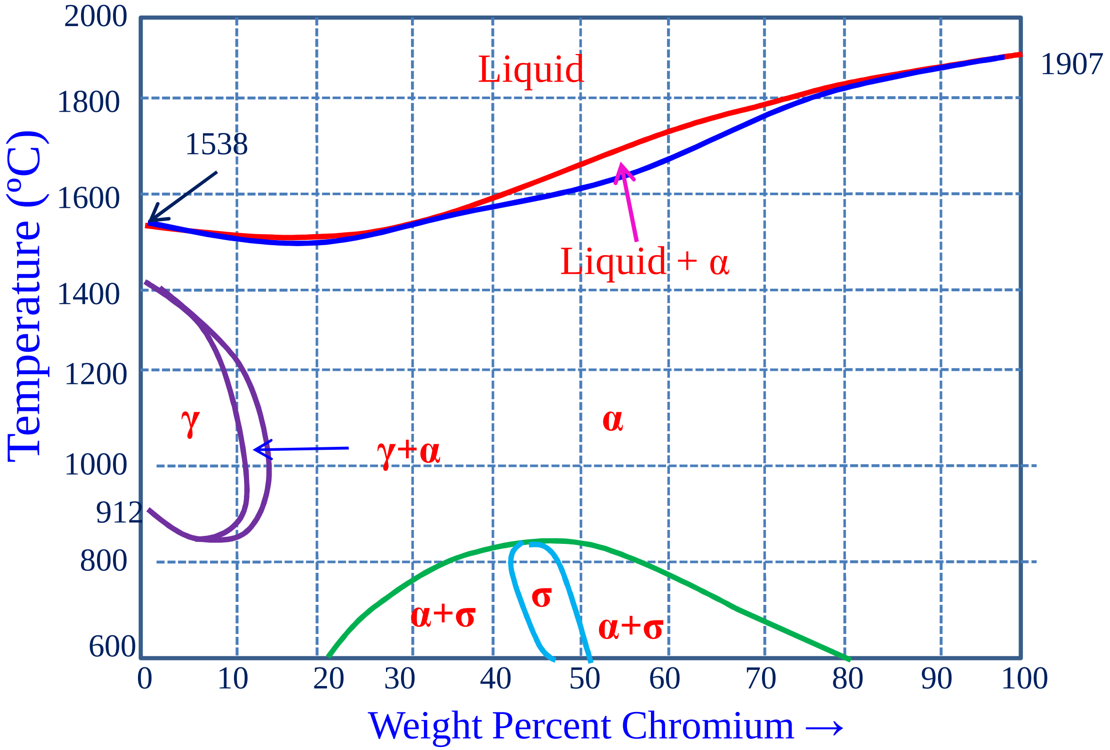
δ Fe ↔ γFe + L at 1360 °C

Summary of Invariant reactions

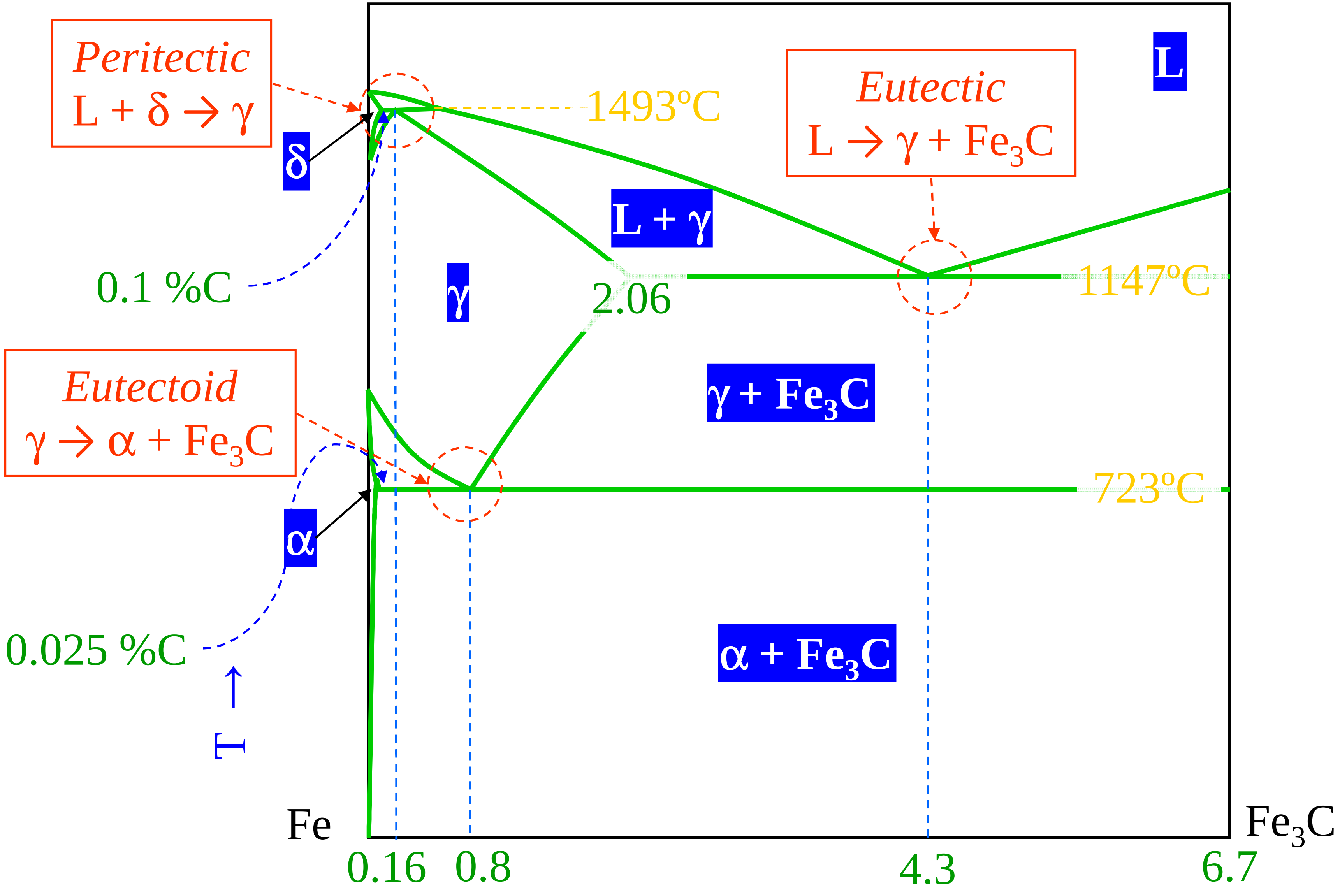
Name of reaction	Phase equilibrium	Schematic representation
Eutectic	$L \leftrightarrow S_1 + S_2$	
Peritectic	$S_1 + L \leftrightarrow S_2$	
Monotectic	$L_1 \leftrightarrow S_1 + L_2$	
Eutectoid	$S_1 \leftrightarrow S_2 + S_3$	
Peritectoid	$S_1 + S_2 \leftrightarrow S_3$	
Monotectoid	$S_{1a} \leftrightarrow S_{1b} + S_2$	
Metatectic	$S_1 \leftrightarrow S_2 + L$	
Syntectic	$L_1 + L_2 \leftrightarrow S$	

Allotropic Transformations

- As we discussed earlier that several metals may exist in more than one type of crystal structure depending upon temperature , Iron, Tin, Manganese and Cobalt are examples of metals which exhibit this property , known as *Allotropy.*
- On an equilibrium diagram, this allotropic change is indicated by a point or points on the vertical line which represents the pure metal. This is illustrated in below figure. In this diagram, the gamma solid solution field is ‘looped’. The pure metal Fe and alloys rich in Fe undergo two transformations.



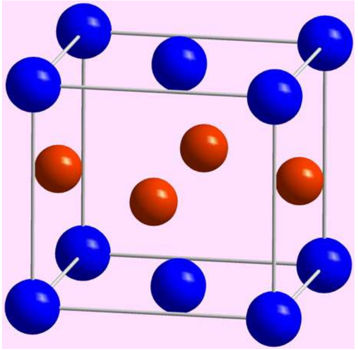
Allotropic Transformations: Fe-Fe_3C System



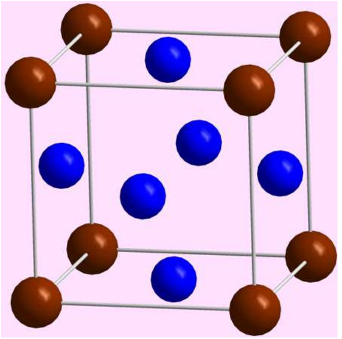
Fe-Cementite diagram

Order-disorder Transformations

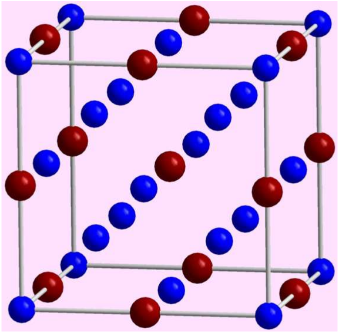
- Ordinarily in the formation of substitutional type of solid solution the solute atoms do not occupy any specific position but are distributed at random in the lattice structure of the solvent. The alloy is said to be in a ‘disordered’ condition.
- Some of these random solid solutions, if cooled slowly, undergo a rearrangement of the atoms where the solute atoms move into definite positions in the lattice. This structure is known as an *ordered solid solution or superlattice*.
- Ordering is most common in metals that are completely soluble in the solid state, and usually the maximum amount of ordering occurs at a simple atomic ratio of the two elements.
- For this reason, the ordered phase is sometimes given a chemical formula, such as AuCu and $AuCu_3$ in the gold-copper alloy system. On the equilibrium diagram, the ordered solutions are frequently designated as α′ , β′ , etc. or α′ , α″ , etc., and the area in which they are found is usually bounded by a dot-dash line.



CuAu



Cu_3Au



Fe_3Al

Order-disorder Transformations

- When the ordered phase has the same lattice structure as the disordered phase, the effect of ordering on mechanical properties is negligible. Hardening associated with the ordering process is most pronounced in those systems where the shape of the unitcell is changed by ordering.

- Regardless of the structure formed as a result of ordering, an important property change produced, even in the absence of hardening, is a significant reduction in electrical resistance. Notice the sharp decrease in electrical resistivity at the compositions which correspond to the ordered phases AuCu and $AuCu_3$.

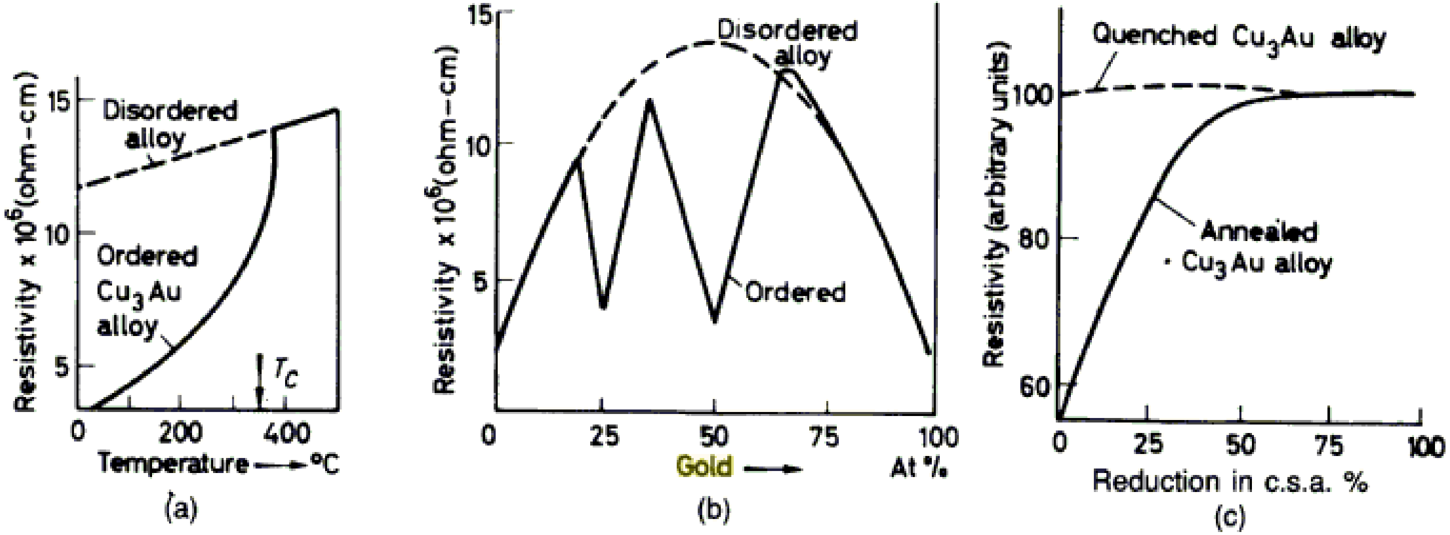
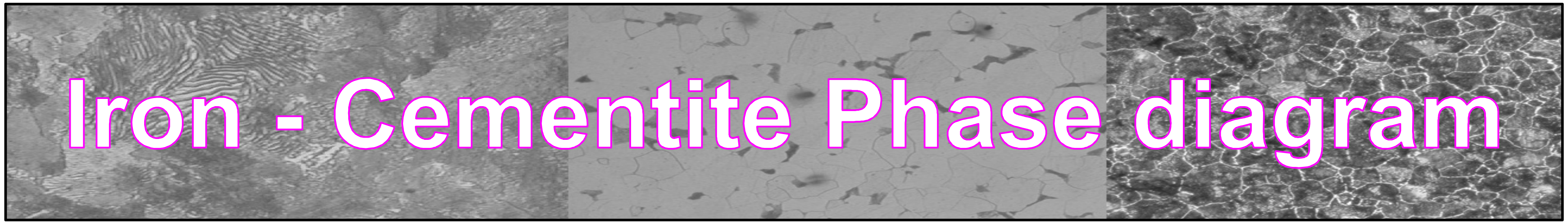


Figure : Effect of (a) temperature, (b) composition, and (c) deformation on the resistivity of copper-gold alloys

Note

- Some of the equilibrium diagrams discussed under the simple types are the same as actual ones. Many alloy systems have diagrams which show more than one type of reaction and are generally more complex than the simple types.
- However, even the most complex diagrams show mainly the reactions that have been covered. The student should be able to label a phase diagram completely; understand the significance of every point, line and area; determine the various reactions that occur at the horizontal lines; and describe the slow cooling and microstructure of any alloy on a binary equilibrium diagram.



Iron - Cementite Phase diagram

Avala Lava Kumar* : Suneeti Purohit : Gautam Behera

Department of Metallurgical & Materials Engineering (MME)

Veer Surendra Sai University of Technology (VSSUT), Burla -768018

**E-mail : lavakumar.vssut@gmail.com*

History

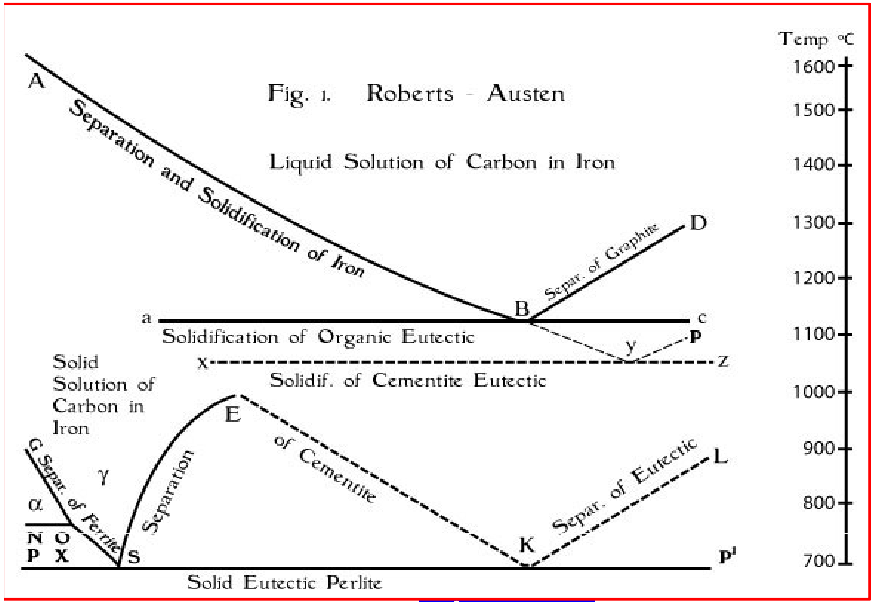


Figure 1

- Iron – carbon (Fe-C) diagram and first phase diagram of any alloy to be established, done by Roberts –Austen in 1898 after whom austenite came to be named. (Figure 1)

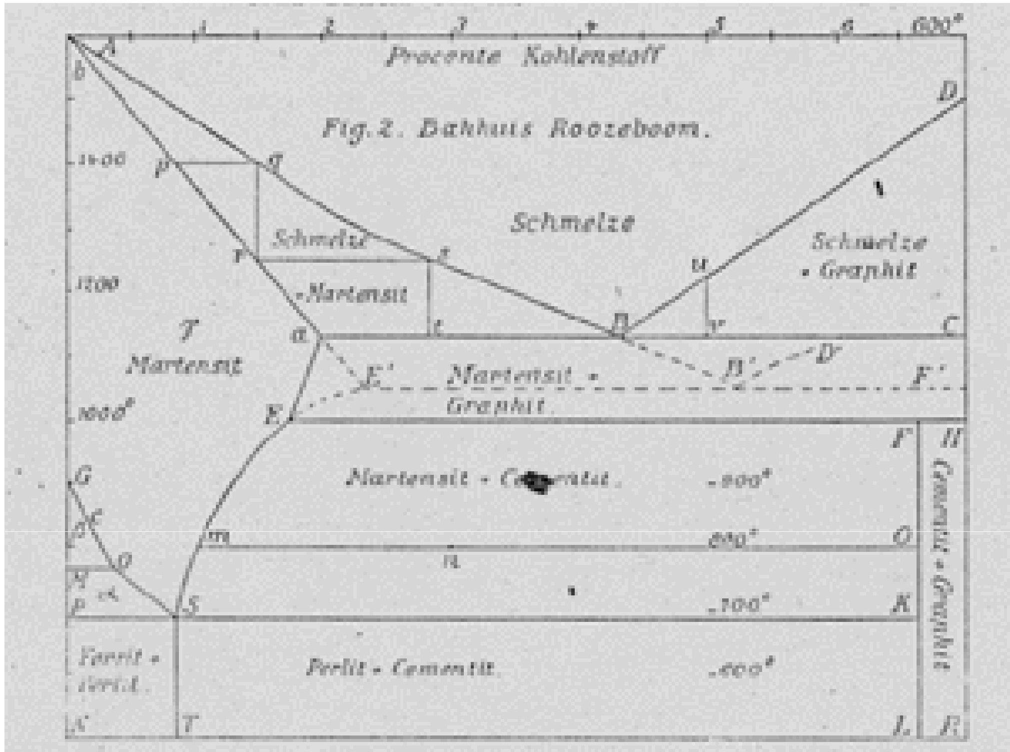
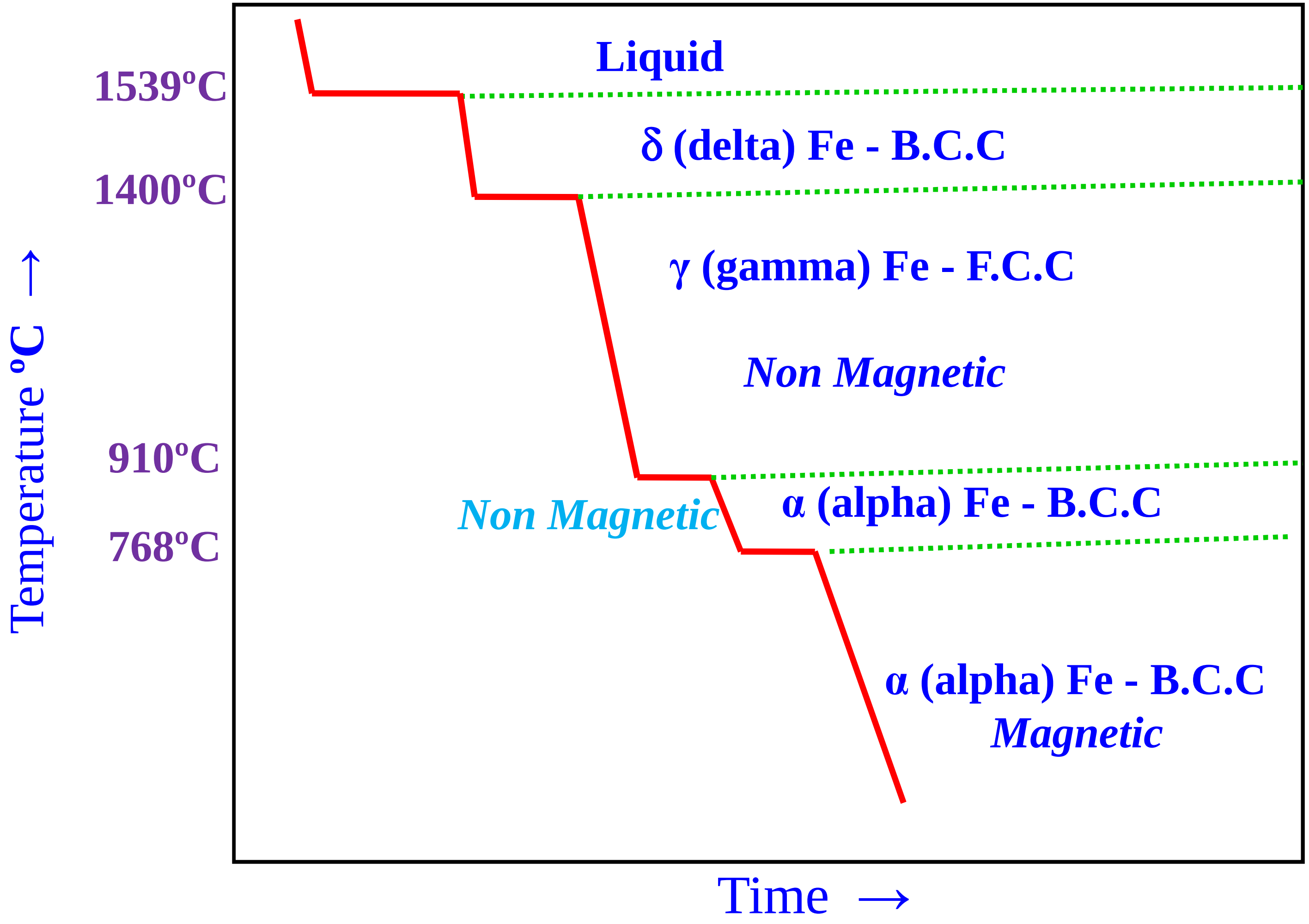


Figure 2

- The Iron Carbon diagram, adjusted by Bakhuis-Roozeboom in 1900. Notice line A-a and the temperature range between 1000 and 1100°C, where carbide formation was suppose to take place as the result of a chemical reaction between graphite and austenite (at that time called martensite! (Figure 2)

Allotropic Transformation in Iron

- Iron is an allotropic metal, which means that it can exist in more than one type of lattice structure depending upon temperature. A cooling curve for pure iron is shown below:



Allotropic Transformations in Iron

There are three more allotropes for pure iron that form under different conditions

ε-iron

The iron having hexagonal close packed structure. This forms at extreme pressure,110 k bars and 490°C. It exists at the centre of the Earth in solid state at around 6000°C and 3 million atmosphere pressure.

FCT-iron

This is face centered tetragonal iron. This is coherently deposited iron grown as thin film on a {100} plane of copper substrate

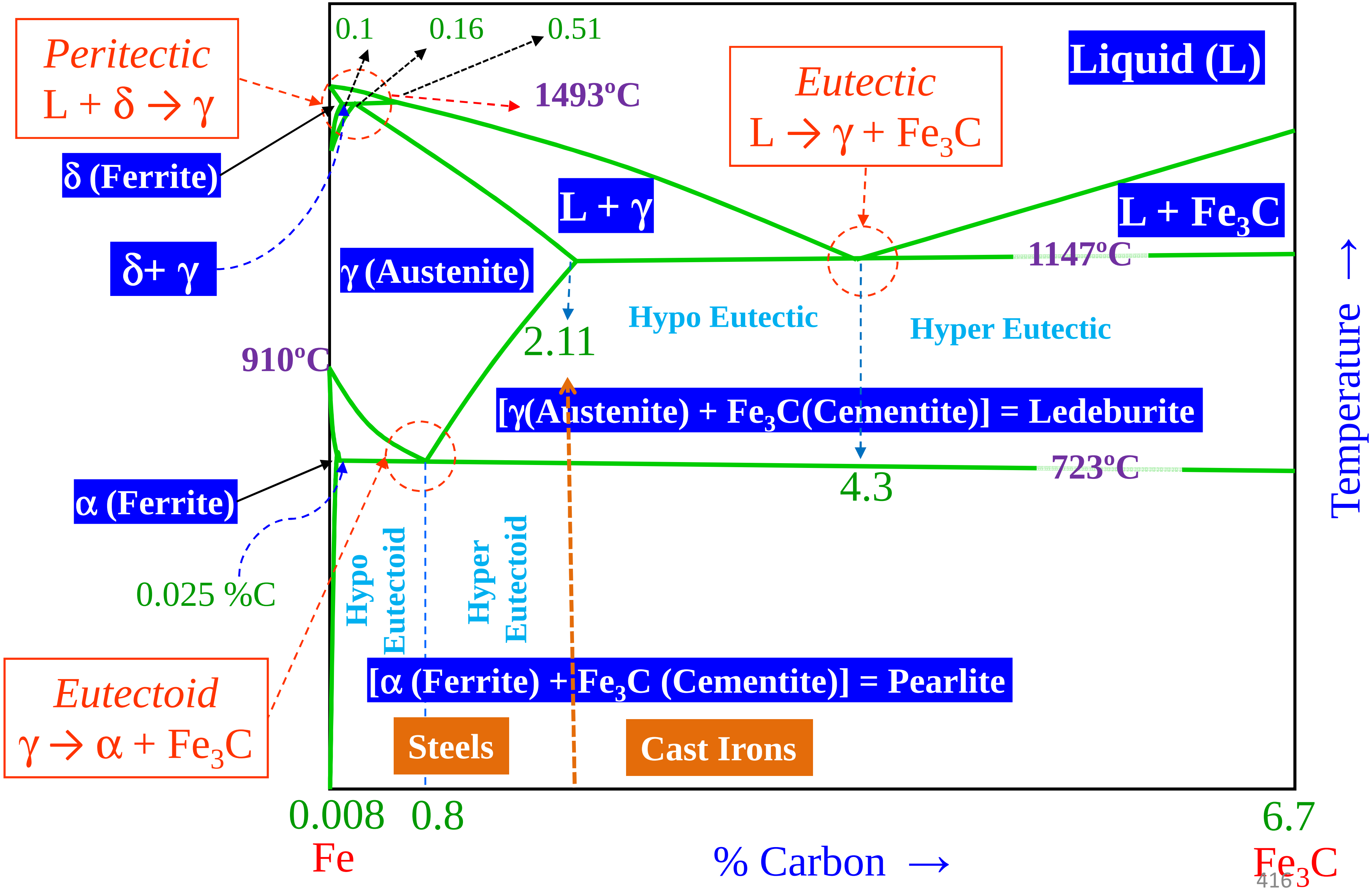
Trigonal-iron

Growing iron on mis-fiting {111} surface of a face centered cubic copper substrate.

Iron – Cementite Phase Diagram

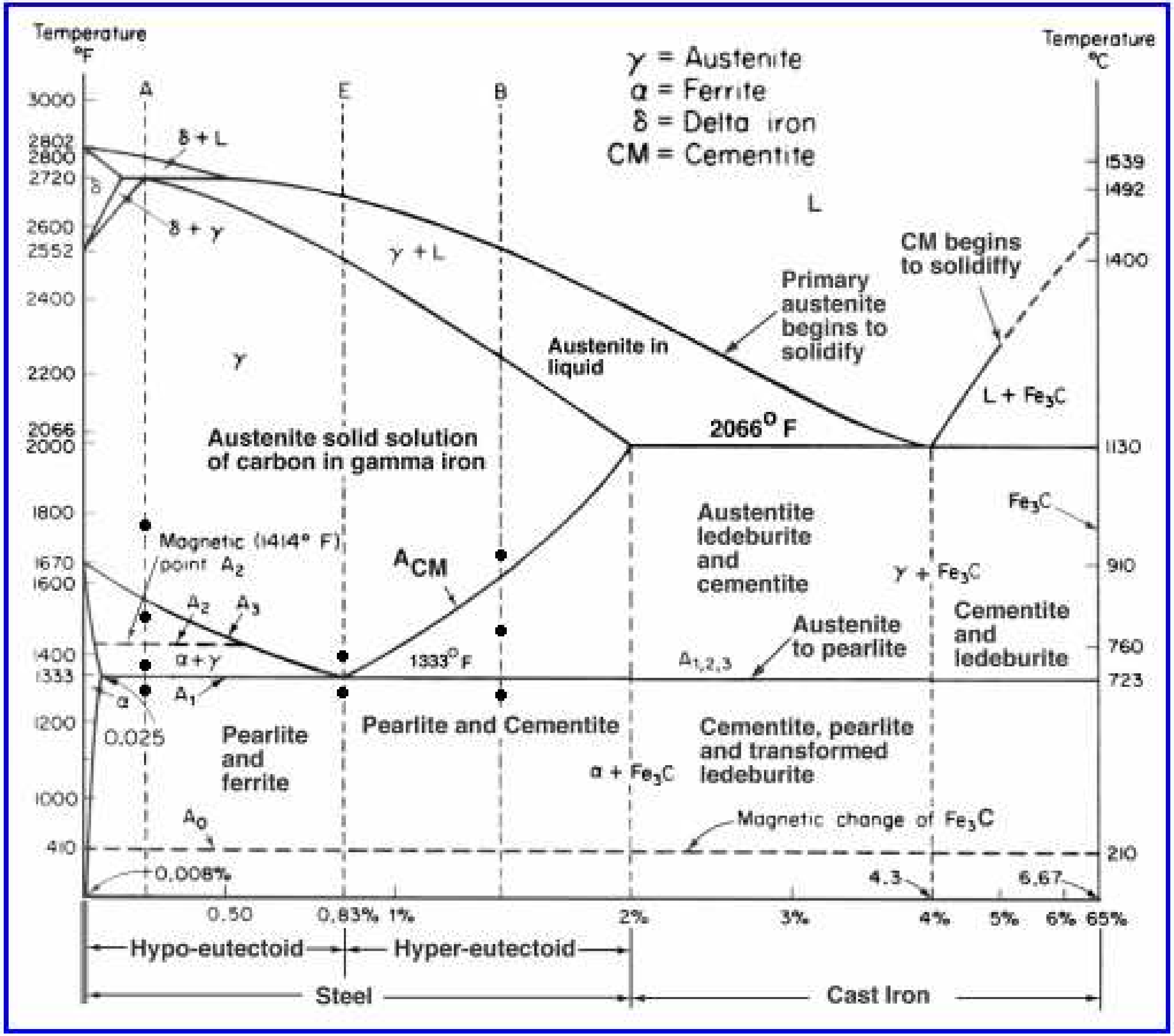
- The Fe-C (or more precisely the Fe-Fe_3C) diagram is an important one. Cementite is a metastable phase and 'strictly speaking' should not be included in a phase diagram. But the decomposition rate of cementite is small and hence can be thought of as 'stable enough' to be included in a phase diagram. Hence, we typically consider the Fe-Fe_3C part of the Fe-C phase diagram.
- A portion of the Fe-C diagram – the part from pure Fe to 6.67 wt.% carbon (*corresponding to cementite*, *Fe_3C) – is technologically very relevant.*
- Cementite is not a equilibrium phase and would tend to decompose into Fe and graphite. This reaction is sluggish and for practical purpose (at the microstructural level) cementite can be considered to be part of the phase diagram. Cementite forms as it nucleates readily as compared to graphite.
- Compositions upto 2.1%C are called steels and beyond 2.1% are called cast irons. *In reality the calssification should be based on 'castability' and not just on carbon content.*
- Heat treatments can be done to alter the properties of the steel by modifying the microstructure → we will learn about this in coming chapters.

Iron – Cementite Phase Diagram



Iron – Cementite Phase Diagram

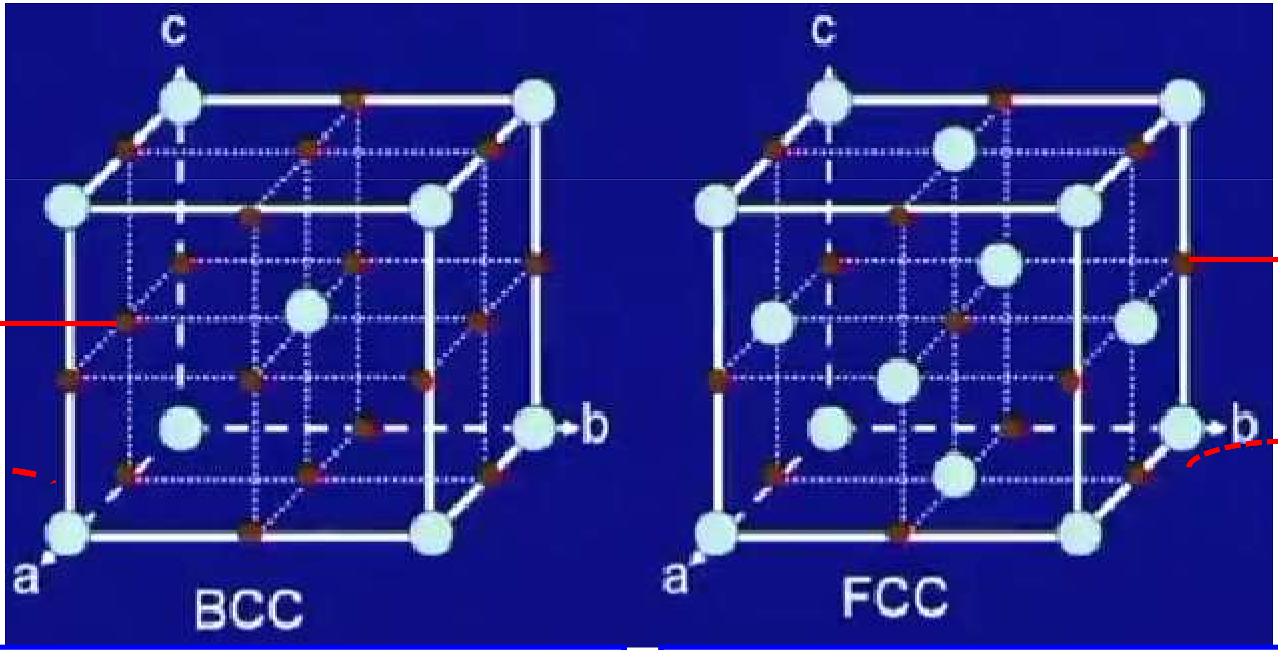
more detailed view of Fe-Fe$_3$C.....!



Carbon Solubility in Iron

Solubility of carbon in Fe = f (structure, temperature)

Where is carbon located in iron lattice ?



Octahedral sites

Octahedral sites

6 faces sharing with two sides (6/2)=3
12 edges sharing with four sides (12/4)=3
Total sites is (3+3), 6 per unit cell
Every one Fe atom we have 3 interstitial sites

One interstitial site in center plus
12 edges sharing with four sides (12/4)=3
Total sites is (1+3), 4 per unit cell
Every one Fe atom we have 1 interstitial site

Carbon Solubility in Iron

Surprising facts…!

- ☐ C dissolves more in the close packed structure (FCC, γ-Fe) (albeit at higher temperatures at 1 atm. pressure– where FCC is stable) than in the open structure (BCC-Fe).
- ☐ C sits in the smaller octahedral void in BCC in preference to the larger tetrahedral void in BCC.

Some relevant explanation…!

- ☐ The octahedral void in FCC is the larger one and less distortion occurs when carbon sits there → this aspect contributes to a higher solubility of C in γ-Fe.
- ☐ The distorted octahedral void in BCC is the smaller one → but *(surprisingly)* carbon sits there in preference to the distorted tetrahedral void (the bigger one). *(we will see in coming slides)*
- ☐ Due to small size of the voids in BCC the distortion caused is more and the solubility of C in α-Fe is small
  - ➢ this is rather surprising at a first glance as BCC is the more open structure
  - ➢ but we have already seen that the number of voids in BCC is more than that in FCC → i.e. BCC has more *number of smaller voids.*

Carbon Solubility in Iron

FCC

Size of Fe atom
CCP crystal

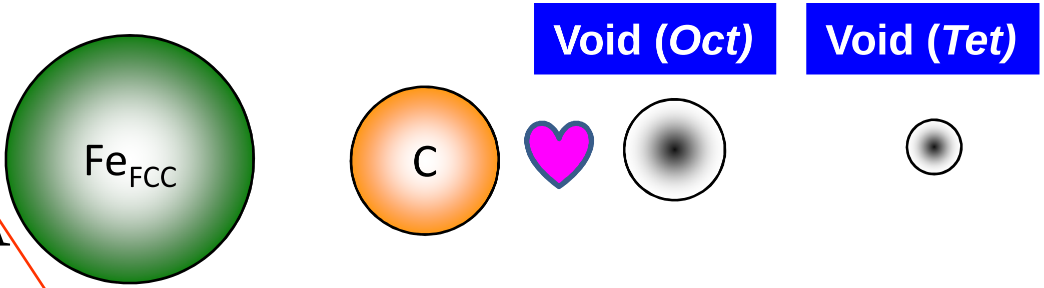
$$r^{Fe}_{FCC} = 1.292\ \mathring{A}$$

Size of the OV

$$x^{Fe}_{FCC}(oct) = 0.534\ \mathring{A}$$

Size of Carbon atom

$$r^{C} = 0.77\ \mathring{A}$$



Relative sizes of voids w.r.t atoms

Note the difference in size of the atoms

BCC

Size of Fe atom
BCC crystal

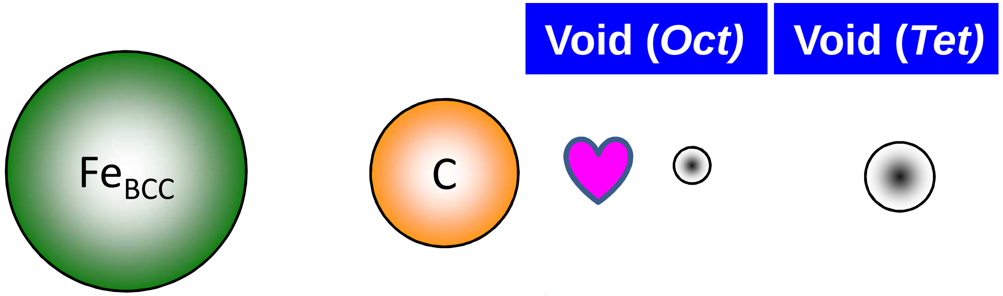
$$r^{Fe}_{BCC} = 1.258\ \mathring{A}$$

Size of the TV

$$x^{Fe}_{BCC}(d.tet) = 0.364\ \mathring{A}$$

Size of the OV

$$x^{Fe}_{BCC}(d.oct) = 0.195\ \mathring{A}$$

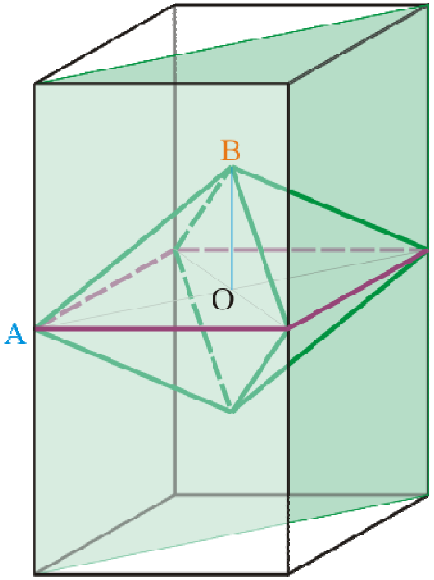


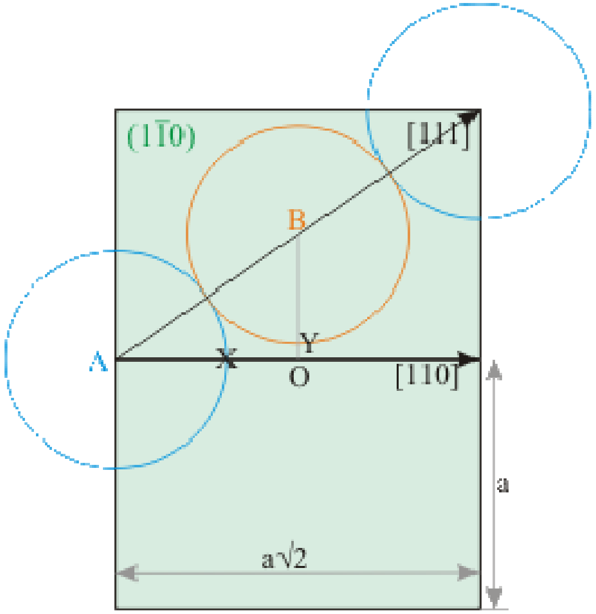
Relative sizes of voids w.r.t atoms

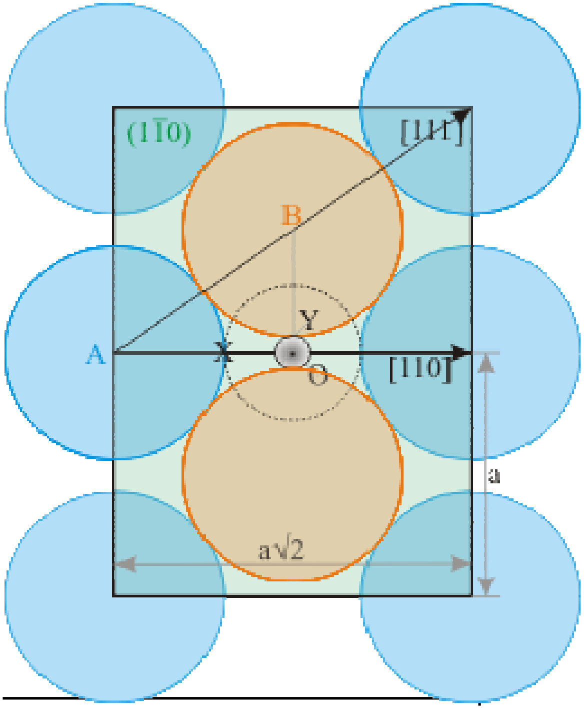
Remember

- ❑ **FCC** Size of the largest atom which can fit into the tetrahedral is 0.225 and octahedral void is 0.414
- ❑ **BCC** Size of the largest atom which can fit into the *d.tetrahedral* is 0.29 and *d.octahedral* void is 0.154

Why carbon preferentially sits in the apparently smaller octahedral void in BCC ?







Ignoring the atom sitting at B and assuming the interstitial atom touches the atom at A

$$OA = r + x_A = \frac{\sqrt{2}a}{2}$$

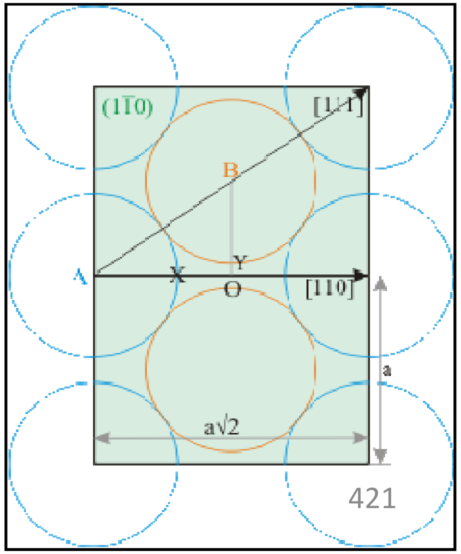
$$r^{Fe}_{BCC} = 1.258\ \mathring{A}$$

$$BCC : \sqrt{3}a = 4r$$

$$r + x_A = \frac{2\sqrt{6}\,r}{3}$$

$$\frac{x_A}{r} = \left(\frac{2\sqrt{6}}{3} - 1\right) = 0.6329$$

$$OX = x_A = 0.796\ \mathring{A} \qquad OY = x_B = 0.195\ \mathring{A} \qquad x^{Fe}_{BCC}(d.tet) = 0.364\ \mathring{A}$$



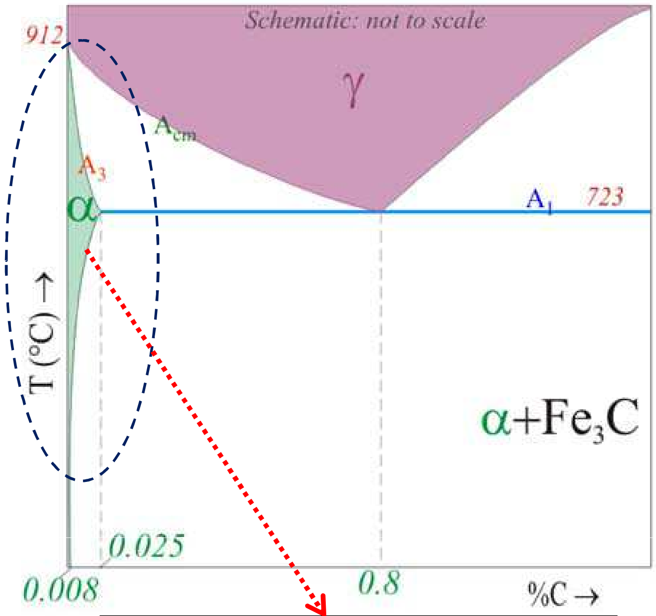
Carbon Solubility in Iron

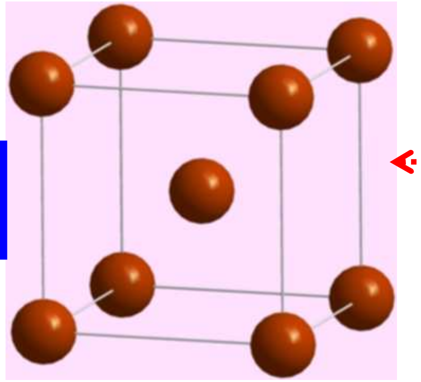
- Actually the octahedral void in BCC is a linear one *(interstitial atom actually touches only two out of the 6 atoms surrounding it)*
- This implies for x/r ratios between 0.15 and 0.63 the interstitial atom has to push only two atoms
- $(x_{carbon}/r_{Fe})_{BCC} \sim 0.6$
- This explains why Carbon preferentially sits in the apparently smaller octahedral void in BCC

Characteristics of phases appeared in Fe-Fe_3C phase diagram

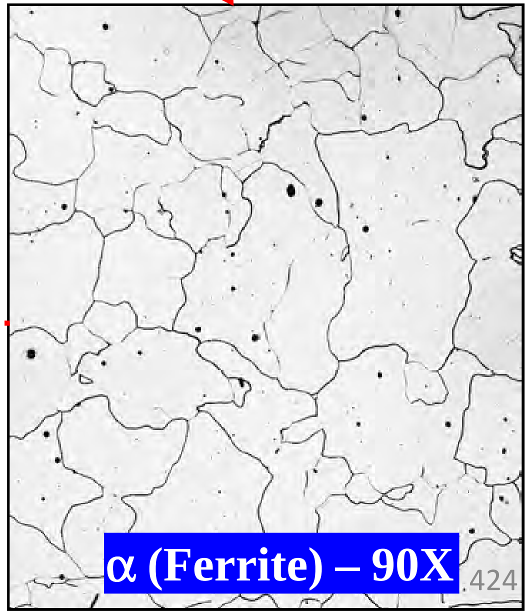
Ferrite (α)

- It is an interstitial solid solution of a small amount of carbon dissolved in α iron. The maximum solubility is 0.025%C at 723ºC and it dissolves only 0.008%C at room temperature. *It is the softest structure that appears on the diagram*
- The crystal structure of ferrite (α) is B.C.C
- Tensile strength – 40,000 psi or 275 Mpa
- Elongation – 40% in 2 in.
- Hardness - < 0 HRC or < 90 HRB





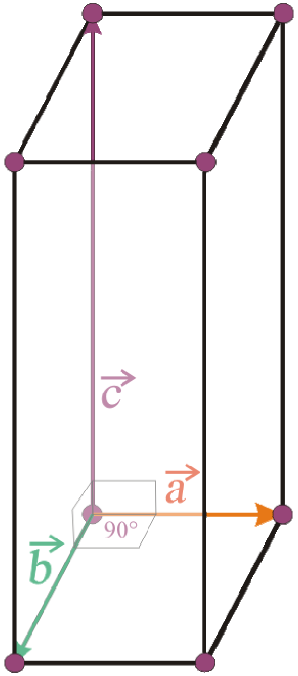
α(Ferrite) contains B.C.C structure



α (Ferrite) – 90X

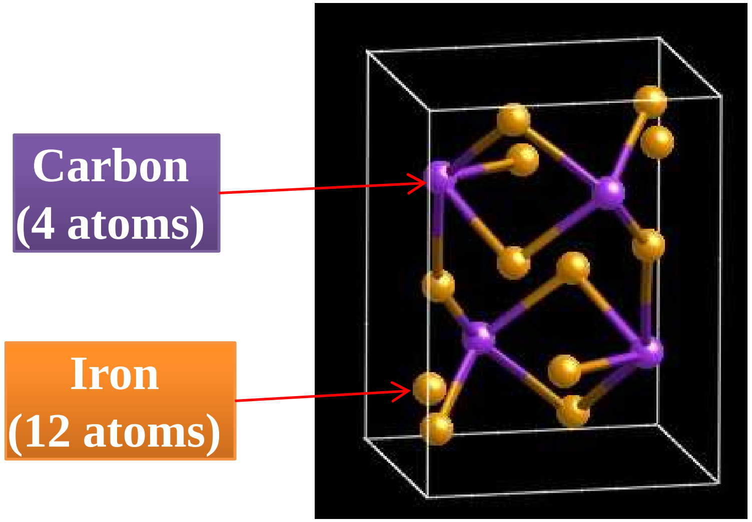
Cementite (Fe_3C)

- Cementite or iron carbide, chemical formula Fe_3C, contains 6.67%C by weight and it is a metastable phase.
- It is typically hard and brittle interstitial compound of low tensile strength (approx. 5000 psi) but high compressive strength.
- It is the hardest structure that appears on the diagram.
- Its crystal structure is orthorhombic

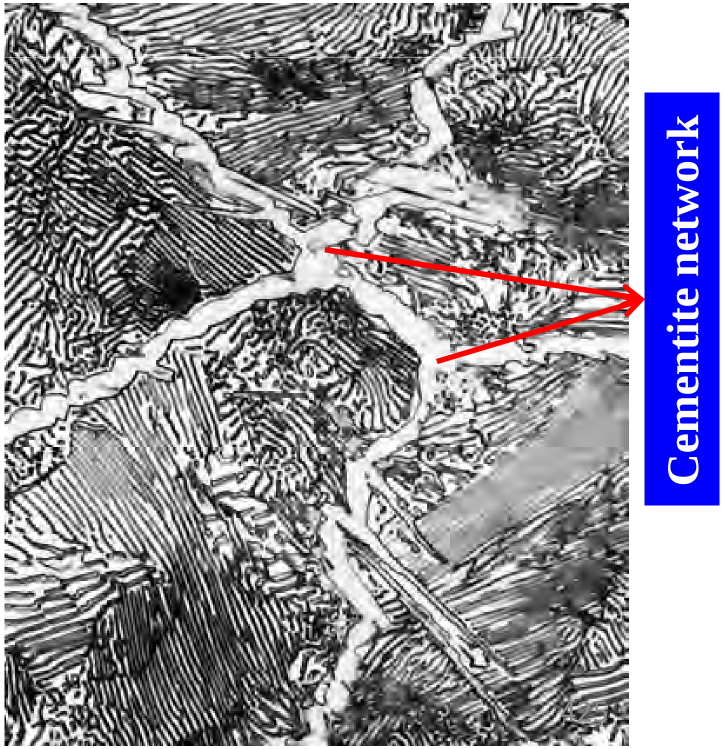


Orthorhombic

$a \neq b \neq c$
$\alpha = \beta = \gamma = 90^o$

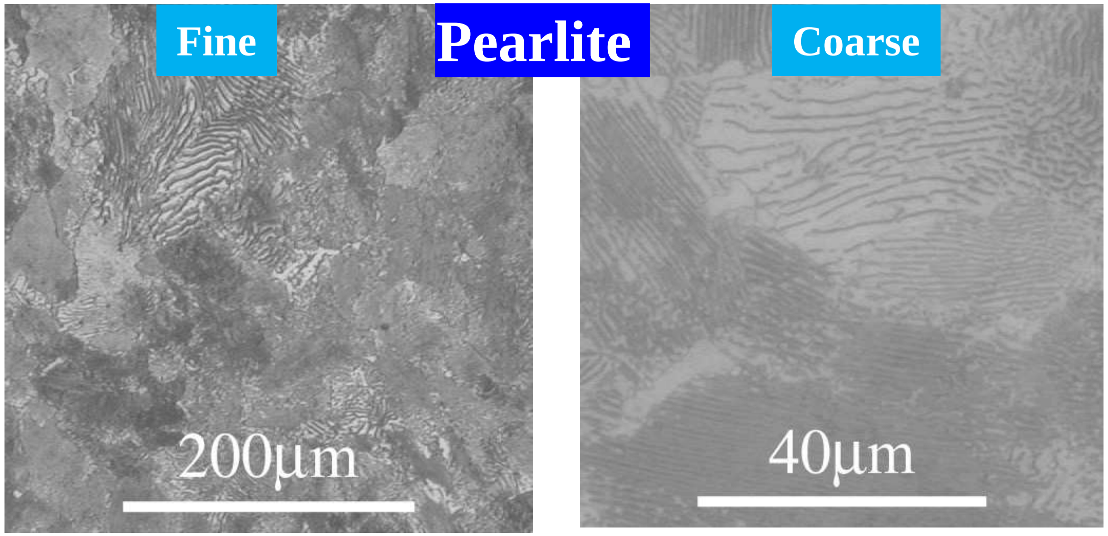

Carbon (4 atoms)

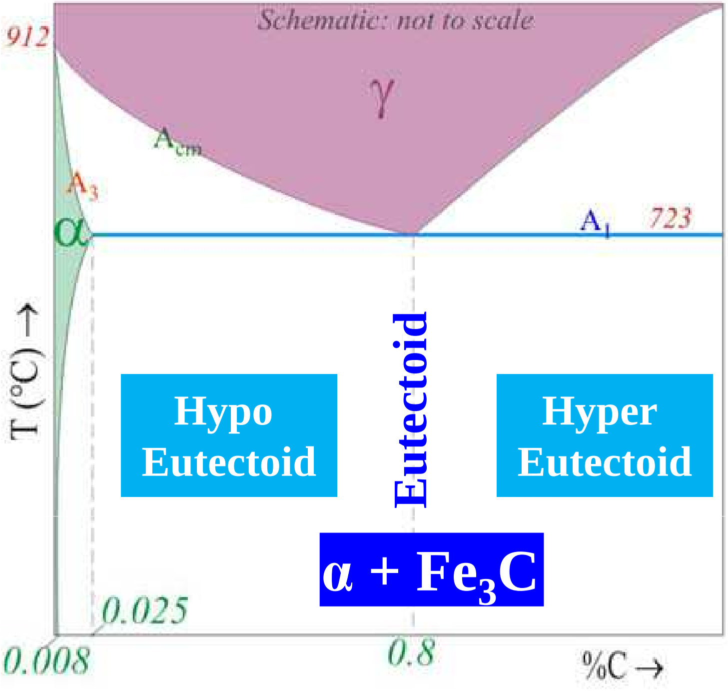
Iron (12 atoms)


Cementite network

Pearlite ($\alpha + Fe_3C$)

- Pearlite is the eutectoid mixture containing 0.80 %C and is formed at 723ºC on very slow cooling.
- It is very fine platelike or lamellar mixture of ferrite and cementite. The fine fingerprint mixture called pearlite is shown in below figure.





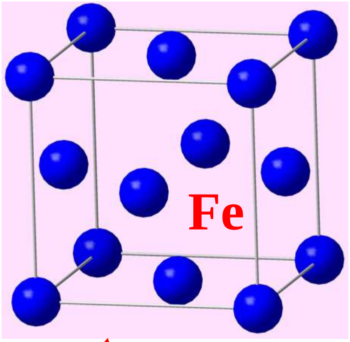
- Tensile strength – 120,000 psi or 825 Mpa
- Elongation – 20 percent in 2 in.
- Hardness – HRC 20, HRB 95-100, or BHN 250-300

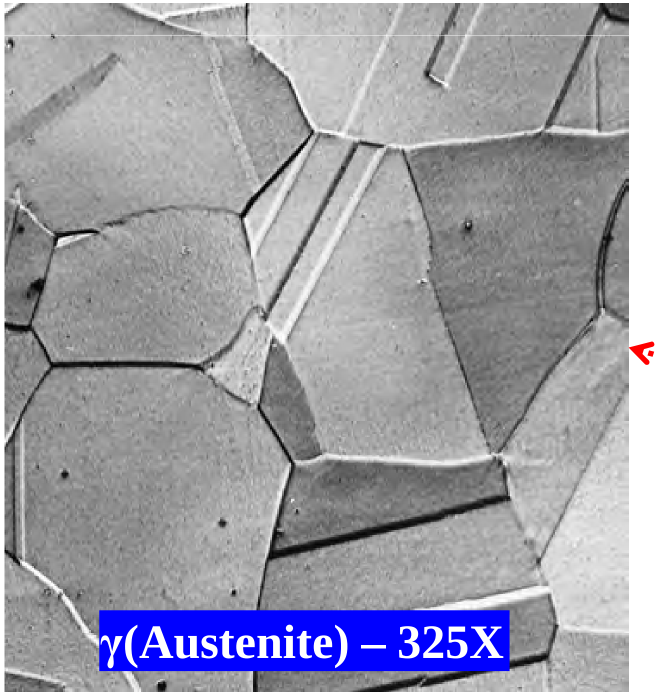
Remember…!

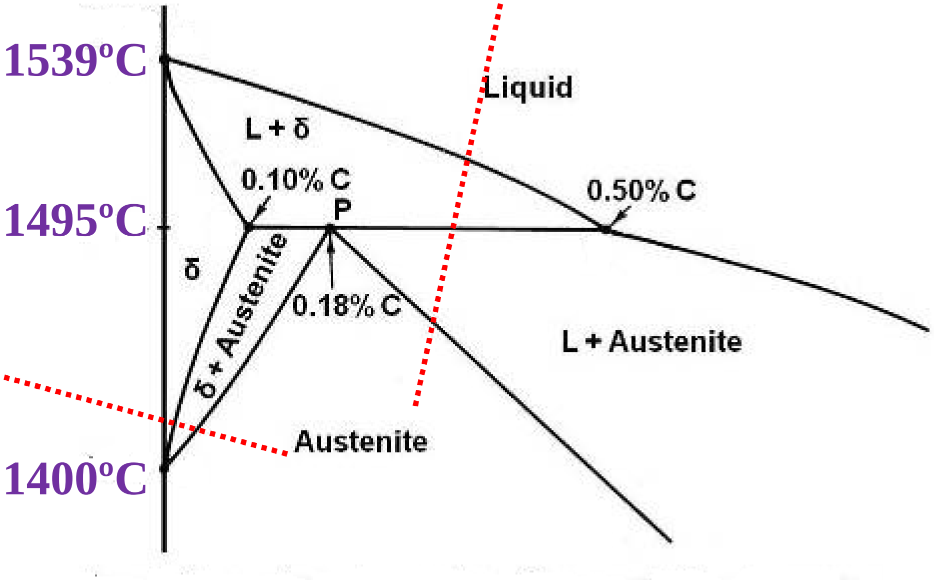
Pearlite is a not a phase but combination of two phases (ferrite + cementite)

Austenite (γ)

- It is an interstitial solid solution of a small amount of carbon dissolved in γ iron. The maximum solubility is 2.1%C at 1147ºC.
- The crystal structure of Austenite (γ) is F.C.C
- Tensile strength – 150,000 psi or 1035 Mpa
- Elongation – 10% in 2 in.
- Hardness - 40 HRC and Toughness is high.

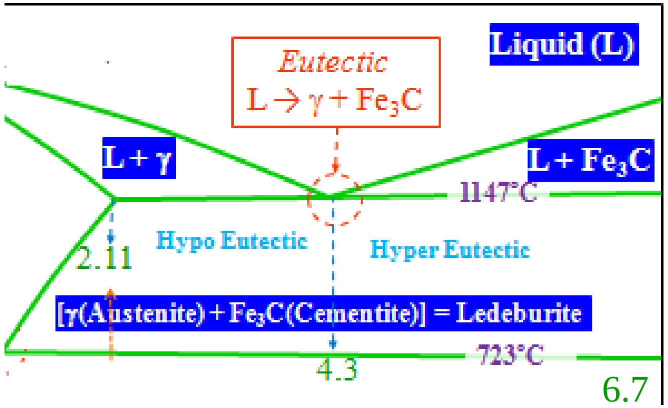



γ(Austenite) – 325X

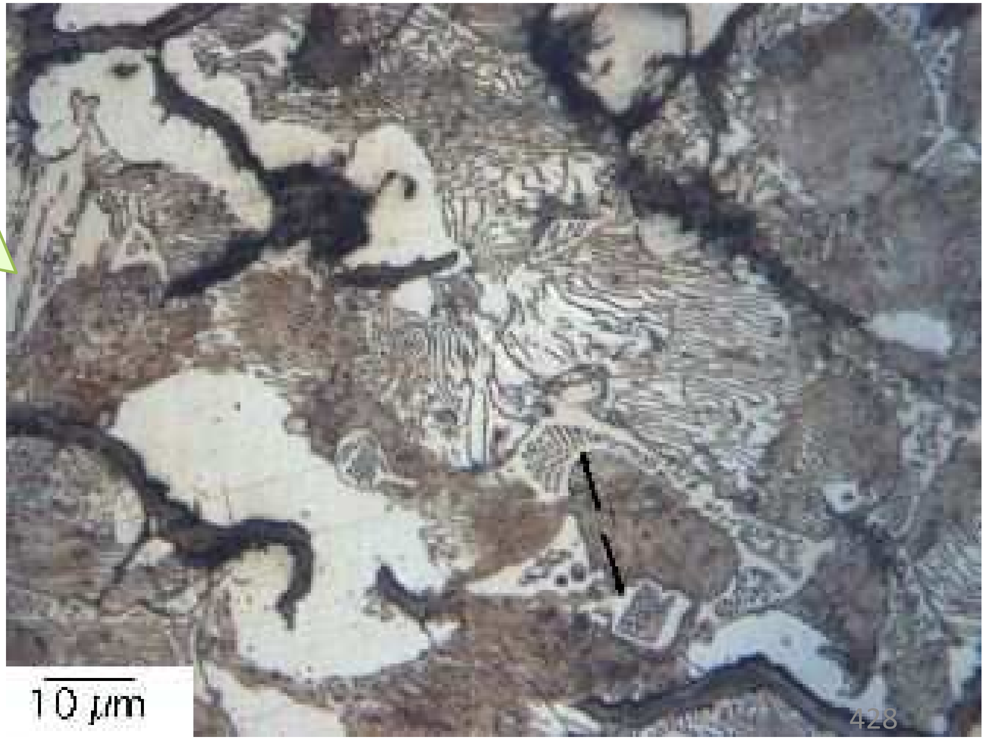


Ledeburite (γ+ Fe_3C)

- ❑ Ledeburite is the eutectic mixture of austenite and cementite. It contains 4.3%C and is formed at 1147ºC
- ❑ Structure of ledeburite contains small islands of austenite are dispersed in the carbide phase.
- ❑ Not stable at room temperature

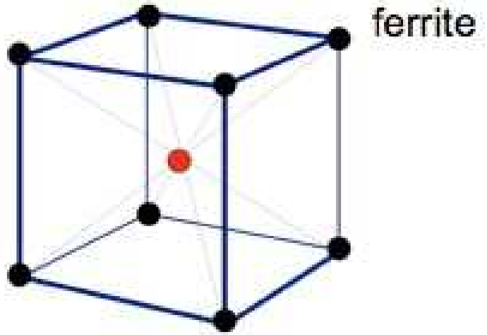


The pearlite is resolved in some regions where the sectioning plane makes a glancing angle to the lamellae. The ledeburite eutectic is highlighted by the arrows. At high temperatures this is a mixture of austenite and cementite formed from liquid. The austenite subsequently decomposes to pearlite.

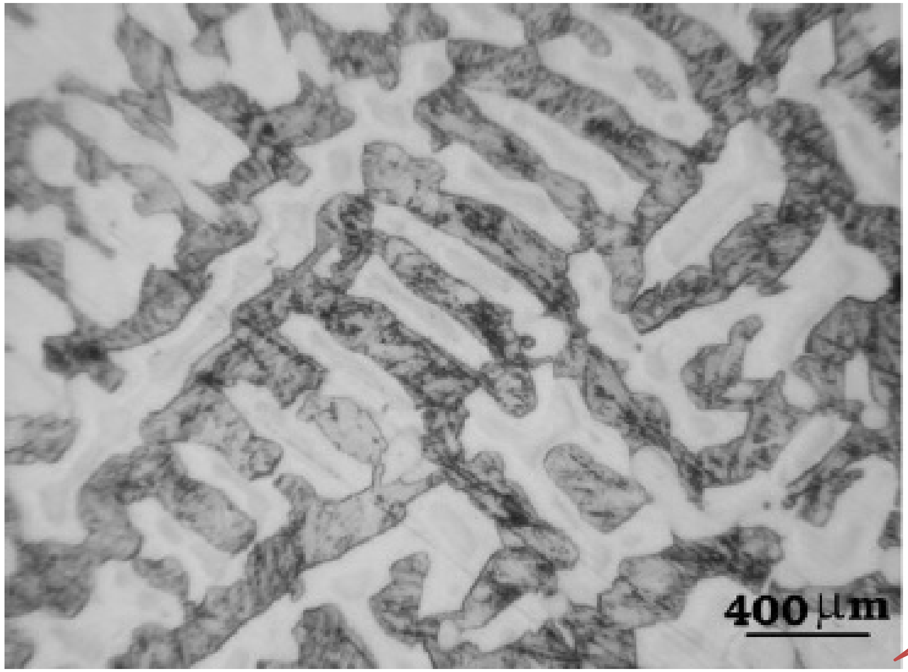


Ferrite (δ)

- Interstitial solid solution of carbon in iron of body centered cubic crystal structure. (δ iron) of higher lattice parameter (2.89Å) having solubility limit of 0.09 wt% at 1495°C with respect to austenite. The stability of the phase ranges between 1394-1539°C.



- This is not stable at room temperature in plain carbon steel. However it can be present at room temperature in alloy steel specially duplex stainless steel.

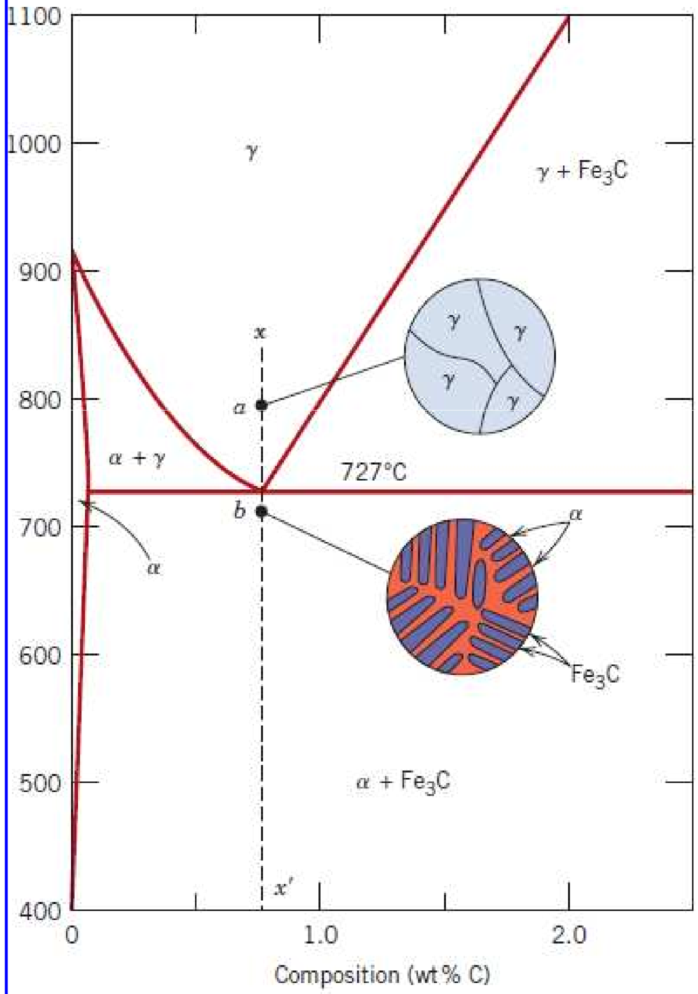


δ-ferrite in dendrite form in as-cast Fe-0.4C-2Mn-0.5Si-2 Al0.5Cu

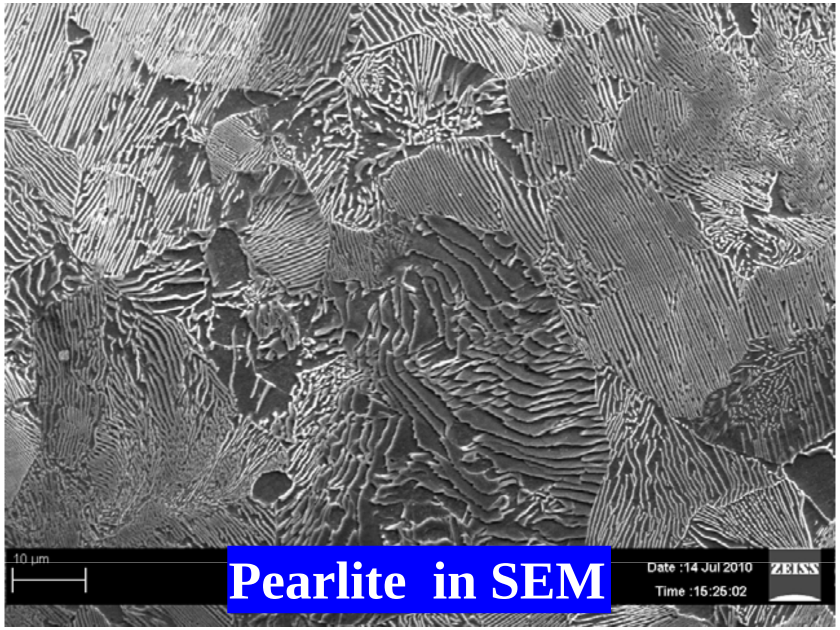
Microstructures involved in eutectoid mixture

Eutectoid reaction

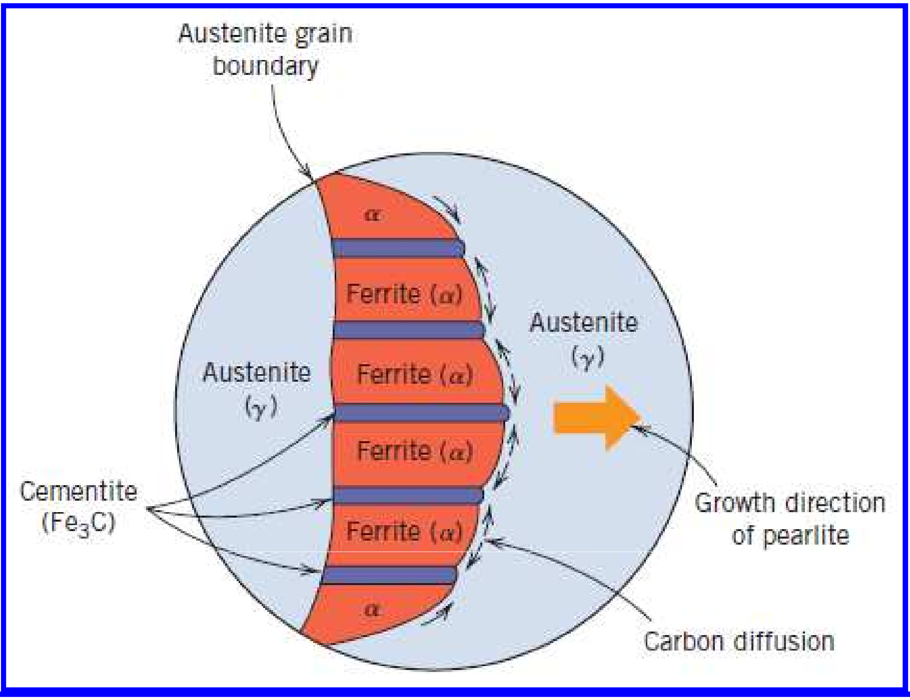
- Phase changes that occur upon passing from the γ region into the α+ Fe_3C phase field.
- Consider, for example, an alloy of eutectoid composition (0.8%C) as it is cooled from a temperature within the γ phase region, say 800ºC – that is, beginning at point ‘a’ in figure and moving down vertical xx’. Initially the alloy is composed entirely of the austenite phase having composition 0.8 wt.% C and then transformed to α+ Fe_3C [pearlite]
- The microstructure for this eutectoid steel that is slowly cooled through eutectoid temperature consists of alternating layers or lamellae of the two phases α and Fe_3C
- The pearlite exists as grains, often termed “colonies”; within each colony the layers are oriented in essentially the same direction, which varies from one colony to other.
- The thick light layers are the ferrite phase, and the cementite phase appears as thin lamellae most of which appear dark.



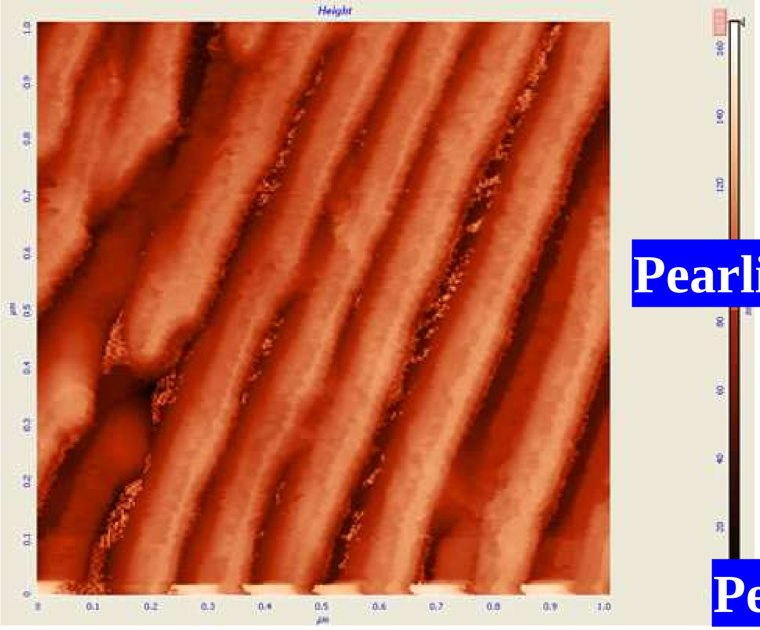
Eutectoid structure



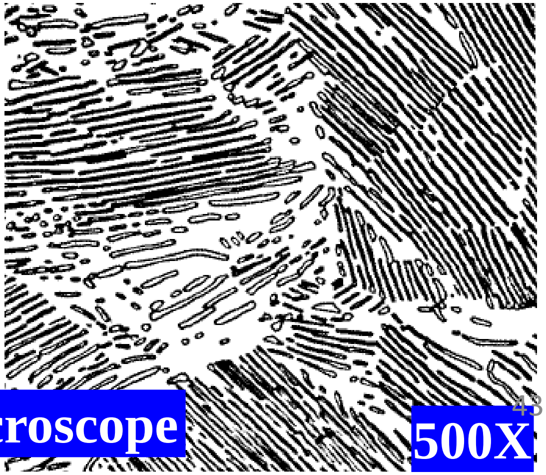
Pearlite in SEM



Schematic representation of the formation of pearlite from austenite; direction of carbon diffusion indicated by arrows



Pearlite in AFM

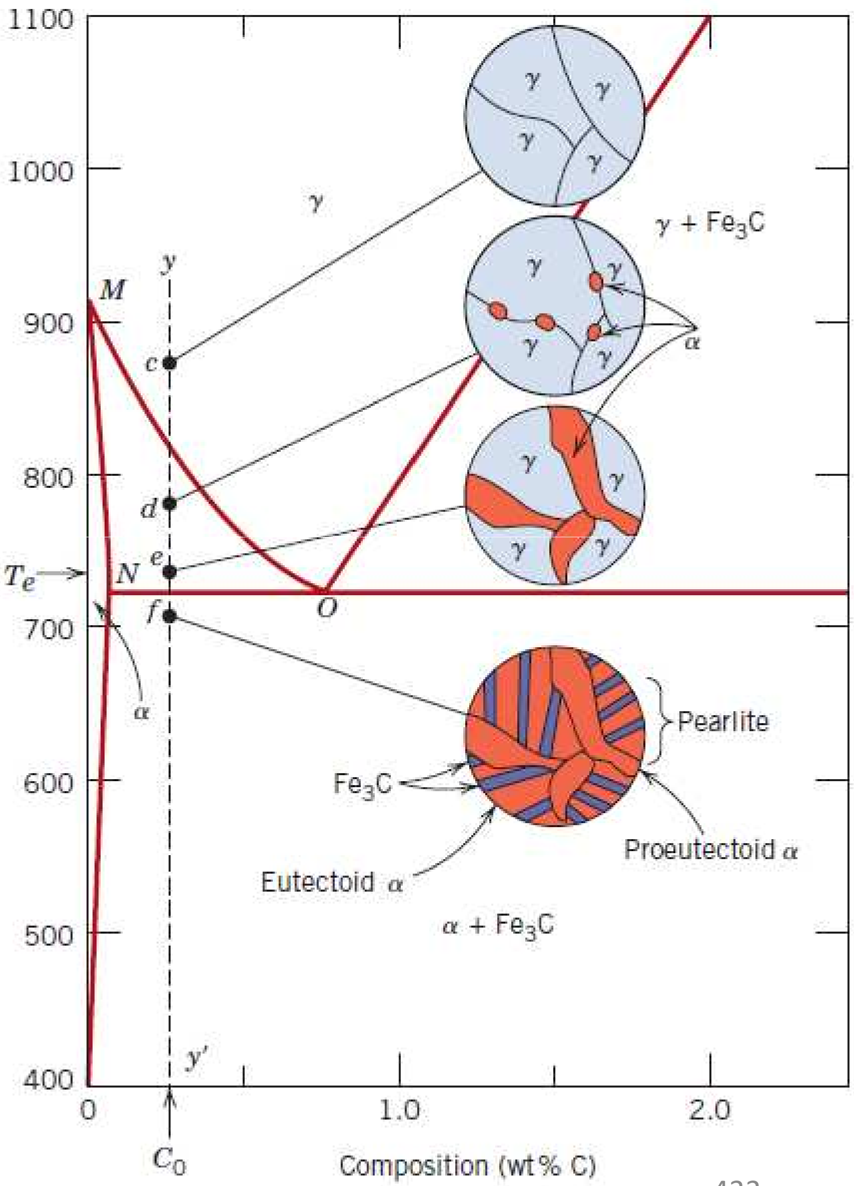


Pearlite in optical microscope

500X

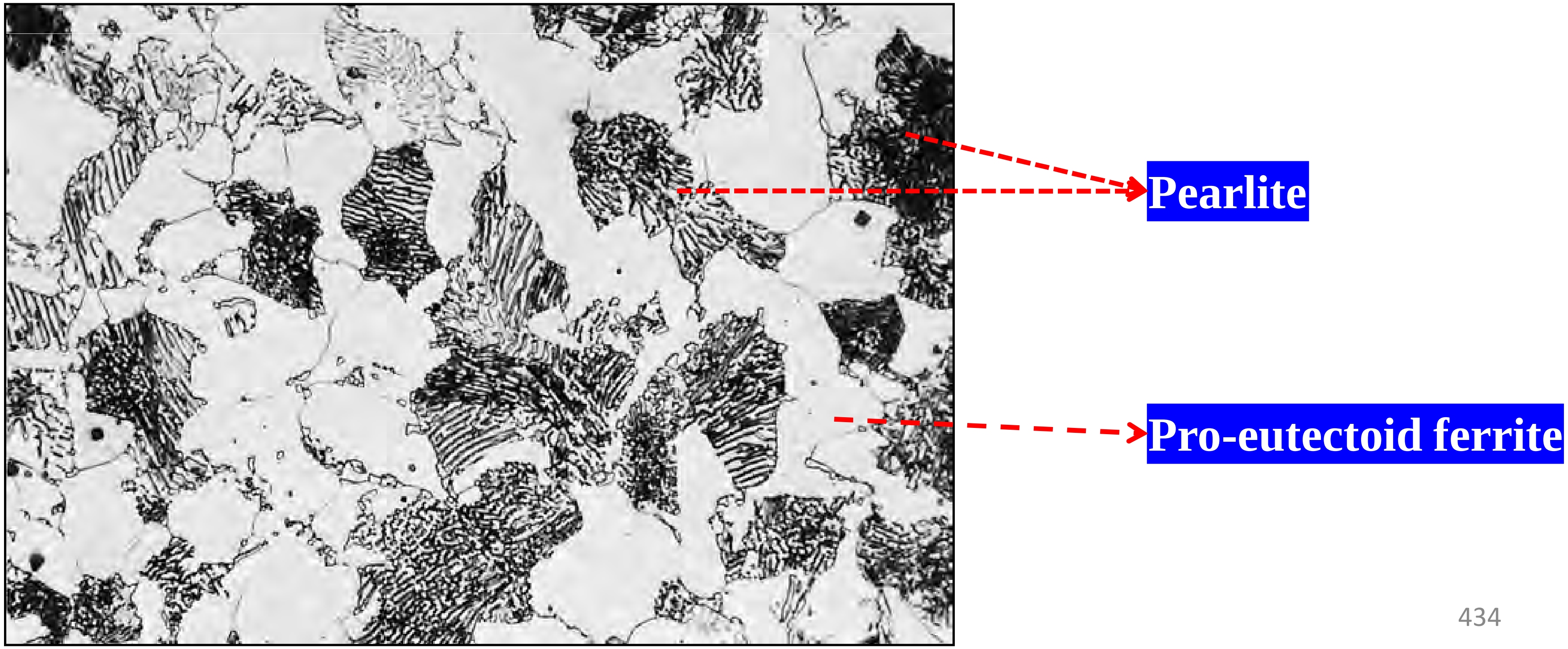
Hypo eutectoid region

- Hypo eutectoid region – 0.008 to 0.8 %C
- Consider vertical line yy’ in figure, at about 875ºC, point c, the microstructure will consist entirely of grains of the γ phase.
- In cooling to point d, about 775ºC, which is within the α+γ phase region, both these phases will coexist as in the schematic microstructure Most of the small α particles will form along the original γ grain boundaries.
- Cooling from point d to e, just above the eutectoid but still in the α+γ region, will produce an increased fraction of the α phase and a microstructure similar to that also shown: the α particles will have grown larger.



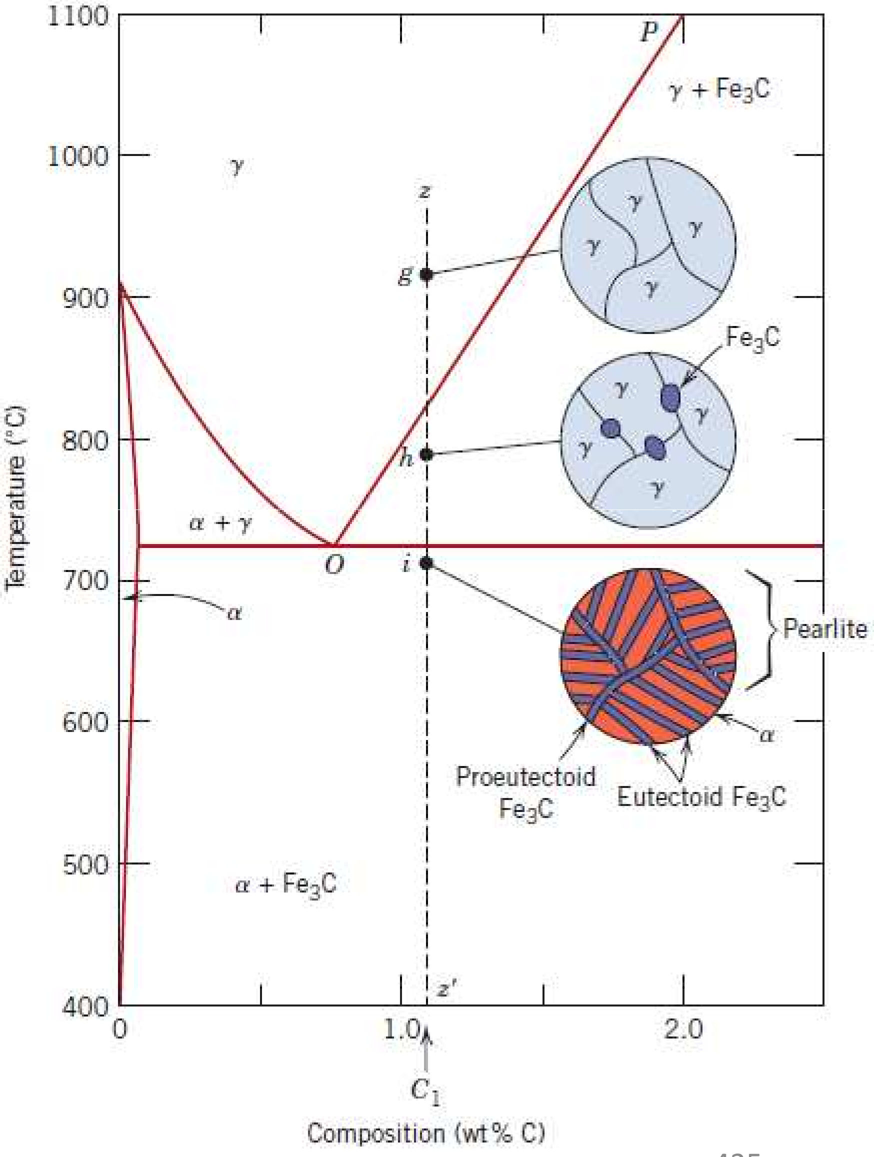
Hypo eutectoid region

- Just below the eutectoid temperature, at point f, all the γ phase that was present at temperature e will transform pearlite. Virtually there is no change in α phase that existed at point e in crossing the eutectoid temperature – it will normally be present as a continuous matrix phase surrounding the isolated pearlite colonies.
- Thus the ferrite phase will be present both in the pearlite and also as the phase that formed while cooling through the α+γ phase region. The ferrite that is present in the pearlite is called eutectoid ferrite, whereas the other, is termed proeutectoid (meaning pre- or before eutectoid) ferrite.

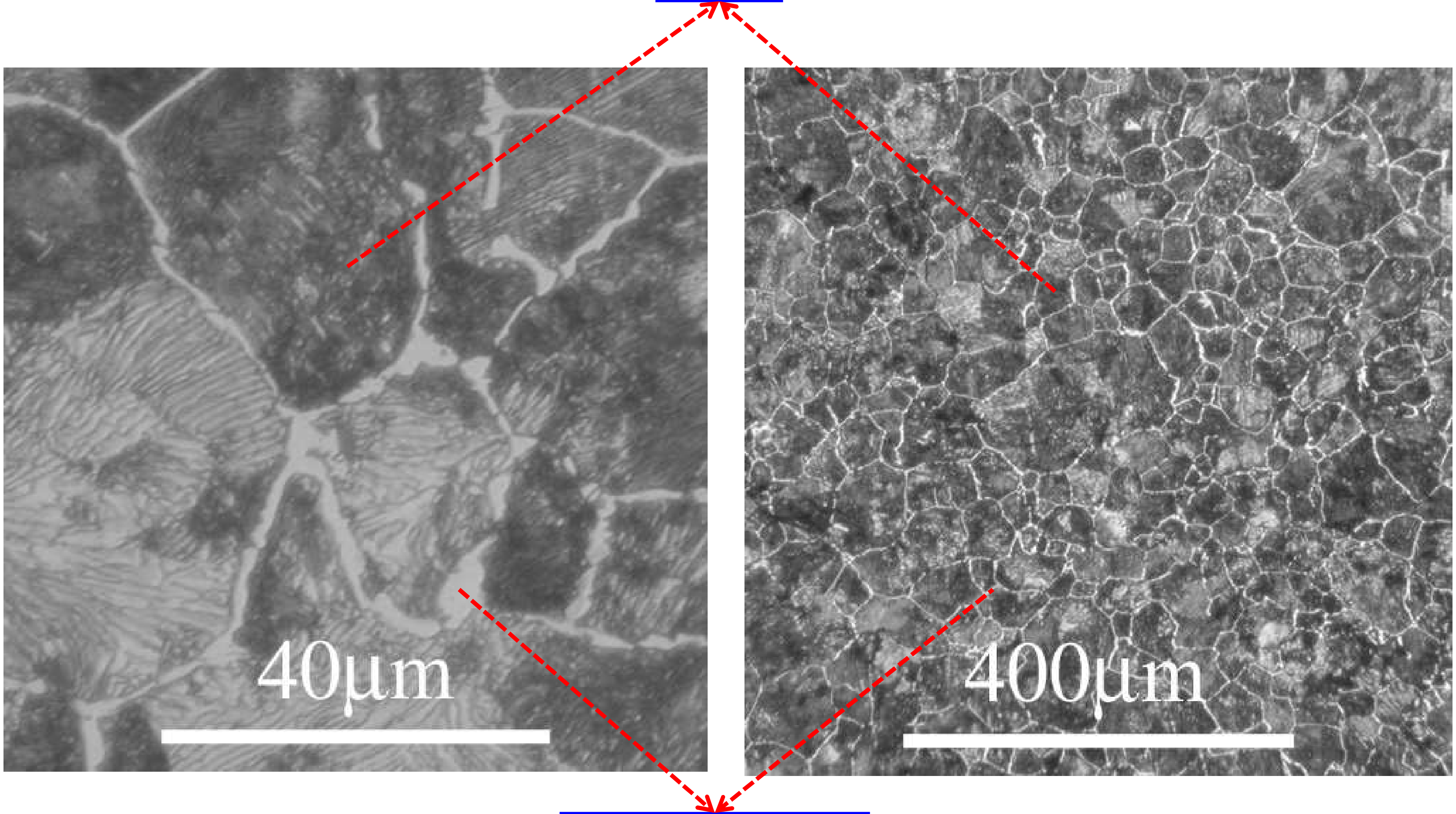


Hyper eutectoid region

- Hyper eutectoid region – 0.8 to 2.1 %C
- Consider an alloy of composition C_1 in figure that, upon cooling, moves down the line zz’. At point g only the γ phase will be present and the microstructure having only gamma grains.
- Upon cooling into the γ+ Fe_3C phase field – say to point h – the cementite phase will began to form along the initial γ grain boundaries, similar to the α phase in point d. this cementite is called *proeutectoid cementite* that which forms before the eutectoid reaction.
- As the temperature is lowered through the eutectoid to point I, all remaining austenite of eutectoid composition is converted into pearlite; thus the resulting microstructure consists of pearlite and proeutectoid cementite as microconstituents.



Hyper eutectoid region



Pearlite

Cementite network

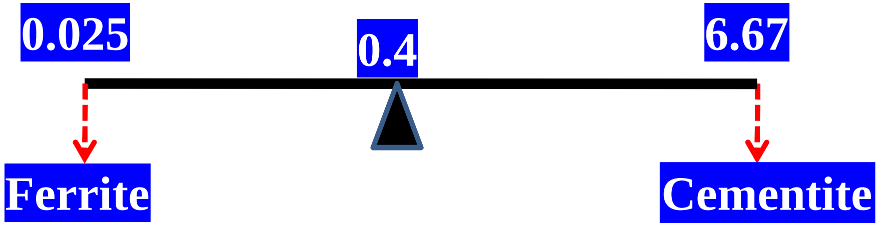
Application of Lever rule in Fe-Fe_3C phase diagram

Solved Example

For a 99.6 wt% Fe-0.40 wt% C at a temperature just below the eutectoid, determine the following:

a) The amount of Fe_3C, ferrite (α) and pearlite

b) The amount of pearlite and proeutectoid ferrite (α)



0.025 **0.4** **6.67**

Ferrite **Cementite**

a) The amount of Fe_3C and ferrite (α)

Percentage of $\mathbf{Fe_3C}$ = $\dfrac{0.4-0.025}{6.67-0.025} * 100$

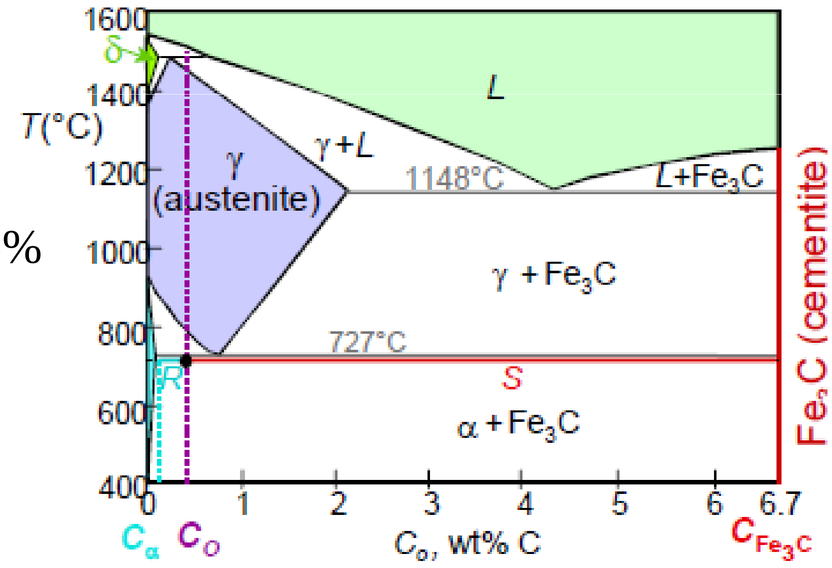
Percentage of Fe_3C in 0.4 %C steel is 5.64 %

Percentage of Ferrite (α) in 0.4 %C steel = (100- 5.64)%

Percentage of ferrite in 0.4 %C steel = 94.36%

or

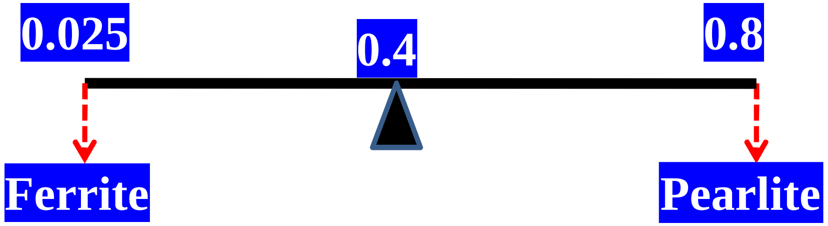
Percentage of ferrite=$\dfrac{6.67-0.4}{6.67-0.025} * 100$ **= 94.36%**



b) Phase fraction of pearlite and proeutectoid ferrite (α)

$$Percentage\ of\ pearlite = \frac{0.4 - 0.025}{0.8 - 0.025} * 100$$

Percentage of pearlite = 48 %



0.025

0.4

0.8

Ferrite

Pearlite

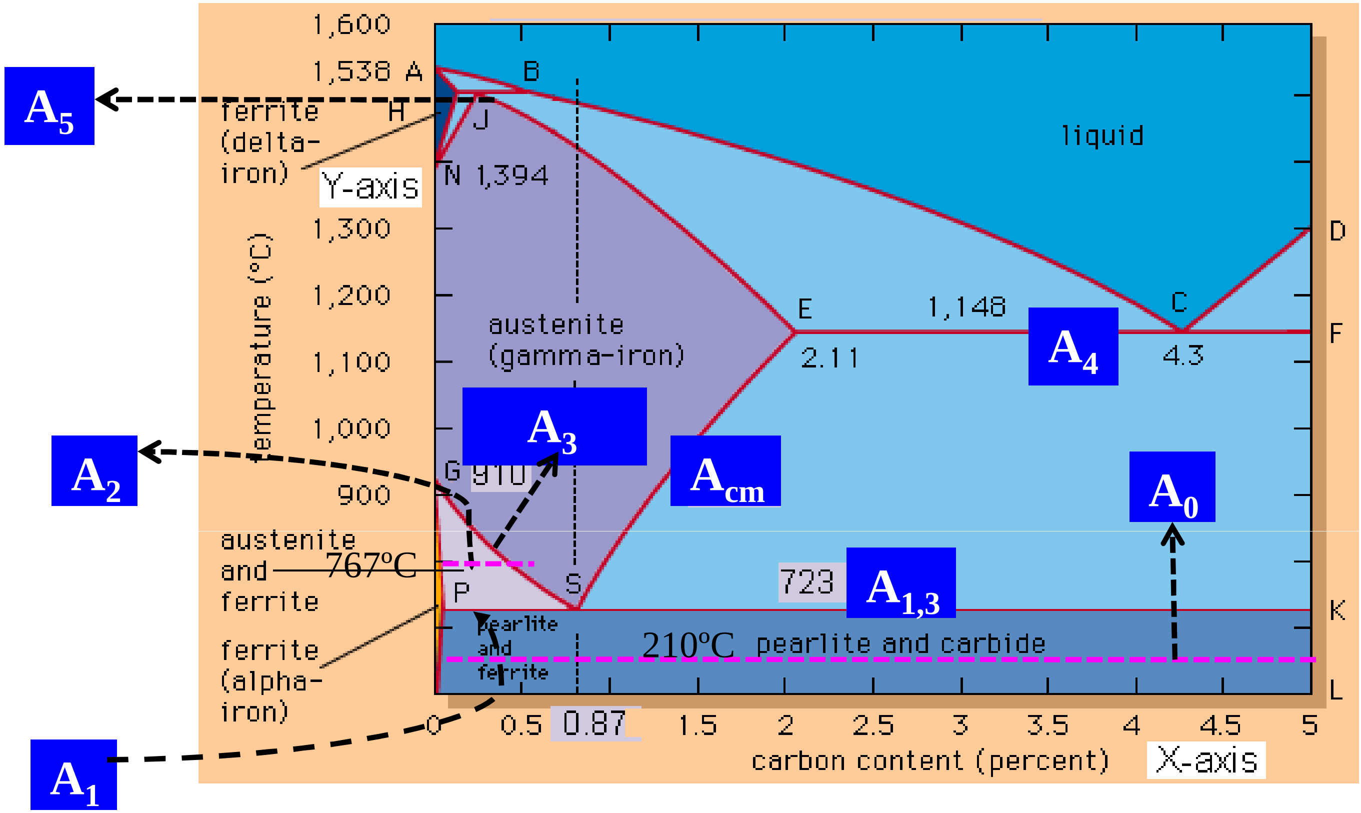
Percentage of proeutectoid ferrite (α) in 0.4 %C steel = (100- 48)%

Percentage of proeutectoid ferrite (α) = 52 %

or

$$Percentage\ of\ proeutectoid\ ferrite = \frac{0.8 - 0.4}{0.8 - 0.025} * 100 = 52\%$$

Critical temperature lines

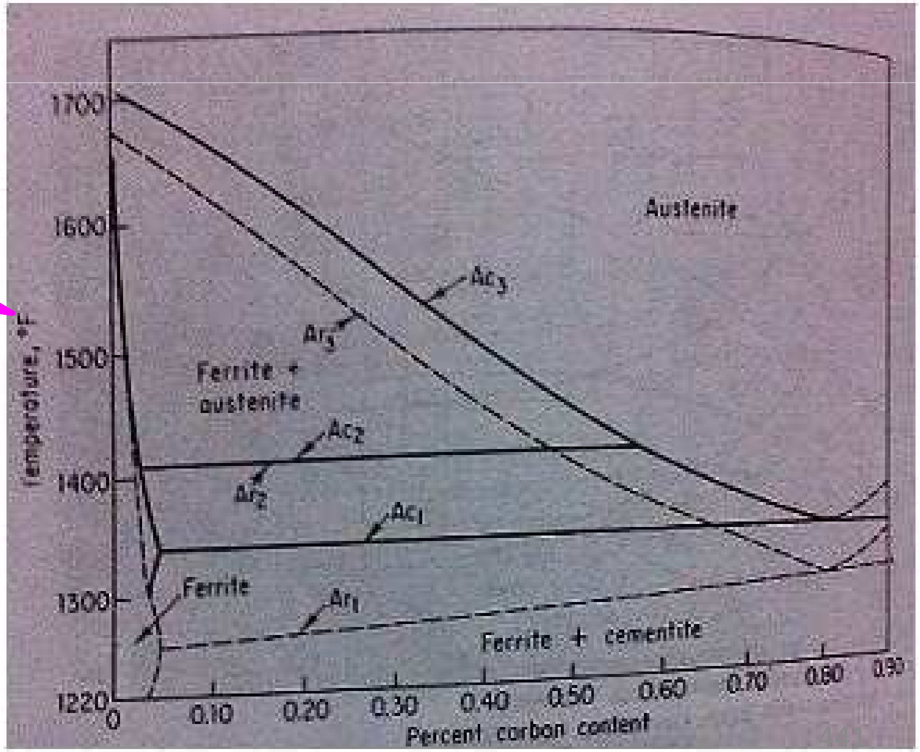


- ❑ In general, A_0 – Subcritical temperature, A_1 - lower critical temperature, A_3 - upper critical temperature, A_4 – Eutectic temperature, A_5 – Peritectic temperature and A_{cm} - γ/γ+cementite phase field boundary.
- ❑ While heating we denoted as Ac_1, Ac_2, Ac_3 etc., *'c' stands for chauffage (French word), which means heating* and while cooling we denoted as Ar_1, Ar_2, Ar_3 etc., *'r' stands for refroidissement, (French word) which means cooling.*

Critical temperature lines

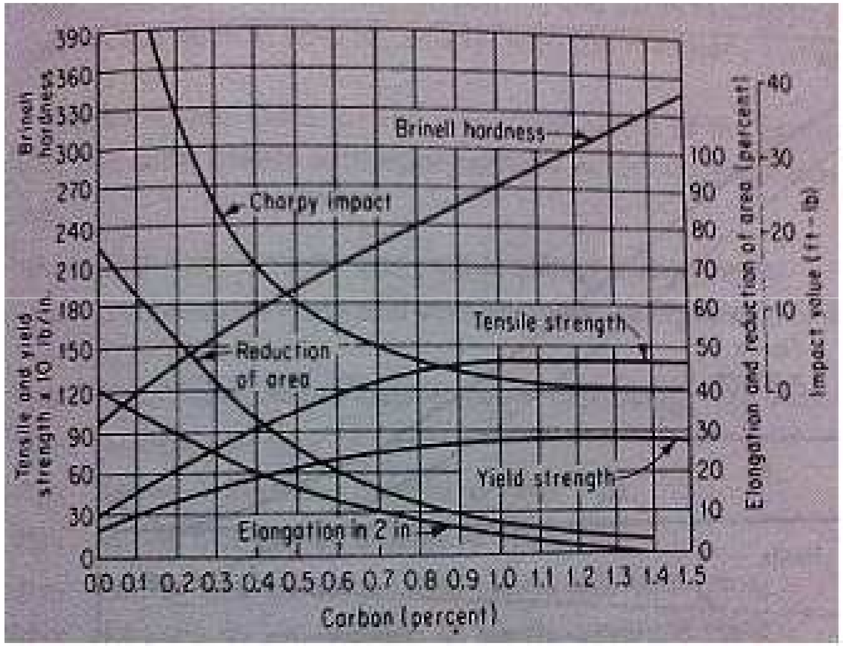
- The upper – and lower critical temperature lines are shown as single lines under equilibrium conditions and are sometimes indicated as A_{e3}, A_{e1} etc. When the critical lines are actually determined, it is found that they do not occur at the same temperature.
- The critical line on heating is always higher than the critical line on cooling. Therefore, the upper critical line of a hypo eutectoid steel on heating would be labeled A_{C3} and the same line on cooling A_{r3}. The rate of heating and cooling has a definite effect on the temperature gap between these lines.

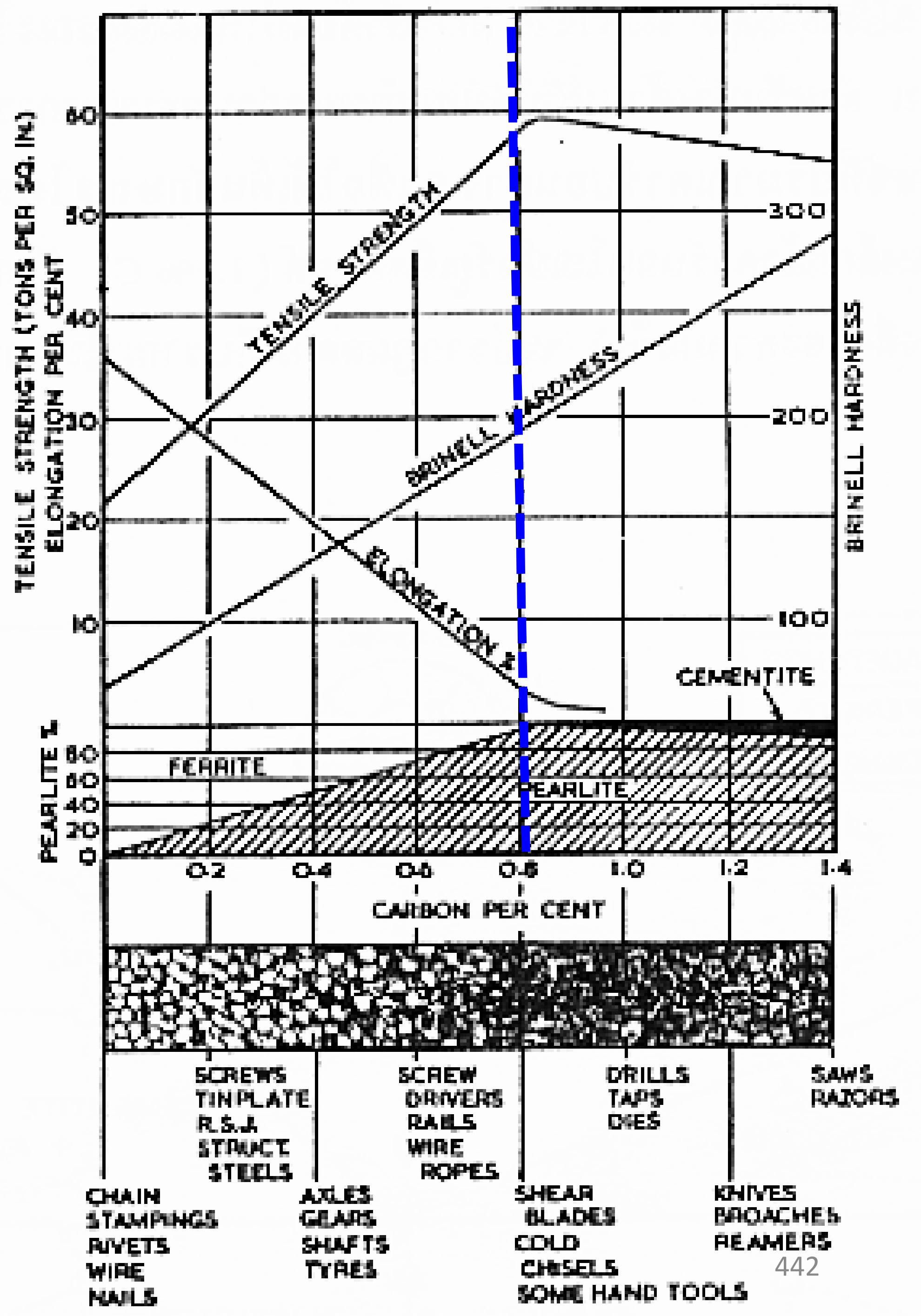
The results of thermal analysis of a series of carbon steels with an average heating and cooling rate of 11°F/min are shown in figure.



Final word…! with infinitely slow heating and cooling they would probably occur at exactly the same temperature.

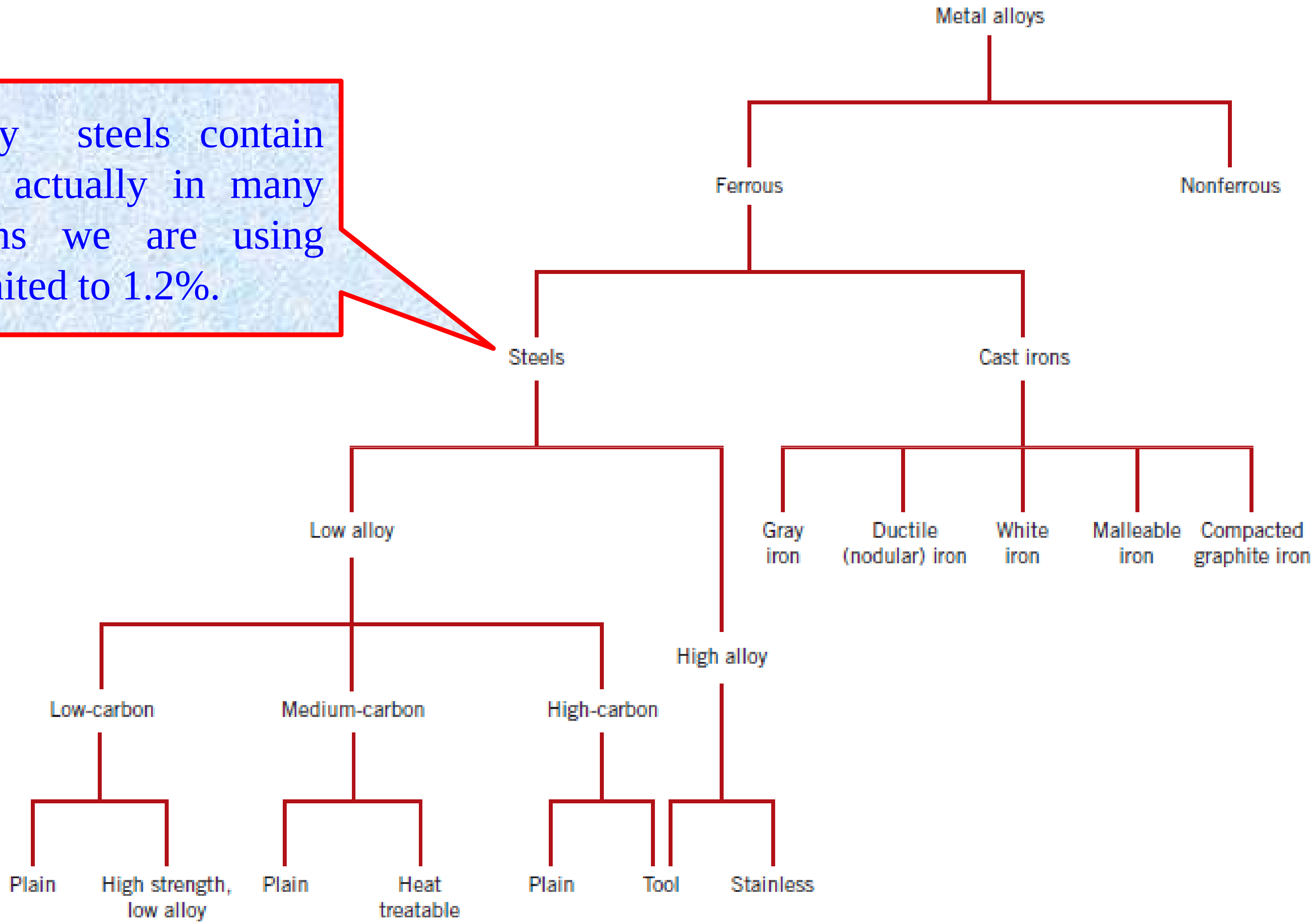
Properties of carbon steels





Classification of metal alloys

Technically steels contain 2.1% but actually in many applications we are using carbon limited to 1.2%.



- Metal alloys
  - Ferrous
    - Steels
      - Low alloy
        - Low-carbon
          - Plain
          - High strength, low alloy
        - Medium-carbon
          - Plain
          - Heat treatable
        - High-carbon
          - Plain
          - Tool
      - High alloy
        - Tool
        - Stainless
    - Cast irons
      - Gray iron
      - Ductile (nodular) iron
      - White iron
      - Malleable iron
      - Compacted graphite iron
  - Nonferrous

Plain stands for only Fe-c with out any alloying element

Classification of steels

Based on method of manufacturer

- ❑ This gives rise to bessemer steel, open hearth steel, electric – furnace steel, crucible steel, etc.

Based on method application

- ❑ This is generally the final use for the steel, such as machine steel, spring steel, boiler steel, structural steel, or tool steel.

Based on % of Carbon

- ❑ Low carbon alloys - (0.025-0.3)%C
- ❑ Medium carbon alloys – (0.3-0.6)%C
- ❑ High carbon alloys – (0.6-1.2)%C

Based on Specifications

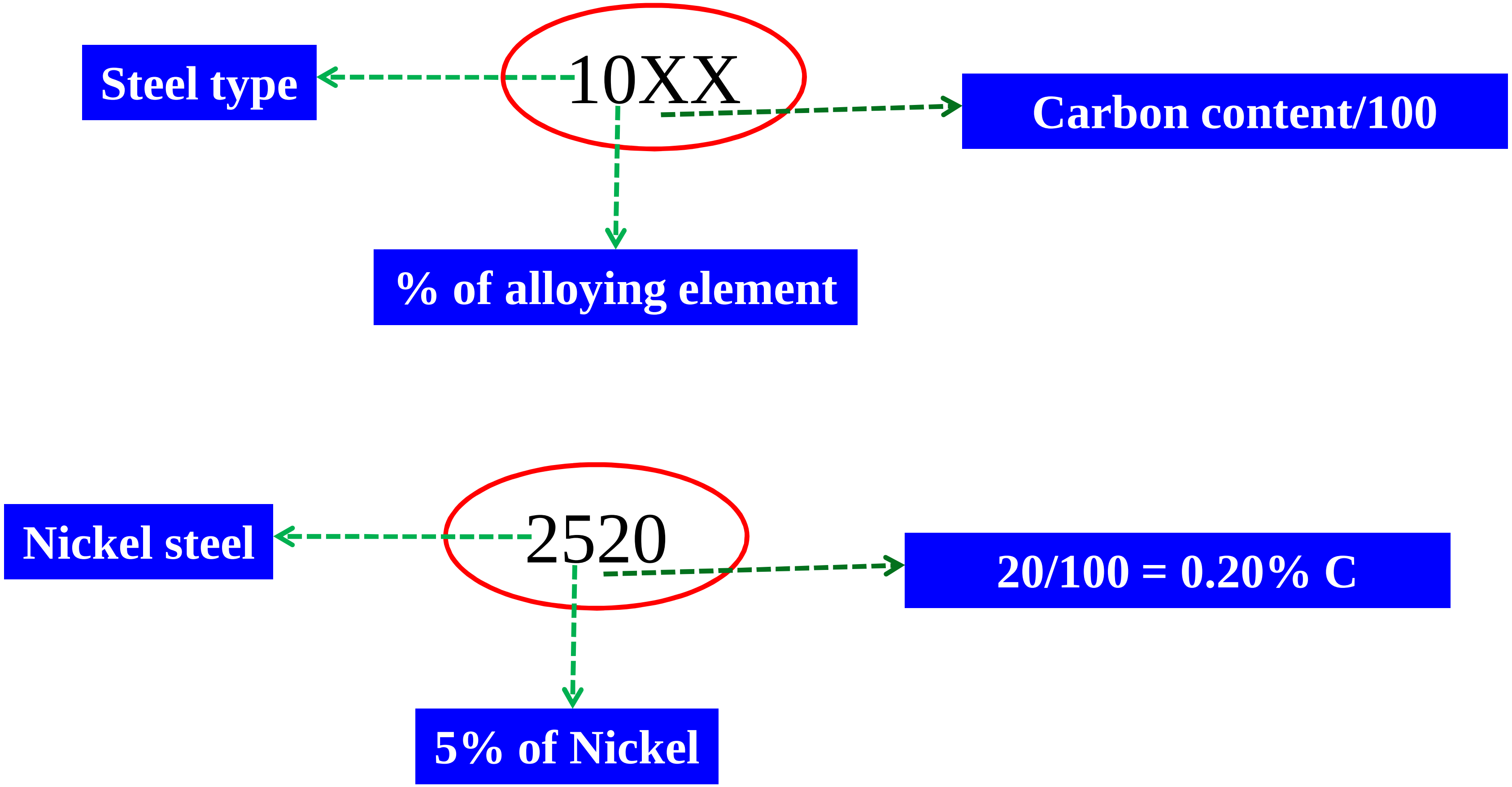
These standard specifications given by different societies, and they developed different series of (Fe-c) alloys based on different compositions. For each type they given a standard series number…!

AISI (American Iron and Steel Institute)
SAE (Society of Automotive Engineering)
JIS ⇨Japanese Standard
DIN ⇨German Standard
TIS ⇨ Thai Standard

AISI –SAE Steel Specification

Series	**Steel type**
10xx	Plain carbon steel
11xx	Plain carbon steel (high S, low P)
12xx	Plain carbon steel (high S, high P)
13xx	Mn-Steel (Mn 1.75%)
23xx	Ni-Steel (Ni 3.00%)
25xx	Ni-Steel (Ni 5.00%)
31xx	Ni-Cr Steel (Ni 1.25%, Cr 0.60%)
33xx	Ni-Cr Steel (Ni 3.50%, Cr 1.50%)
40xx	Molybdenum steel (Mo 0.20 or 0.25)
41xx	Chrom – Moly steel (Cr 0.50, 0.80, or 0.95. Mo 0.12,0.20 or 0.30
43xx	No-Cr-Mo steel
44xx	Molybdenum 0.53
92xx	Silicon steel (Si 2.0%) ……etc.

AISI –SAE Steel Specification



10XX

Steel type

Carbon content/100

% of alloying element

2520

Nickel steel

20/100 = 0.20% C

5% of Nickel

Iron - Graphite Phase diagram

Avala Lava Kumar* : Suneeti Purohit : Gautam Behera

Department of Metallurgical & Materials Engineering (MME)

Veer Surendra Sai University of Technology (VSSUT), Burla -768018

**E-mail : lavakumar.vssut@gmail.com*

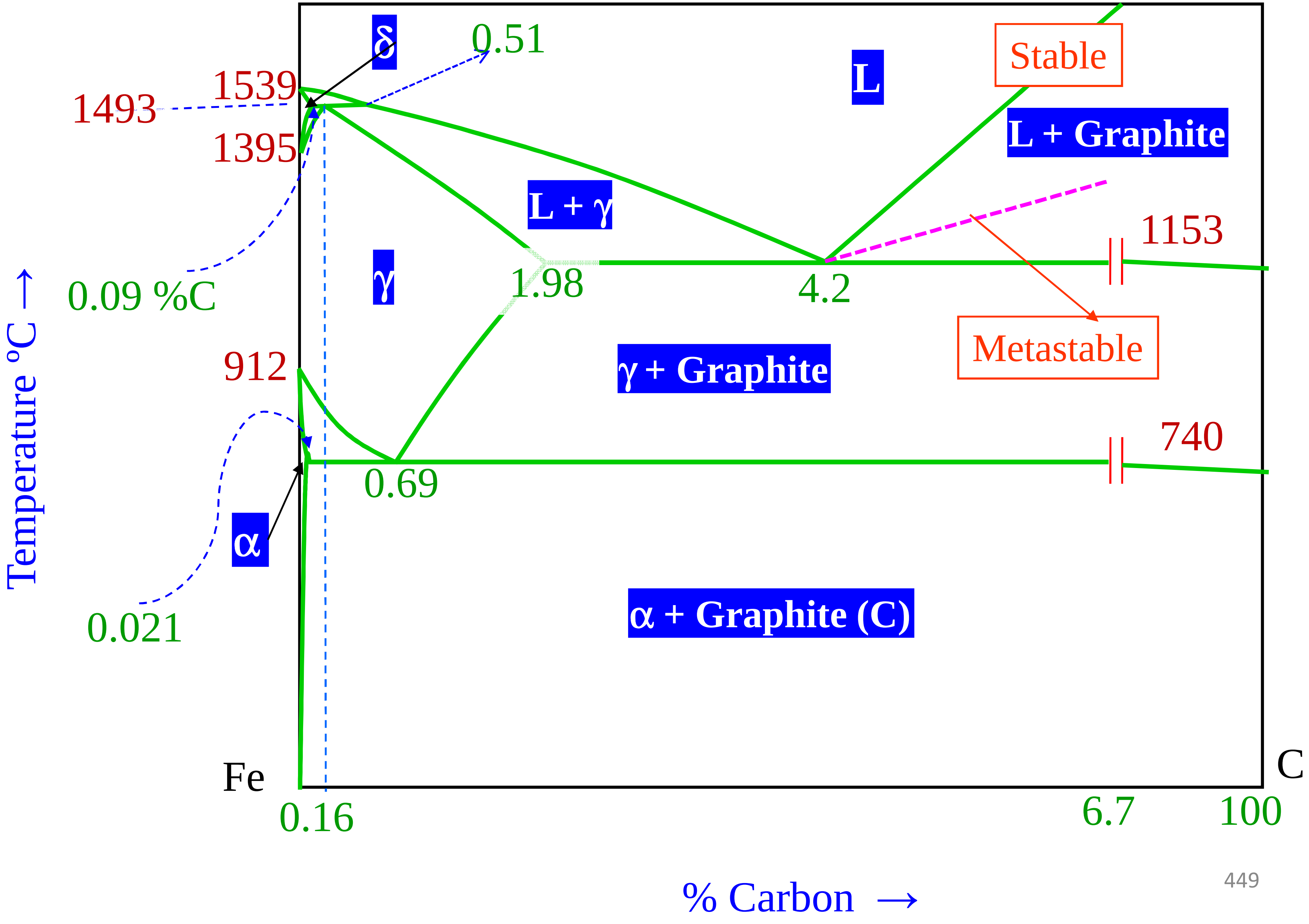
Iron – Graphite Phase Diagram

- The true equilibrium diagram for iron and carbon is generally considered as iron-graphite phase diagram *(next slide)*. Earlier we learn about iron-iron carbide phase diagram and it is not a true equilibrium diagram, generally it is called metastable iron - iron carbide phase diagram.
- Cementite (Fe_3C) is a metastable compound, and under some circumstances it can be made to dissociate or decompose to form ferrite and graphite, according to the reaction

$$Fe_3C \longrightarrow 3Fe + C$$

- For explain of cast irons we will refers to both Iron-Iron carbide phase diagram and Iron-Graphite phase diagram.
- Cast irons are a class of ferrous alloys with carbon contents above 2.14 wt%; in practice, however, most cast irons contain between 3.0 and 4.5 wt% C and, in addition, other alloying elements .
- The ductility of cast iron is very low and brittle, it cannot be rolled, drawn, or worked at room temperature. However they melt readily and can be cast into complicated shapes which are usually machined to final dimensions. Since casting is the only suitable process applied to these alloys, they are known as cast irons.

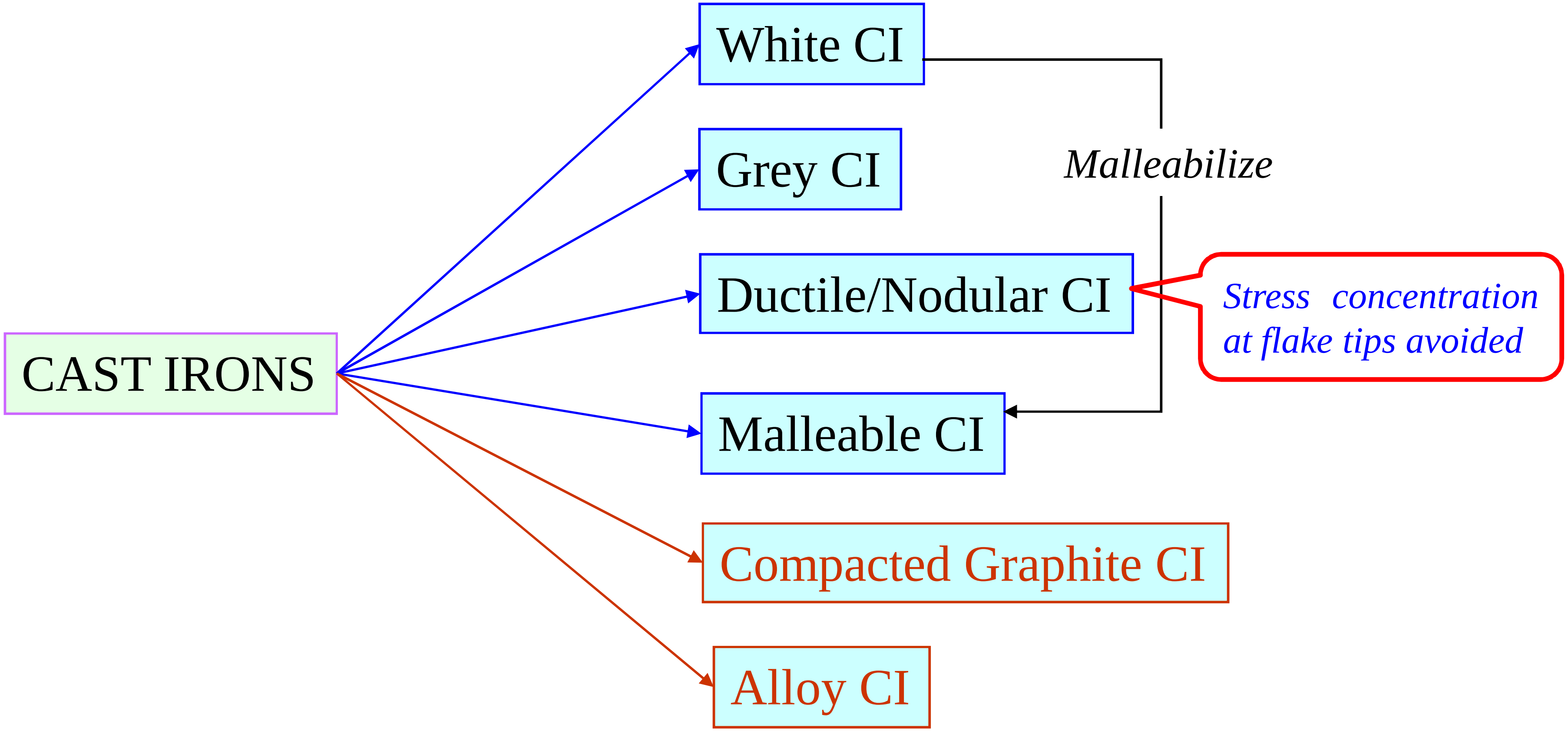
Iron – Graphite Phase Diagram



A brief history of cast irons

- Cast iron has its earliest origins in china between 700 and 800B.C. until this period ancient furnaces could not reach sufficiently high temperatures.
- The use of this newly discovered form of iron varied from simple tools to a complex chain suspension bridge erected approximately 56A.D.
- The next significant development in cast iron was the first use of coke in 1730 by an English founder named Darby.
- Due to this revolution, better casts were available for more versatile roles, such as James Watt’s first steam engine, constructed in 1794.
- In 1810, Swedish chemist Bergelius, and German physicists Stromever discovered that by adding silicon to the furnace, along with scrap and pigiron, consistently cast iron is produced.
- In 1885 Turner added ferrosilicon to white iron to produce stronger gray iron castings.
- In the late 20th century the major use of cast irons consisted of pipes, thermal containment units, and certain machine or building entities which were necessary to absorb continuous vibrations.

Classification of cast irons



CAST IRONS

White CI

Grey CI

Ductile/Nodular CI

Malleable CI

Compacted Graphite CI

Alloy CI

Malleabilize

Stress concentration at flake tips avoided

Good castability ⇒ C > 2.4%

White Cast Iron

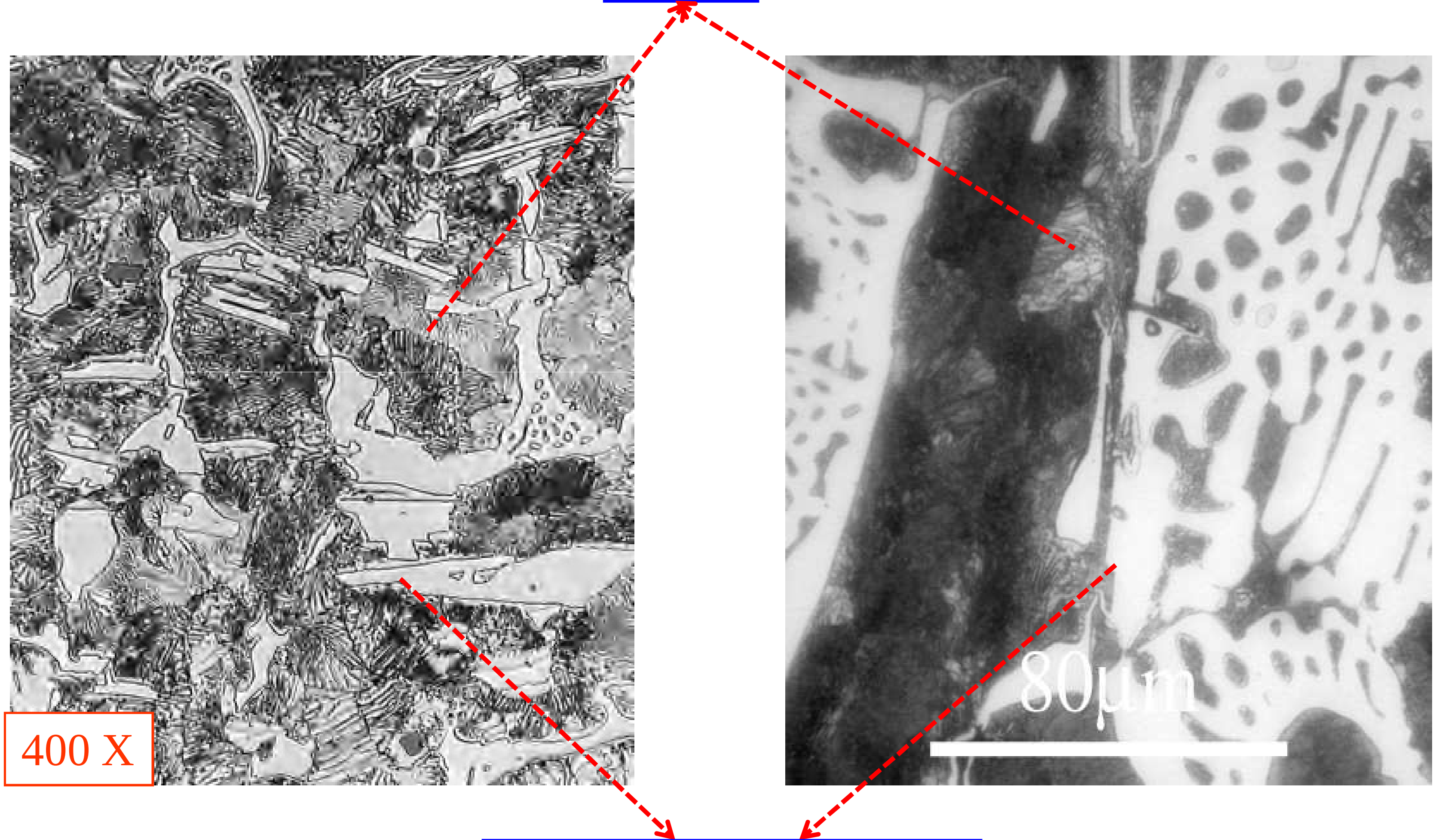
- ❑ In which all the C is in the combined form as Fe_3C (Cementite)
- ❑ The typical microstructure of white cast iron *(see next slide)*, consisting of dendrites of transformed austenite (pearlite) in a white interdendritic network of cementite.

Microstructure → Pearlite + Ledeburite + Cementite

- ❑ White cast iron contains a relatively large amount of cementite as a continuous interdendritic network, it makes the cast iron hard and wear-resistant but extremely brittle and difficult to machine.
- ❑ ‘completely white’ cast irons are limited in engineering applications because of this brittleness and lack of machinability. mainly used in liners for cement mixers, ball mills and extrusion nozzles.
- ❑ A large tonnage of white cast iron is used as a starting material for the manufacturer of malleable cast iron.
- ❑ Hardness : 375 to 600 BHN
- ❑ Tensile strength : 135-480 Mpa, Compressive strength: 1380 -1725 Mpa

White Cast Iron

Pearlite



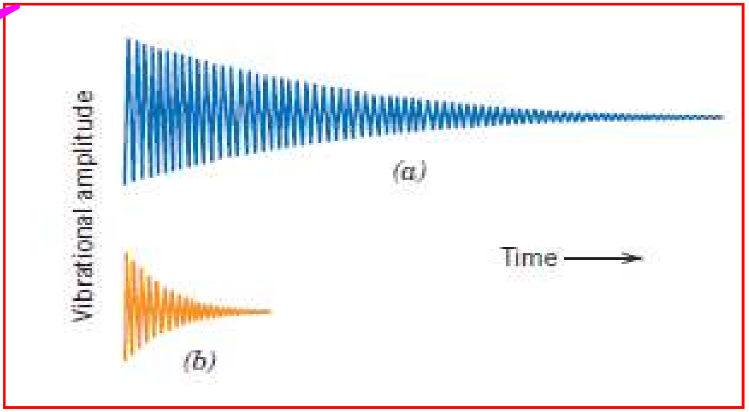
White cementite network

Grey Cast Iron

- This group is one of the most widely used alloys of iron, containing between 2.5 to 4 percent of carbon with other alloying elements.
- In the manufacture of gray cast iron the tendency of cementite to separate into graphite and austenite or ferrite is favored by controlling alloy additions and cooling rates.
- These alloys solidify by first forming primary austenite. The initial appearance of combined carbon is in the cementite resulting from the eutectic reaction. With proper control of carbon content, temperature and the proper amount of graphitizing elements notably silicon, magnesium cerium and, alloy will follow the stable iron – graphite equilibrium diagram.
- For most of these cast irons, the graphite exists in the form of flakes (similar to corn flakes), which are normally surrounded by an α-ferrite or pearlite matrix.
- Mechanically, gray iron is comparatively weak and brittle in tension as a consequence of its microstructure; the tips of graphite flakes are sharp and pointed, and may serve as points of stress concentration when an external tensile stress is applied. Strength and ductility are much higher under compressive loads.

Grey Cast Iron

- Gray irons are very effective in damping vibrational energy. Base structures for machines and heavy equipment that are exposed to vibrations are frequently constructed of this material. In addition, gray irons exhibit a high resistance to wear. Furthermore, in the molten state they have a high fluidity at casting temperature, which permits casting pieces having intricate shapes; also, casting shrinkage is low. Finally, and perhaps most important, gray cast irons are among the least expensive of all metallic materials.
- Gray irons having different type of microstructures, it may be generated by adjustment of composition and/or by using an appropriate heat treatment. For example, lowering the silicon content or increasing the cooling rate may prevent the complete dissociation of cementite to form graphite. Under these circumstances the microstructure consists of graphite flakes embedded in a pearlite matrix.



Comparison of the relative vibrational damping capacities of *(a) steel and (b) gray cast iron*

Grey Cast Iron

Role of silicon

- Silicon increases fluidity and influences the solidification of the molten metal and it decreases Eutectivity i.e., the eutectic composition is shifted to the left approximately 0.30% carbon for each 1% silicon, which effectively depresses the temperature at which the alloy begins o solidify.
- Si promotes graphitization → ~ effect as ↓ cooling rate
- As the silicon content is increased, the austenite field decreases in area, the eutectoid carbon content is lowered, and the eutectoid transformation occurs over a broadening range.
- Solidification over a range of temperatures permits the nucleation and growth of Graphite flakes
- Change in interfacial energy between γ/L & Graphite/L brought about by Si
- Careful control of the silicon content and cooling rate is required to graphitize the eutectic and proeutectoid cementite, but not the eutectoid cementite, in order to end up with a pearlitic gray iron of high strength.

Grey Cast Iron

Role of Sulfur

- Most commercial gray irons contain between 0.06 and 0.12% sulfur. The effect of sulfur on the form of carbon is the reverse of silicon. The higher the sulfur content, the greater will be the combined carbon, thus tending to produce a hard, brittle white iron.

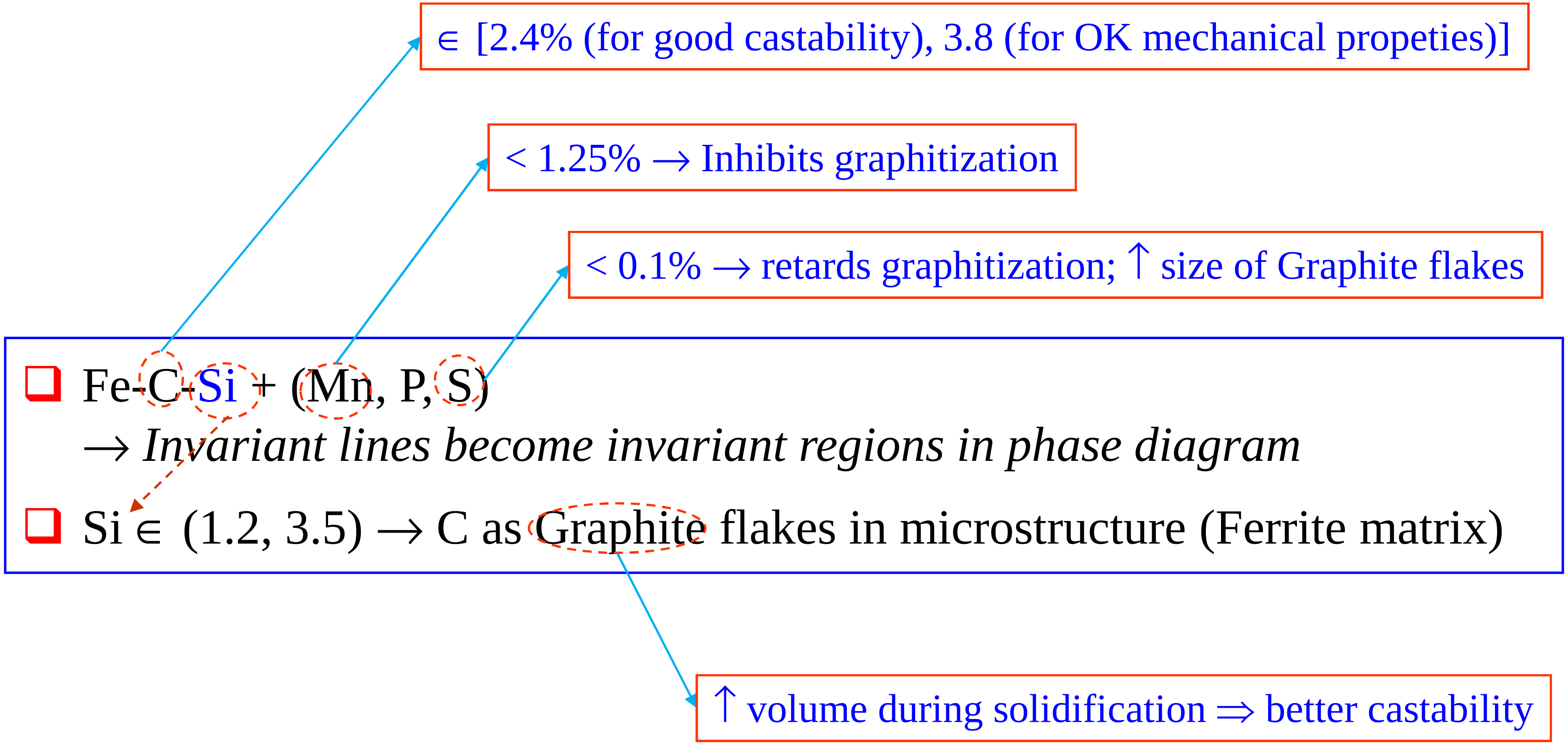
Role of Manganese

- Manganese is a carbide stabilizer, tending to increase the amount of combined carbon, but it is much less potent than sulfur. Excess manganese (>1.25%) has little effect on solidification and only weakly retards primary graphitization. On eutectoid graphitization, however, Mn is strongly carbide stabilizing.

Role of Phosphorus

- Most gray irons contain between 0.10 to 0.90% phosphorus. Most of the ‘P’ combines with the iron to form iron phosphide (Fe_3P).This iron phosphide forms a ternary eutectic known as *steadite*, contains cementite and austenite (*at room temperature pearlite*).
- Fluidity ↑, Primary graphitization ↑ and extends the range of eutectic freezing

Grey Cast Iron



∈ [2.4% (for good castability), 3.8 (for OK mechanical propeties)]

< 1.25% → Inhibits graphitization

< 0.1% → retards graphitization; ↑ size of Graphite flakes

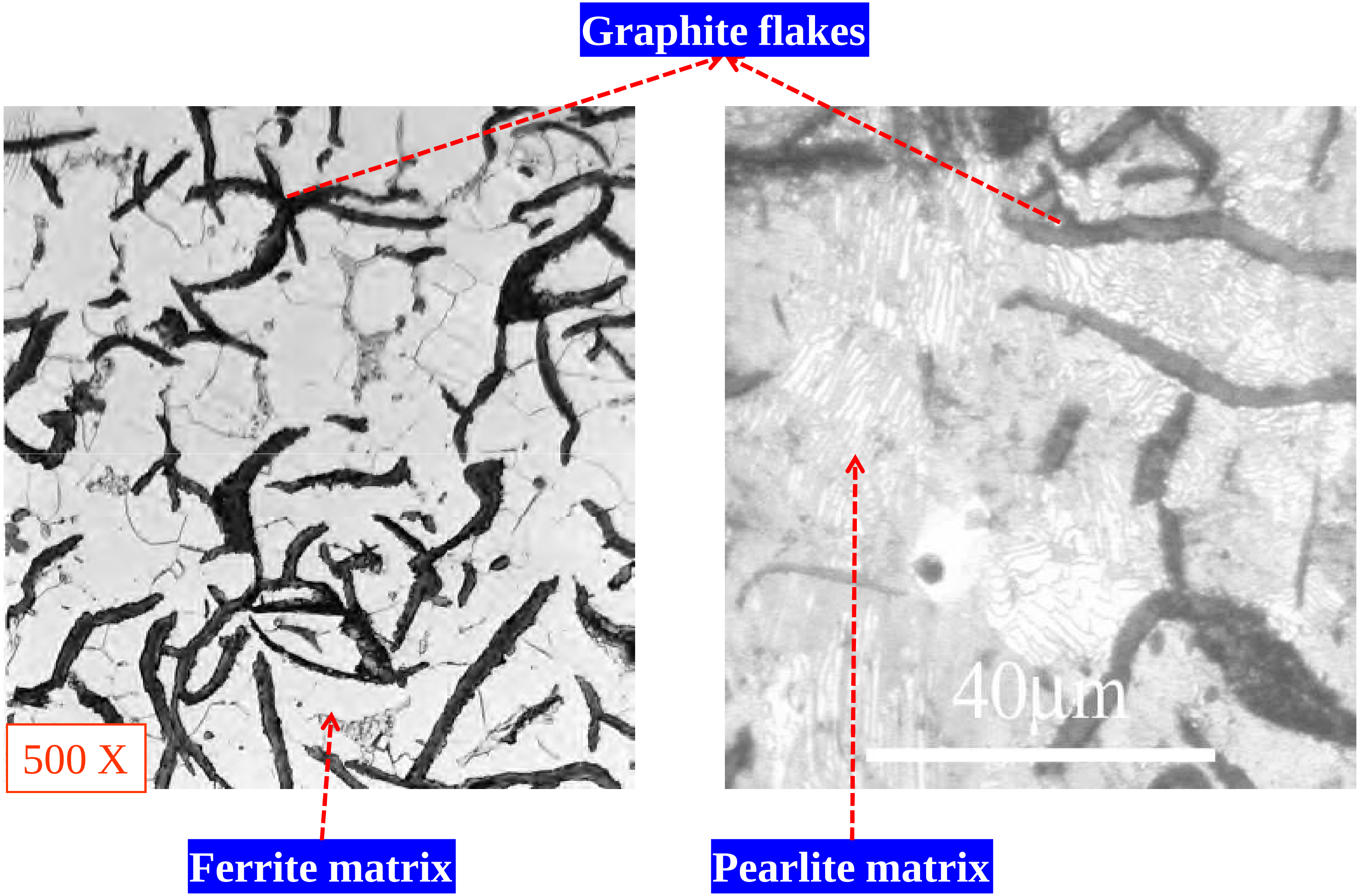
- ❑ Fe-C-Si + (Mn, P, S)
  → *Invariant lines become invariant regions in phase diagram*
- ❑ Si ∈ (1.2, 3.5) → C as Graphite flakes in microstructure (Ferrite matrix)

↑ volume during solidification ⇒ better castability

$$\text{L} \rightarrow \underbrace{\gamma + (Fe_3C)}_{Ledeburite} \rightarrow \underbrace{\alpha + Fe_3C}_{Pearlite} + (Fe_3C)$$

$$\text{Si} \uparrow \Rightarrow \overleftarrow{C_{eutectoid}}$$

Grey Cast Iron



Graphite flakes

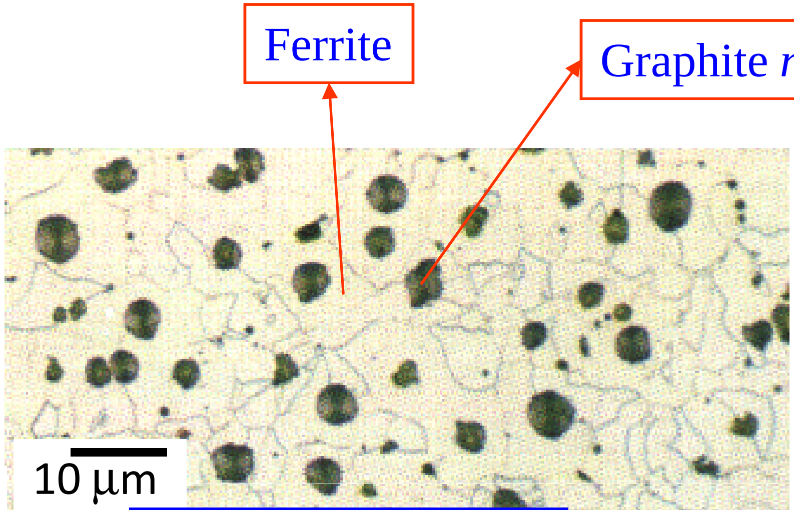
Ferrite matrix

Pearlite matrix

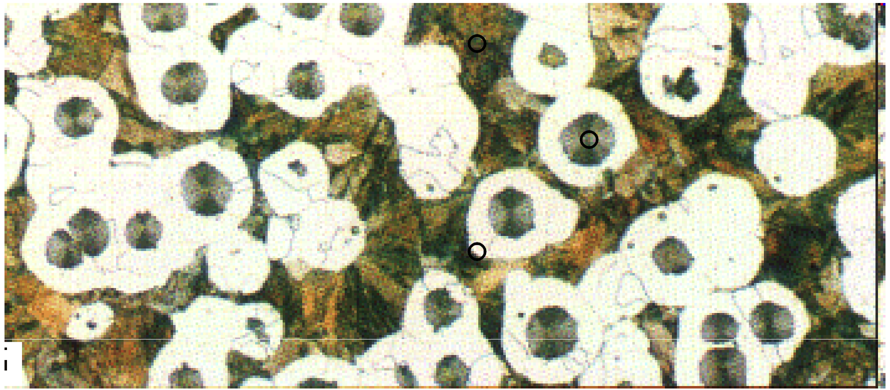
Ductile Cast Iron

- Ductile cast iron also called as Nodular cast iron, Spheroidal graphite cast iron, and Spherulitic cast iron.
- Graphite nodules instead of flakes *(in 2D section)*
- Mg, Ce, Ca (or other spheroidizing) elements are added
- The elements added to promote spheroidization react with the solute in the liquid to form heterogeneous nucleation sites
- The alloying elements are injected into mould before pouring
- It is thought that by the modification of the interfacial energy the ‘c’ and ‘a’ growth direction are made comparable leading to spheroidal graphite morphology
- The graphite phase usually nucleates in the liquid pocket created by the proeutectic γ

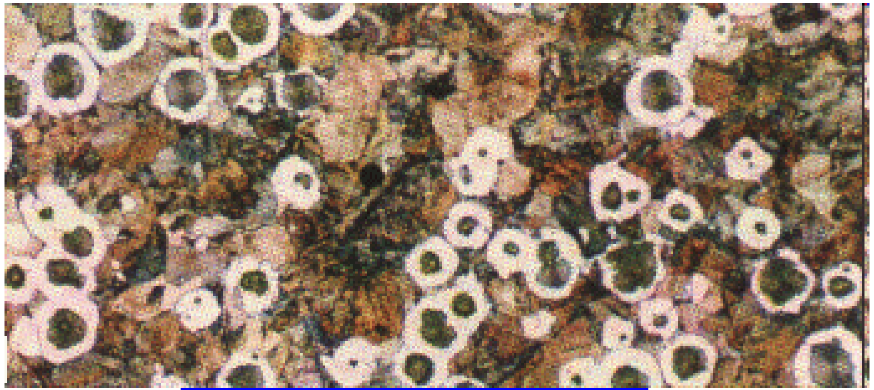
Ductile Cast Iron



With Ferritic Matrix

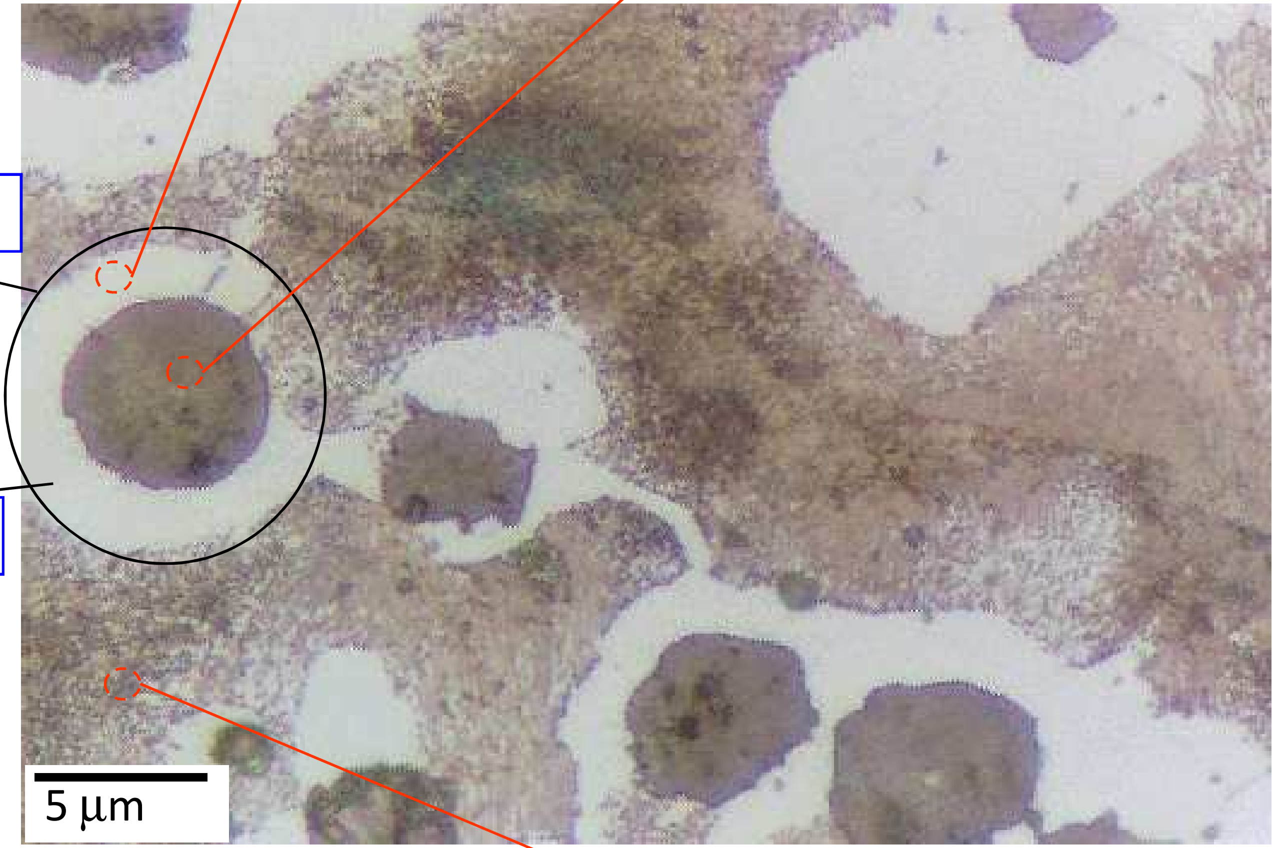


With (Ferrite + Pearlite) Matrix



With Pearlitic matrix

Ductile Cast Iron



Ferrite *(White)*

Graphite *(black)*

Bull’s Eye

Ferrite

Pearlite *(grey)*

Malleable Cast Iron

- ☐ As we discussed earlier that cementite is actually a metastable phase. There is a tendency for cementite to decompose into iron and carbon. This tendency to form free carbon is the basis for the manufacture of malleable cast iron.
- ☐ The reaction of $Fe_3C \rightarrow 3Fe + C$ is favored by elevated temperatures, the existence of solid nonmetallic impurities, higher carbon contents, and the presence of elements that aid the decomposition of Fe_3C.

$$\text{White Cast Iron} \xrightarrow[\text{To Increase Ductility}]{\text{Malleabilize}} \text{Malleable Cast Iron}$$

$$Fe_3C\ (\text{WCI}) \xrightarrow[\text{2 stage heat treatment}]{>48\,hrs} \text{Graphite Temper Nodules (Malleable Iron)}$$

Malleable Cast Iron

Stage I

- (940-960)°C *(Above eutectoid temperature)*
- Competed when all Cementite → Graphite

A: Low T structure (Ferrite + Pearlite + Martensite) → (γ + Cementite)

B: Graphite nucleation at γ/Cementite interface

(rate of nucleation increased by C, Si)

(Si $\downarrow$ solubility of C in $\gamma \Rightarrow \uparrow$ driving force for growth of Graphite)

C: Cementite dissolves → C joining growing Graphite plates

Time for Graphitization in Stage I

Spacing between Cementite and Graphite →
$\downarrow$ *spacing* $\Rightarrow \downarrow$ *time (obtained by faster cooling of liquid)*

Addition of Alloying elements
→ *which increase the nucleation rate of Graphite temper nodules*

Si $\uparrow \Rightarrow$ t $\downarrow$

Malleable Cast Iron

Stage II

- (720-730)°C *(Below eutectoid temperature)*
- After complete graphitization in Stage I → Further Graphitization

☐ Slow cool to the lower temperature such that γ does not form Cementite

☐ C diffuses through γ to Graphite temper nodules
(called Ferritizing Anneal)

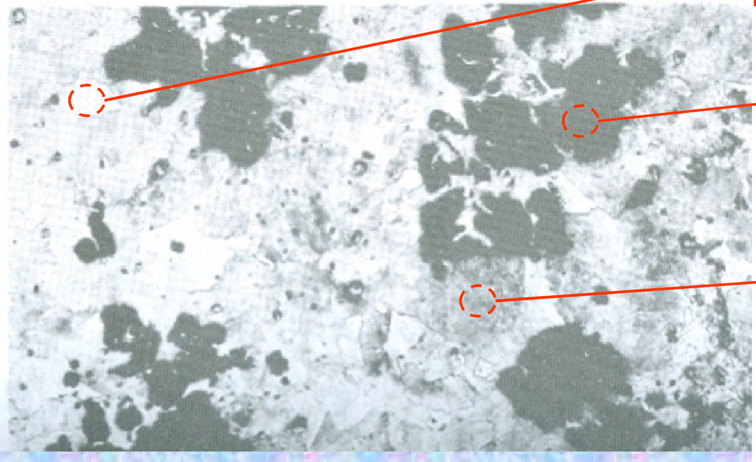
☐ *Full* Anneal in Ferrite + Graphite two phase region

☐ *Partial* Anneal *(Insufficient time in Stage II Graphitization)*
γ → Ferrite is partial and the remaining γ transforms to Pearlite
⇒ γ → Pearlite + Ferrite + Graphite

☐ If quench after Stage I ⇒ γ → Martensite *(+ Retained Austenite(RA))*
(Graphite temper nodules are present in a matrix of Martensite and RA)

Malleable Cast Iron

Pearlitic Matrix



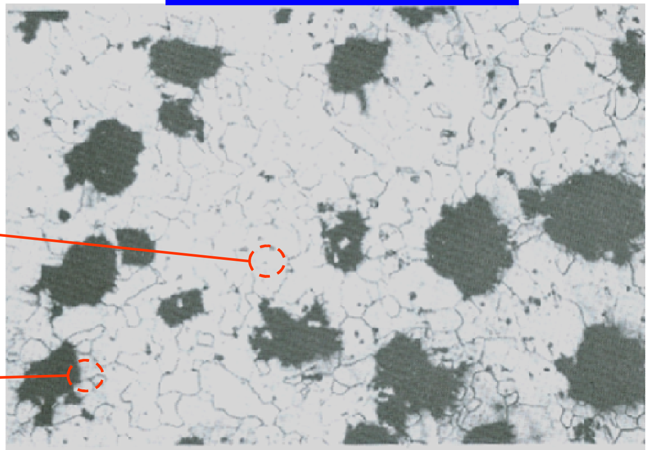
Ferrite *(White)*

Graphite *(black)*

Pearlite *(grey)*

Partially Malleabilized Iron
→ Incomplete Ferritizing Anneal

Ferritic Matrix



Ferrite *(White)*

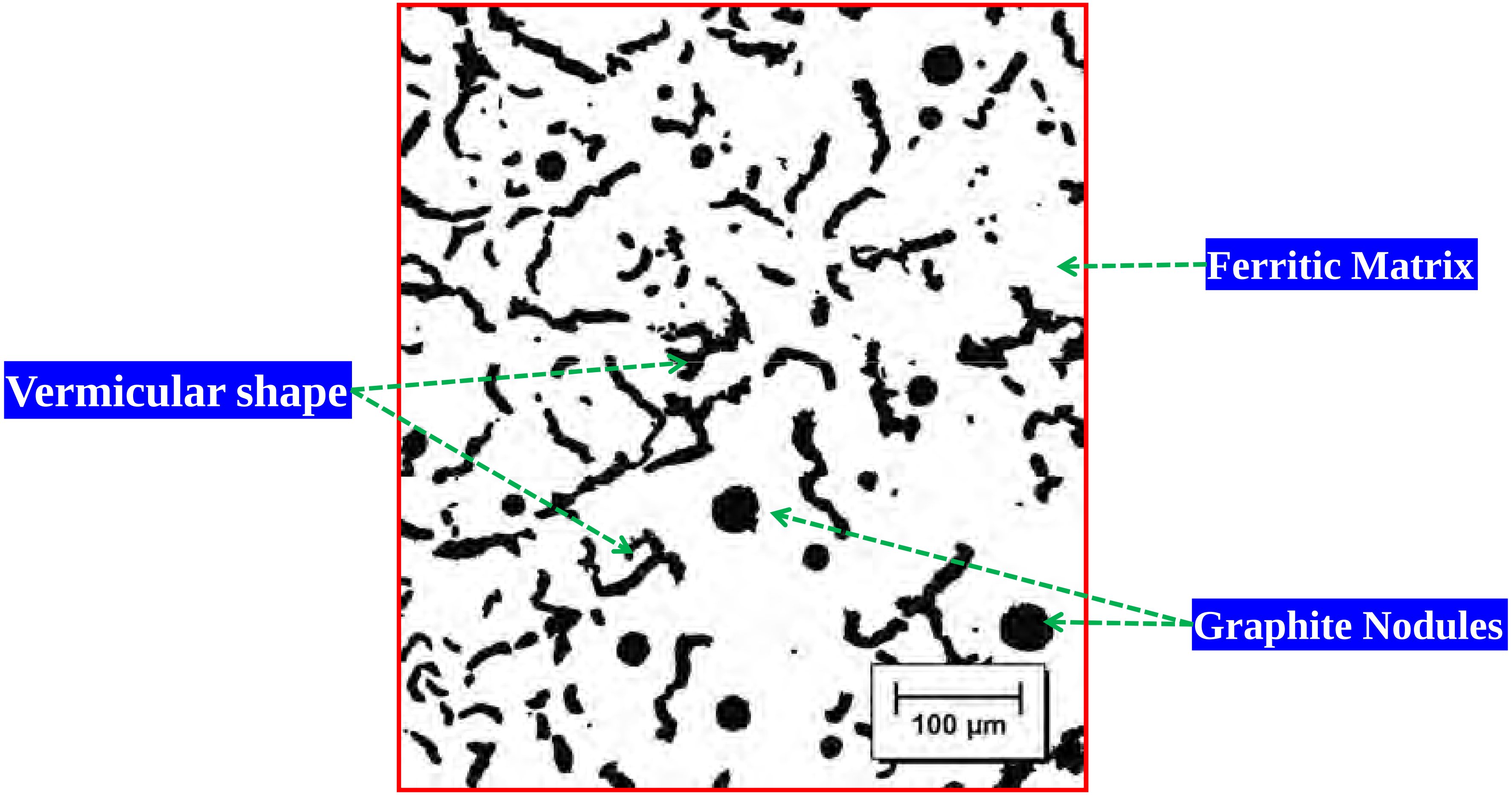
Graphite *(black)*

Fully Malleabilized Iron
→Complete Ferritizing Anneal

Compacted Graphite Cast Iron

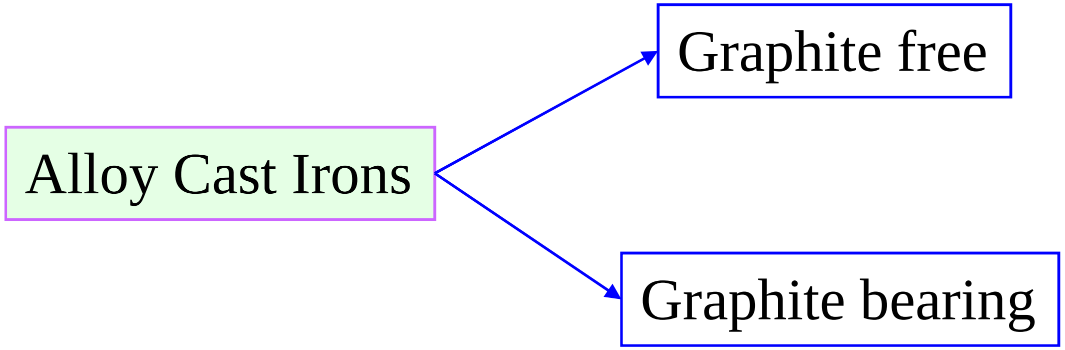
- ❑ A relatively recent addition to the family of cast irons is *compacted graphite (CGI).*
- ❑ Micro structurally, the graphite in CGI alloys has a worm-like (or vermicular) shape; a typical CGI microstructure. In a sense, this microstructure is intermediate between that of gray iron and ductile iron and, in fact, some of the graphite (less than 20%) may be as nodules.
- ❑ The chemistries of CGIs are more complex than for the other cast iron types; compositions of Mg, Ce and other additives must be controlled so as to produce a microstructure that consists of the worm-like graphite particles, while at the same time limiting the degree of graphite nodularity, and preventing the formation of graphite flakes. Furthermore, depending on heat treatment, the matrix phase will be pearlite and/or ferrite.
- ❑ CGI are now being used in a number of important applications – these include: diesel engine blocks, exhaust manifolds, gearbox housings, brake discs for high speed trains and flywheels.

Compacted Graphite Cast Iron



Alloy Cast Iron

- Cr, Mn, Si, Ni, Al
- ↑ the range of microstructures
- Beneficial effect on many properties
  - ↑ high temperature oxidation resistance
  - ↑ corrosion resistance in acidic environments
  - ↑ wear/abaration resistance



Alloy Cast Irons

Graphite free

Graphite bearing

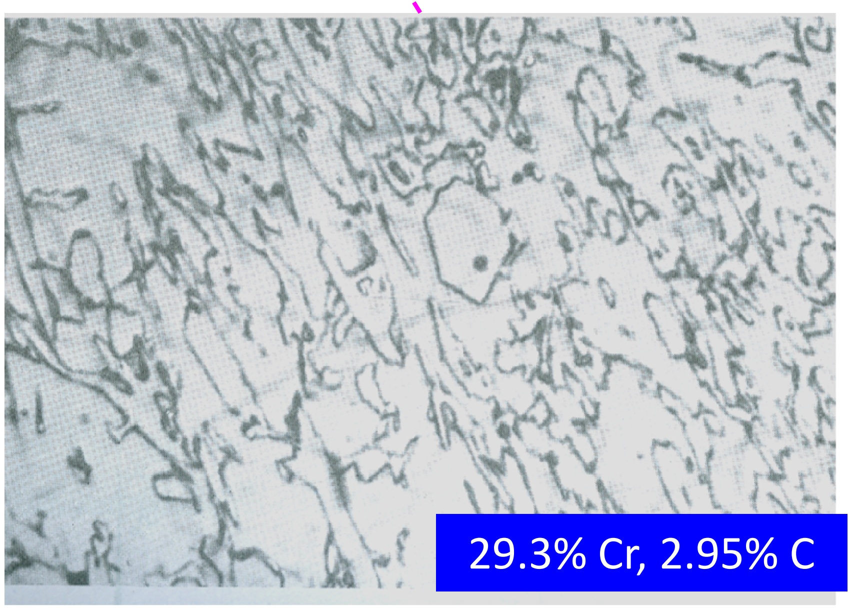
Chromium addition (12- 35 wt %)

- Excellent resistance to oxidation at high temperatures
- High Cr Cast Irons are of 3 types:

❑ 12-28 % Cr ➢ matrix of Martensite + dispersed carbide

❑ 29-34 % Cr ➢ matrix of Ferrite + dispersion of alloy carbides $[(Cr,Fe)_{23}C_6, (Cr,Fe)_7C_3]$

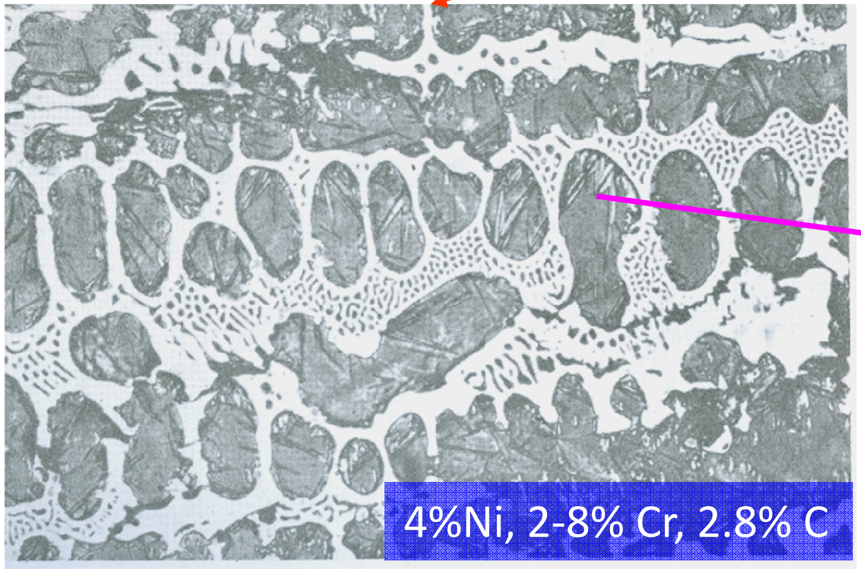
❑ 15-30 % Cr + 10-15 % Ni ➢ stable γ + carbides $[(Cr,Fe)_{23}C_6, (Cr,Fe)_7C_3]$
Ni stabilizes Austenite structure



29.3% Cr, 2.95% C

Nickel Hard Cast Iron

- ❑ Stabilizes Austenitic structure
- ❑ ↑ Graphitization *(suppresses the formation of carbides)*
- ❑ (Cr counteracts this tendency of Ni for graphitization)
- ❑ ↓ Carbon content in Eutectic
- ❑ Moves nose of TTT diagram to higher times ⇒ easy formation of Martensite
- ❑ Carbide formation in presence of Cr increases the hardness of the eutectic structure → Ni Hard Cast Irons (4%Ni, 2-8% Cr, 2.8% C)



Good abrasion resistance

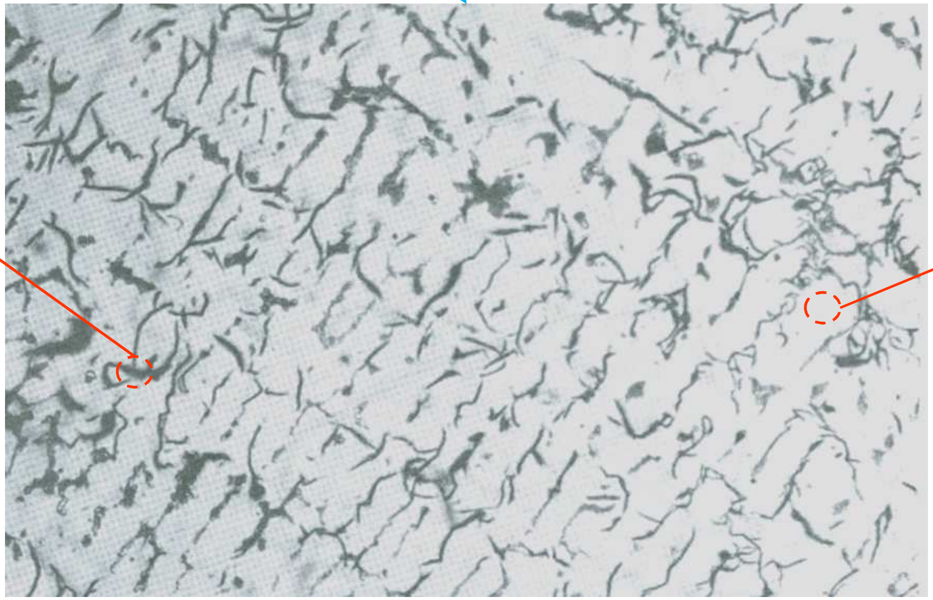
Needles of Martensite

Transformation sequence

- ➢ Crystallization of primary γ
- ➢ Eutectic liquid → γ + alloy carbide
- ➢ γ → Martensite

Nickel Resist Cast Iron

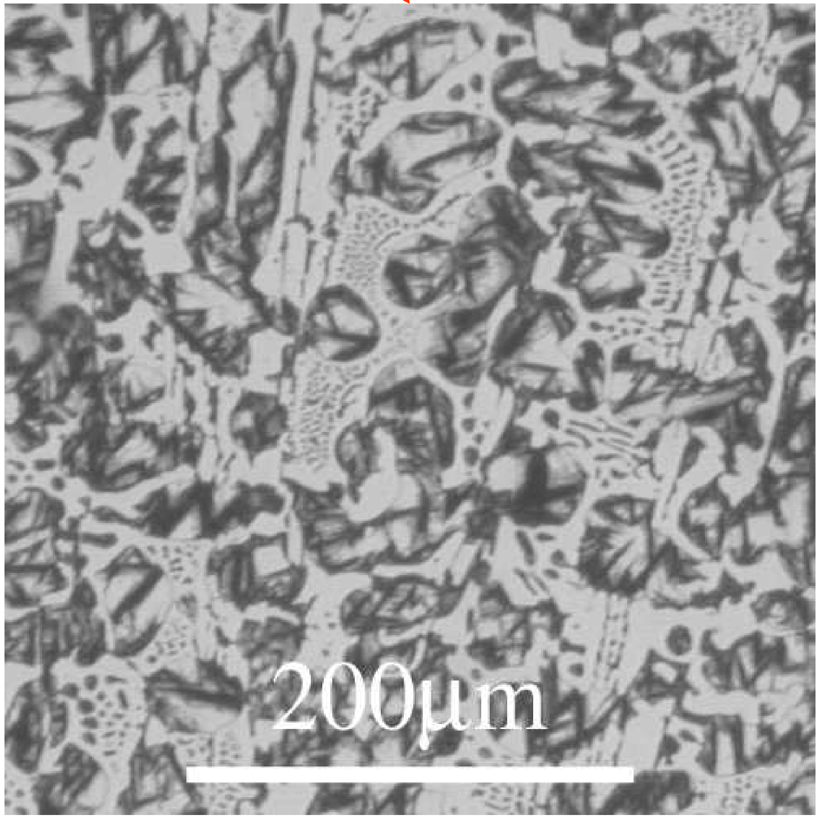
- Ni Resist Iron: 15-30% Ni + small amount of Cr:
- ❑ Austenitic Dendrites + Graphite plates/flakes + interdendritic carbides due to presence of Cr
- ❑ Resistant to oxidation (used in chemical processing plants, sea water, oil handling operations…)


Graphite plates

Dendrites of γ

Silicon (Silal) Cast Iron

- Silal Iron (trade name): Alloy CI with 5% Si
- ☐ Si allows solidification to occur over larger temperature range → promotes graphitization
- ☐ Forms surface film of iron silicate → resistant to acid corrosion



Some other types…!

Chilled Cast Iron

- *Chilled –iron castings are made by casting the molten metal against a metal chiller, resulting in a surface of white cast iron. This hard, abrasion-resistant white iron surface or case is backed up by a softer gray iron core.*
- *This case-core structure is obtained by careful control of the overall alloy composition and adjustment of the cooling rate.*

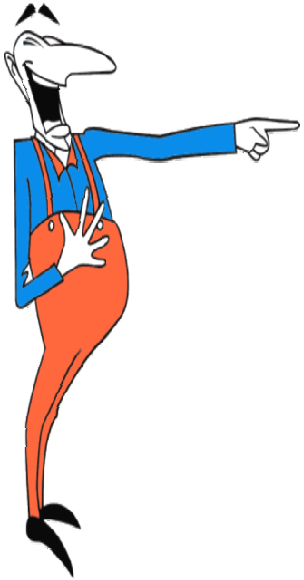
Mottled Cast Iron

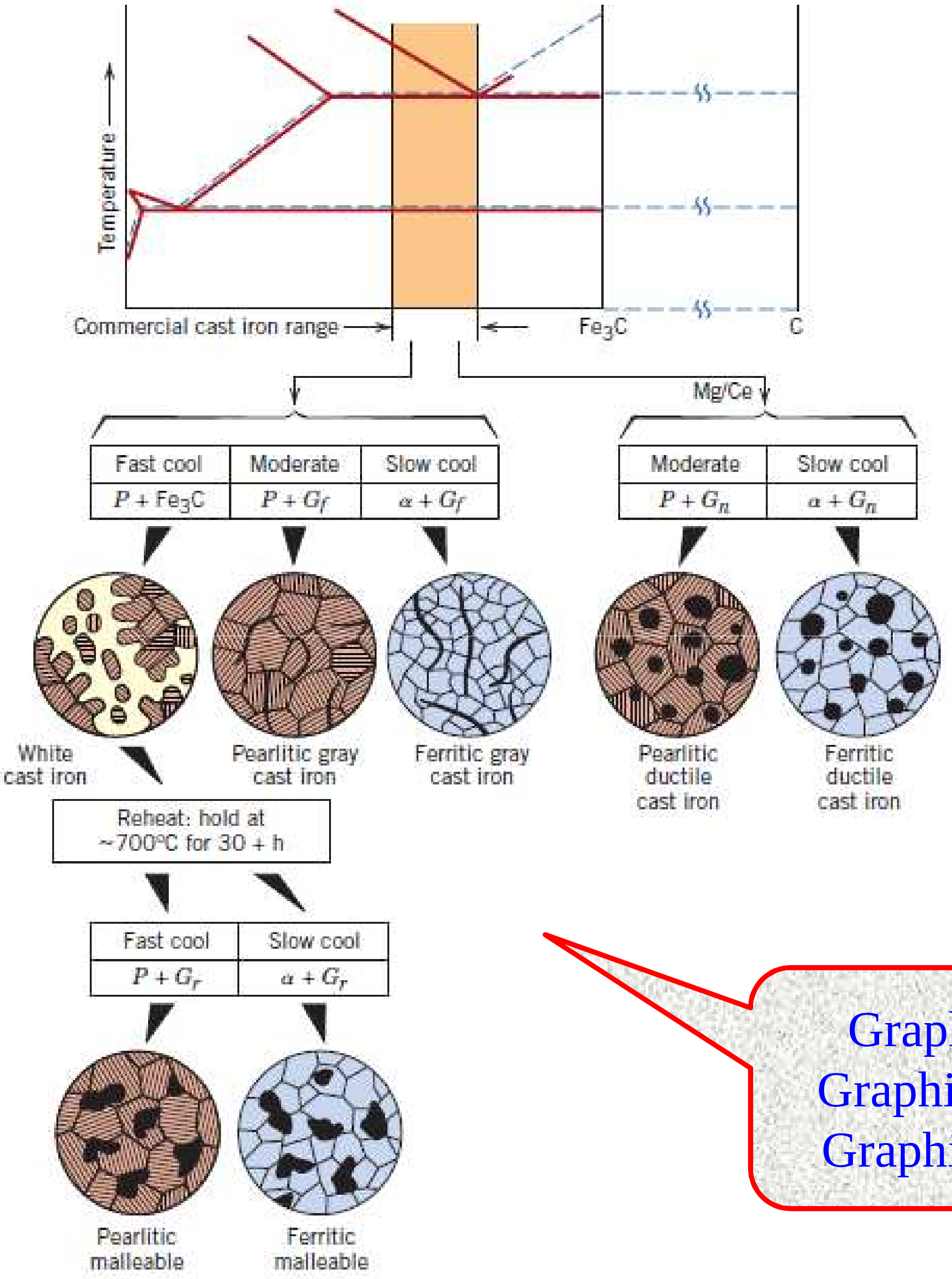
- *Solidifying at a rate with extremes between those for chilled and gray irons, thus exhibiting micro structural and metallurgical characteristics of both*

High-Alloy Graphitic Irons

- *Produced with microstructures consisting of both flake and nodule structures. Mainly utilized for applications requiring a combination of high strength and corrosion resistance.*

Summary





Graphite flake - G_f
Graphite nodules - G_n
Graphite rosettes - G_r

Heat Treatment of Steel

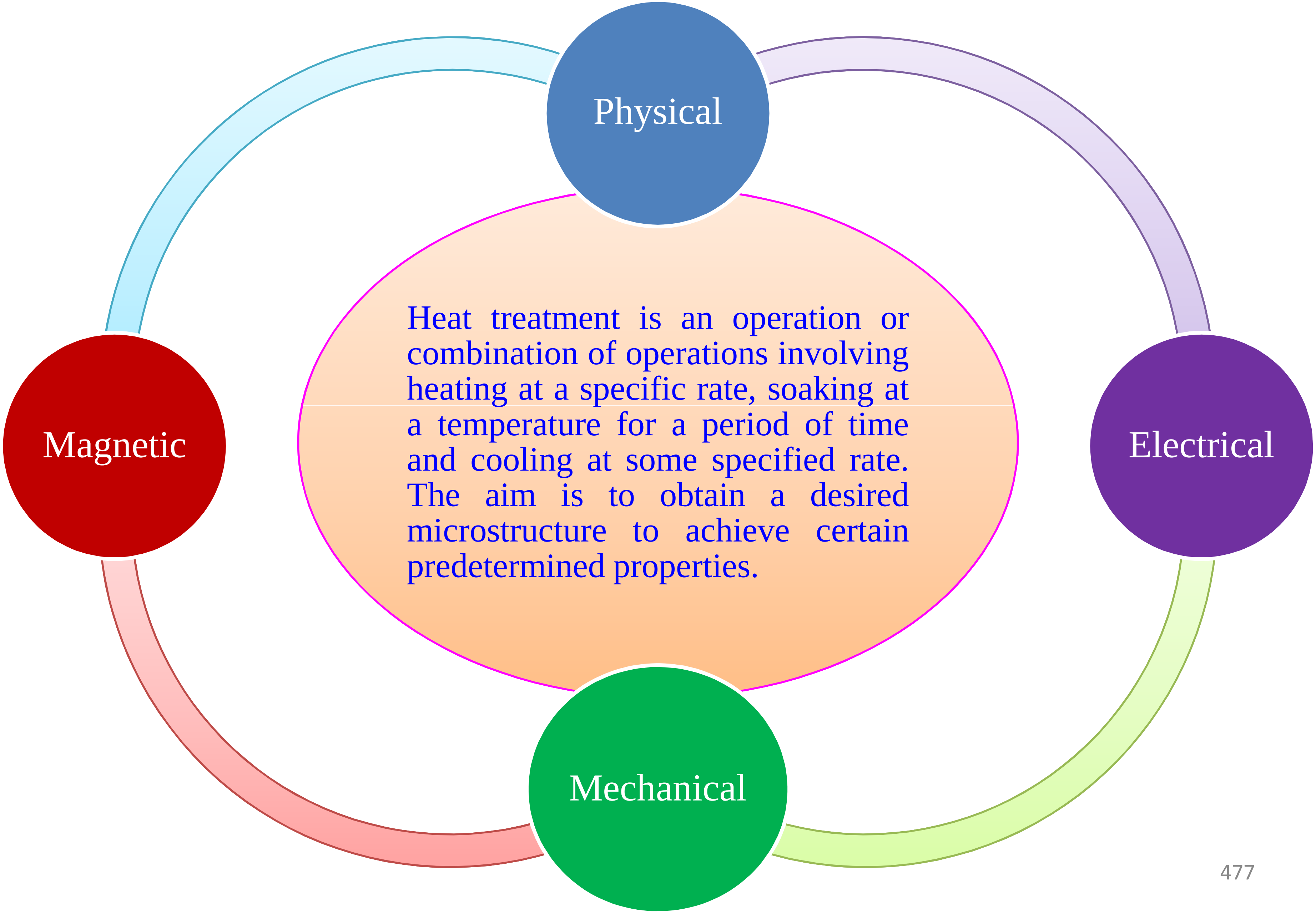
Avala Lava Kumar* : Suneeti Purohit : Gautam Behera

Department of Metallurgical & Materials Engineering (MME)

Veer Surendra Sai University of Technology (VSSUT), Burla -768018

**E-mail : lavakumar.vssut@gmail.com*

Definition of Heat treatment

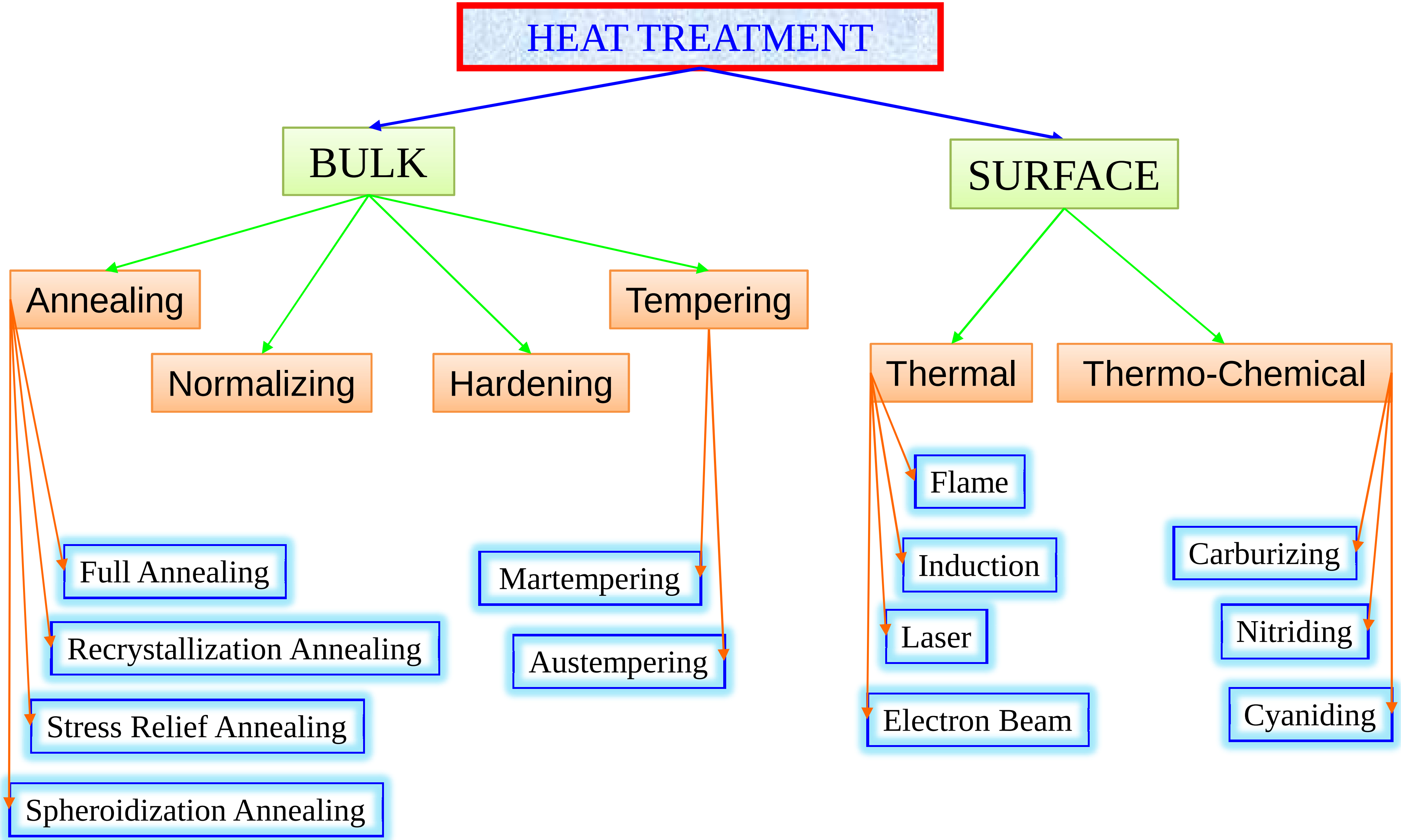


Heat treatment is an operation or combination of operations involving heating at a specific rate, soaking at a temperature for a period of time and cooling at some specified rate. The aim is to obtain a desired microstructure to achieve certain predetermined properties.

Objectives of Heat Treatment Processes

- To increase strength, hardness and wear resistance (*bulk hardening, surface hardening*)
- To increase ductility and softness (*Tempering, Recrystallization Annealing*)
- To increase toughness (*Tempering, Recrystallization annealing*)
- To obtain fine grain size (*Recrystallization annealing, Full annealing, Normalizing*)
- To remove internal stresses induced by differential deformation by cold working, non-uniform cooling from high temperature during casting and welding (*Stress relief annealing*)
- To improve machinability (*Full annealing and Normalizing*)
- To improve cutting properties of tool steels (*Hardening and Tempering*)
- To improve surface properties (*surface hardening, high temperature resistance-precipitation hardening, surface treatment*)
- To improve electrical properties (*Recrystallization, Tempering, Age hardening*)
- To improve magnetic properties (*Hardening, Phase transformation*)

Classification



HEAT TREATMENT

BULK

SURFACE

Annealing

Normalizing

Hardening

Tempering

Thermal

Thermo-Chemical

Full Annealing

Recrystallization Annealing

Stress Relief Annealing

Spheroidization Annealing

Martempering

Austempering

Flame

Induction

Laser

Electron Beam

Carburizing

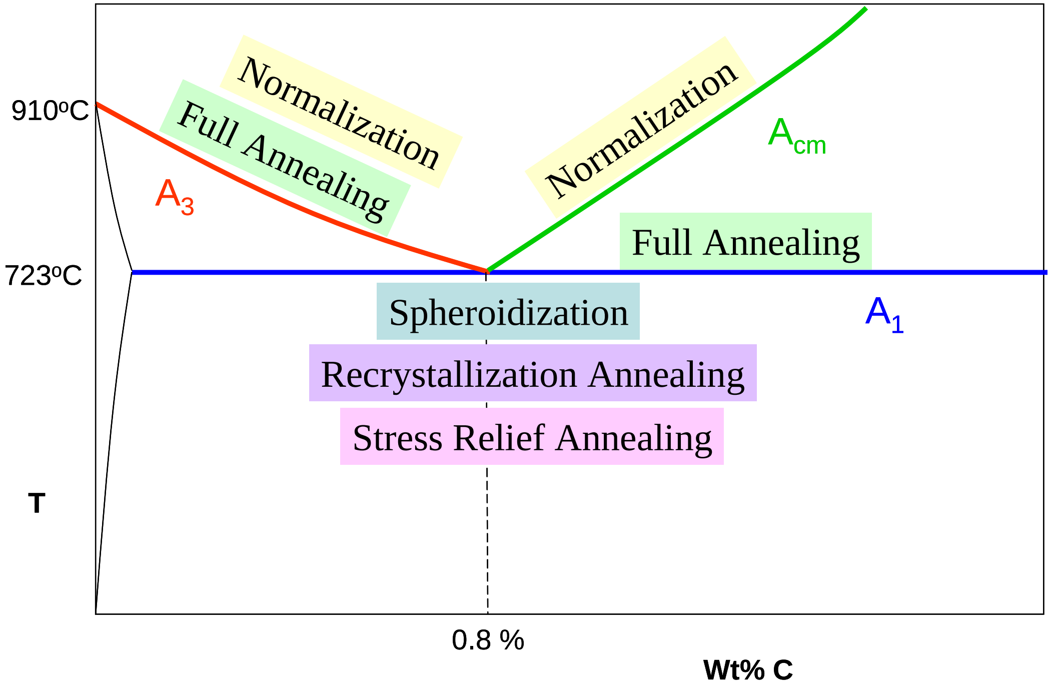
Nitriding

Cyaniding

Annealing

Full Annealing

- ❑ The steel is heated above A_3 (for hypo-eutectoid steels) | A_1 (for hyper-eutectoid steels) →(hold) →then the steel is furnace cooled to obtain Coarse Pearlite
- ❑ Coarse Pearlite has ↓ Hardness, ↑ Ductility
- ❑ Not above A_{cm} →to avoid a continuous network of proeutectoid cementite along grain boundaries (→path for crack propagation)



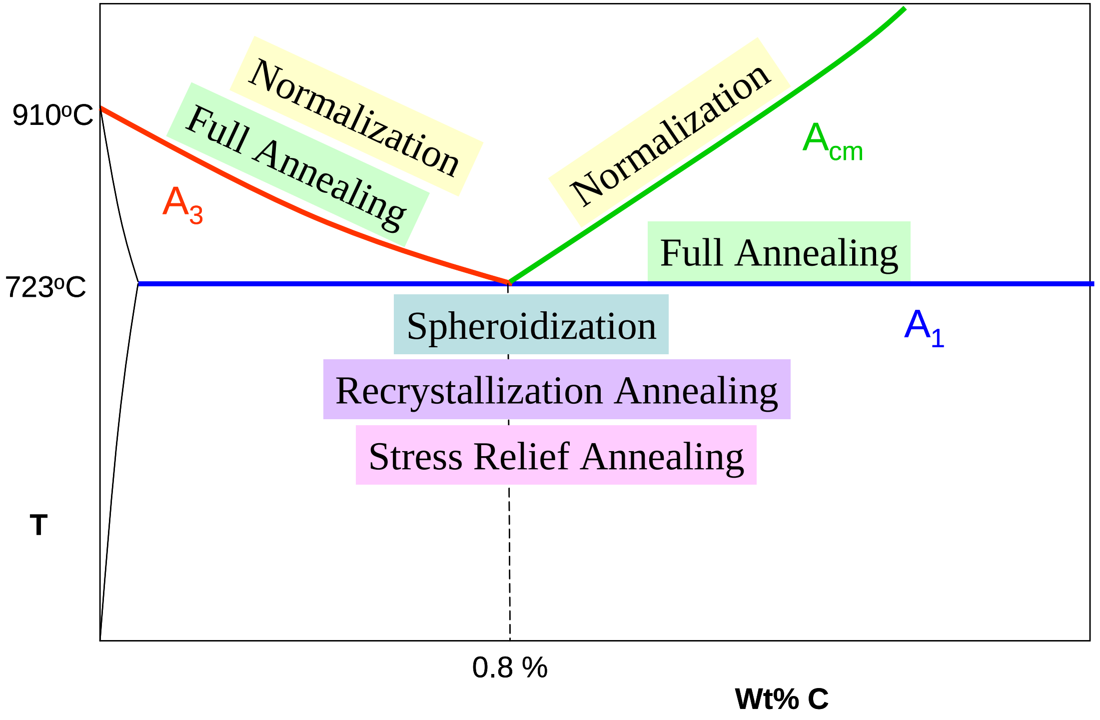
Annealing

Recrystallization Annealing

- ❑ The Heat below A_1 → Sufficient time → Recrystallization

  Cold worked grains → New stress free grains

- ❑ Used in between processing steps (e.g. Sheet Rolling)

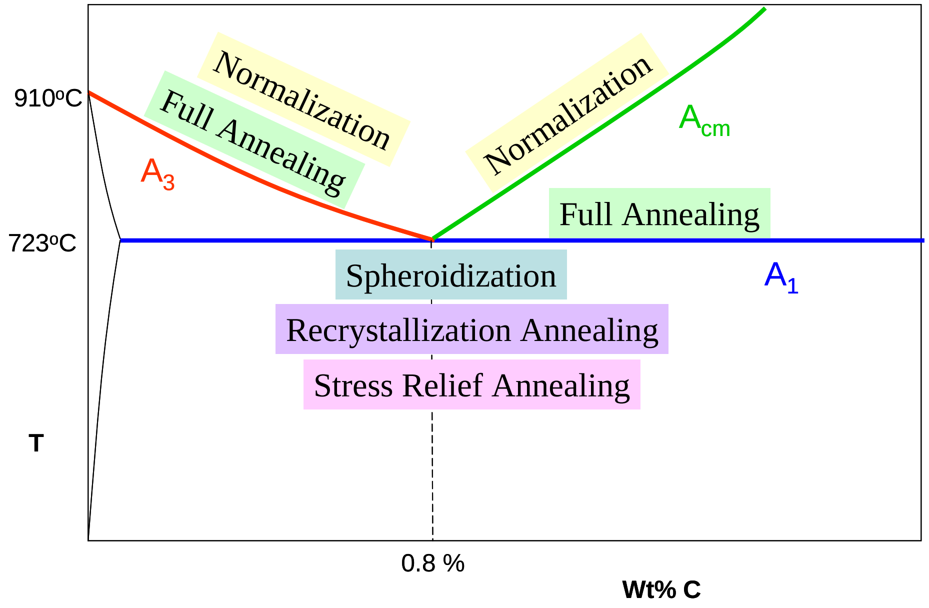


Annealing

Stress Relief Annealing

Residual stresses → Heat below A_1 → Recovery → Annihilation of dislocations, polygonization

- → Differential cooling
- → Martensite formation
- → Machining and cold working
- → Welding



Annealing

Spheroidization Annealing

Heat below/above A_1 (Prolonged holding*)
Cementite plates → Cementite spheroids → ↑ Ductility

- ❑ *Used in high carbon steel requiring extensive machining prior to final hardening and tempering*
- ❑ *Driving force is the reduction in interfacial energy*

- ❑ The spheroidized structure is desirable when minimum hardness, maximum ductility, or(in high-carbon steels) maximum machinability is important.
- ❑ Low-carbon steels are seldom spheroidized for machining, because in the spheroidized condition they are excessively soft and "gummy".
- ❑ Medium-carbon steels are sometimes spheroidization annealed to obtain maximum ductility.

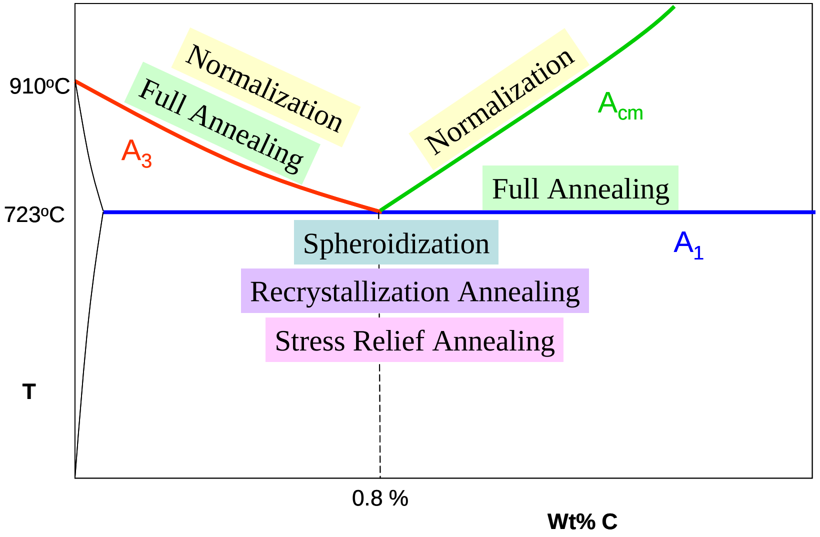
**If the steel is kept too long at the spheroidized-annealing temperature, the cementite particles will coalesce and become elongated thus reducing machinability*

Normalizing

Heat above A_3 | A_{cm} → Austenization → Air cooling → Fine Pearlite (Higher hardness)

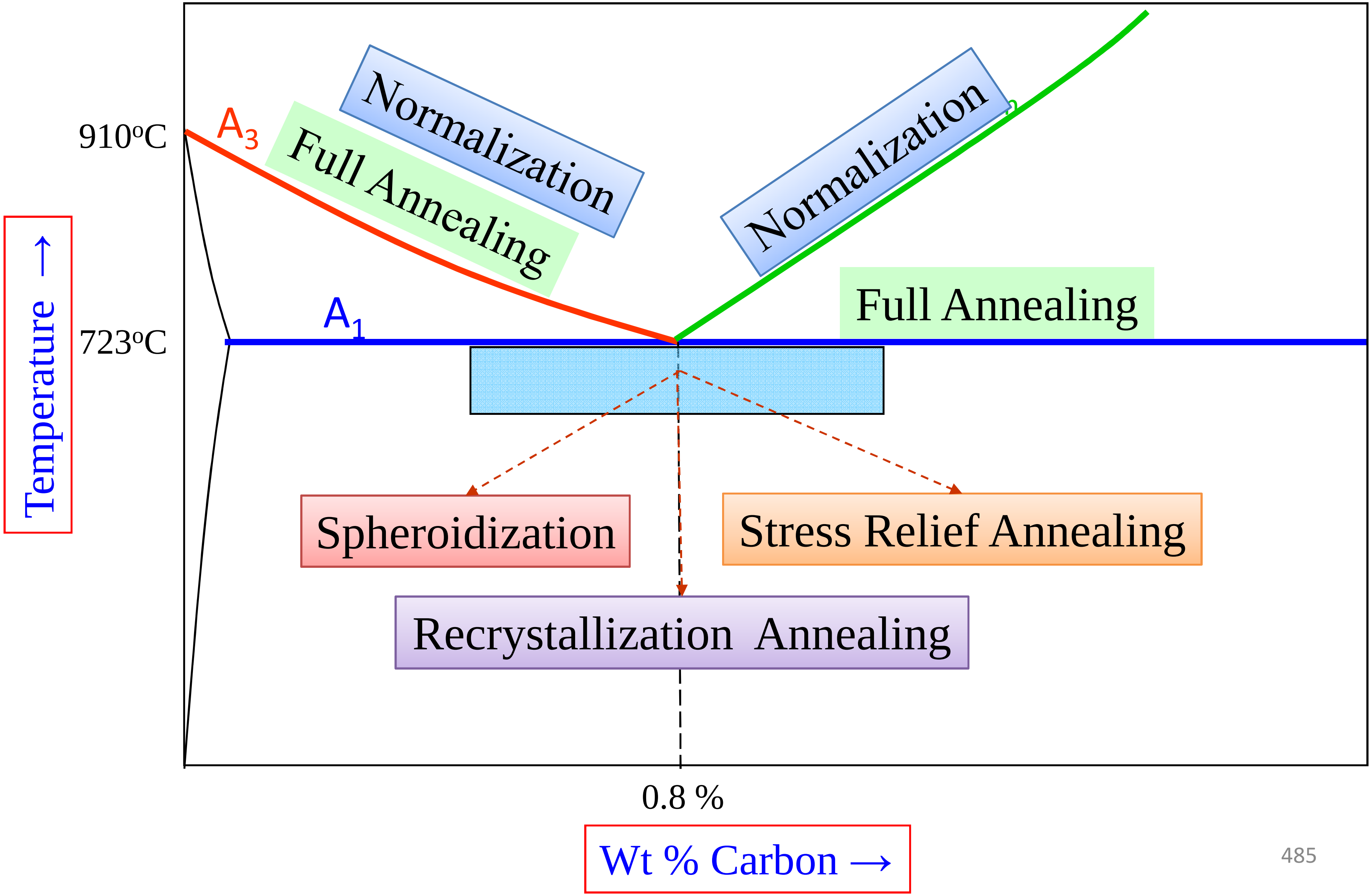
Purposes

- Refine grain structure prior to hardening
- To harden the steel slightly
- To reduce segregation in casting or forgings



- In hypo-eutectoid steels normalizing is done 50°C above the annealing temperature
- In hyper-eutectoid steels normalizing done above A_{cm} → due to faster cooling cementite does not form a continuous film along GB

Ranges of temperature where Annealing, Normalizing and Spheroidization treatment are carried out for hypo- and hyper-eutectoid steels.



Hardening

Heat above A_3 | A_{cm} → Austenization → Quench (higher than critical cooling rate)

- ☐ Under slow cooling rates, the carbon atoms are able to diffuse out of the austenite structure and it leads to gamma to alpha transformation . This process involves nucleation and growth and it is time dependent.
- ☐ With a still further increase in cooling rate, insufficient time is allowed for the carbon to diffuse out of solution, and although some movement of the iron atoms takes place, the structure cannot become B.C.C. while the carbon is trapped in solution.
- ☐ *The resultant structure is called Martensite, is a supersaturated solid solution of carbon trapped in a body-centered tetragonal structure and it is a metastable phase.*
- ☐ The highly distorted lattice structure is the prime reason for the high hardness of martensite.
- ☐ After drastic cooling, martensite appears microscopically as a white needlelike or acicular structure or lenticular, sometimes described as pile of straw.

Characteristics of Martensite

- Shape of the Martensite formed →Lenticular (or thin parallel plates)
- Associated with shape change (shear)
- This condition requires:
    1) Bain distortion → Expansion or contraction of the lattice along certain crystallographic directions leading to homogenous pure dilation
    2) Secondary Shear Distortion →Slip or twinning
    3) Rigid Body rotation

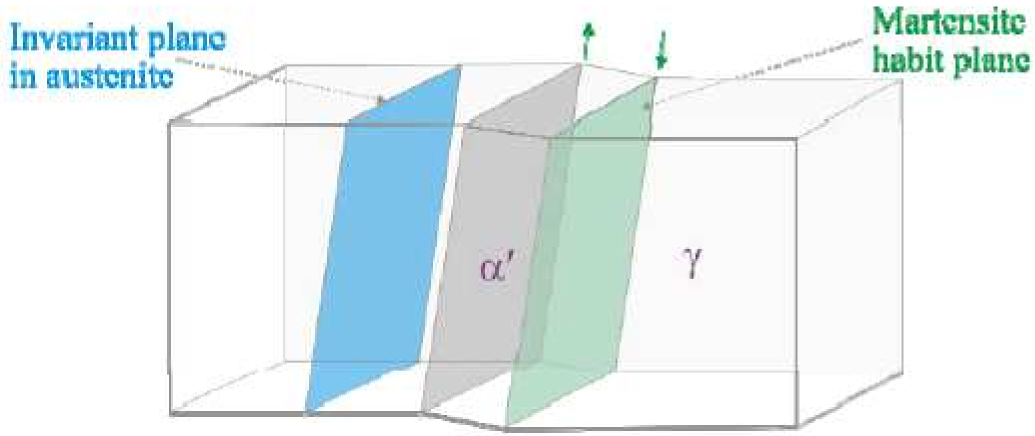
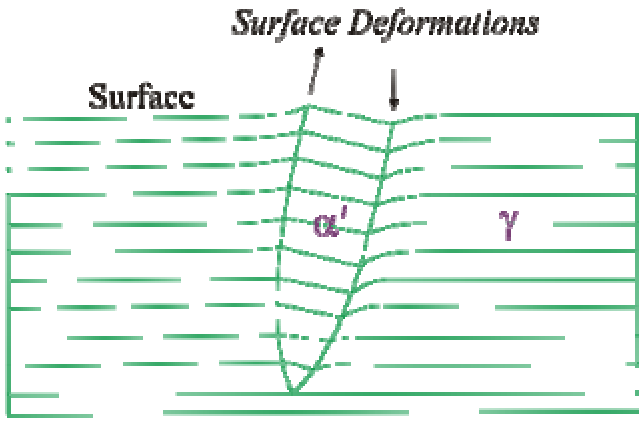


Illustration of the coherence of the martensitic plate with the surrounding austenite

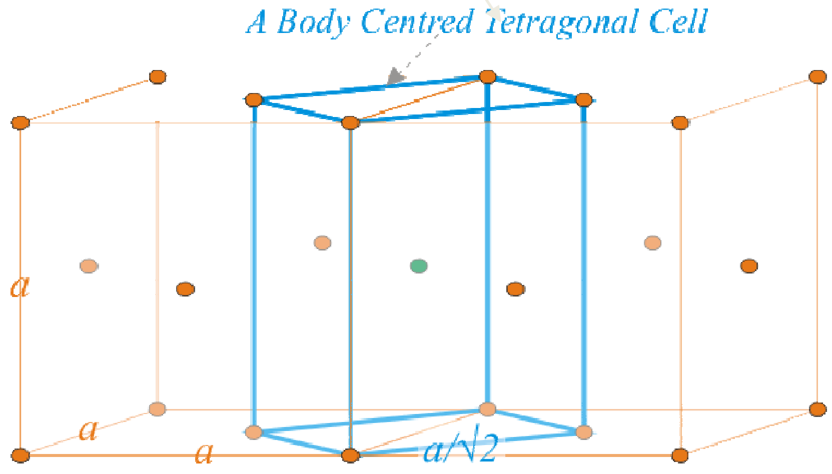


Characteristics of Martensite

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

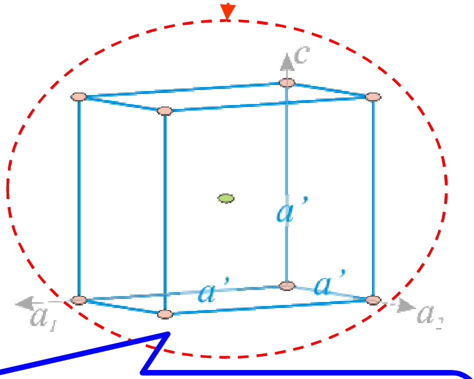
$$\underset{0.8\,\%C}{\gamma\,(FCC)} \xrightarrow{Quench} \underset{0.8\,\%C}{\alpha'\,(BCT)}$$

FCC Austenite alternate choice of Cell



FCC → BCC

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

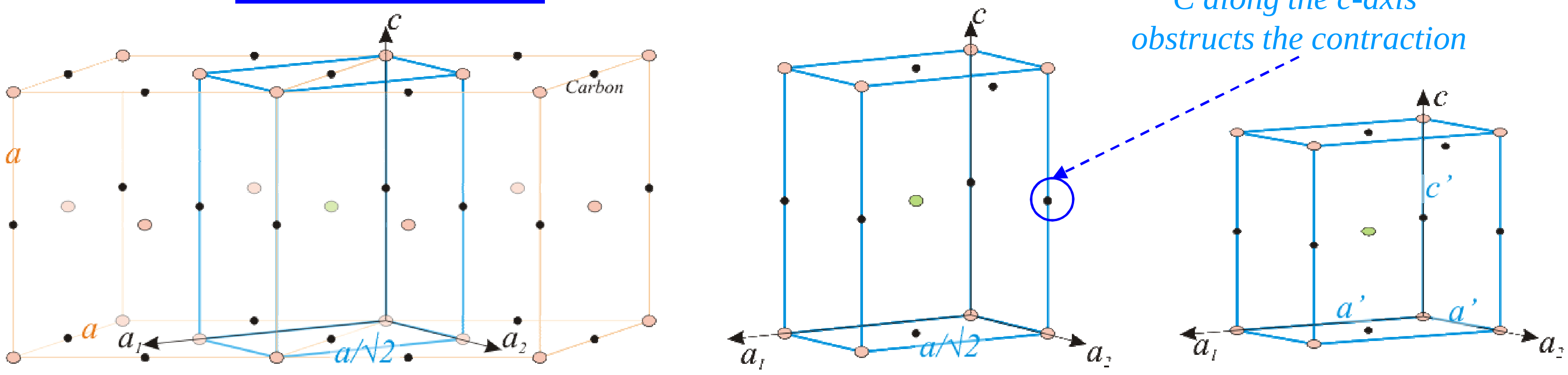


~20% contraction of *c-axis*
~12% expansion of *a-axis*

Characteristics of Martensite

- ❑ In the presence of Carbon in the octahedral voids of CCP (FCC) γ-Fe (as in the schematic below) → the contraction along the c-axis is impeded by the carbon atoms. *(Note that only a fraction of the octahedral voids are filled with carbon as the percentage of C in Fe is small).*
- ❑ However the a_1 and a_2 axis can expand freely. This leads to a product with c/a ratio (c'/a') >1
- ❑ In this case there is an overall increase in volume of ~4.3% *(depends on the carbon content)* → the Bain distortion*.

Bain distortion



C along the c-axis obstructs the contraction

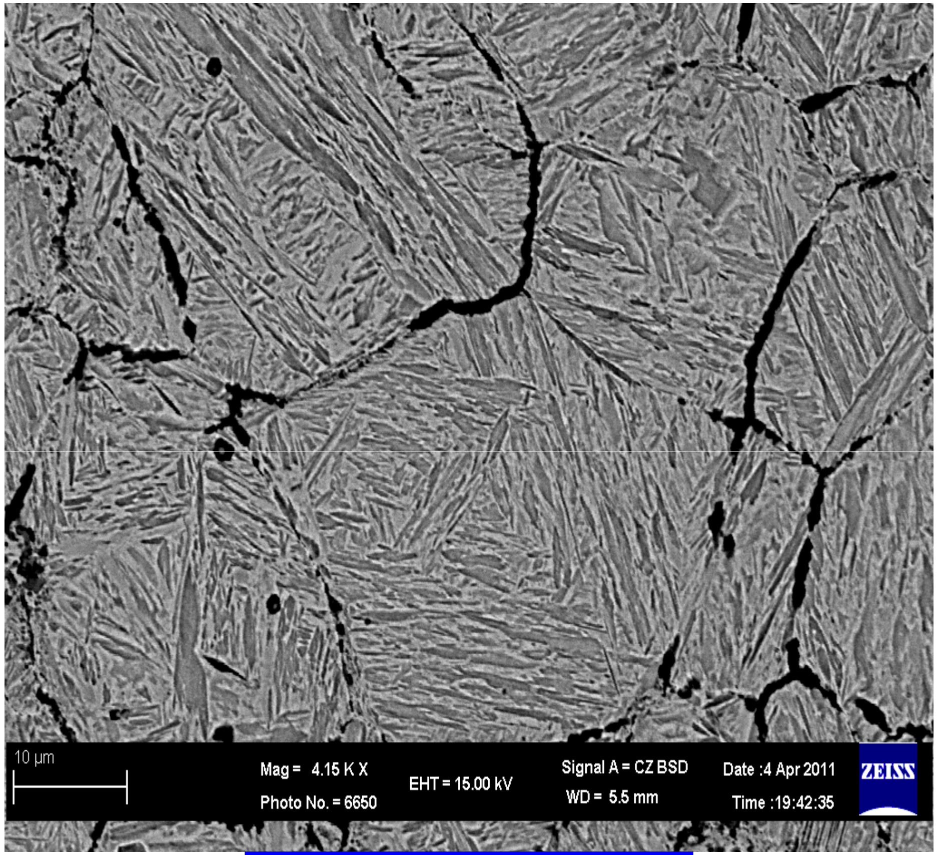
Tetragonal Martensite

Austenite to Martensite → ~4.3 % volume increase

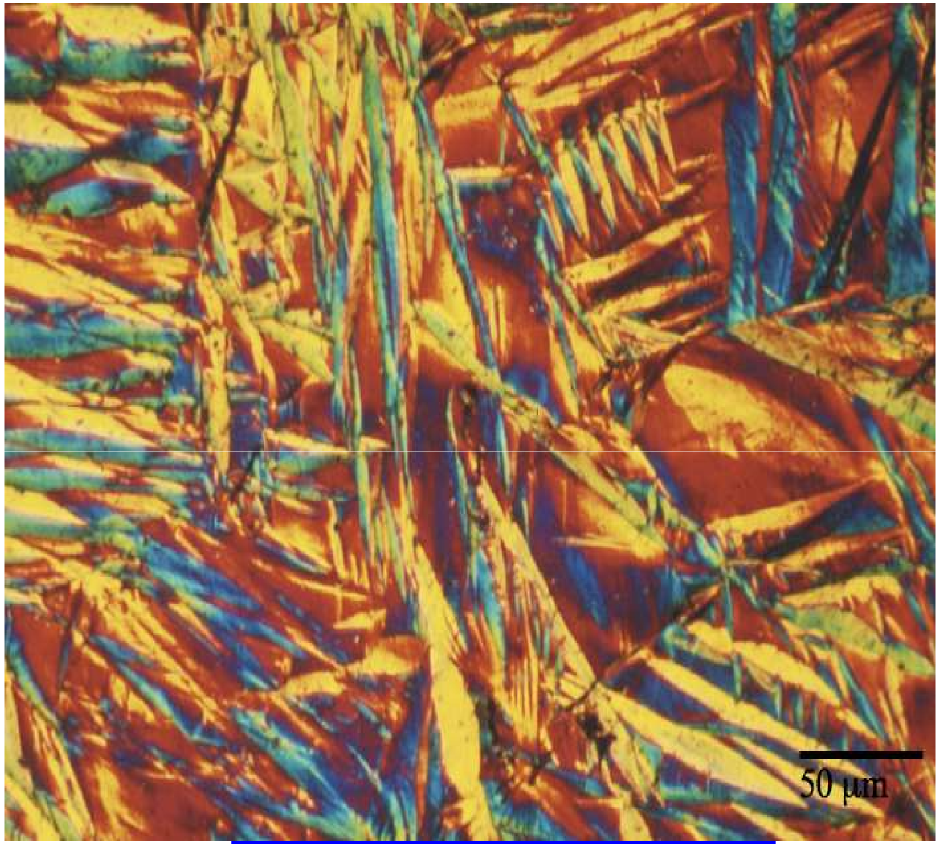
---

* *Homogenous dilation of the lattice (expansion/contraction along crystallographic axis) leading to the formation of a new lattice is called Bain distortion. This involves minimum atomic movements.*

Microstructures of Martensite



Fe-0.6%C steel
Martensite plates

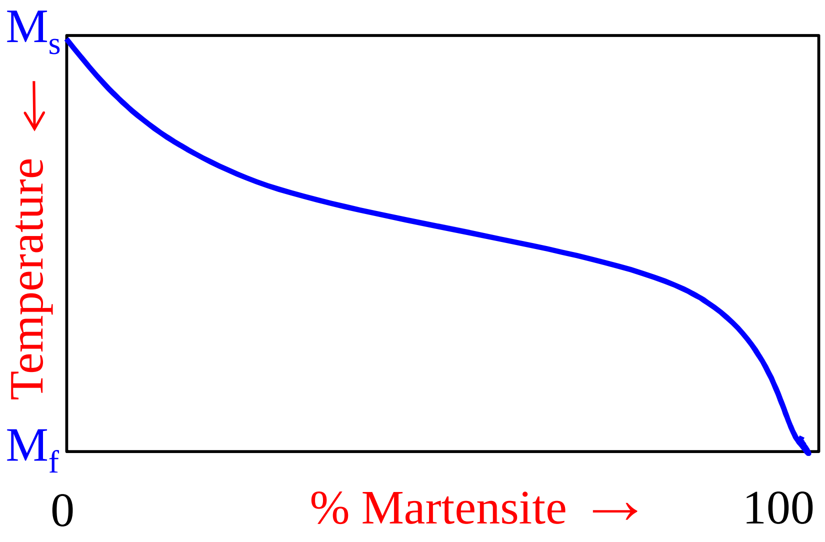


Fe, C 0.8 (Wt%)
Martensite plates

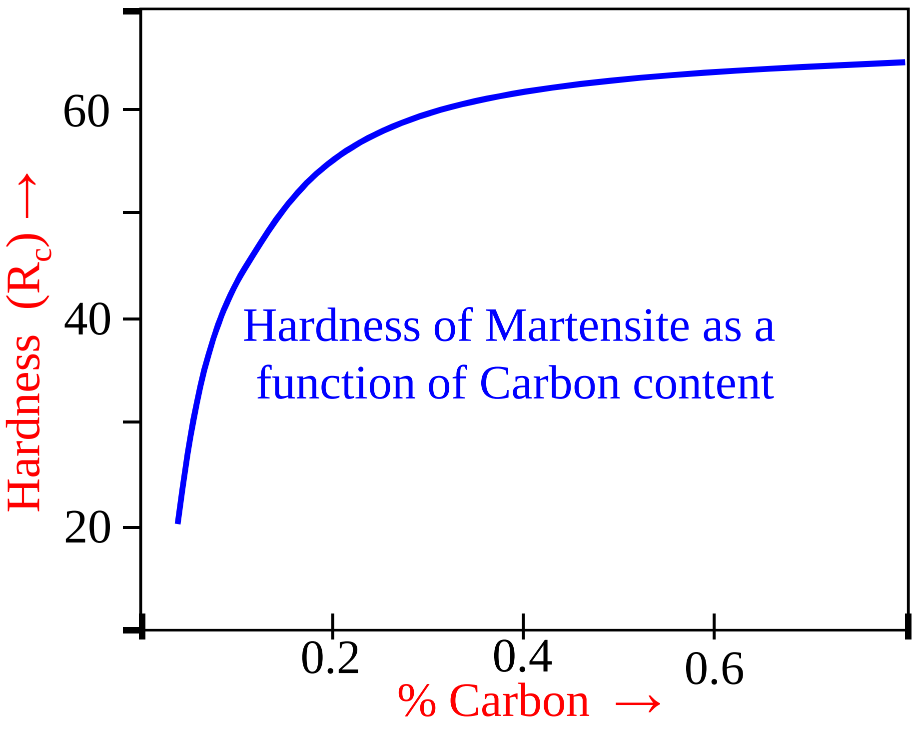
Characteristics of Martensite

- The Martensitic transformation occurs without composition change
- The transformation occurs by shear without need for diffusion and is called diffusion less transformation
- The atomic movements (*shearing)* required are only a fraction of the inter atomic spacing
- The shear changes the shape of the transforming region
  - → results in considerable amount of shear energy
  - → plate-like shape of Martensite
- The amount of martensite formed is a function of the temperature to which the sample is quenched and not of time
- Hardness of martensite is a function of the carbon content
  - → but high hardness steel is very brittle as martensite is brittle
- Steel is reheated to increase its ductility
  - → this process is called TEMPERING

Characteristics of Martensite

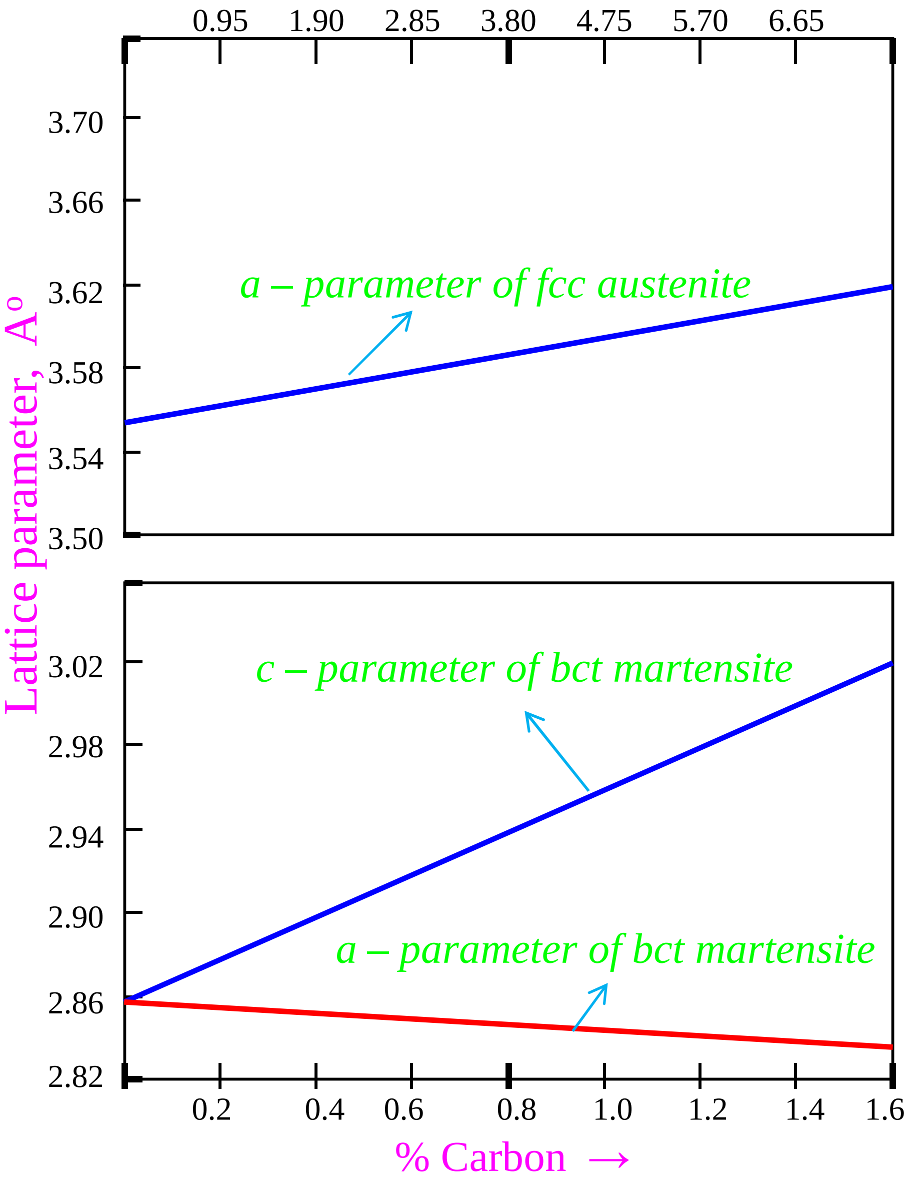


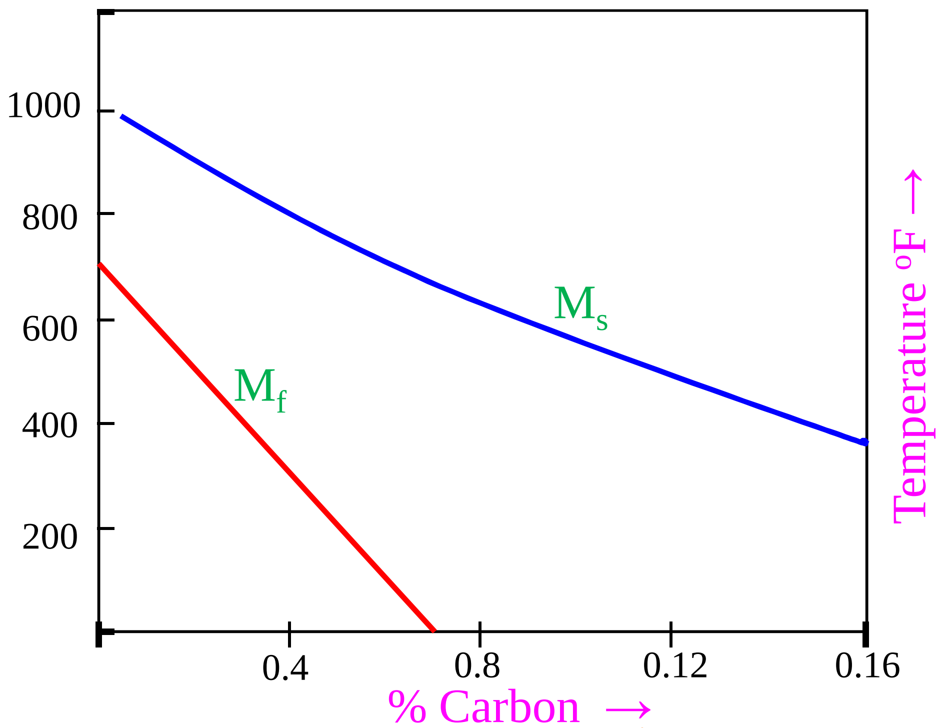
Martensite start - M_s and *Martensite finish* - M_f



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

Characteristics of Martensite



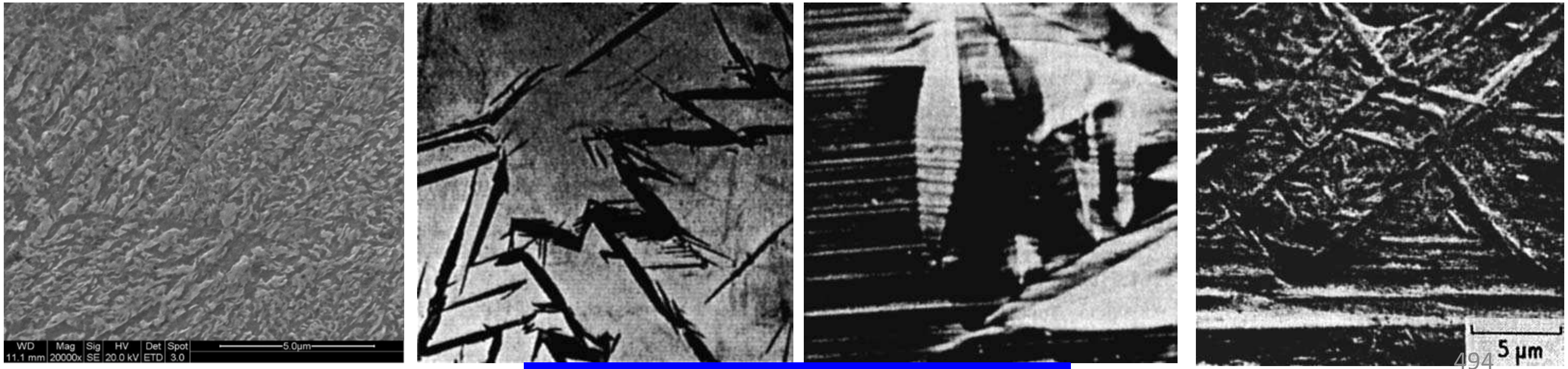


Influence of carbon on the martensite range

Effect carbon on lattice parameters of austenite and martensite

Characteristics of Martensite

- The martensite transformation, for many years, was believed to be unique for steel. However, in recent years, this martensite type of transformation has been found in a number of other alloy systems, such as iron-nickel, copper-zinc, and copper-aluminum.
- The basic purpose of hardening is to produce a fully martensitic structure, and the minimum cooling rate (per second) that will avoid the formation of any of the softer products of transformation is known as the *critical cooling rate*.
- The critical cooling rate, determined by chemical composition and austenitic grain size, is an important property of a steel since it indicates how fast a steel must be cooled in order to form only martensite



More structures of martensitic structure

Time-Temperature-Transformation (TTT) Diagrams

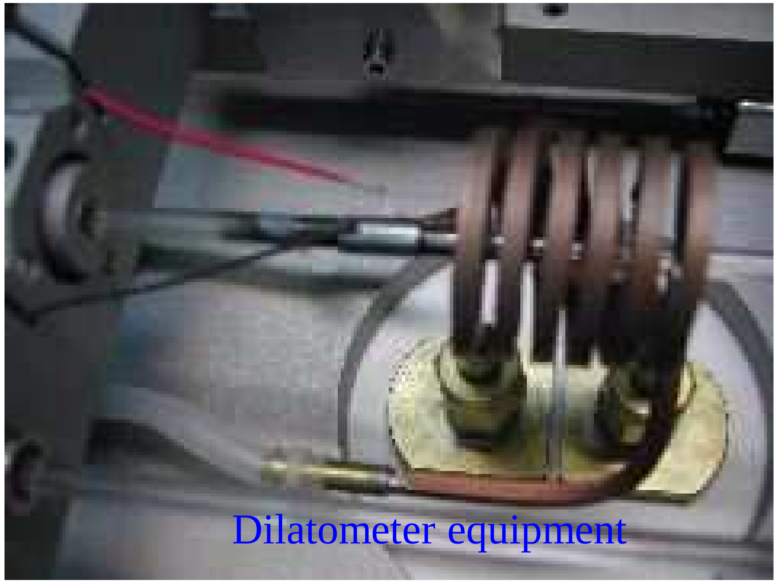
- ❑ Davenport and Bain were the first to develop the TTT diagram of eutectoid steel. They determined pearlite and bainite portions whereas Cohen later modified and included M_S and M_F temperatures for martensite.
- ❑ There are number of methods used to determine TTT diagrams. The most popular method is salt bath techniques combined with metallography and hardness measurement with addition of this we have other techniques like dilatometry, electrical resistivity method, magnetic permeability, *in situ* diffraction techniques (X-ray, neutron), acoustic emission, thermal measurement techniques, density measurement techniques and thermodynamic predictions.
- ❑ TTT diagrams, also called as Isothermal (*temperature constant)* Transformation diagrams.
- ❑ TTT diagrams give the kinetics of isothermal transformations.
- ❑ For every composition of steel we should draw a different TTT diagram.

Equipments for determination of TTT Diagrams

Salt bath I
Austenitisation heat treatment

Salt bath II
Low-temperature for isothermal treatment

Sample and fixtures
for dilatometric measurements

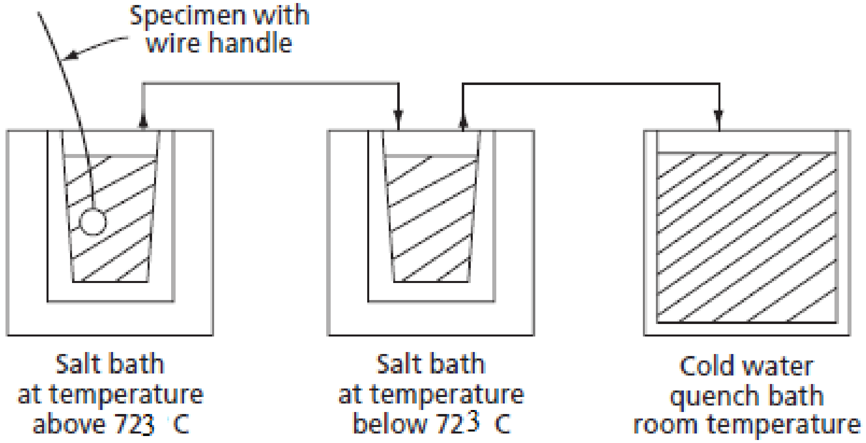


Dilatometer equipment

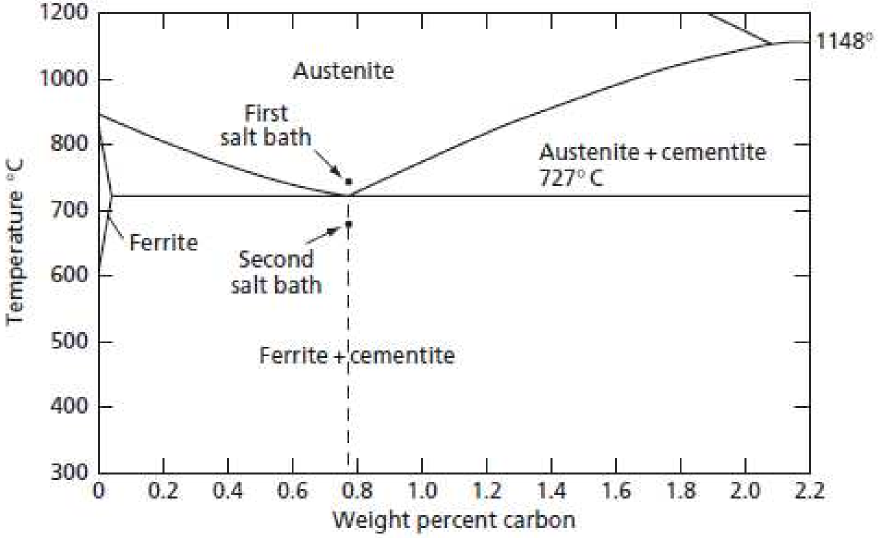
Determination of TTT diagram for eutectoid steel

- For the determination of isothermal transformation (or) TTT diagrams, we consider *molten salt bath technique* combined with metallography and hardness measurements.
- In *molten salt bath technique* two salt baths and one water bath are used. Salt bath I is maintained at austenising temperature (780˚C for eutectoid steel). Salt bath II is maintained at specified temperature at which transformation is to be determined (below A_{e1}), typically 700-250°C for eutectoid steel. Bath III which is a cold water bath is maintained at room temperature.
- In bath I number of samples are austenite at A_1+20-40°C for eutectoid, A_3+20-40°C for hypo-eutectoid steel and A_{Cm}+20-40°C for hyper-eutectoid steels for about an hour.
- Then samples are removed from bath I and put in bath II and each one is kept for different specified period of time say t_1, t_2, t_3, t_4,…..........,t_n etc. After specified times, the samples are removed and quenched in cold water. The microstructure of each sample is studied using metallographic techniques. The type, as well as quantity of phases, is determined on each sample.

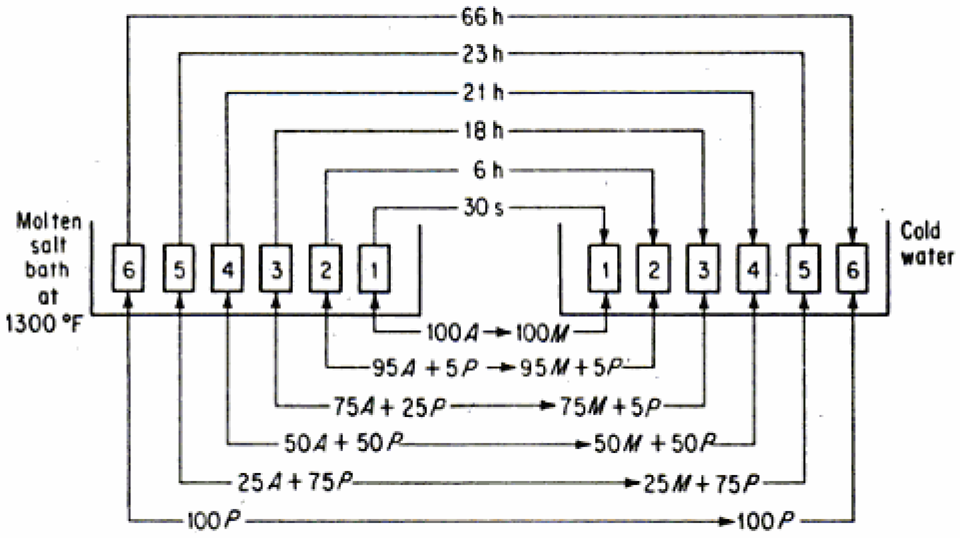
Determination of TTT diagram for eutectoid steel



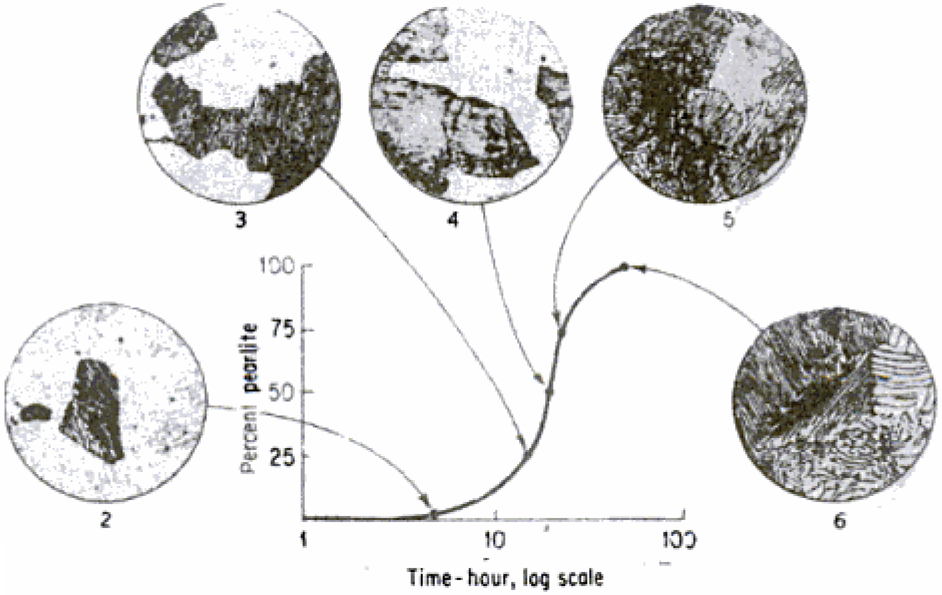
Simple experimental arrangement for determining
The kinetics of isothermal austenitic transformation



Eutectoid section of the iron - carbon diagram

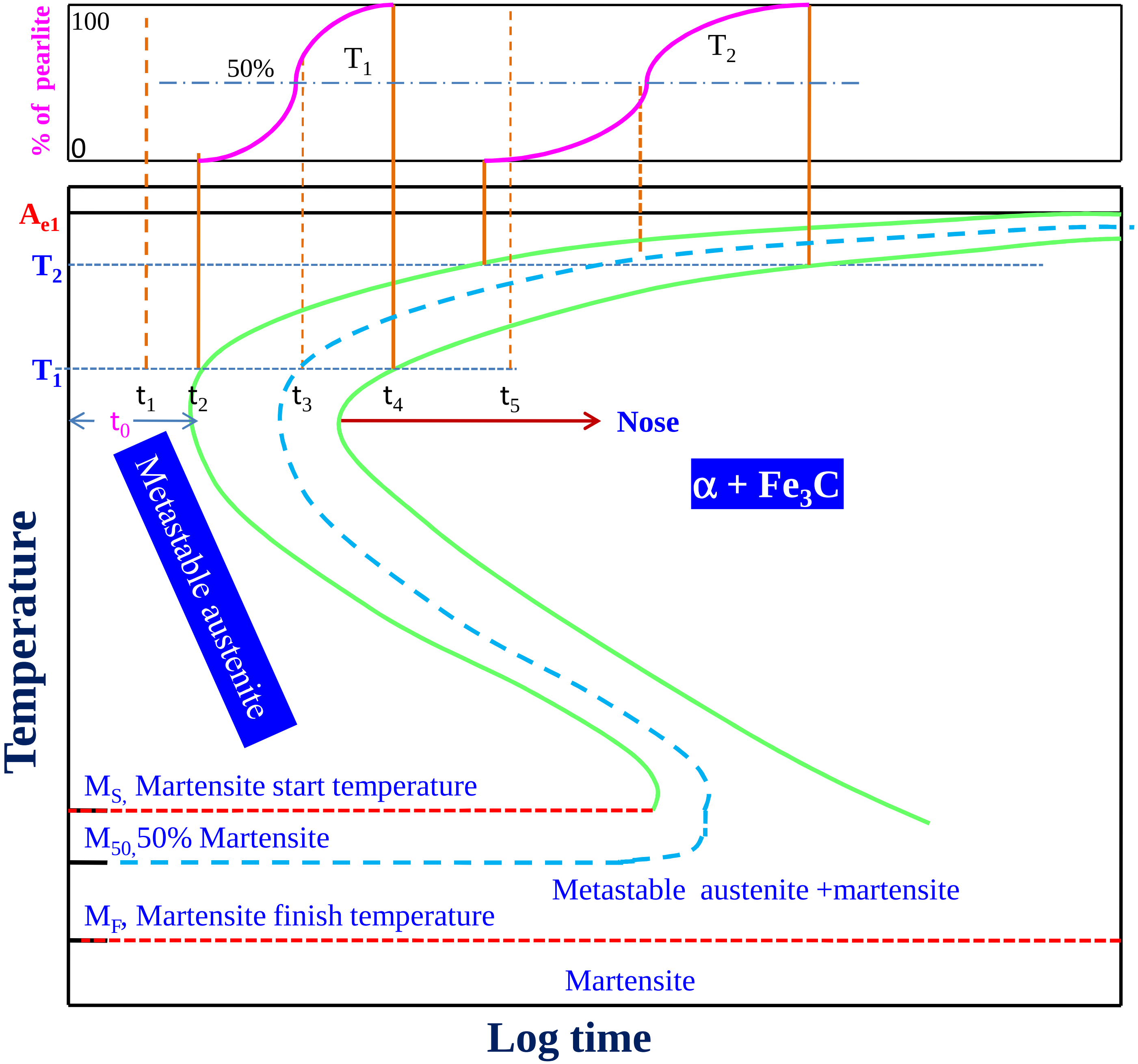


The progress of austenite transformation
A-austenite, P-pearlite, M-martensite



TTT curve of austenite to pearlite for 1080 steel

Determination of TTT diagram for eutectoid steel



✓At T_1, incubation period for pearlite=t_2, Pearlite finish time =t_4

✓Minimum incubation period t_0 at the nose of the TTT diagram,

Important points to be noted:

- ✓ The x-axis is log scale. ‘Nose’ of the ‘C’ curve is in ~sec and just below **T_E** transformation times may be ~day.
- ✓ The starting phase (left of the C curve) has to γ.
- ✓ To the right of finish C curve is (γ+ Fe_3C) phase field. This phase field has more labels included.

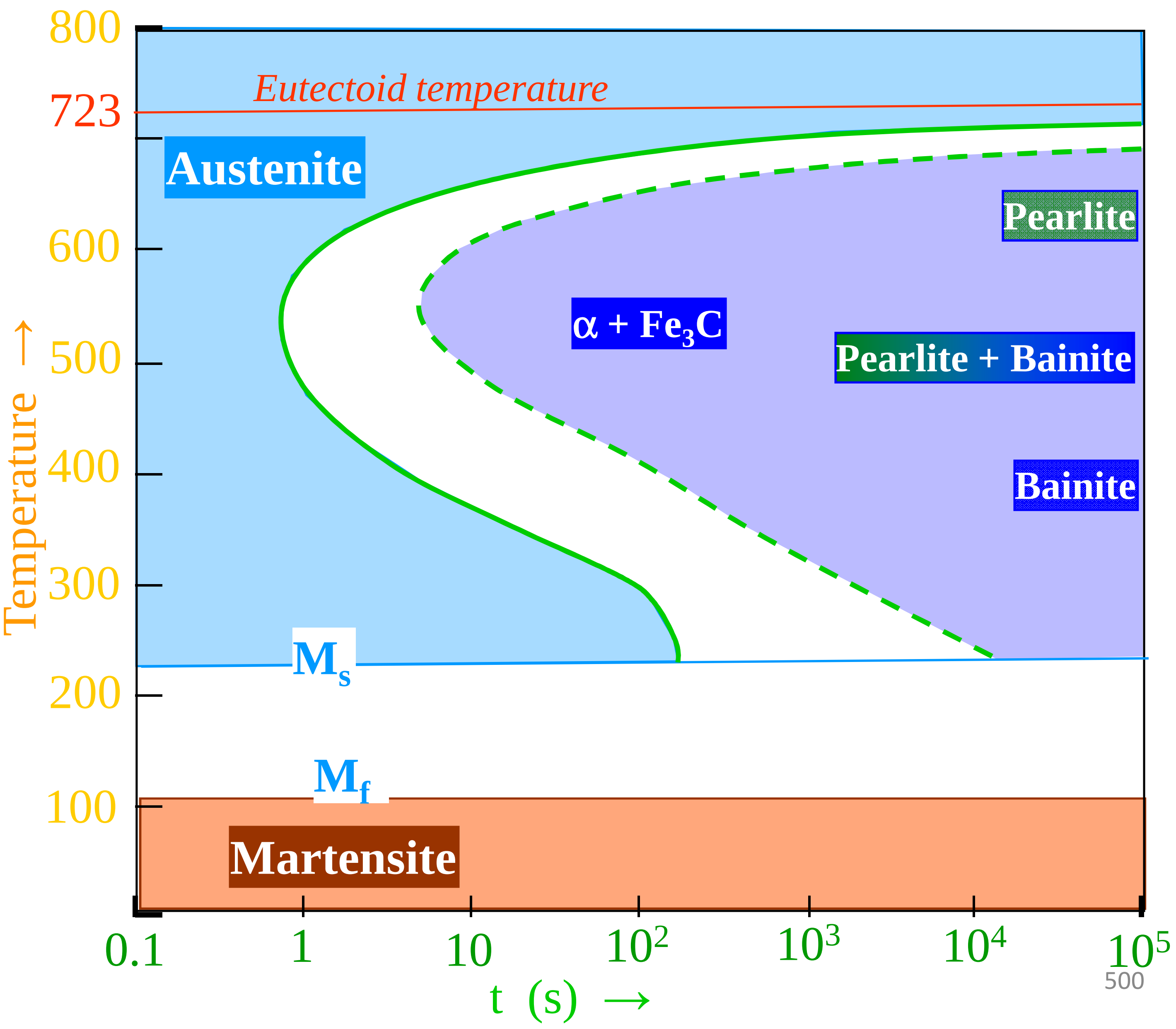
Isothermal Transformation diagram for eutectoid steel

Important points to be noted:

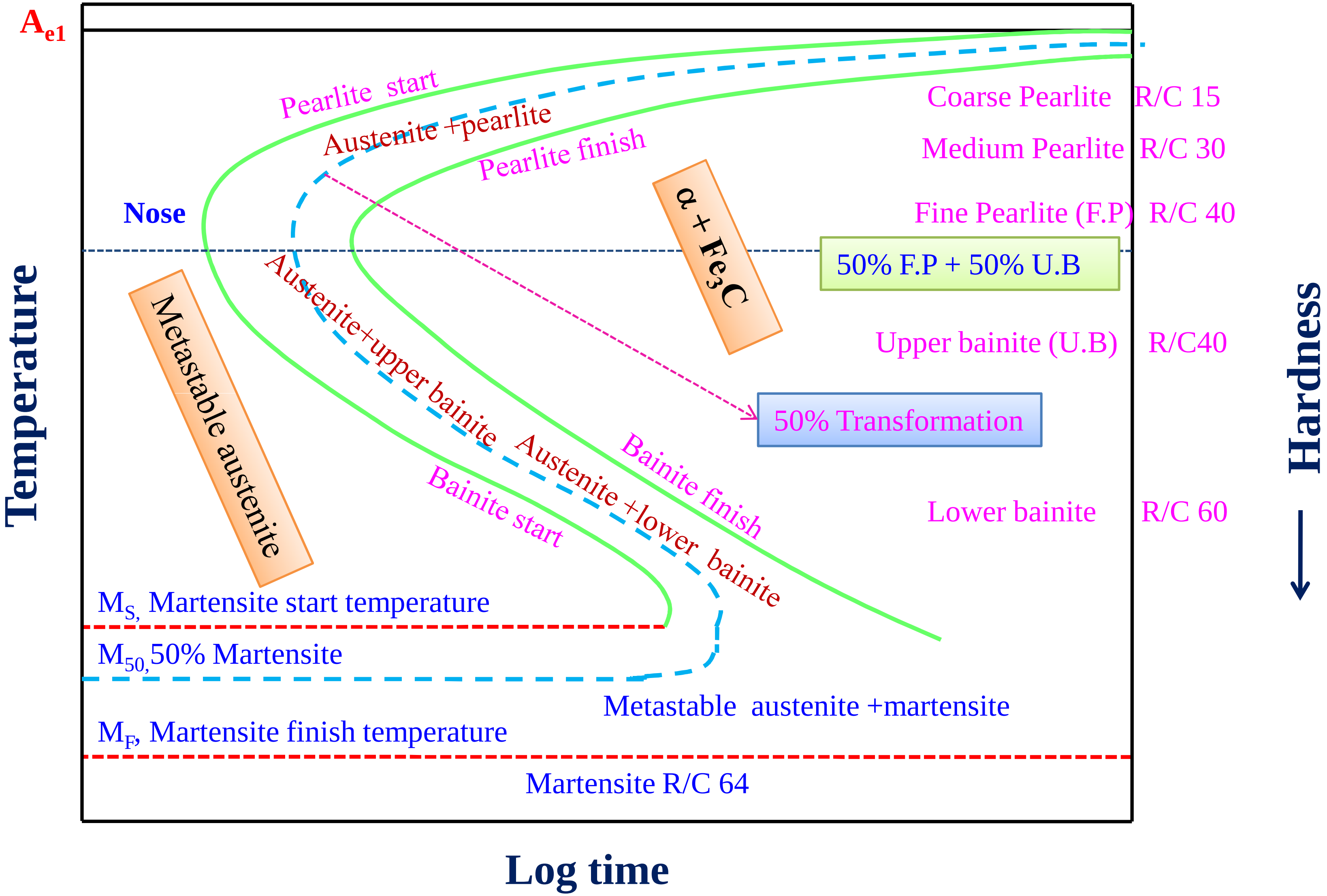
✓ The x-axis is log scale. 'Nose' of the 'C' curve is in ~sec and just below **T_E** transformation times may be ~day.

✓ The starting phase (left of the C curve) has to γ.

✓ To the right of finish C curve is (γ+ Fe_3C) phase field. This phase field has more labels included.



Possible phases in TTT diagram for eutectoid steel



A_{e1}

Pearlite start

Austenite +pearlite

Pearlite finish

$\alpha + Fe_3C$

Nose

Metastable austenite

Austenite+upper bainite

Austenite +lower bainite

Bainite start

Bainite finish

50% F.P + 50% U.B

50% Transformation

Coarse Pearlite R/C 15

Medium Pearlite R/C 30

Fine Pearlite (F.P) R/C 40

Upper bainite (U.B) R/C40

Lower bainite R/C 60

Hardness ↓

M_S, Martensite start temperature

M_{50}, 50% Martensite

Metastable austenite +martensite

M_F, Martensite finish temperature

Martensite R/C 64

Temperature

Log time

Isothermal Transformation diagram for eutectoid steel

- As pointed out before one of the important utilities of the TTT diagrams comes from the overlay of micro-constituents (microstructures) on the diagram.
- Depending on the T, the (γ+ Fe_3C) phase field is labeled with micro-constituents like Pearlite, Bainite.
- The time taken to 1% transformation to, say pearlite or bainite is considered as transformation start time and for 99% transformation represents transformation finish.
- We had seen that TTT diagrams are drawn by instantaneous quench to a temperature followed by isothermal hold.
- Suppose we quench below (~225°C, below the temperature marked M_s), then Austenite transforms via a diffusionless transformation *(involving shear) to a (hard)* phase known as Martensite. Below a temperature marked M_f this transformation to Martensite is complete. Once γ is exhausted it cannot transform to (γ + Fe_3C).
- Hence, we have a new phase field for Martensite. The fraction of Martensite formed is not a function of the time of hold, but the temperature to which we quench (between M_s and M_f).
- Strictly speaking cooling curves (including finite quenching rates) should not be overlaid on TTT diagrams *(remember that TTT diagrams are drawn for isothermal holds!).*

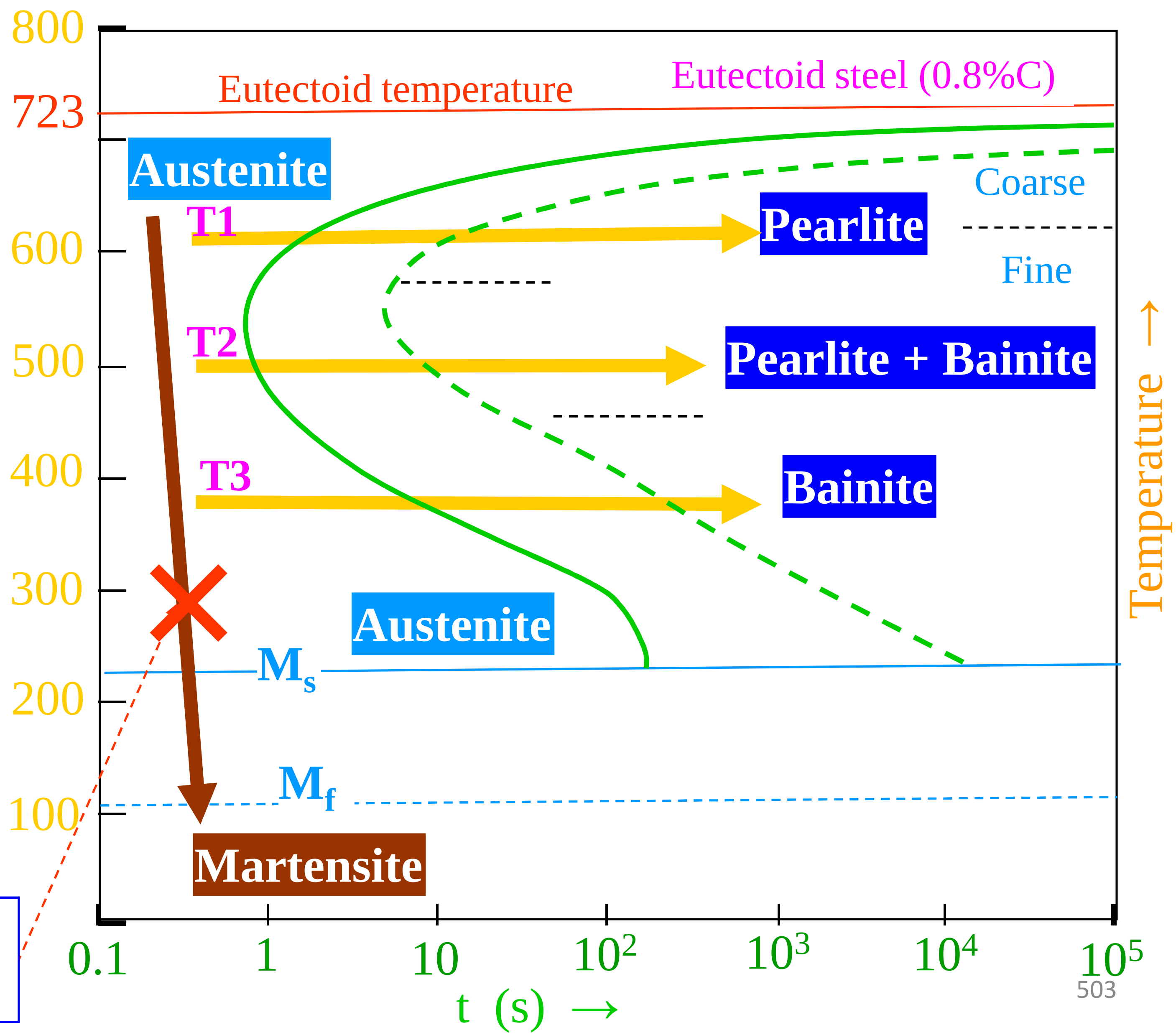
Isothermal Transformation diagram for eutectoid steel

✓ Isothermal hold at: (i) T1 gives us Pearlite, (ii) T2 gives Pearlite+Bainite, (iii) T3 gives Bainite. *Note that Pearlite and Bainite are both α+Fe_3C (but their morphologies are different).*

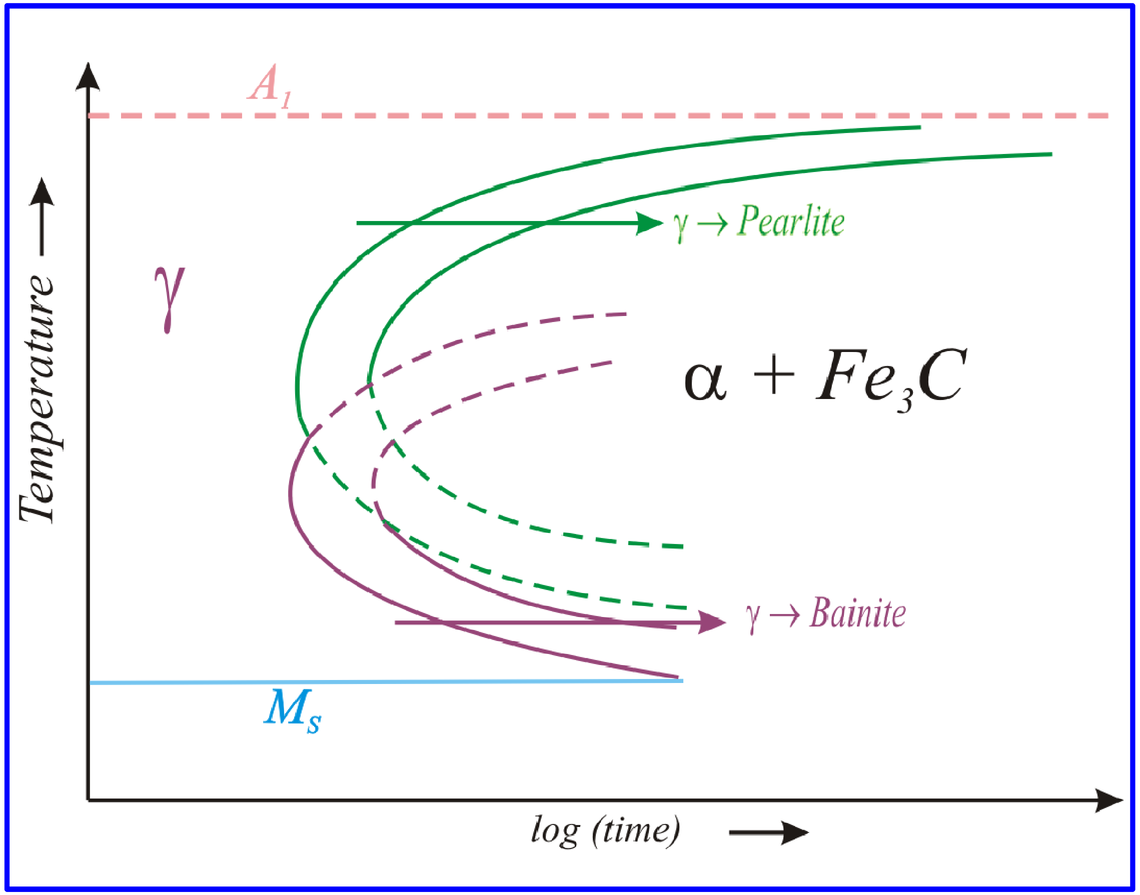
✓ To produce Martensite we should quench at a rate such as to avoid the nose of the start 'C' curve. Called the critical cooling rate.

✓ If we quench between M_s and M_f we will get a mixture of Martensite and γ *(called retained Austenite).*

Not an isothermal transformation



Isothermal Transformation diagram for eutectoid steel



In principle two curves exist for Pearlitic and Bainitic transformations

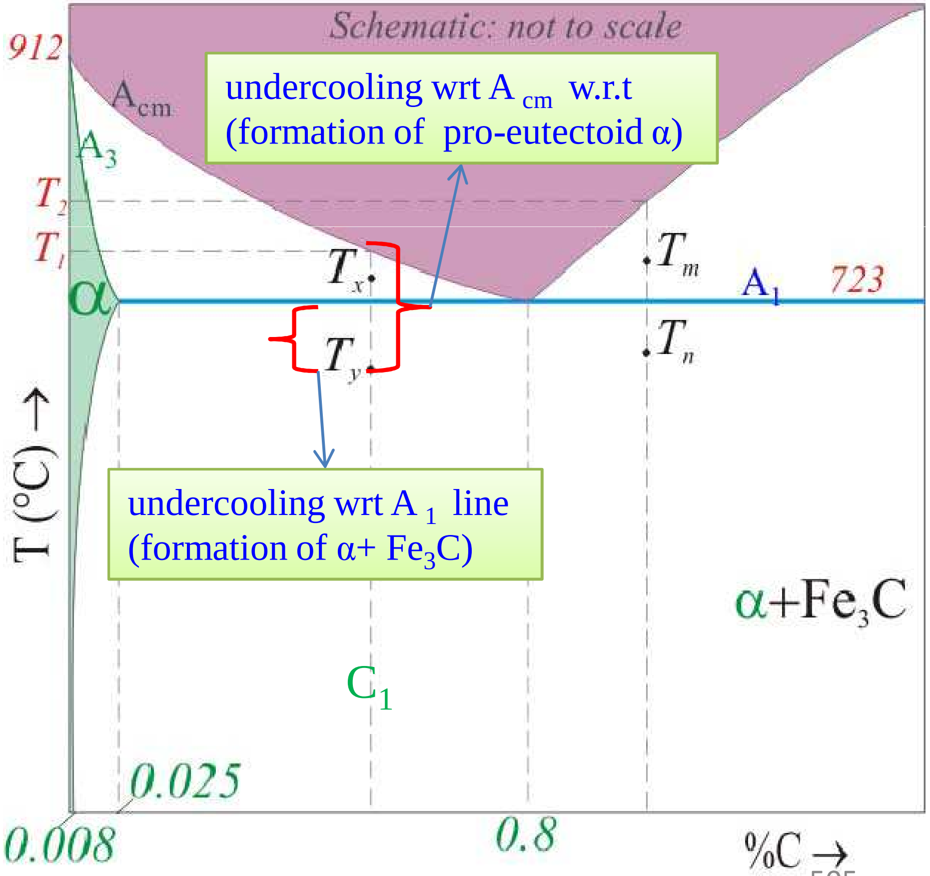
→ they are usually not resolved in plain C steel

(In alloy steels they can be distinct)

TTT diagram for Hypo eutectoid steel

- In hypo- (and hyper-) eutectoid steels (say composition C_1) there is one more branch to the ‘C’ curve-NP *(next slide: marked in red).*
- The part of the curve lying between T_1 and T_E (marked in fig : n*ext slide*) is clear, because in this range of temperatures we expect only pro-eutectoid α to form and the final microstructure will consist of α and γ. *(E.g. if we cool to T_x and hold).*

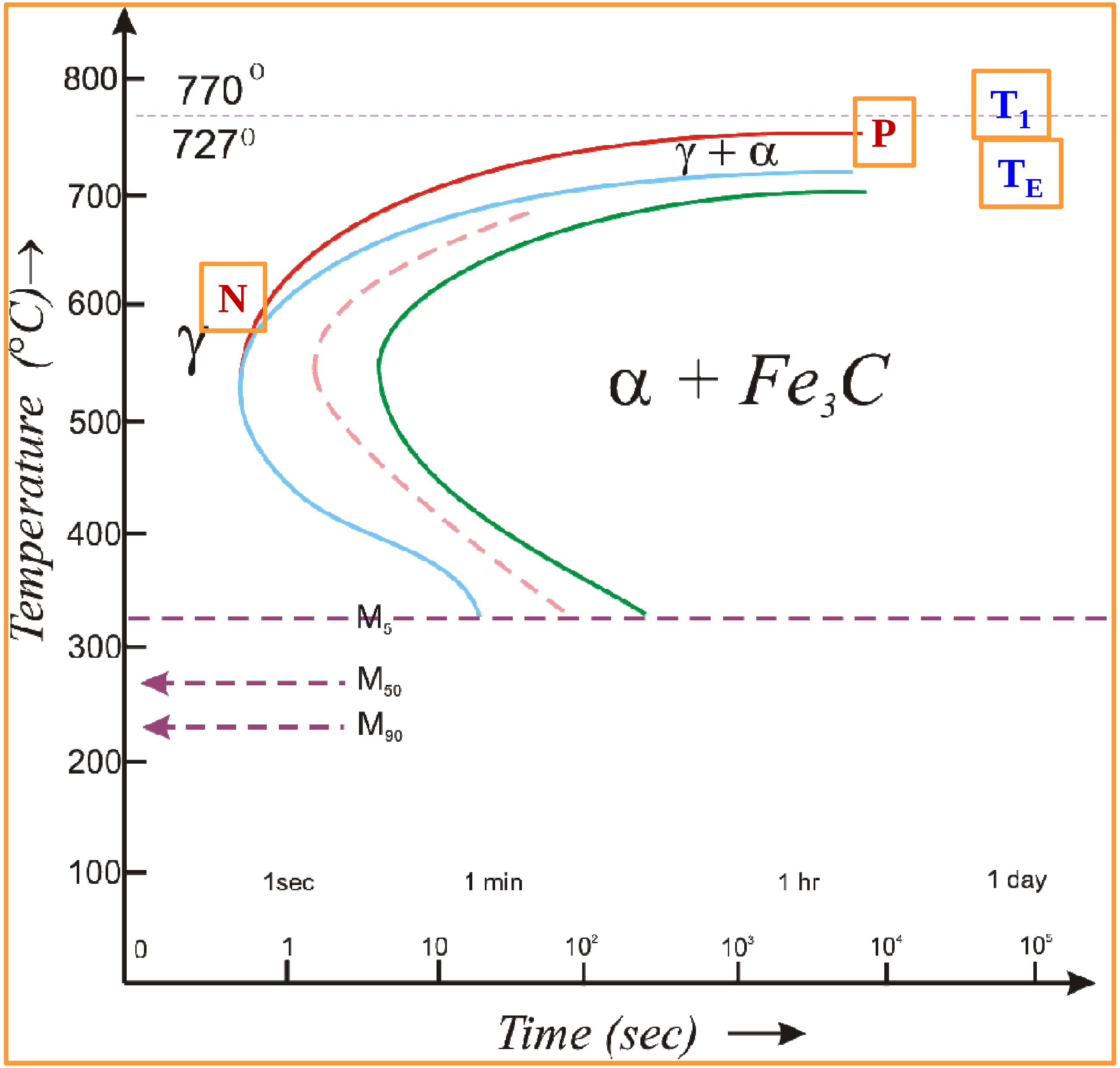
- The part of the curve below T_E is a bit of a ‘mystery’ *(since we are instantaneously cooling to below T_E, we should get a mix of α+ Fe_3C → what is the meaning of a ‘pro’-eutectoid phase in a TTT diagram? (remember ‘pro-’ implies ‘pre-’)*
- Suppose we quench instantaneously an hypo-eutectoid composition C_1 to T_x we should expect the formation of α+Fe_3C (and not pro-eutectoid α first).
- The reason we see the formation of pro-eutectoid α first is that the undercooling w.r.t to A_{cm} is more than the undercooling w.r.t to A_1. Hence, there is a higher propensity for the formation of pro-eutectoid α.



undercooling wrt A_{cm} w.r.t (formation of pro-eutectoid α)

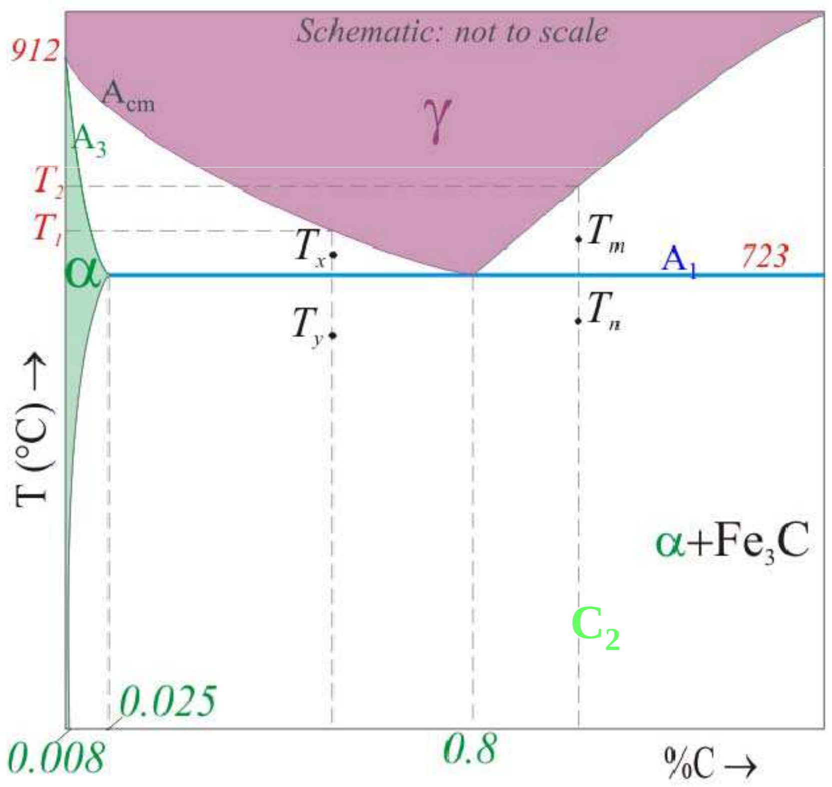
undercooling wrt A_1 line (formation of α+ Fe_3C)

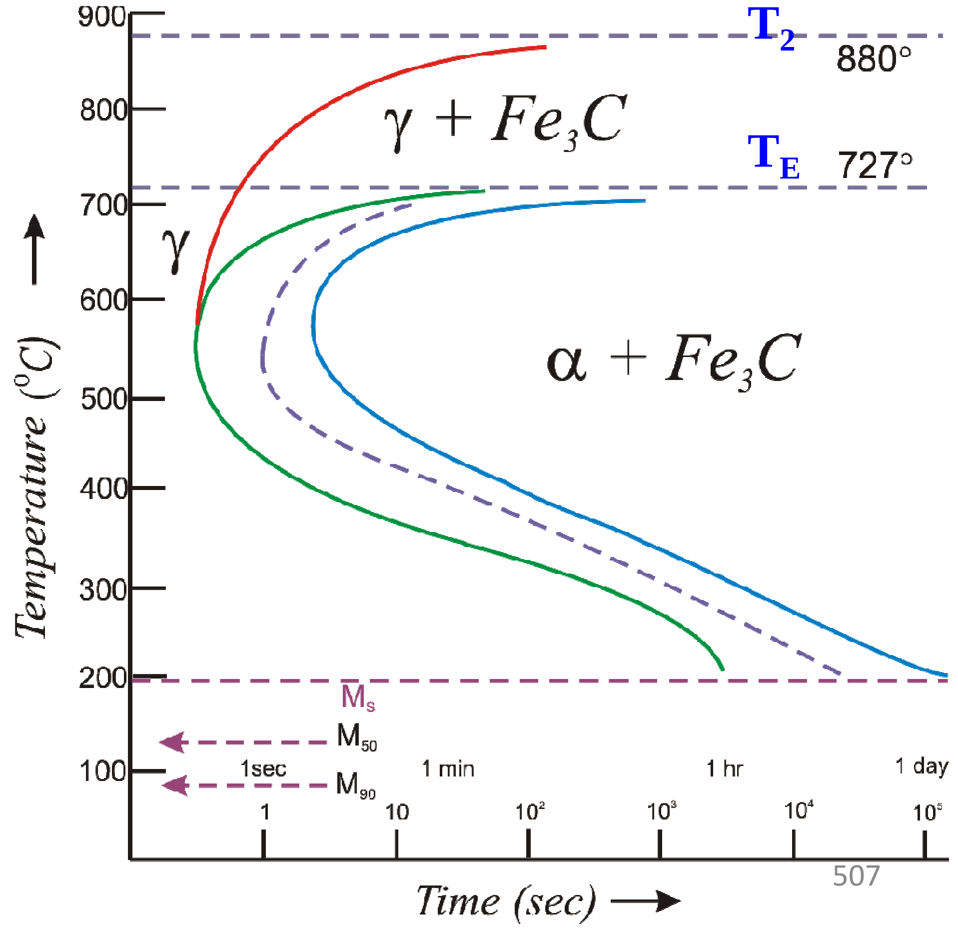
TTT diagram for Hypo eutectoid steel



TTT diagram for Hyper eutectoid steel

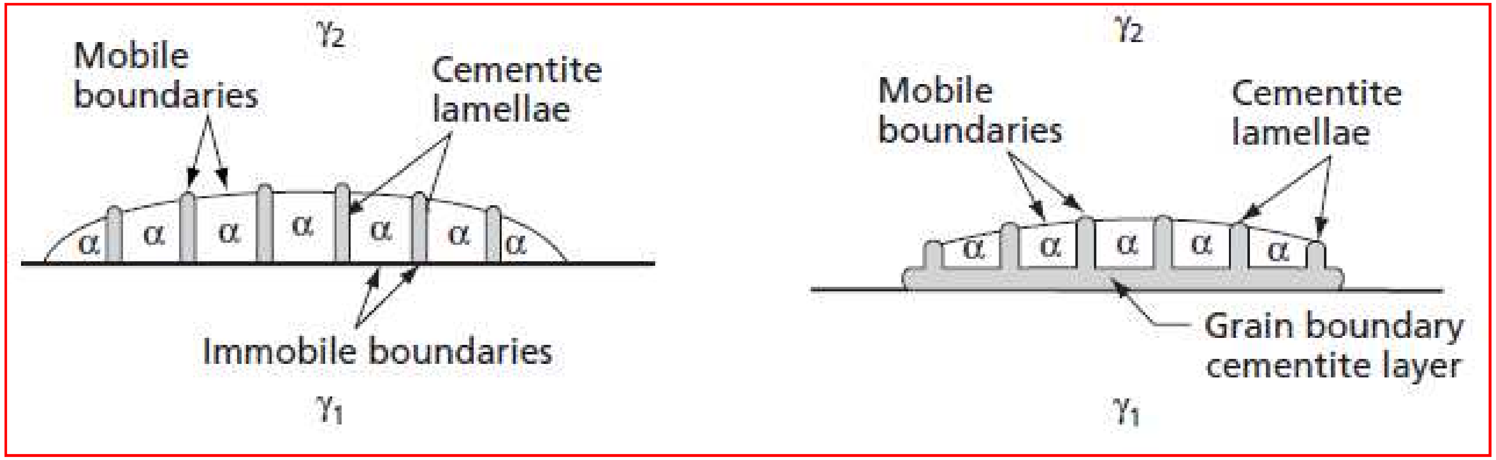
- Similar to the hypo-eutectoid case, hyper-eutectoid compositions C_2 have a γ+Fe_3C branch.
- For a temperature between T_2 and T_E (say T_m (not melting point- just a label)) we land up with γ+Fe_3C.
- For a temperature below T_E (but above the nose of the 'C' curve) (say T_n), first we have the formation of pro-eutectoid Fe_3C followed by the formation of eutectoid γ+Fe_3C.



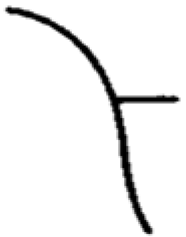


Transformation to Pearlite

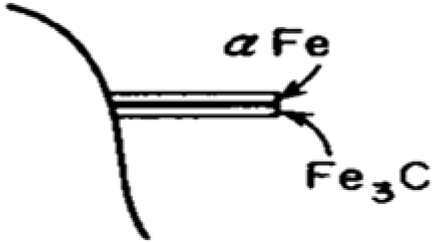
- ❑ The transformation product above the nose region is pearlite. The pearlite microstructure is the characteristic lamellar structure of alternate layers of ferrite and cementite.
- ❑ As the transformation temperature decreases, the characteristic lamellar structure is maintained, but the spacing between the ferrite and carbide layers becomes increasingly smaller until the separate layers cannot be resolved with the light microscope.
- ❑ As the temperature of transformation and the fineness of the pearlite decreases, it is apparent that the hardness will increase.



Transformation to Pearlite

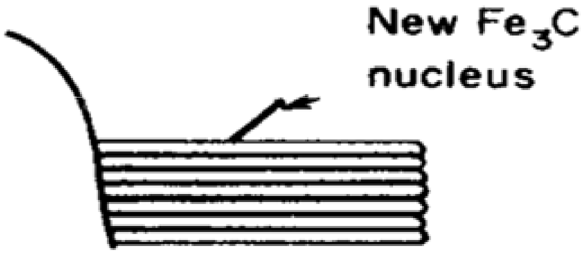


Initial Fe_3C nucleus



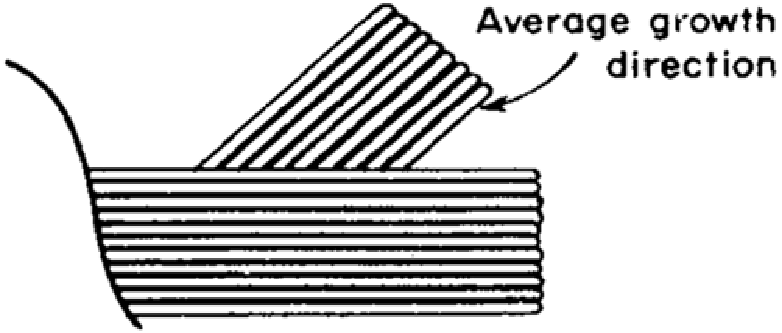
*Fe_3C plate full grown,
α-Fe is nucleus*

*α-Fe plates are now grown
new Fe_3C plates nucleated*



*new Fe_3C plates nucleated
on different orientation*

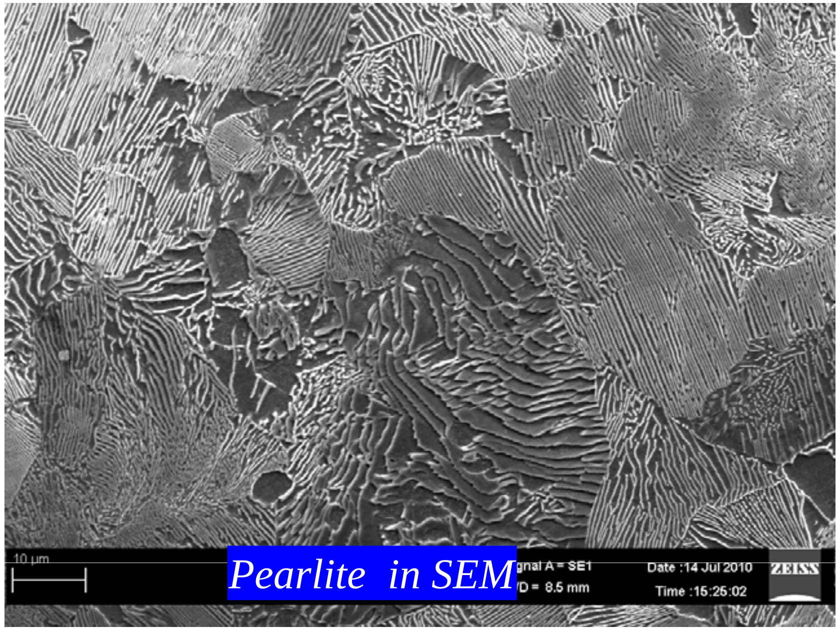
$\gamma \rightarrow \alpha + Fe_3C$



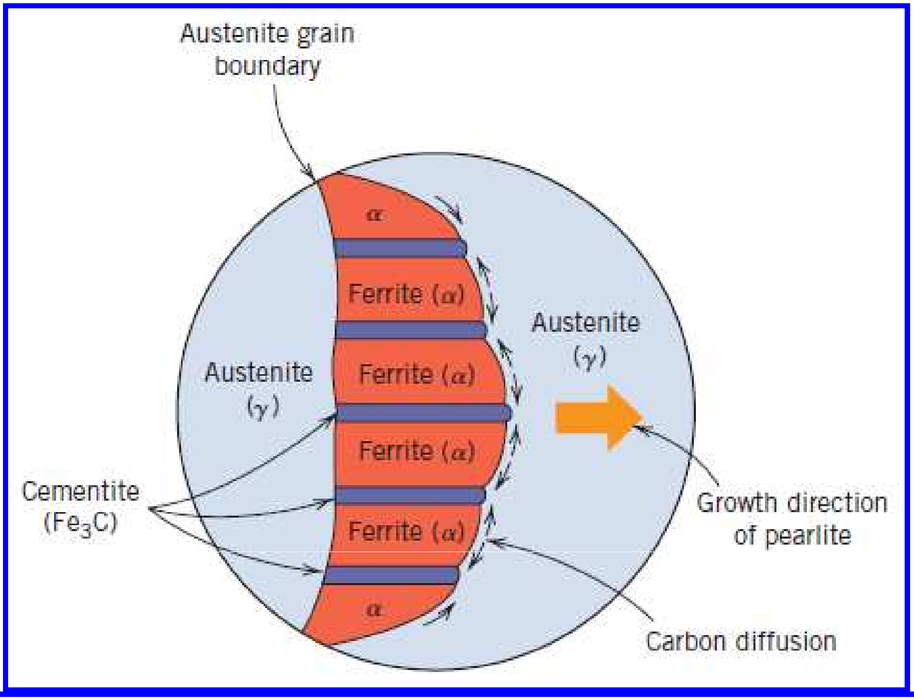
New colony of advanced stage of growth

- ❑ Nucleation and growth
- ❑ Heterogeneous nucleation at grain boundaries
- ❑ Interlamellar spacing is a function of the temperature of transformation
- ❑ Lower temperature → finer spacing → higher hardness

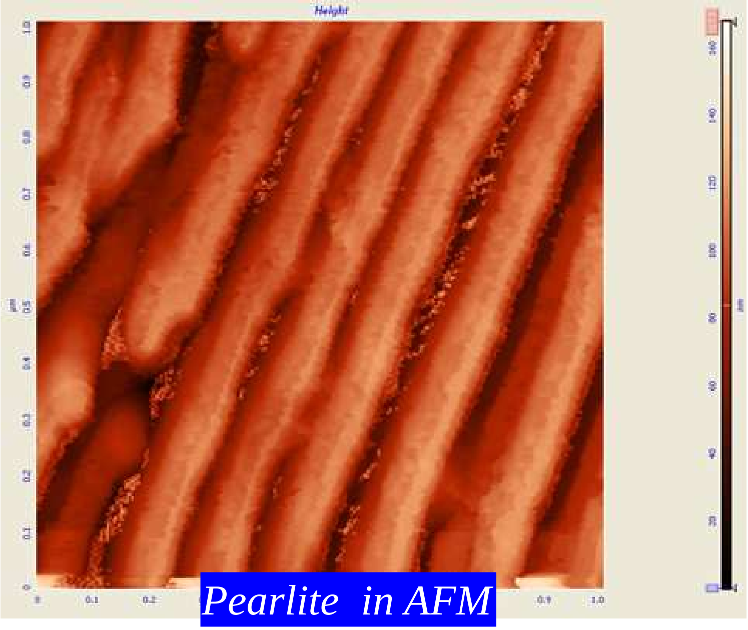
Pearlitic structure



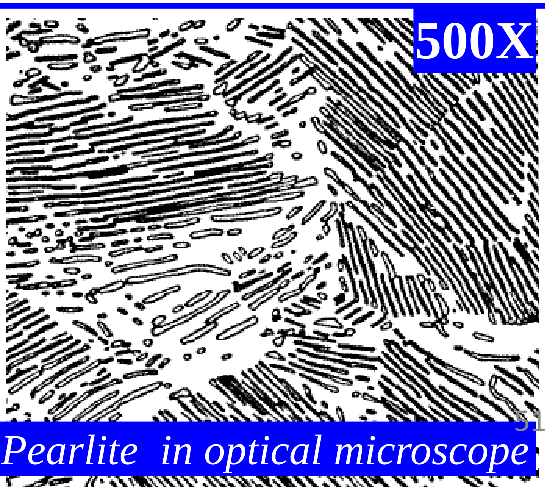
Pearlite in SEM



Schematic representation of the formation of pearlite from austenite; direction of carbon diffusion indicated by arrows



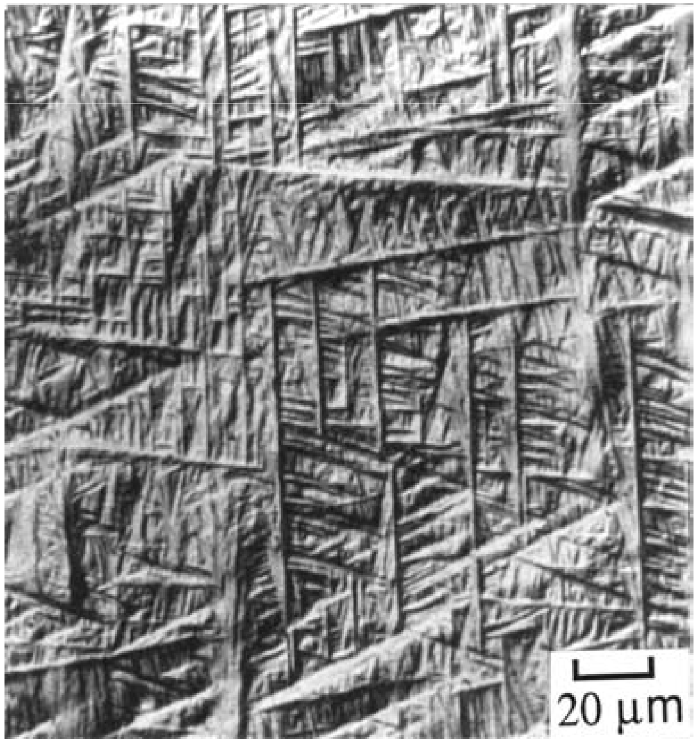
Pearlite in AFM



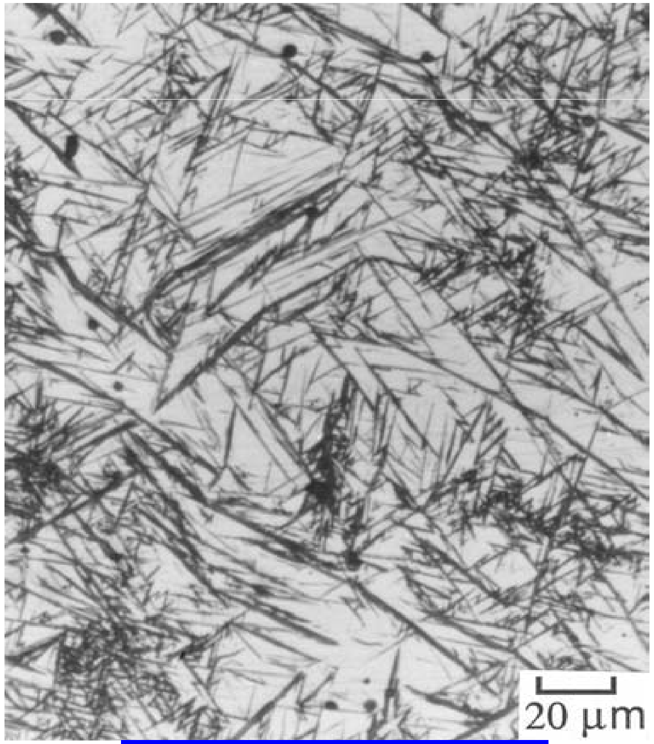
Pearlite in optical microscope

Transformation to Bainite

- In between the nose region of approximately 510˚C and the M_s temperature, a new, dark-etching aggregate of ferrite and cementite appears. This structure, named after E.C.Bain, is called bainite.
- At upper temperatures of the transformation range, it resembles pearlite and is known as upper or feathery bainite. At low temperatures it appears as a black needlelike structure resembling martensite and is known as lower or acicular banite.

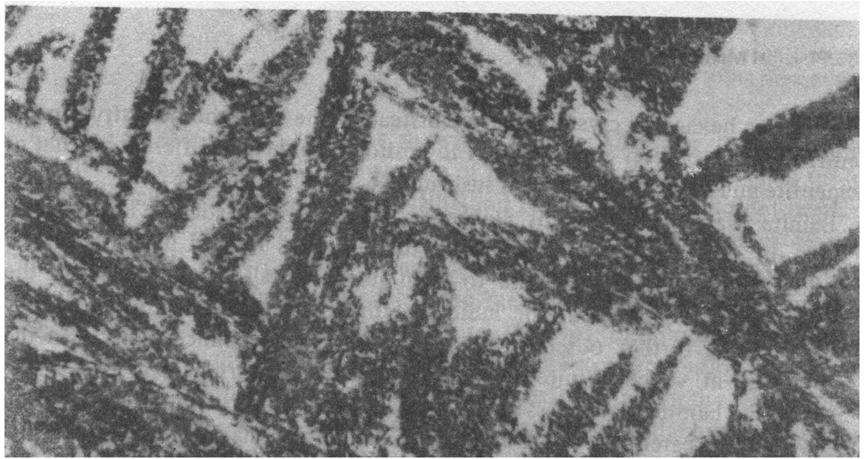


Upper or Feathery bainite

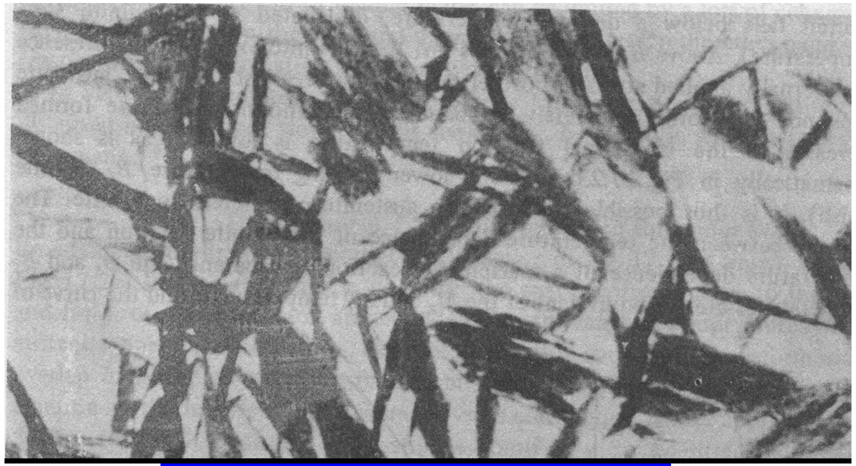


Lower or Acicular bainite

Transformation to Bainite



Bainite formed at 348°C

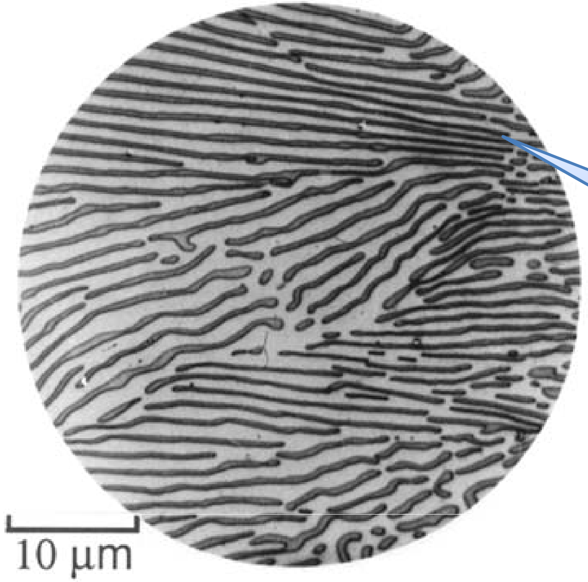


Bainite formed at 278°C

$$\gamma \longrightarrow \alpha + Fe_3C^{**}$$

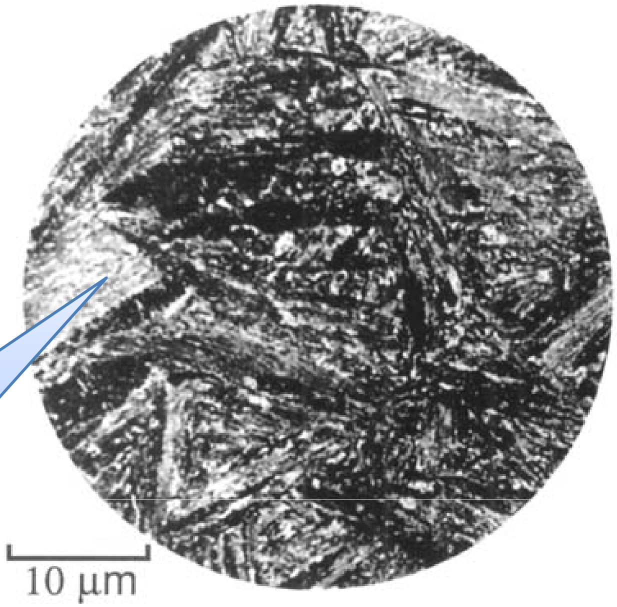
- Pearlite is nucleated by a carbide crystal, bainite is nucleated by a ferrite crystal, and this results in a different growth pattern.
- Acicular, accompanied by surface distortions
- ** Lower temperature → carbide could be ε carbide (hexagonal structure, 8.4% C)
- Bainite plates have irrational habit planes
- Ferrite in Bainite plates possess different orientation relationship relative to the parent Austenite than does the Ferrite in Pearlite

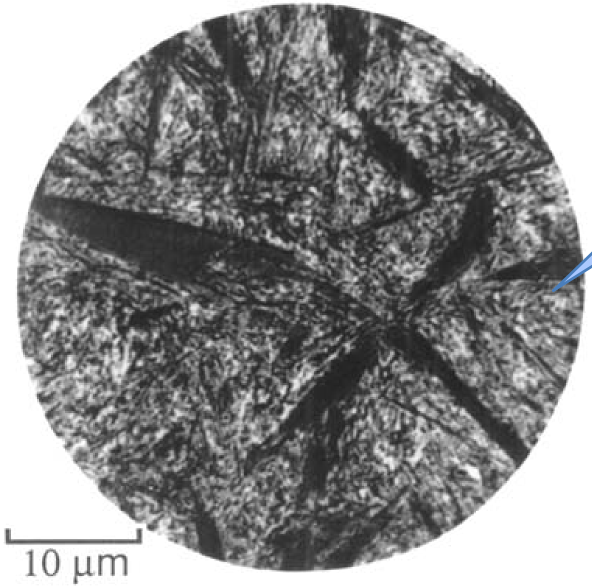
Microstructures in a eutectoid steel



Pearlite formed at 720˚C

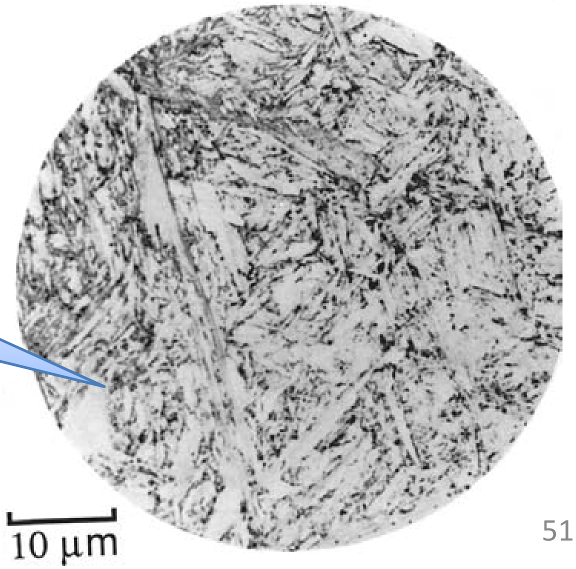
Bainite obtained by isothermal transformation at 290˚C



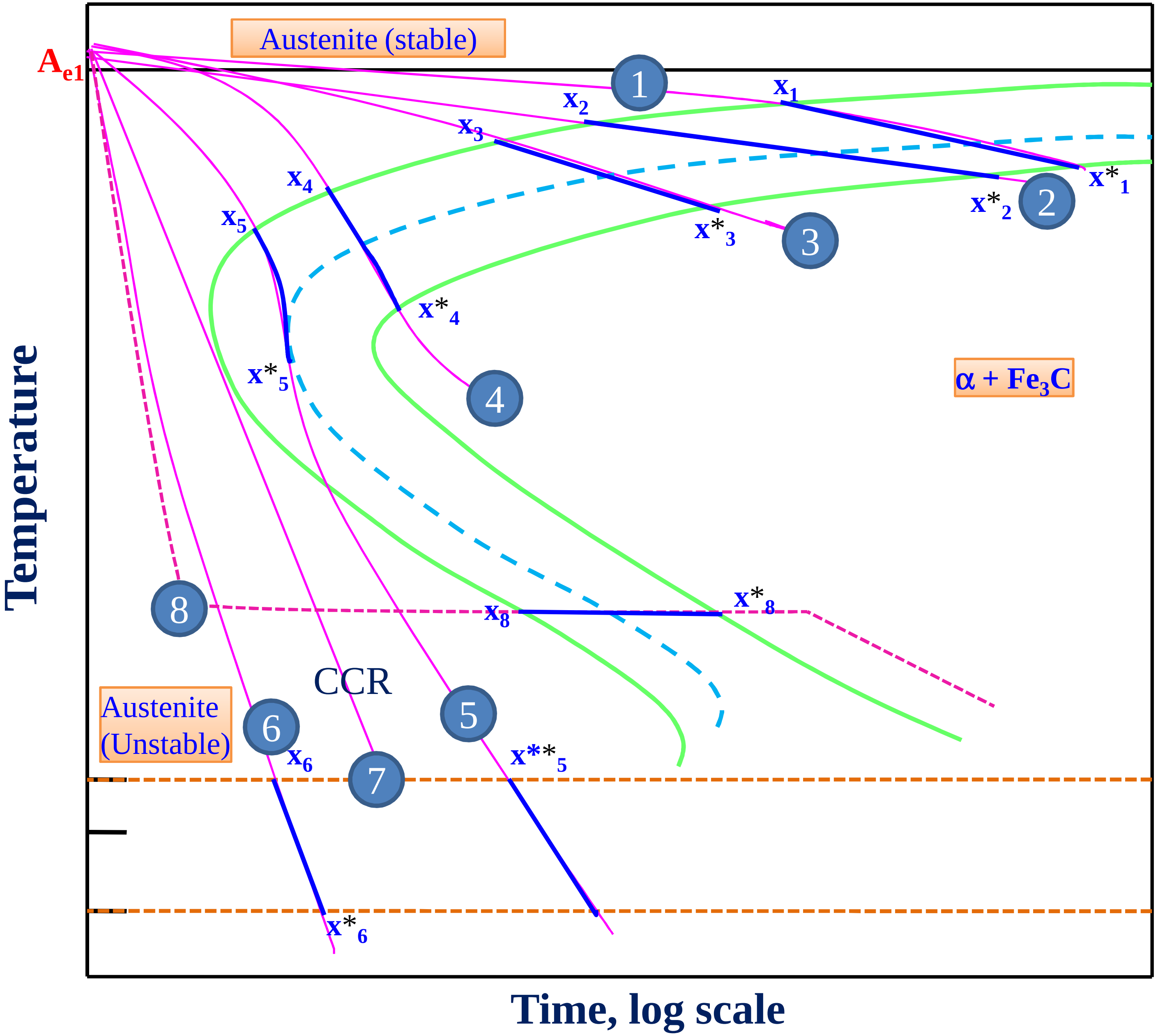


Bainite obtained by isothermal transformation at 180˚C

Martensite



Cooling curves and the I-T diagram



Cooling curves and the I-T diagram

Curve 1

Cooling curve 1 shows a very slow cooling rate typical of conventional annealing transformation will start at $x_{1,}$ ends at $x^*_{1,}$ and there is a slight temperature difference in temperature between the beginning and end of transformation, there will be a slight difference in the fineness of pearlite formed at the beginning and at the end.

Curve 2

Cooling curve 2 shows ‘isothermal’ cooling and was developed directly from the IT diagram. The process is carried out by cooling the material rapidly from above the critical range to a predetermined temperature in the upper portion of the I-T diagram and holding for the time indicate to produce complete transformation. In contrast to conventional annealing, this treatment produces a more uniform microstructure and hardness.

Curve 3

Cooling curve 3 is a faster cooling rate than annealing and may be considered typical of normalizing. The diagram indicates that transformation will start at $x_{3,}$ with the formation of coarse pearlite, and ends at $x^*_{3,}$ with the formation of medium pearlite. Here, we are clearly observing the temperature difference between $x_3 - x^*_3$ and $x_1 - x^*_1$, so that microstructure will show a greater variation in fineness of pearlite.

Cooling curves and the I-T diagram

Curve 4

Cooling curve 4, typical of a slow oil quench, is similar to the one just described, and the microstructure will be a mixture of medium and fine pearlite.

Curve 5

Cooling curve 5, typical of an intermediate cooling rate, will start to transform at x_5 to fine pearlite in a relative short time. After some temperature, the cooling curve is going in a direction of decreasing percent transformed. Since pearlite cannot form austenite on cooling, the transformation must stop at $x^*_{5.}$ The microstructure at this point will consists, fine pearlite surrounding with austenitic grains. It will remain in this condition until the M_s line is crossed $x^{**}_{5.}$ The remaining austenite now transforms to martensite. The final microstructure consists, martensite and fine nodular pearlite largely concentrated along the original austenite grain boundaries.

Curve 6

Cooling curve 6, typical of drastic quench, is rapid enough to avoid transformation in the nose region. It remains austenitic until the M_s line is reached at $x_{6.}$ Transformation to martensite will take place between the M_s and M_F lines. The final microstructure will be entirely martensite of high hardness.

Cooling curves and the I-T diagram

Curve 7

Cooling curve 7, which is tangent to the nose, would be the approximate critical cooling rate (CCR) for the steel. Any cooling rate slower than the one indicated will cut the curve above the nose and form some softer transformation product. Any cooling rate faster than the one illustrated will form only martensite. To obtain a fully Martensitic structure it is necessary to avoid transformation in the nose region.

Curve 8

It is possible to form 100 % pearlite or 100% martensite by continuous cooling, but it is not possible to form 100% bainite. A complete bainitic structure may be formed only by cooling rapidly enough to miss the nose of the curve and then holding in the temperature range at which bainite is formed until transformation is complete. This is illustrated by cooling curve 8. It is apparent that continuously cooled steel samples will contain only small amounts of bainite, and this is probably the reason why this structure was not recognized until the isothermal study.

Factors affecting on TTT diagram

- Composition of steel
  - → carbon wt%,
  - → alloying element wt%

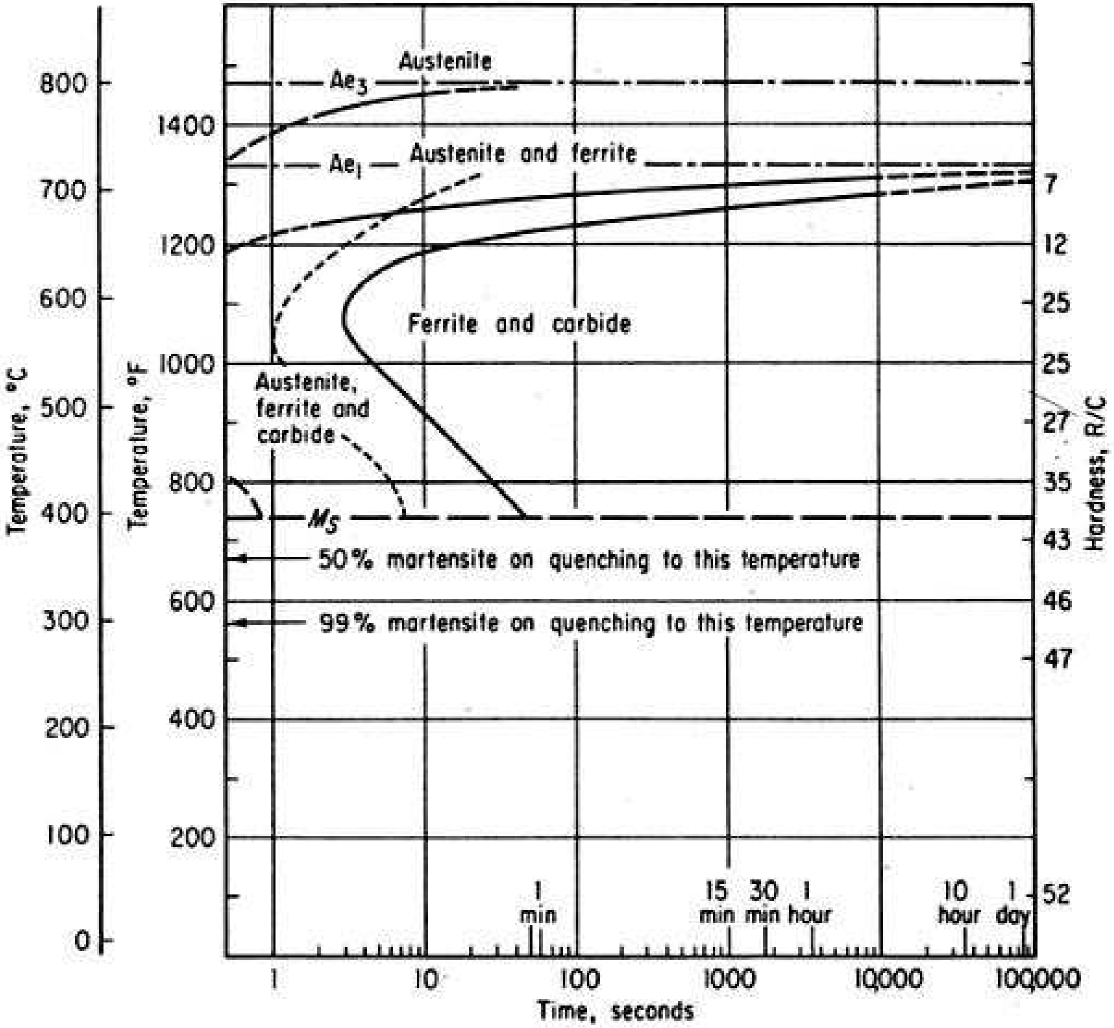
- Grain size of austenite

- Heterogeneity of austenite

Composition

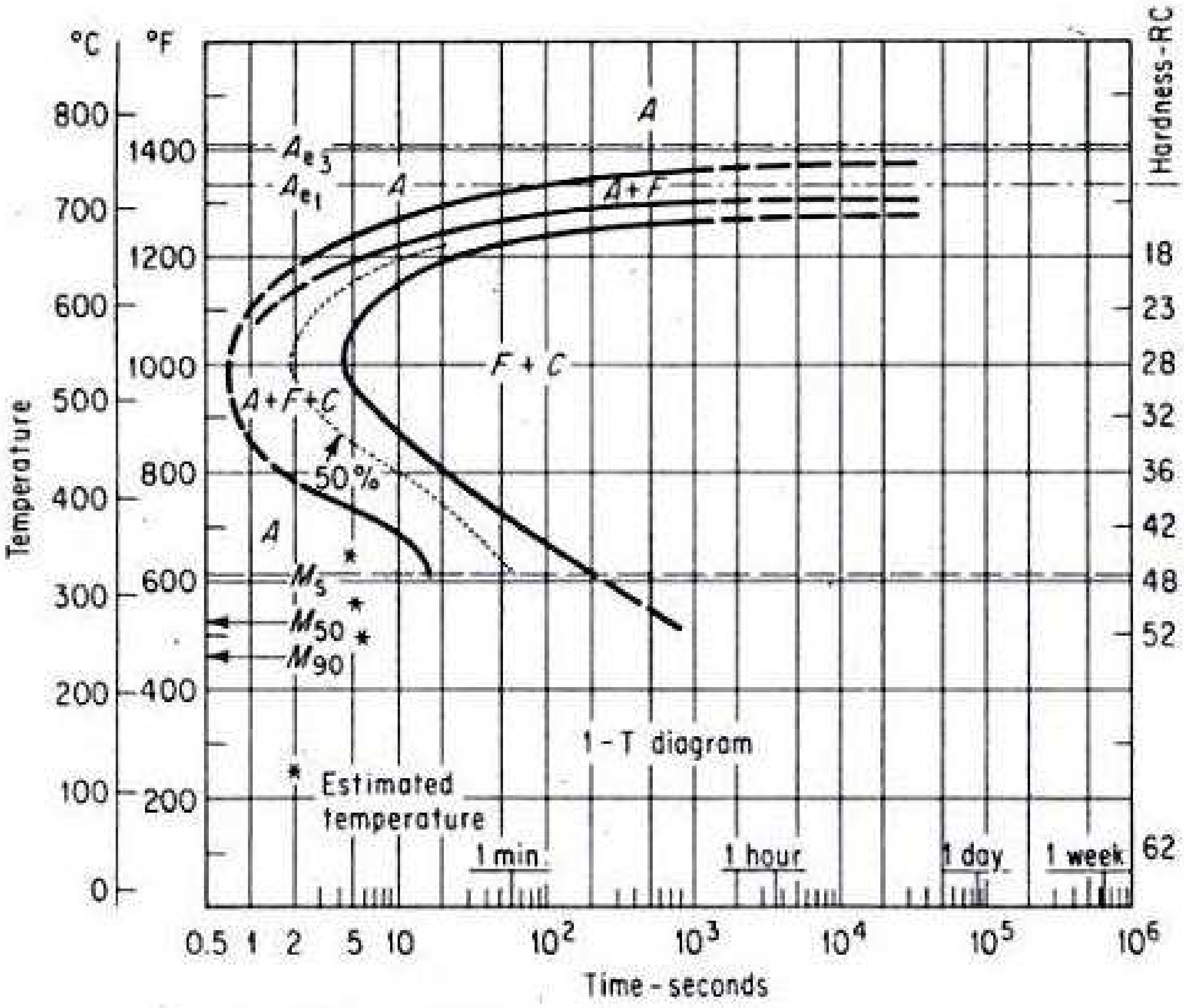
- ☐ With some limitations, an increase in carbon or alloy content or in grain size of the austenite always retards transformation (*moves curves to the right*), at least at temperatures at or above the nose region. This in turn slows up the critical cooling rate, making is easier to form martensite.
- ☐ This retardation is also reflected in the greater hardenability, or depth of penetration of hardness, of steel with higher alloy content or larger austenitic grain size.

I.T diagram of a 1035 steel



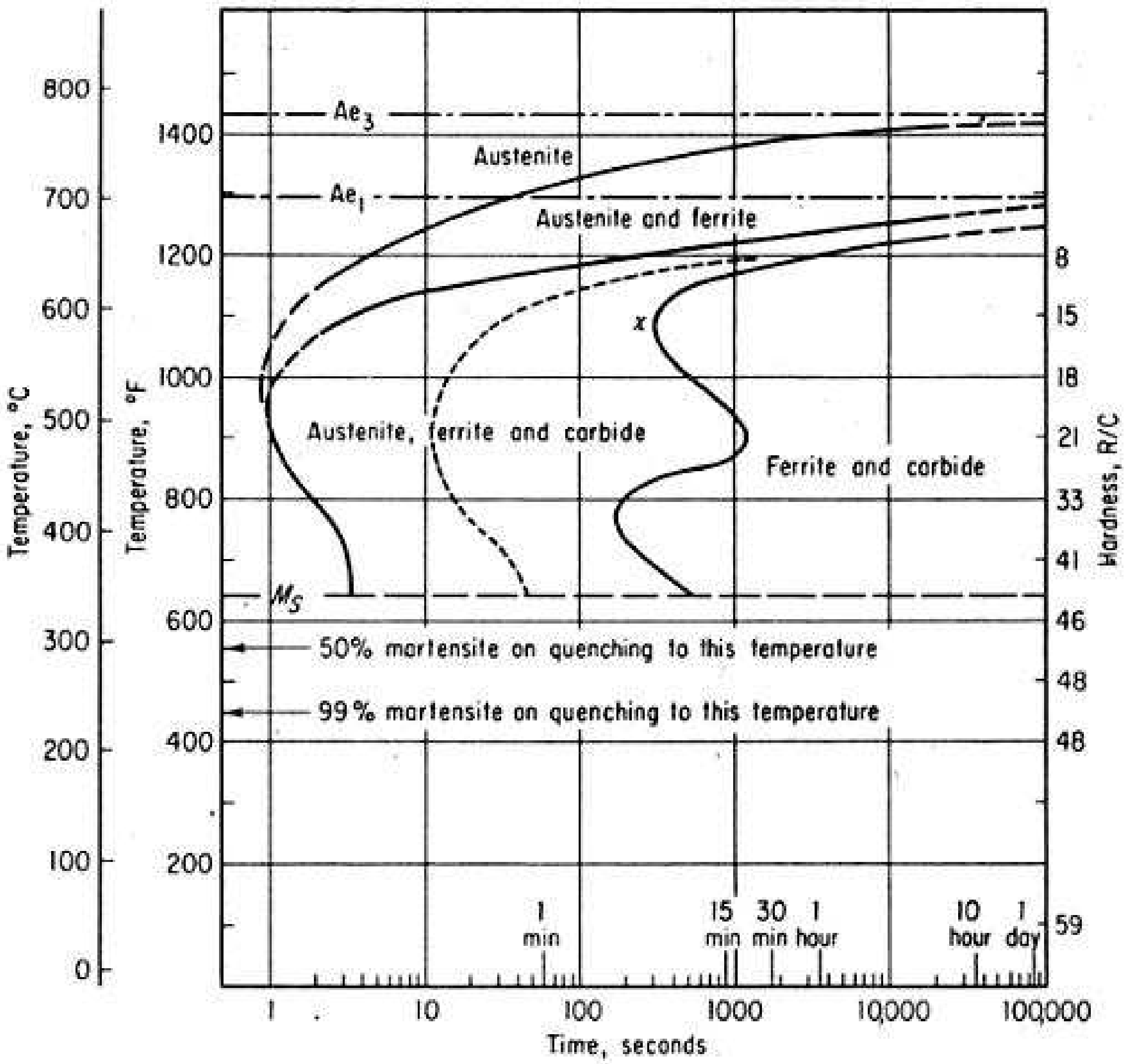
This is a hypo-eutectoid steel, notice the presence of the austenite to ferrite region. The nose of the curve is not visible, indicating that it is very difficult to cool this steel fast enough to obtain only martensite. The microstructure of a low carbon steel water quenched shows a white ferrite network surrounding the gray low carbon martensite areas.

I.T diagram of a 1050 steel



The microstructure of a medium carbon steel water quenched, shows dark areas of fine pearlite that seem to outline some of the previous austenite grain boundaries, some dark feathery bainite, and substantially more martensite as the matrix than appeared in the low carbon steel.

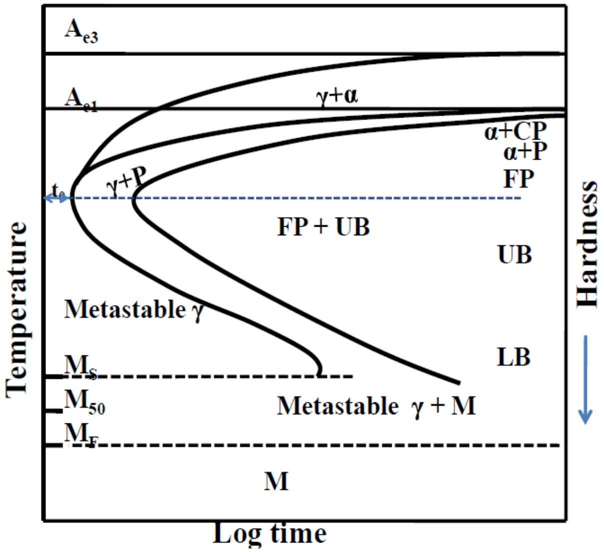
I.T diagram of a 1335 steel



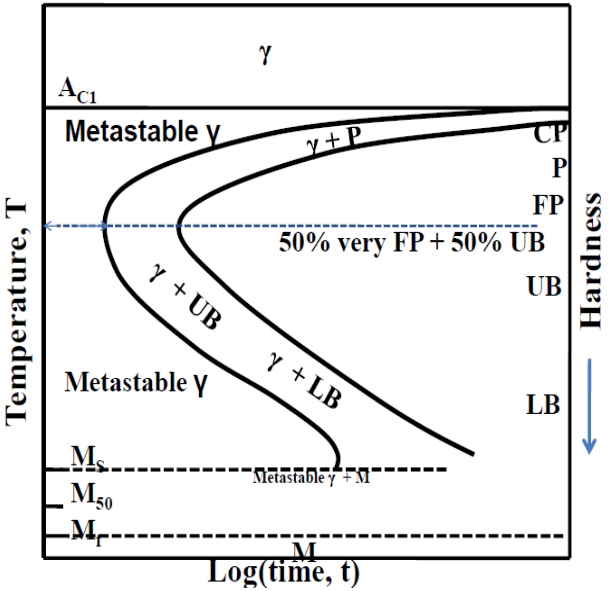
Alloy additions tend in general to delay the start of transformation and to increase the time for its completion, they differ greatly in both magnitude and nature of their effects. Above diagram shows the 1335 manganese steel.

Heterogeneity of austenite

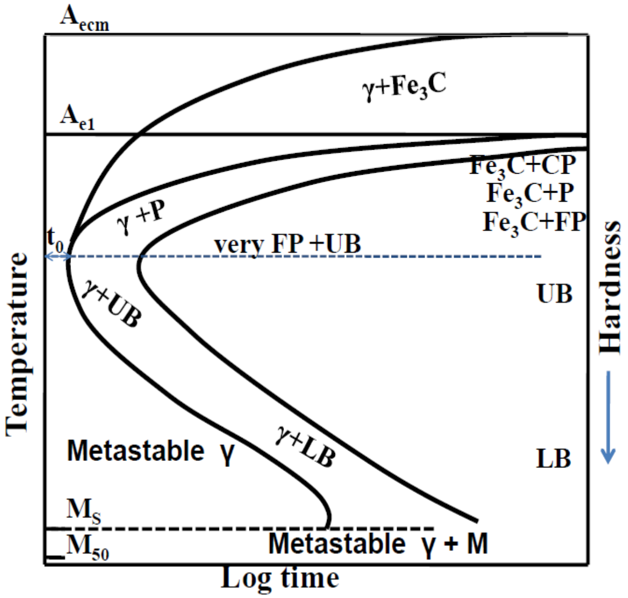
- Heterogenous austenite increases transformation time range, start to finish of ferritic, pearlitic and bainitic range as well as increases the transformation temperature range in case of martensitic transformation and bainitic transformation. Undissolved cementite, carbides act as powerful inocculant for pearlite transformation. Therefeore heterogeneity in austenite increases the transformation time range in diffussional transformation and temperature range of shear transformation products in TTT diagram.



TTT diagram for hypo-eutectoid steel



TTT diagram for eutectoid steel



TTT diagram for hyper-eutectoid steel

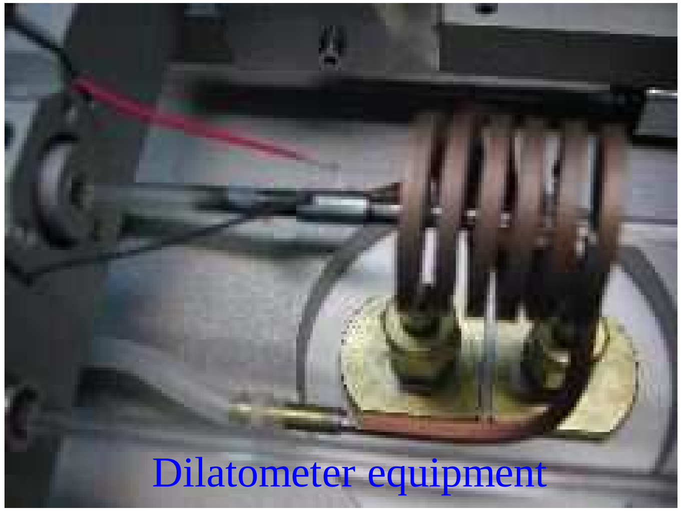
Continuous Cooling Transformation diagrams

- The TTT diagrams are also called Isothermal Transformation Diagrams, because the transformation times are representative of isothermal hold treatment (following a instantaneous quench).
- In practical situations we follow heat treatments (T-t procedures/cycles) in which (typically) there are steps involving cooling of the sample. The cooling rate may or may not be constant. The rate of cooling may be slow (as in a furnace which has been switch off) or rapid (like quenching in water).
- Hence, in terms of practical utility TTT curves have a limitation and we need to draw separate diagrams called Continuous Cooling Transformation diagrams (CCT), wherein transformation times (also: products & microstructure) are noted using constant rate cooling treatments. A diagram drawn for a given cooling rate (dT/dt) is typically used for a range of cooling rates (thus avoiding the need for a separate diagram for every cooling rate).
- However, often TTT diagrams are also used for constant cooling rate experiments- keeping in view the assumptions & approximations involved.
- The CCT diagram for eutectoid steel is considered next.
- *Important difference between the CCT & TTT transformations is that in the CCT case Bainite cannot form.*

Determination of CCT diagram for eutectoid steel

- CCT diagrams are determined by measuring some physical properties during continuous cooling. Normally these are specific volume and magnetic permeability. However, the majority of the work has been done through specific volume change by dilatometric method. This method is supplemented by metallography and hardness measurement.
- In dilatometry the test sample is austenitised in a specially designed furnace and then controlled cooled. Sample dilation is measured by dial gauge/sensor. Slowest cooling is controlled by furnace cooling but higher cooling rate can be controlled by gas quenching


Sample and fixtures
for dilatometric measurements


Dilatometer equipment

Determination of CCT diagram for eutectoid steel

- Cooling data are plotted as temperature versus time (Fig. a). Dilation is recorded against temperature (Fig. b). Any slope change indicates phase transformation. Fraction of transformation roughly can be calculated based on the dilation data as explained below.

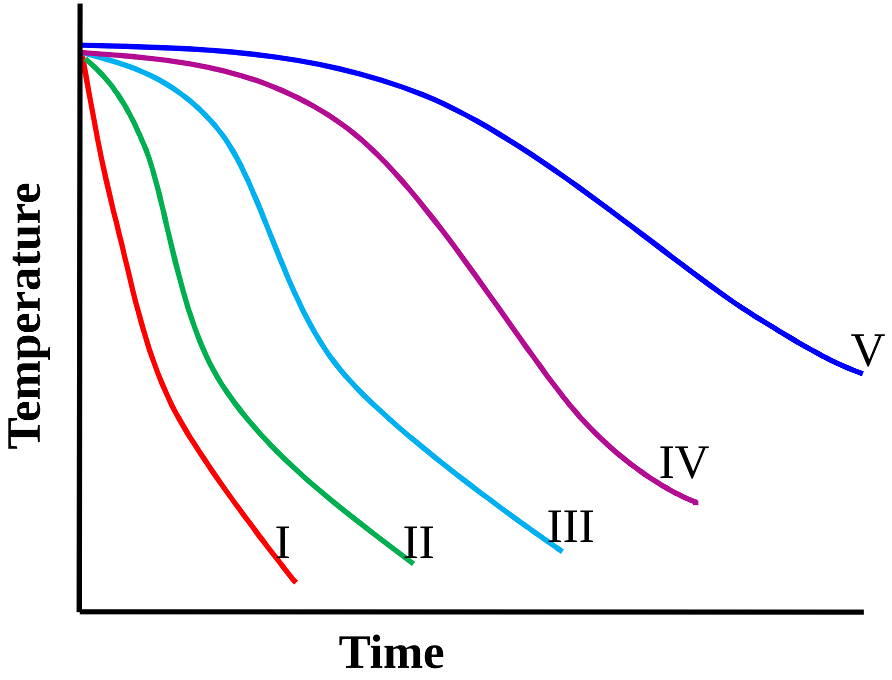


Fig. a : Schematic cooling curves

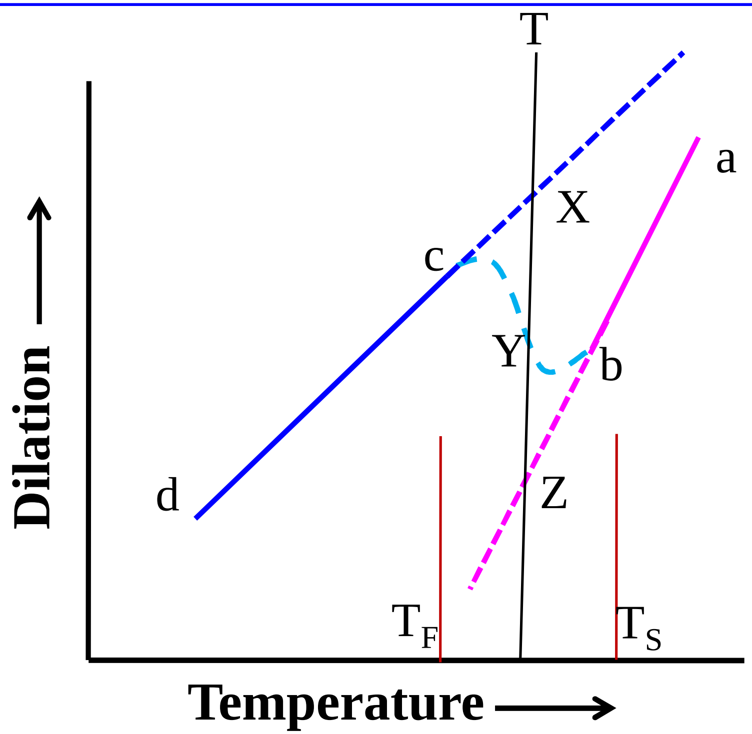


Fig. b : Dilation-temperature plot for a cooling curve

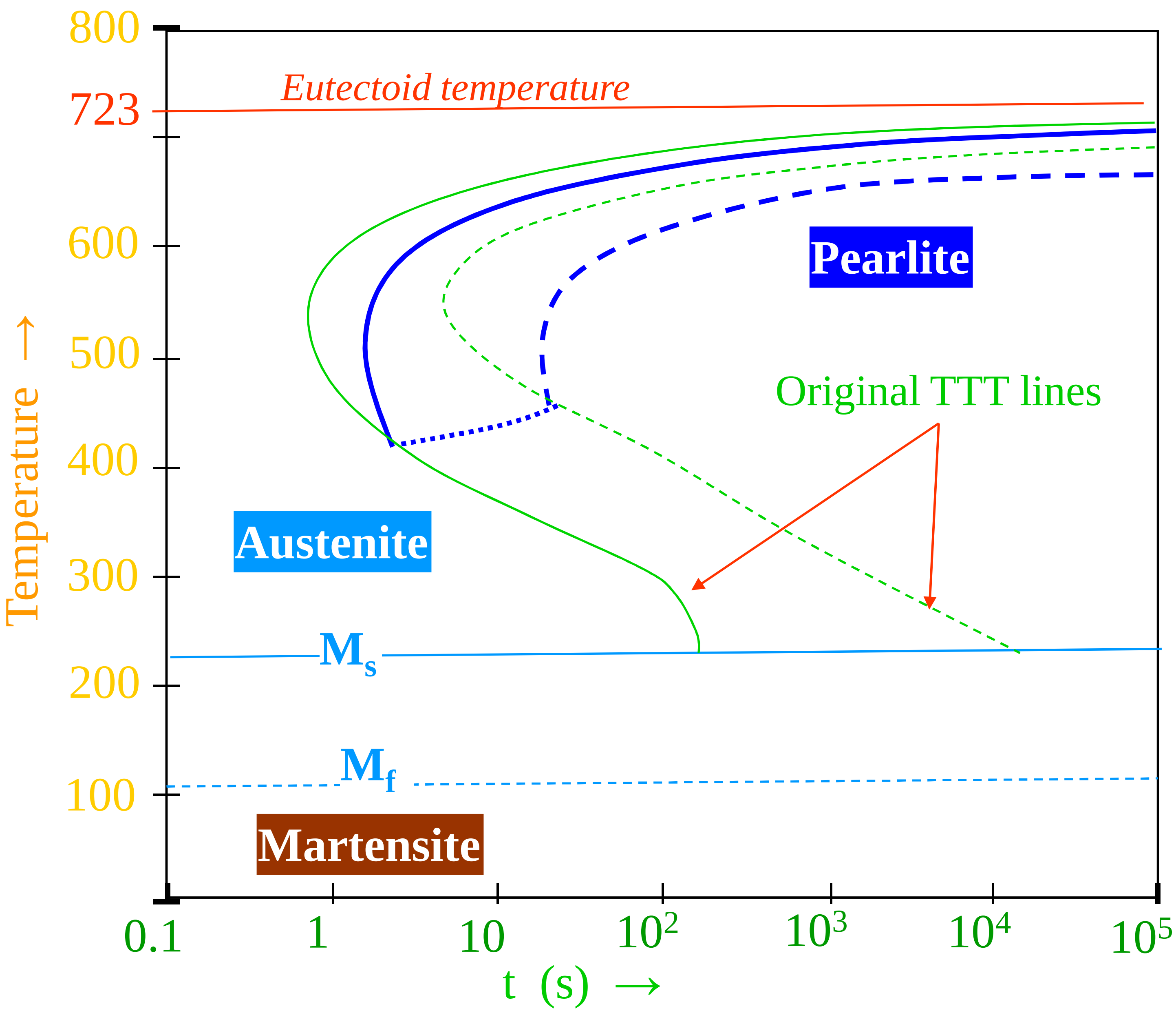
Determination of CCT diagram for eutectoid steel

- In **Fig. a** curves I to V indicate cooling curves at higher cooling rate to lower cooling rate respectively. **Fig. b** gives the dilation at different temperatures for a given cooling rate/schedule.
- In general slope of dilation curve remains unchanged while amount of phase or the relative amount of phases in a phase mixture does not change during cooling (or heating) however sample shrink or expand i.e. dilation takes place purely due to thermal specific volume change because of change in temperature.
- Therefore in **Fig. b** dilation from a to b is due to specific volume change of high temperature phase austenite. But at T_S slope of the curve changes. Therefore transformation starts at T_S. Again slope of the curve from c to d is constant but is different from the slope of the curve from a to b. This indicates there is no phase transformation between the temperature from c to d but the phase/phase mixture is different from the phase at a to b.
- Slope of the dilation curve from b to c is variable with temperature. This indicates the change in relative amount of phase due to cooling. The expansion is due to the formation of low density phase(s). Some part of dilation is compensated by purely thermal change due to cooling. Therefore dilation curve takes complex shape. i.e first slope reduces and reaches to a minimum value and then increases to the characteristic value of the phase mixture at c.

Determination of CCT diagram for eutectoid steel

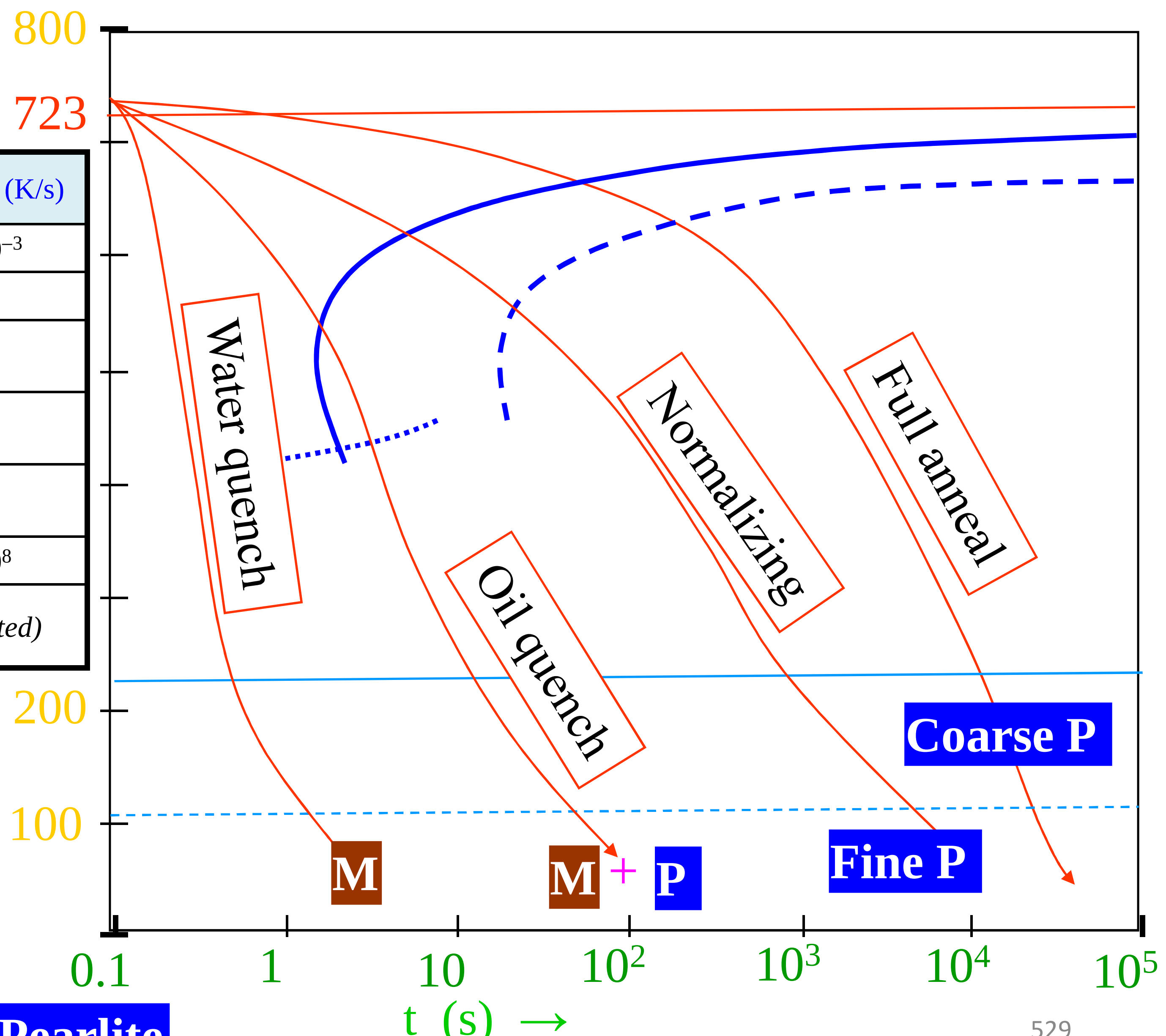
- Therefore phase transformation start at b i.e. at temperature T_S and transformation ends or finishes at c or temperature T_F. The nature of transformation has to be determined by metallography. When austenite fully transforms to a single product then amount of transformation is directly proportional to the relative change in length. For a mixture of products the percentage of austenite transformed may not be strictly proportional to change in length, however, it is reasonable and generally is being used.
- Cumulative percentage of transformation at in between temperature T is equal to YZ/XZ*100 where X, Y and Z are intersection point of temperature T line to extended constant slope curve of austenite (ba), transformation curve (bc) and extended constant slope curve of low temperature phase (cd) respectively.
- So at each cooling rate transformation start and finish temperature and transformation temperature for specific amount (10 %, 20%, 30% etc.) can also be determined. For every type of transformation, locus of start points, isopercentage points and finish points give the transformation start line, isopercentage lines and finish line respectively and that result CCT diagram. Normally at the end of each cooling curve hardness value of resultant product at room temperature and type of phases obtained are shown.

CCT curves for eutectoid steel



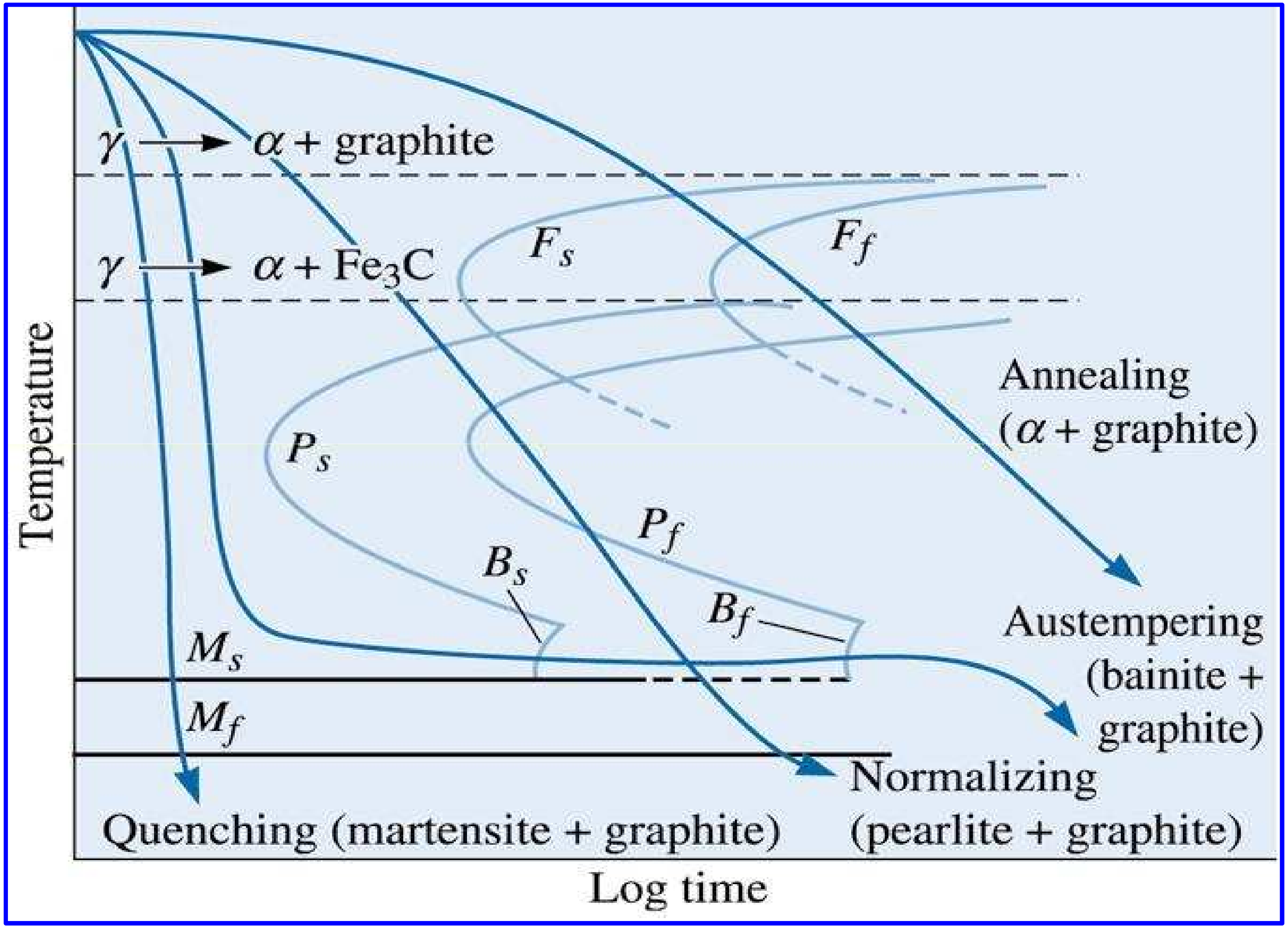
Different cooling treatments for eutectoid steel

Process	Cooling rate (K/s)
Annealing	10^{-5} – 10^{-3}
Air Cooling	1 – 10
Oil Quenching	~100
Water Quenching	~500
Splat Quenching	10^{5}
Melt-Spinning	10^{6} – 10^{8}
Evaporation, sputtering	10^{9} *(expected)*



M = Martensite **P = Pearlite**

Transformation diagram for cast iron



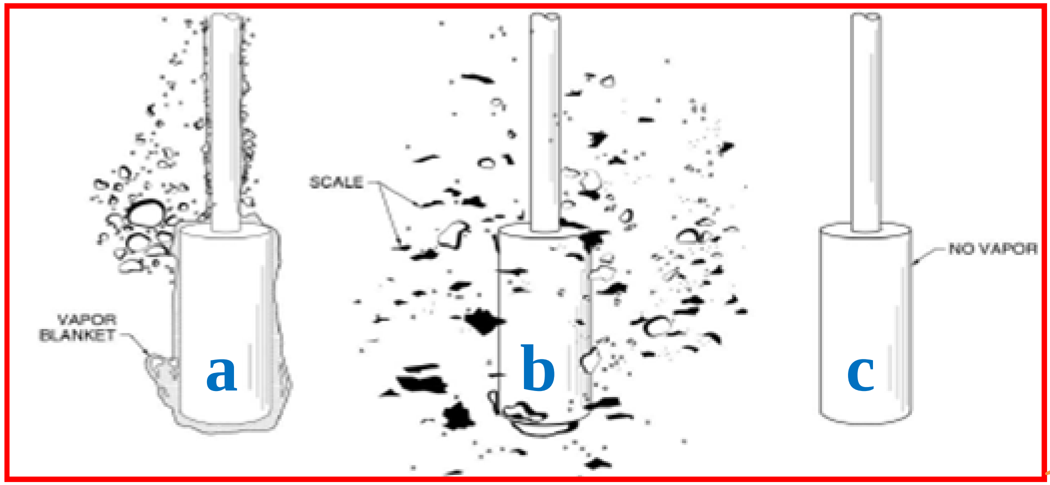
Homogeneity of austenite

- This refers to the uniformity in carbon content of the austenite grains. If a hypo-eutectoid steel is heated for hardening, when the A_1 line is crossed, the austenite grains formed from pearlite will contain 0.8 percent carbon.
- With continued heating, the austenite grains formed from pro-eutectoid ferrite will contain very little carbon, so that when the A_3 line is crossed, the austenite grains will not be uniform in carbon content.
- Upon quenching, the austenite grains leaner in carbon, having a fast critical cooling rate, tend to transform to nonmartensitic structures, while those richer in carbon, having a slower critical cooling rate, tend to form martensite. This results a non uniform microstructure with variable hardness . This condition may be avoided by very slow heating, so that uniformity is established by carbon diffusion during heating. *It is recommended that the material be held at the austenitizing temperature 1hour for each inch of thickness or diameter*
- The recommended austenitizing temperature for hypo-eutectoid steels is about 30˚C above the A_3 line. This same as the recommended annealing temperature.
- For hyper-eutectoid steels the recommended austenitizing temperature is usually between the A_{cm} and $A_{3,1}$ lines.
- The A_{cm} line rises so steeply that an excessively high temperature may be required to dissolve all the proeutectoid cementite in the austenite. This tends to develop undesirable coarse austenitic grain size, with danger of cracking on cooling.

Quenching

Mechanism

- The properties of materials alter by different heat treating processes by varying the cooling rate followed by quenching. If the actual cooling rate (ACR) exceeds the critical cooling rate, only martensite will result. If the actual cooling rate is less than the critical cooling rate (CCR), the part will not completely harden. So that, difference in cooling rates leads to variation in properties. *At this point, it is necessary to understand the mechanism of heat removal during quenching.*
- A cooling curve shows the variation of temperature with time during quenching. A cooling rate, however, shows the rate of change of temperature with time.
- The cooling rate at any temperature may be obtained from the cooling curve by drawing a tangent to the curve at that temperature and determining the slope of the tangent. It is apparent that the cooling rate is constantly changing with time.



a- Vapor-blanket cooling stage
b- Vapor-transport cooling stage
c- Liquid cooling stage

Quenching

Vapor-blanket cooling stage

- ❑ In this stage, quenching medium is vaporized at the surface of the metal and forms a thin stable layer.
- ❑ Cooling is by conduction and radiation.
- ❑ Cooling rate is relatively slow

Vapor-transport cooling stage

- ❑ This stage starts when the metal has cooled to a temperature at which the vapor film is no longer stable. Wetting of the metal surface by the quenching medium and violent boiling occur. Heat is removed from the metal very rapidly as the latent heat of vaporization. This is the fastest stage of cooling.

Liquid cooling stage

- ❑ This stage starts when the surface temperature of the metal reaches the boiling point of the quenching liquid .
- ❑ Vapor no longer forms, so cooling is by conduction and convection through the liquid. The rate of cooling is slowest in this stage.

Factors affecting on Quenching

Many factors determine the actual cooling rate. The most important are the type of quenching medium, the temperature of the quenching medium, the surface condition of the part, and the size and mass of the part.

Quenching Medium

- ❑ Brine solution (Water solution of 10% sodium chloride)
- ❑ Tap water
- ❑ Fused or liquid salts
- ❑ Soluble oil and water solutions
- ❑ Oil
- ❑ Air

Temperature of Quenching Medium

- ❑ Generally, as the temperature of the medium rises, the cooling rate decreases. This is due to the increase in persistence of the vapor-blanket stage. This is particular true of water and brine.
- ❑ In another case, an increase in cooling rate with a rise in temperature of the medium. In the case of oil, as the temperature of the oil rises there is a tendency for the cooling rate to decrease due to the persistence of the vapor film. However, as the temperature of the oil rises it also become more fluid, which increase the rate of heat conduction through the liquid.

Factors affecting on Quenching

Severity of quench values of some typical quenching conditions

Process	Variable	H Value
Air	No agitation	0.02
Oil quench	No agitation	0.2
"	Slight agitation	0.35
"	Good agitation	0.5
"	Vigorous agitation	0.7
Water quench	No agitation	1.0
"	Vigorous agitation	1.5
Brine quench (saturated Salt water)	No agitation	2.0
"	Vigorous agitation	5.0
Ideal quench		∞

If the increase in rate of heat conduction is greater than the decrease due to persistence of the vapor film, the net result will be an increase in the actual cooling rate. However if the reverse is true, then the result will be decrease in cooling rate.

Severity of Quench as indicated by the heat transfer equivalent H

$$H = \frac{f}{K} \qquad [m^{-1}]$$

f → heat transfer factor
K → Thermal conductivity

Note that apart from the nature of the quenching medium, the vigorousness of the shake determines the severity of the quench. When a hot solid is put into a liquid medium, gas bubbles form on the surface of the solid (interface with medium). As gas has a poor conductivity the quenching rate is reduced. Providing agitation (shaking the solid in the liquid) helps in bringing the liquid medium in direct contact with the solid; thus improving the heat transfer (and the cooling rate). The H value/index compares the relative ability of various media (gases and liquids) to cool a hot solid. Ideal quench is a conceptual idea with a heat transfer factor of ∞ (⇒ H = ∞)

Factors affecting on Quenching

Surface condition

- ☐ When the steel is exposed to an oxidizing atmosphere, because of the presence of water vapor or oxygen in the furnace a layer of iron oxide called *scale* is formed. Experiments have shown that a thin layer of scale has very little effect on the actual cooling rate, but that a thick layer of scale (0.005 inch in deep) retards the actual cooling rate.
- ☐ There is also the tendency for parts of the scale to peel off the surface when the piece is transferred from the furnace to the quench tank, thus giving rise to a variation in cooling rate at different points on the surface. *The presence of scale is need to be considered only if the actual cooling rate is very close to critical cooling rate.*
- ☐ To minimize the formation of scale, we have different methods depend upon part being heat treated, type of furnace used, availability of equipment and cost.
  - ✓ Copper plating
  - ✓ Protective atmosphere
  - ✓ Liquid salt pots
  - ✓ Cast iron chips

Factors affecting on Quenching

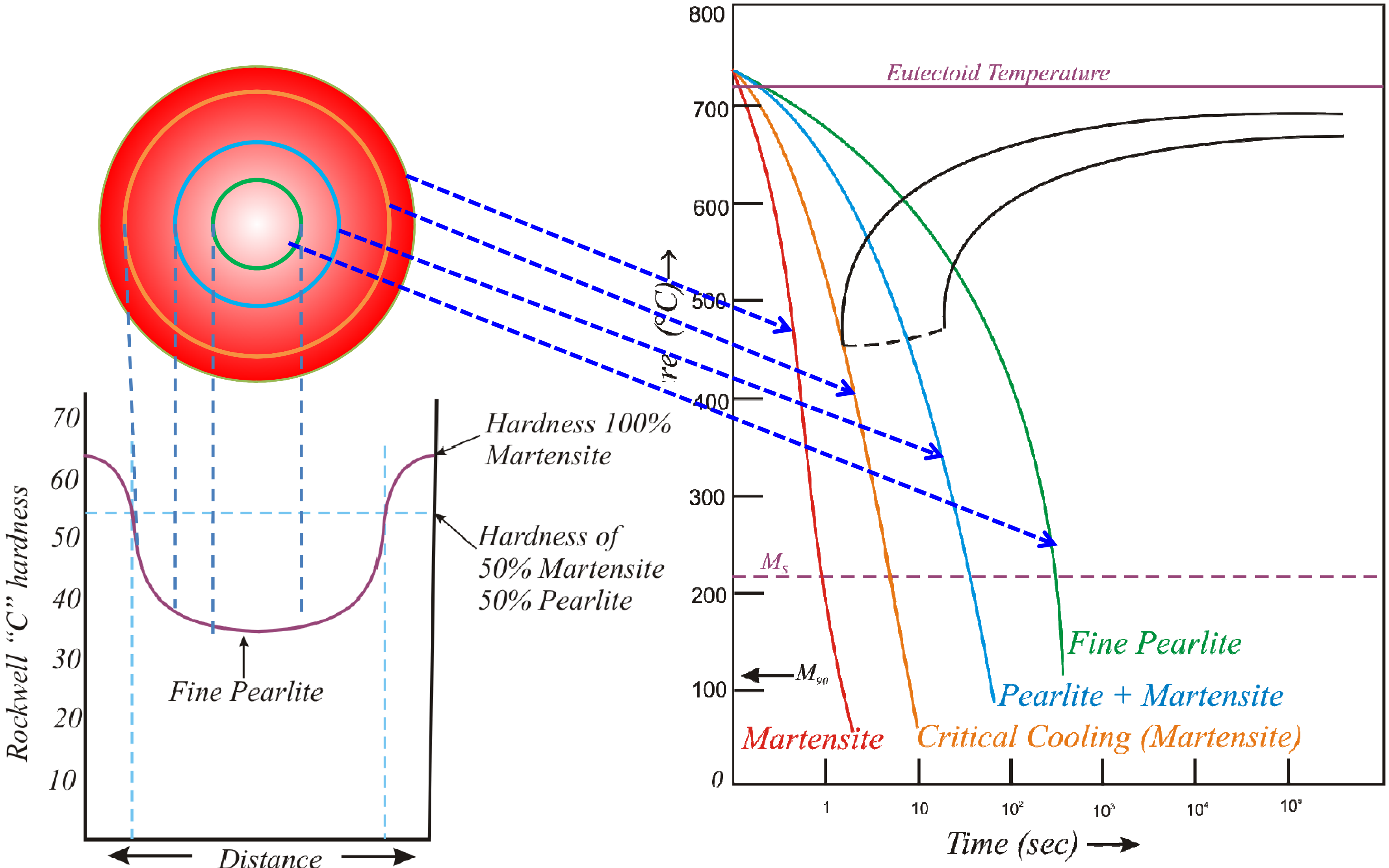
Size and mass

- ☐ The ratio of surface area to mass is an important factor in determining the actual cooling rate, because only the surface of a part which is in contact with the quenching medium.
- ☐ Thin plates and small diameter wires have a large ratio of surface area to mass and therefore rapid cooling rates.

$$For\ Cylinder \qquad \frac{Surface area}{Mass} = \left(\frac{\pi DL}{(\pi/4)D^2 L\rho} \right)$$

- ☐ The calculation shows that the ratio is inversely proportional to diameter if the diameter is increased, the ratio of surface area to mass decreases, and the cooling rate decreases.
- ☐ The heat in the interior of the piece must be removed by conduction, through the body of the piece, eventually reaching the surface and the quenching medium. Therefore the cooling rate in the interior is less than that at the surface.
- ☐ If such variation in cooling rates exists across the radius of a bar during cooling, it is to be anticipated that variations in hardness would be evident when the bars are cut and hardness surveys made on the cross section. A considerable temperature difference between the surface and the center during quenching (*see in next slide*).
- ☐ This temperature difference will give rise to stresses during heat treatment called residual stresses, which may result in distortion and cracking of the piece.

Hardness profile in a cylinder from surface to interior

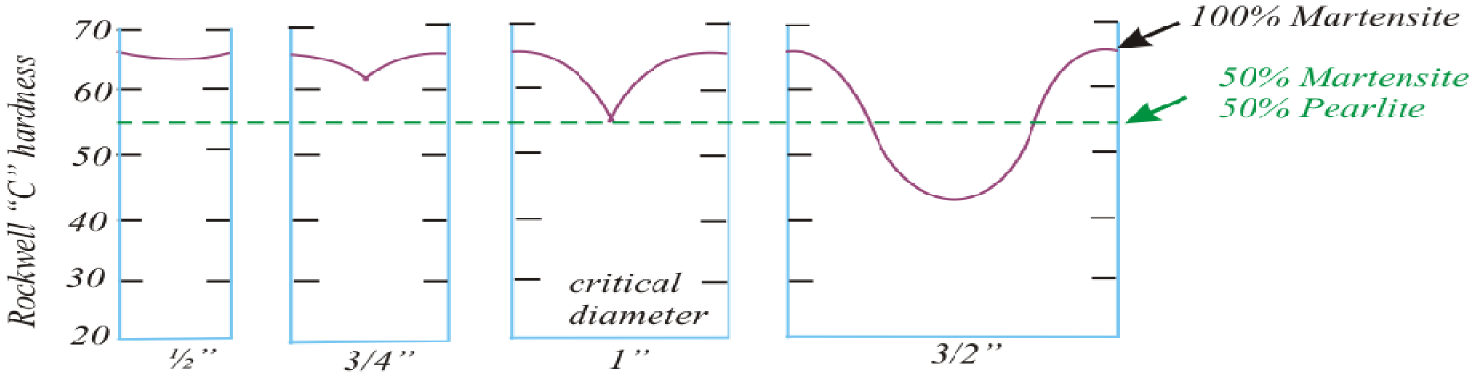


Typical hardness test survey made along a diameter of a quenched cylinder

Schematic showing variation in cooling rate from surface to interior leading to different microstructures

Hardenability

- From the earlier study, we seen that, hardness profile various from case to core. It leads to an important conclusion that, by varying the diameter of cylinder with same composition will give the different hardness profiles, i.e., depth of hardness is different from different size of samples. Generally this diagrams called as hardness-penetration diagrams or hardness-traverse diagrams.
- Hardenability is the ability of a steel to partially or completely transform from austenite to some fraction of martensite at a given depth below the surface, when cooled under a given condition.
- For example, a steel of a high hardenability can transform to a high fraction of martensite to depths of several millimeters, under relatively slow cooling, such as an oil quench, whereas a steel of low hardenability may only form a high fraction of martensite to a depth of less than a millimeter, even under rapid cooling such as a water quench. *Hardenability therefore describes the capacity of the steel to harden in depth under a given set of conditions.*

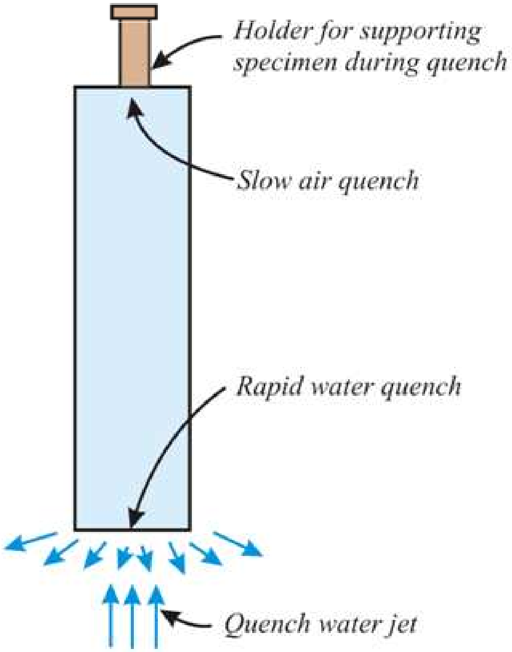


Hardenability

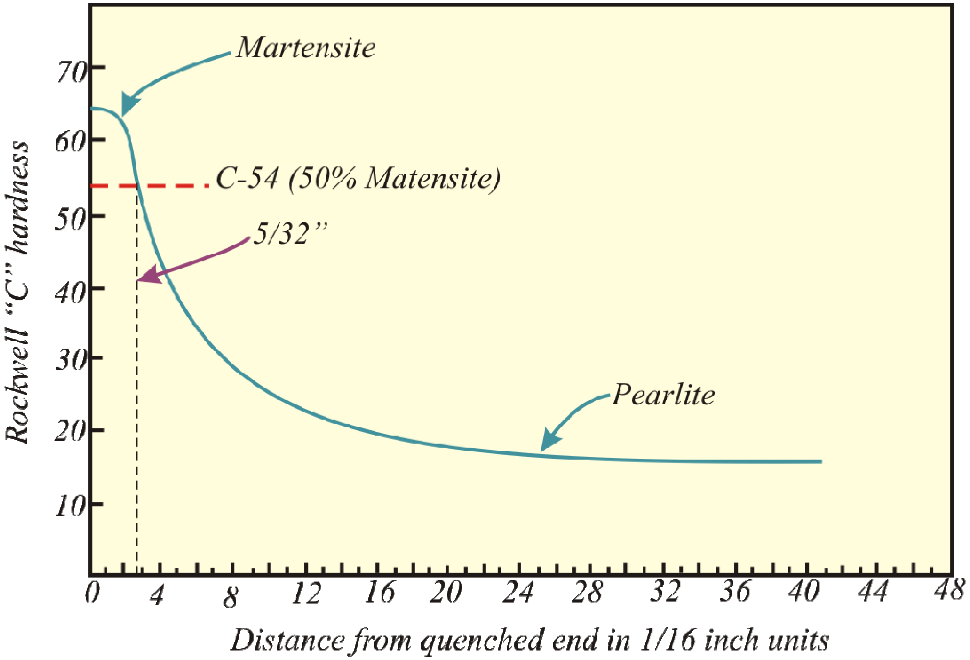
- Increase in the hardenability or depth of penetration of the hardness may be accomplished by either of two methods:
  1. With the actual cooling rates fixed, slow up the critical cooling rate (shift the I-T curve to the right) by adding alloying elements or coarsening the austenitic grain size.
  2. With the I-T curve fixed, increase the actual cooling rates by using a faster quenching medium or increasing circulation.
- *Since increasing cooling rates increase the danger of distortion or cracking, the addition of alloying elements is the more popular method of increasing hardenability.*
- Steels with high hardenability are needed for large high strength components, such as large extruder screws for injection moulding of polymers, pistons for rock breakers, aircraft undercarriages etc.
- Steels with low hardenability may be used for smaller components, such as chisels and gears etc.
- The most widely used method of determining hardenability is the end-quench hardenability test or the Jominy test, commonly called as Jominy End Quench test.

Jominy End Quench Test

- ❑ In conducting this test, a 1 inch round specimen 4 inch long is heated uniformly to the proper austenising temperature. It is then removed from the furnace and placed on a fixture where a jet of water impinges on the bottom face of the sample.
- ❑ After 10 min. on the fixture, the specimen is removed, and to cut along the longitudinal direction. And then Rockwell C scale hardness readings are taken at 1/16 inch, intervals from the quenched end. The results are expressed as a curve of hardness values Vs. distance from the quenched end. A typical hardenability curve shown below for eutectoid steel.



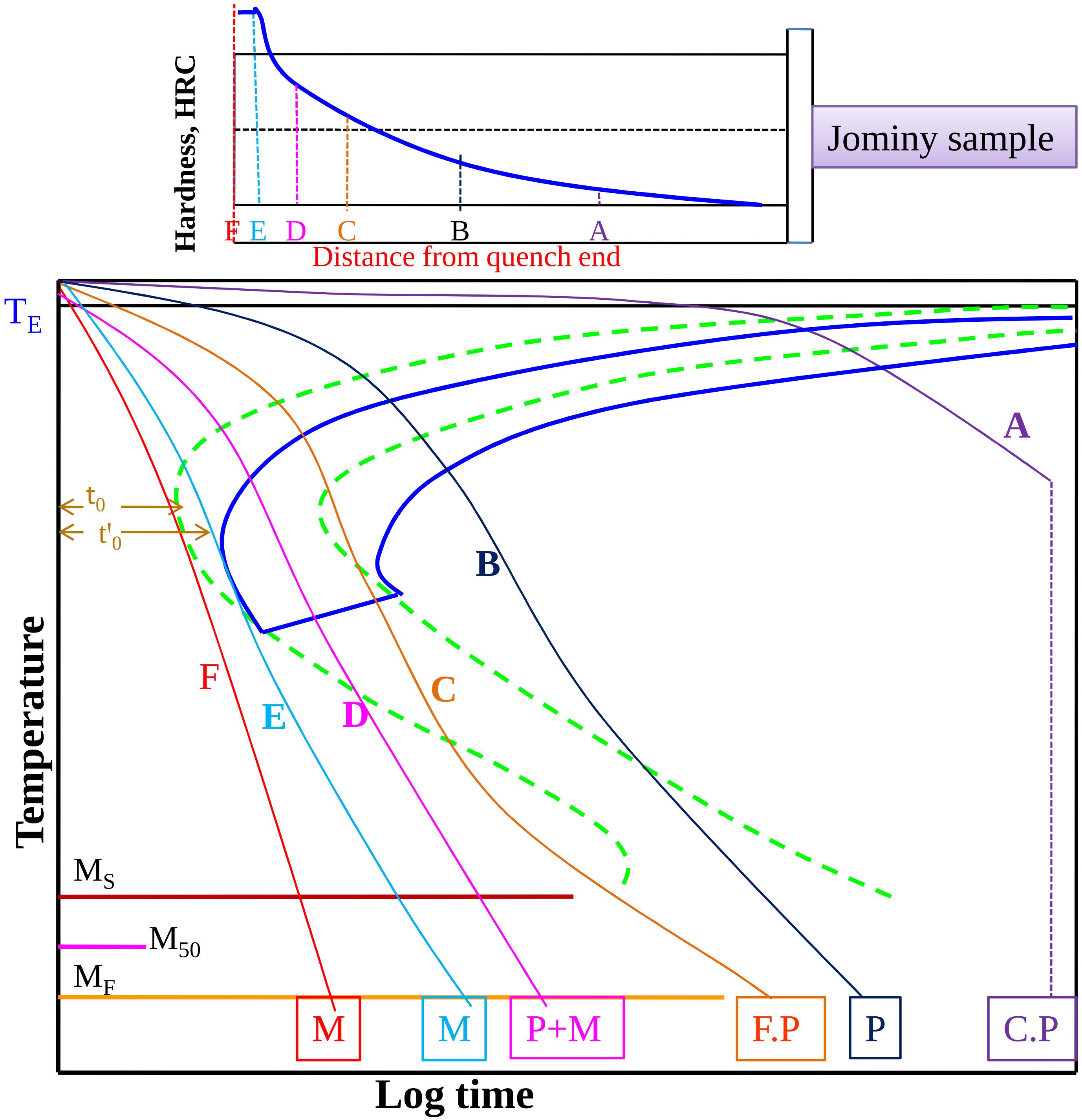
Jominy Sample



Variation of hardness along a Jominy bar

Jominy End Quench Test

- A number of Jominy end quench samples are first end- quenched for a series of different times and then each of them (whole sample) is quenched by complete immersion in water to freeze the already transformed structures.
- Cooling curves are generated putting thermocouple at different locations and recording temperature against cooling time during end quenching. Microstructures at the point where cooling curves are known, are subsequently examined and measured by quantitative metallography. Hardness measurement is done at each investigated point.
- Based on metallographic information on investigated point the transformation start and finish temperature and time are determined. The transformation temperature and time are also determined for specific amount of transformation.
- These are located on cooling curves plotted in a temperature versus time diagram. The locus of transformation start, finish or specific percentage of transformation generate CCT diagram (*see next slide*).
- A, B, C, D, E, F are six different locations on the Jominy sample shown in *Figure (before slide)* that gives six different cooling rates. The cooling rates A, B, C, D, E, F are in increasing order. The corresponding cooling curves are shown on the temperature log time plot. At the end of the cooling curve phases are shown at room temperature. Variation in hardness with distance from Jominy end is also shown in the diagram.



t_o=Minimum incubation period at the nose of the TTT diagram,
t'_o=minimum incubation period at the nose of the CCT diagram

M – Martensite
P – Pearlite
F.P – Fine pearlite
C.P – Coarse pearlite
M_S – Martensite start
M_F – Martensite finish
T_E – Eutectoid temp.

Tempering

- ☐ Tempering is the re-heat treatment processes, to relieve the residual stresses and improve the ductility and toughness of steel. In other words, tempering is a processes to optimize the strength and toughness of steel.
- ☐ With the increase in temperature, carbon diffusion becomes appreciable and the metastable martensite decomposes to more stable products. Four stages of tempering are known.

Stage I

- ☐ Stage I of temperature extends from room temperature to 200°C. During this stage, the martensite decomposes to two phases: a low carbon martensite with 0.2%C some times known as black martensite, and ε (HCP, $Fe_{2.4}C$), a transition carbide.
- ☐ With increase in the carbon content of the steel, more ε-carbide forms. It precipitates very fine form and resolves only under the electron microscope. The hardening effect due to this precipitation is usually offset by the softening effect associated with the loss of carbon in martensite.

Tempering

Stage II

- ❑ Stage II tempering occurs in the range of 250-400°C changes the epsilon carbide to orthorhombic cementite, the low-carbon martensite becomes BCC ferrite, and any retained austenite is transformed to lower bainite as a function of time. The carbide are too small to be resolved by the optical microscope, and the entire structure etches rapidly to a black mass formerly called troostite.

Stage III

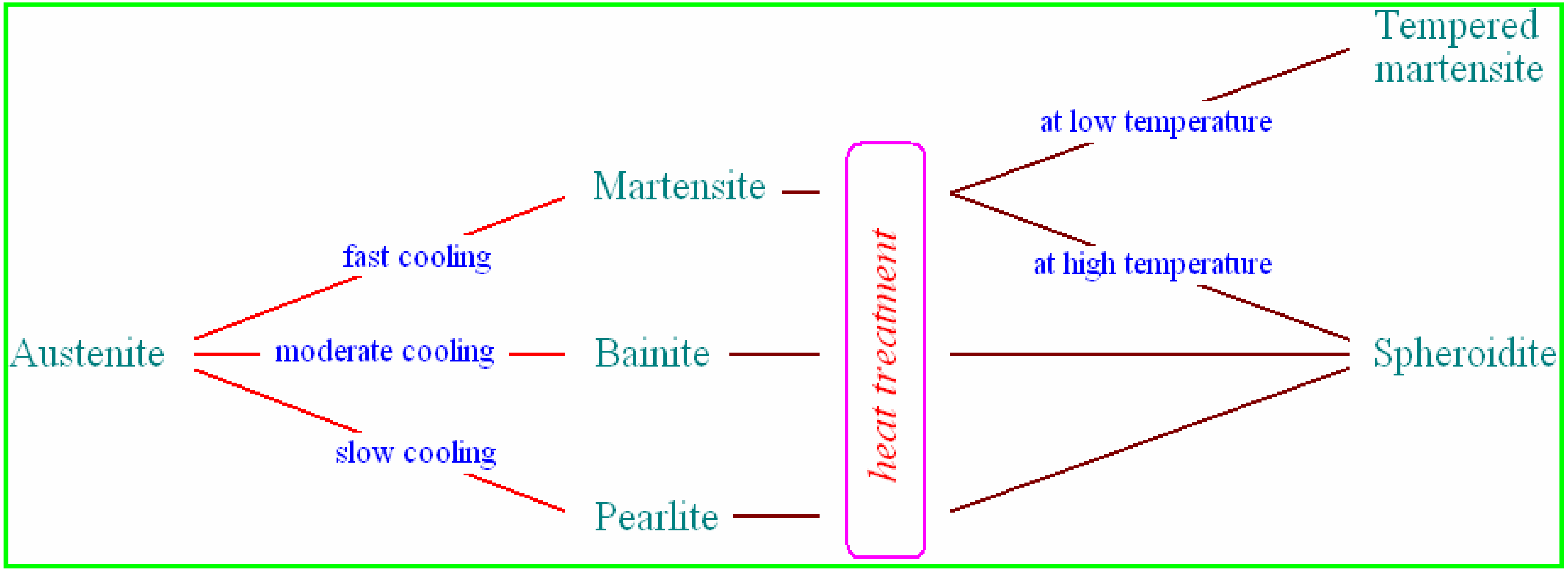
- ❑ Stage III tempering in the range of 400-650°C continues the growth of the cementite particles. This coalescence of the carbide particles allows more of the ferrite matrix to be seen, causing the sample to etch lighter than the low temperature product. In this structure formerly known as sorbite, it is resolvable above 500X, under electron microscopy it is clearly visible.

Stage IV

- ❑ Stage IV tempering in the range from 650-720°C produces large, globular cementite particles. This structure is very soft and tough and is similar to the spheroidized cementite structure. Spheroidite is the softest yet toughest structure that steel may have.

Tempering

- For many years , metallurgists divided the tempering processes into definite stages. For microstructures appearing in these stages was given names like Black Martensite, troostite and sorbite. However, the changes in microstructures are so gradual that it is more realistic to call the product of tempering at any temperature simply tempered martensite.



A schematic of possible transformations involving austenite decomposition

Tempering

- Tempering of some steels may result in a reduction of toughness what is known as temper embrittlement.
- This may be avoided by (1) compositional control, and/or (2) tempering above 575°C or below 375°C, followed by quenching to room temperature.
- The effect is greatest in Martensite structures, less severe in bainite structures and least severe in pearlite structures.
- It appears to be associated with the segregation of solute atoms to the grain boundaries lowering the boundary strength.
- Impurities responsible for temper brittleness are: P, Sn, Sb and As. Si reduces the risk of embrittlement by carbide formation. Mo has a stabilizing effect on carbides and is also used to minimize the risk of temper brittleness in low alloy steels.

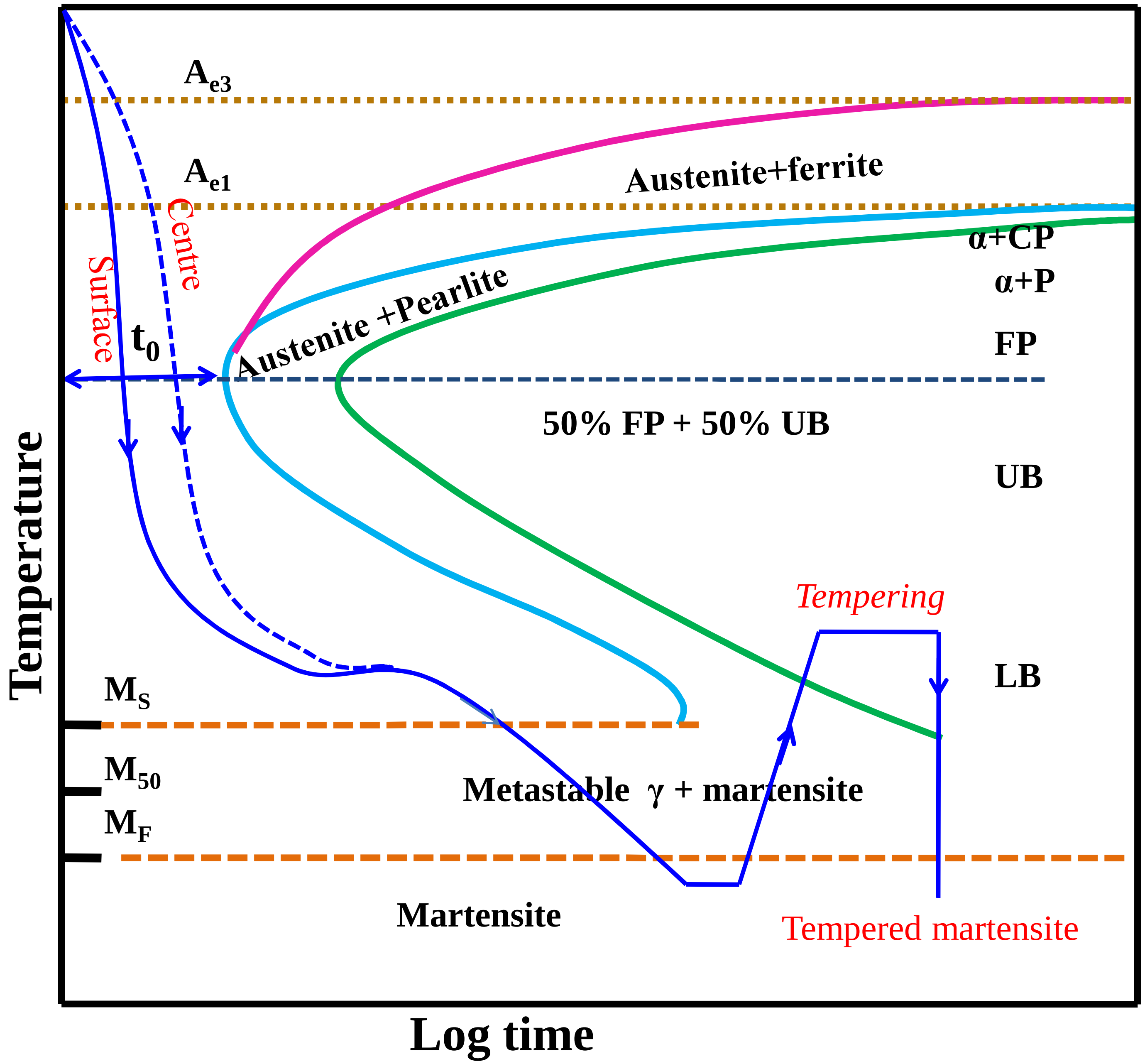
Summary

$$\underset{Martensite}{\alpha'\,(BCT)} \xrightarrow{Temper} \underset{Ferrite}{\alpha\,(BCC)} + \underset{Cementite}{\mathrm{Fe_3C}\,(OR)}$$

Martempering

- This heat treatment is given to oil hardenable and air hardenable steels and thin section of water hardenable steel sample to produce martensite with minimal differential thermal and transformation stress to avoid distortion and cracking.
- The steel should have reasonable incubation period at the nose of its TTT diagram and long bainitic bay.
- The sample is quenched above M_S temperature in a salt bath to reduce thermal stress (instead of cooling below M_F directly) Surface cooling rate is greater than at the centre.
- The cooling schedule is such that the cooling curves pass behind without touching the nose of the TTT diagram. The sample is isothermally hold at bainitic bay such that differential cooling rate at centre and surface become equalize after some time.
- The sample is allowed to cool by air through M_S-M_F such that martensite forms both at the surface and centre at the same time due to not much temperature difference and thereby avoid transformation stress because of volume expansion. The sample is given tempering treatment at suitable temperature.

Martempering

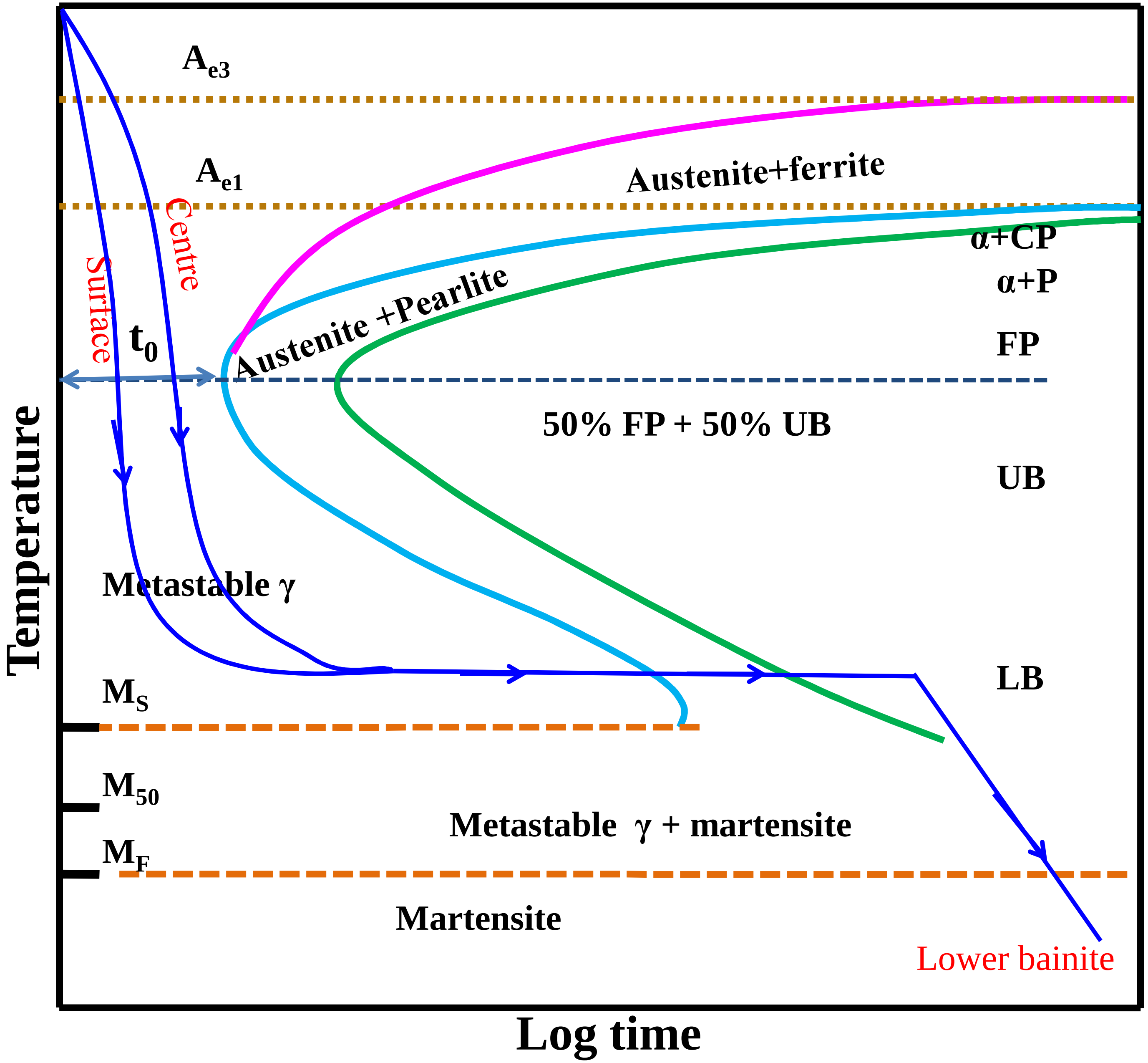


γ=austenite
α=ferrite
CP=coarse pearlite
P=pearlite
FP=fine pearlite
t_0=minimum incubation period
UB=upper bainite
LB=lower bainite
M=martensite
M_S=Martensite start temperature
M_{50}=temperature at which 50% martensite is obtained
M_F= martensite finish temperature

Austempering

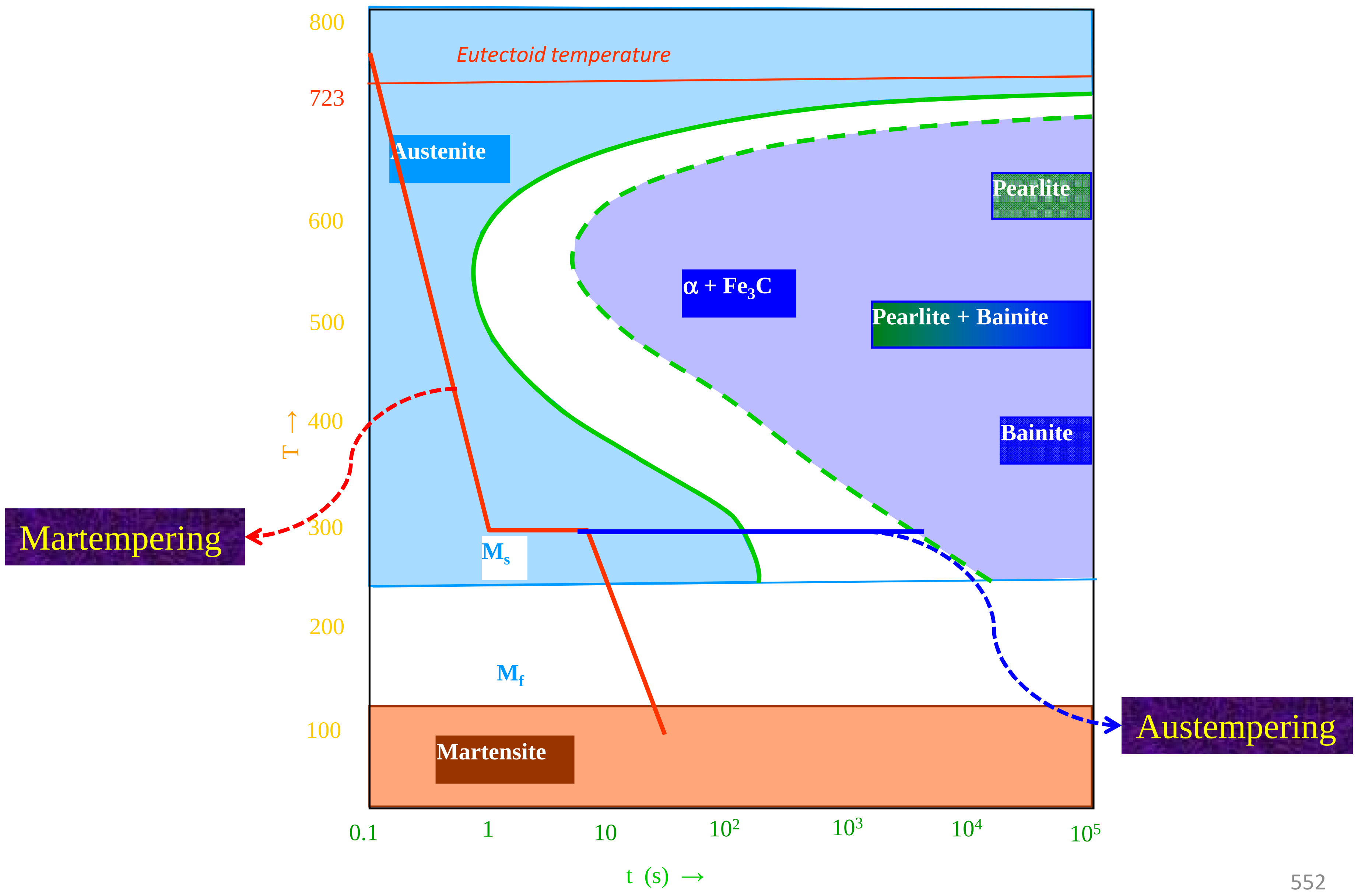
- Austempering heat treatment is given to steel to produce lower bainite in high carbon steel without any distortion or cracking to the sample.
- The heat treatment is cooling of austenite rapidly in a bath maintained at lower bainitic temperature (above M_s) temperature (avoiding the nose of the TTT diagram) and holding it here to equalize surface and centre temperature and till bainitic finish time.
- At the end of bainitic reaction sample is air cooled. The microstructure contains fully lower bainite. This heat treatment is given to 0.5-1.2 wt%C steel and low alloy steel.
- The product hardness and strength are comparable to hardened and tempered martensite with improved ductility and toughness and uniform mechanical properties. Products do not required to be tempered.

Austempering



γ=austenite
α=ferrite
CP=coarse pearlite
P=pearlite
FP=fine pearlite
t_0=minimum incubation period
UB=upper bainite
LB=lower bainite
M=martensite
M_S=Martensite start temperature
M_{50}=temperature at which 50% martensite is obtained
M_F= martensite finish temperature

Comparison between Martempering & Austempering



ALLOY STEELS

- Various elements like Cr, Mn, Ni, W, Mo etc are added to plain carbon steels to create alloy steels
- The alloys elements move the nose of the TTT diagram to the right → this implies that a slower cooling rate can be employed to obtain martensite → increased HARDENABILITY
- The *'C' curves* for pearlite and bainite transformations overlap in the case of plain carbon steels → in alloy steels pearlite and bainite transformations can be represented by separate *'C' curves*

Role of Alloying Elements

Element Added

- Segregation / phase separation
- Solid solution
  - Interstitial
  - Substitutional
- Compound (new crystal structure)

Plain Carbon Steel

- + Simplicity of heat treatment and lower cost
- – Low hardenability
- – Loss of hardness on tempering
- – Low corrosion and oxidation resistance
- – Low strength at high temperatures

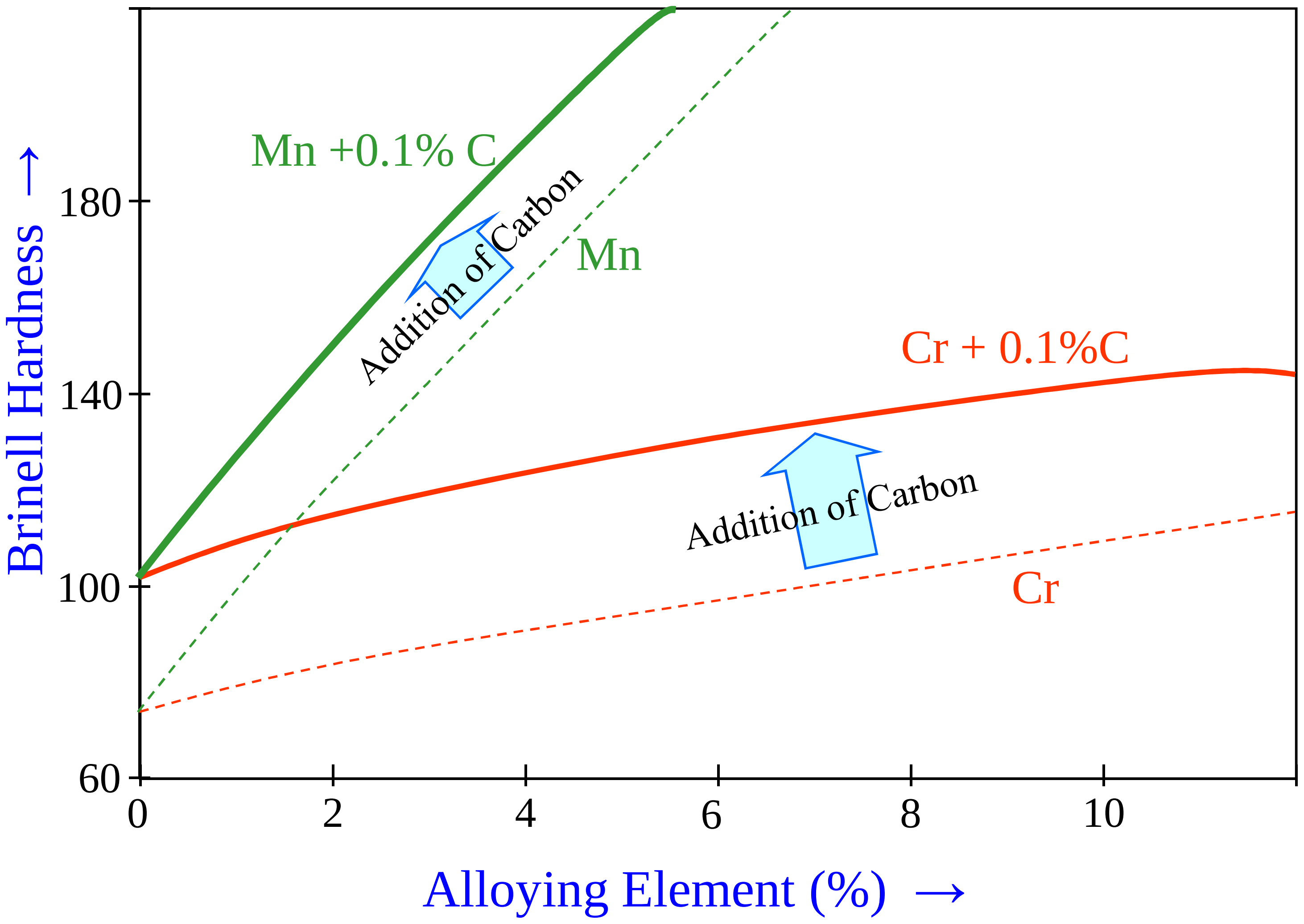
Alloying elements

- ↑ hardenability
- Provide a fine distribution of alloy carbides during tempering
- ↑ resistance to softening on tempering
- ↑ corrosion and oxidation resistance
- ↑ strength at high temperatures
- Strengthen steels that cannot be quenched
- Make easier to obtain the properties throughout a larger section
- ↑ Elastic limit (no increase in toughness)

- Alter temperature at which the transformation occurs
- Alter solubility of C in α or γ Iron
- Alter the rate of various reactions

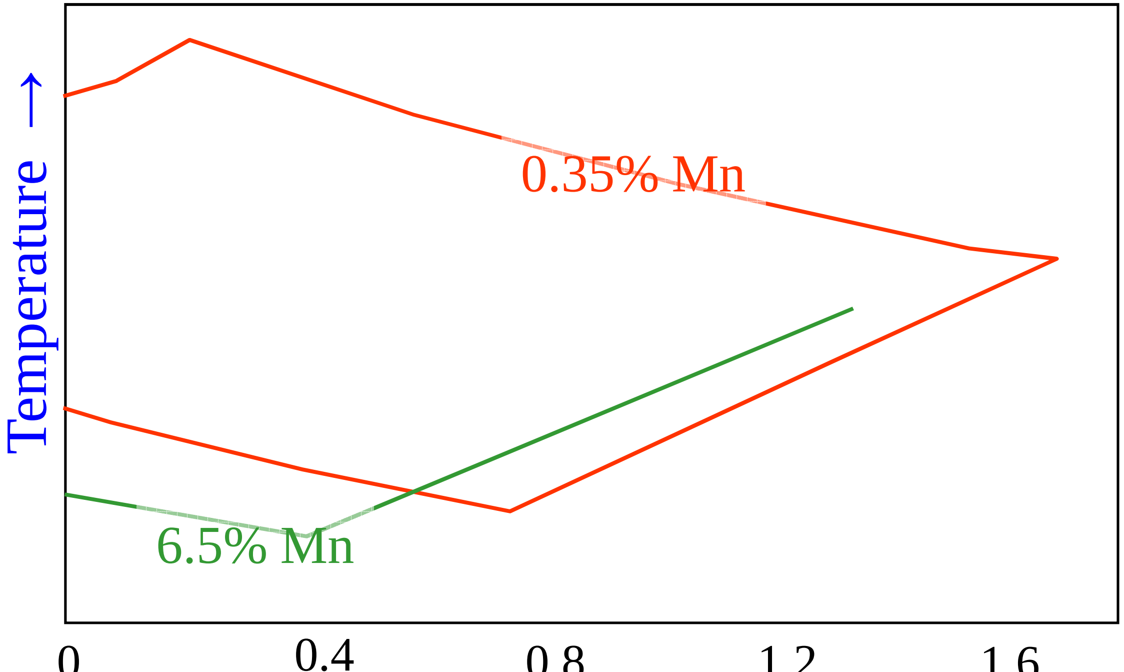
Sample elements and their role

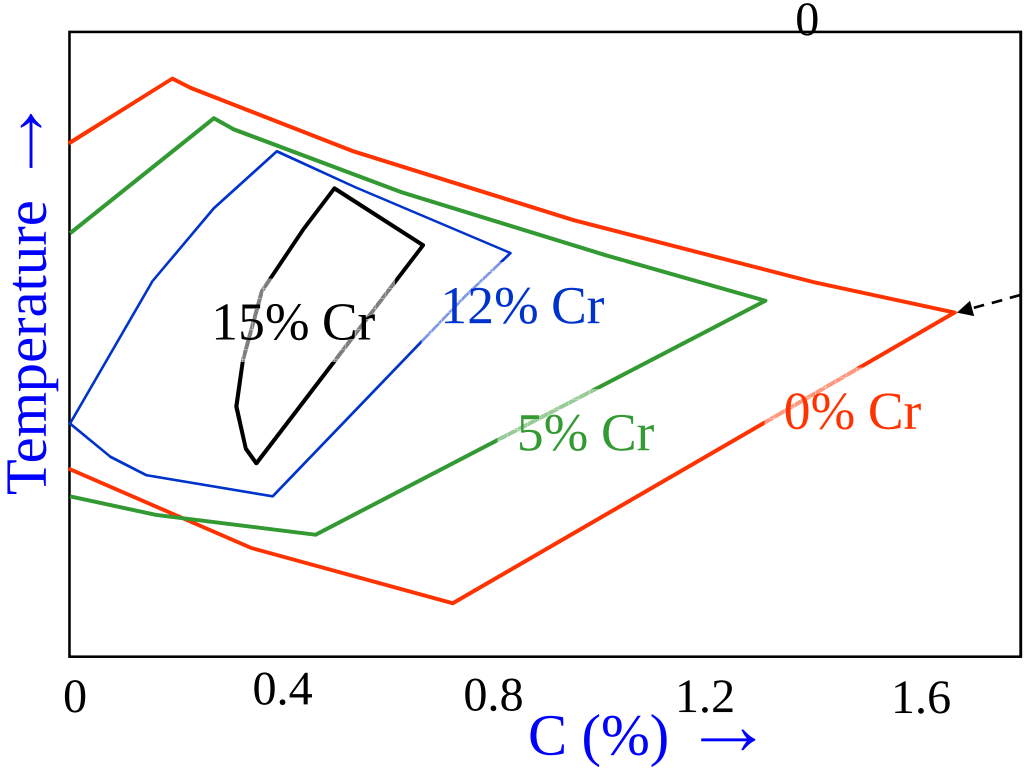
- ❑ **P** ▶Dissolves in ferrite, larger quantities form iron phosphide → brittle (cold-shortness)
- ❑ **S** ▶Forms iron sulphide, locates at grain boundaries of ferrite and pearlite poor ductility at forging temperatures (hot-shortness)
- ❑ **Si** ▶ (0.2-0.4%) increases elastic modulus and UTS
- ❑ **Cu** ▶0.8 % soluble in ferrite, can be used for precipitation hardening
- ❑ **Pb** ▶Insoluble in steel
- ❑ **Cr** ▶Corrosion resistance, Ferrite stabilizer, ↑ hardness/strength, > 11% forms passive films, carbide former
- ❑ **Ni** ▶ Austenite stabilizer, ↑ strength ductility and toughness,
- ❑ **Mo**▶ Dissolves in α & γ, forms carbide, ↑ high temperature strength, ↓ temper embrittlement, ↑ strength, hardenability



Alloying elements increase hardenability but the major contribution to hardness comes from Carbon

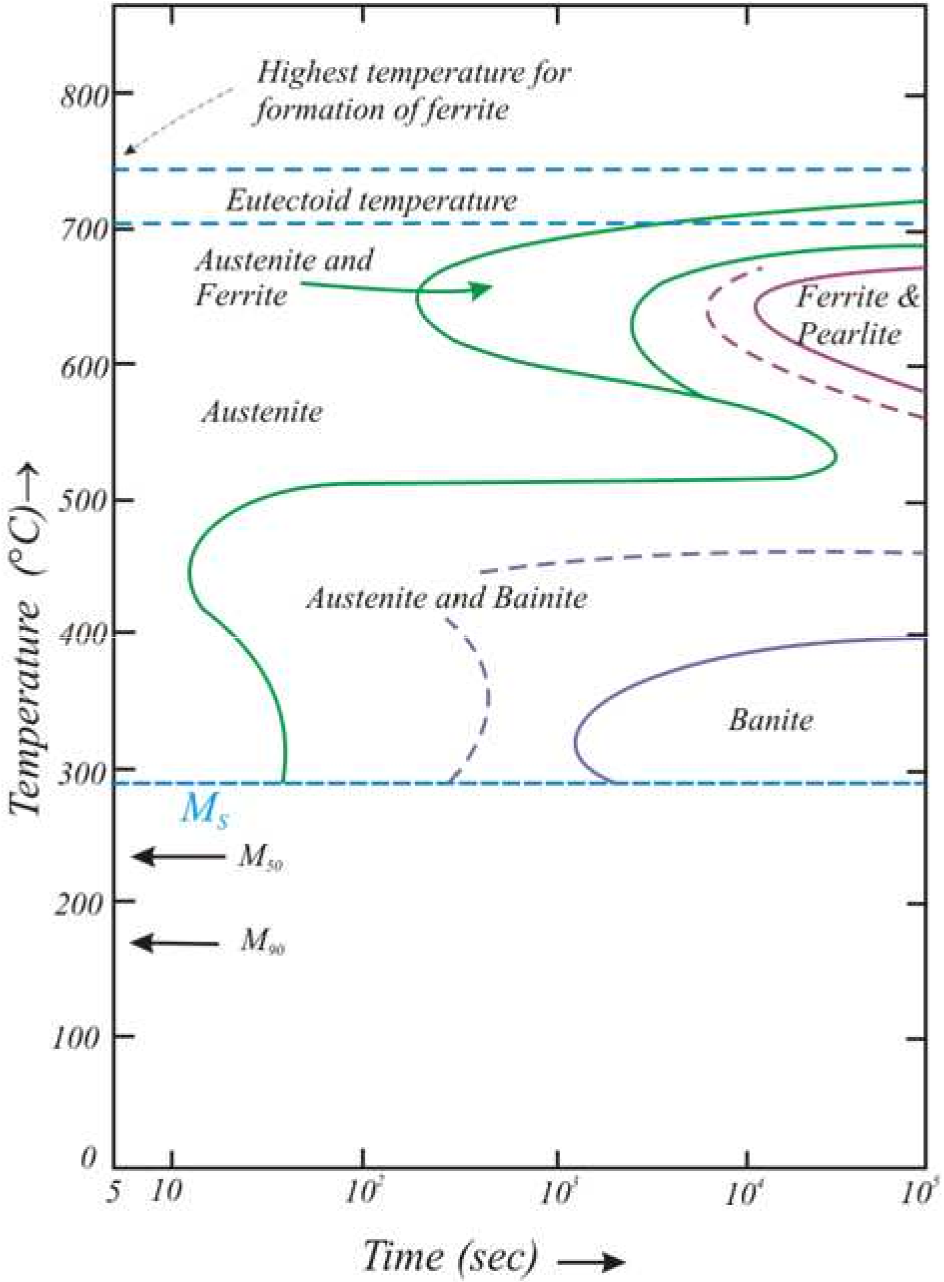
- Mn, Ni are Austenite stabilizers





Outline of the γ phase field

- Cr is Ferrite stabilizer
- Shrinking γ phase field with ↑ Cr

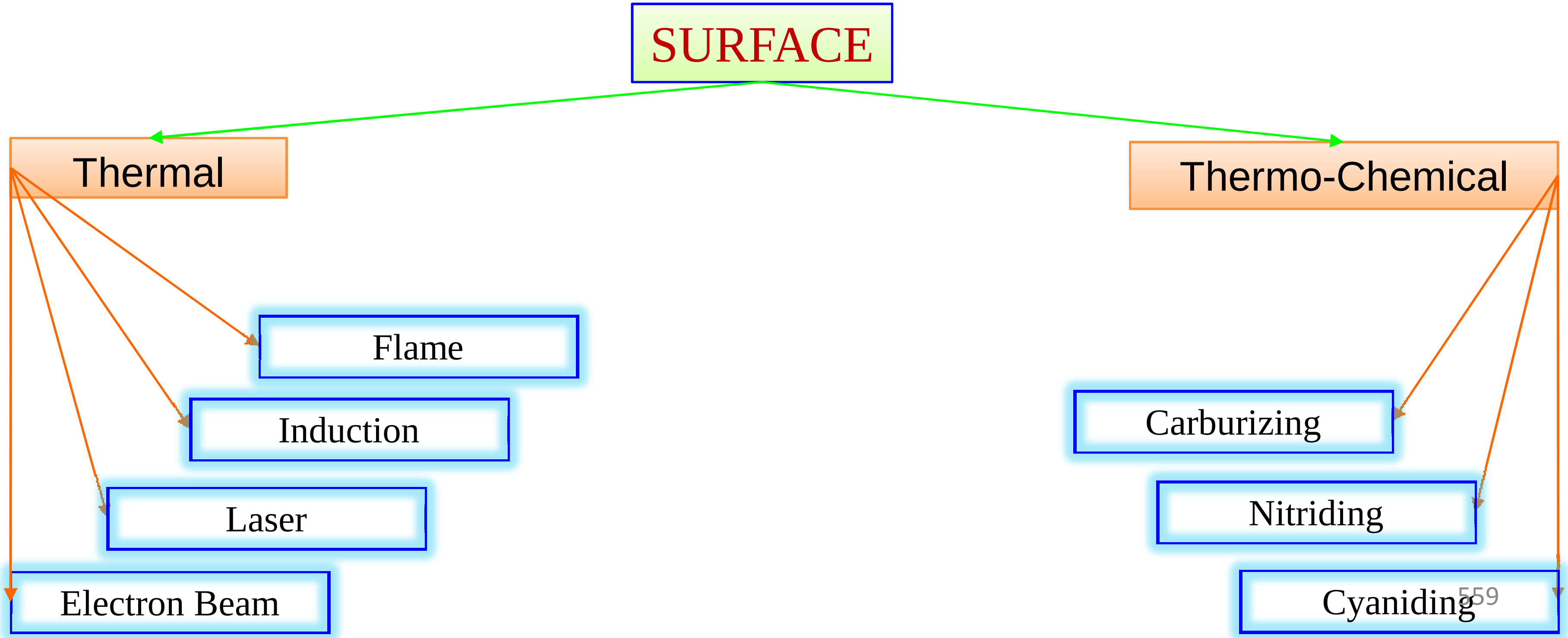


TTT diagram of low alloy steel (0.42% C, 0.78% Mn, 1.79% Ni, 0.80% Cr, 0.33% Mo)

U.S.S Carilloy Steels, United States Steel Corporation, Pittsburgh, 1948)

Surface Hardening Treatments

- Numerous industrial applications require a hard wear resistant surface called the *case*, and a relatively soft, tough inside called the *core*. Example: Gears
- They are two different categories. They are thermo chemical and thermo mechanical treatments. Thermo chemical treatment is related to change in chemical composition and In Thermo mechanical treatment, there is no change of chemical composition of the steel and are essentially shallow- hardening methods.
- A detailed flow chart is given below related to surface hardening treatments.



SURFACE

Thermal

Thermo-Chemical

Flame

Induction

Laser

Electron Beam

Carburizing

Nitriding

Cyaniding

Thermo Chemical Treatments

Carburizing

- Carburizing is the most widely used method of surface hardening. Here, the surface layers of a low carbon steel (<0.25) is enriched with carbon up to 0.8-1.0%. The source of carbon may be a solid medium, a liquid or a gas.
- In all cases, the carbon enters the steel at the surface and diffuses into the steel as a function of time at an elevated temperature. Carburizing is done at 920-950°C. at this temperature the following reaction takes place

$$\boxed{Fe + 2CO \longrightarrow Fe_{(c)} + CO_2}$$

- Where $\mathrm{F}\mathbf{e}_{\mathbf{(c)}}$ represents carbon dissolved in austenite. the rate of diffusion of carbon in austenite, at a given temperature is dependent upon the diffusion coefficient and the carbon concentration gradient.
- The carburizing equation given previously, $Fe+2CO \longrightarrow Fe_{(c)} + CO_2$ is reversible and may proceed to the left, removing carbon from the surface layer if the steel is heated in an atmosphere containing carbon dioxide (CO_2). This is called decarburization.

Carburizing

- Decarburization may be prevented by using an endothermic gas atmosphere in the furnace to protect the surface of the steel from oxygen, carbon dioxide and water vapor.
- An endothermic gas atmosphere is prepared by reacting relatively rich mixtures of air and hydrocarbon gas (usually natural gas) in an externally heated generator in the presence of a nickel catalyst.

Liquid Carburizing

- Liquid carburizing is a method of case hardening steel by placing it in a bath (8% NaCN, 82% $BaCl_2$ and 10% NaCl) of molten cyanide so that carbon will diffuse from the bath into the metal and produce a case comparable to one resulting from pack or gas carburizing.
- Liquid carburizing may be distinguished from cyaniding by the character and composition of the case produced. The cyanide case is higher in nitrogen and lower in carbon; the reverse is true of liquid carburized cases.

$$BaCl_2 + 2NaCN \longrightarrow Ba(CN)_2 + 2NaCl$$

$$Ba(CN)_2 + Fe \longrightarrow Fe_{(C)} + Ba(CN)_2$$

Pack Carburizing

- In *pack carburizing*, the article s to be carburized are packed in a box, embedding them in a powdery mixture of 85% charcoal and 15% of energizers such as $BaCO_3$. The box is sealed with fireclay and loaded into the furnace kept at 930°C. The residual air in the box combines with carbon to produce CO. The energizer decomposes as below :

$$BaCO_3 \longrightarrow \mathrm{BaO} + CO_2$$

$$CO_2 + C \longrightarrow 2CO$$

- The carbon enters the steel through the following reaction:

$$Fe + 2CO \longrightarrow Fe_{(c)} + CO_2$$

- If selective carburization is to be done, copper is electroplated to a thickness of ~0.05 mm in regions where carburization is not desired. Alternatively, a refractory paste of fireclay mixed with asbestos can be applied. Control of temperature and penetration depth is less in pack carburizing as compared to liquid and gas carburizing. Also, direct quench from the carburizing temperature to harden the surface is not possible.

Gas Carburizing

- ❑ The steel is heated in contact with carbon monoxide and/or a hydrocarbon which is readily decomposed at the carburizing temperature.
- ❑ A mixture consisting of 5-15% methane (or propane) in a neutral carrier gas is used. The methane decomposes according to the following reaction:

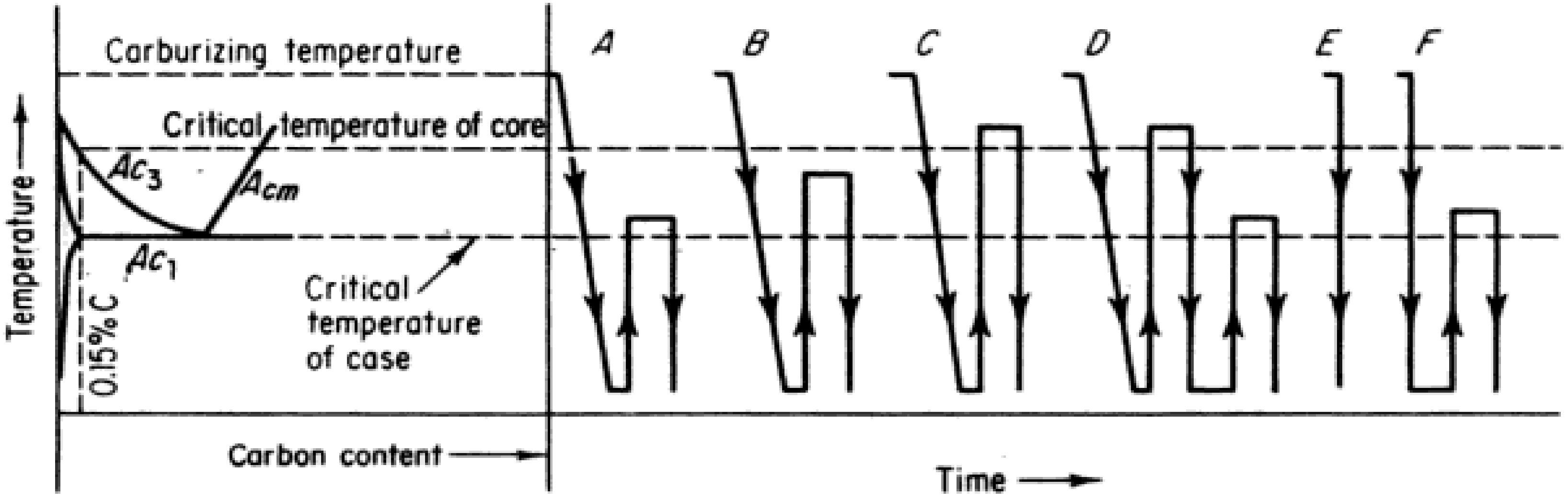
$$CH_4 + Fe \longrightarrow 2H_2 + Fe_{(c)}$$

- ❑ The carbon potential of the gas mixture increases with increasing concentration of methane. Too large a concentration or too high a gas velocity releases carbon faster than it can be absorbed and may result in soot formation on the surface.
- ❑ Closer control of temperature and case depth is possible in gas carburizing, as compared to pack carburizing. Also, post quenching can be done directly.

Heat treatment after carburizing

- ❑ Since steel is carburized in the austenite region, direct quenching from the carburizing temperature will harden both the case and core will harden both the case and core if the cooling rate is greater than the critical cooling rate. Direct quenching of coarse grained steels often leads to brittleness and distortion, so that this treatment should be applied only to fine grained steels. *A diagrammatic representation of various hardening treatments for carburized steels shown in next slide.*

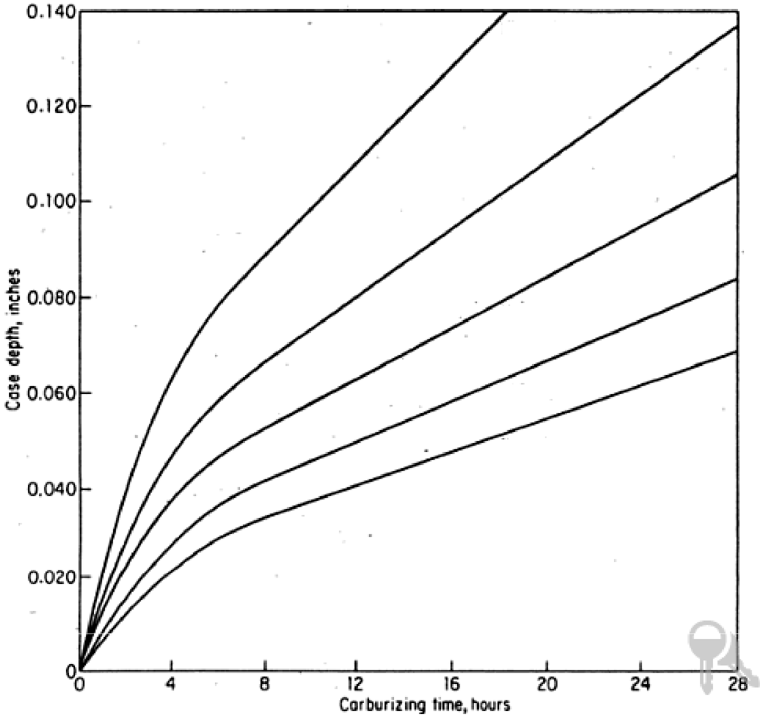
Heat treatment after carburizing

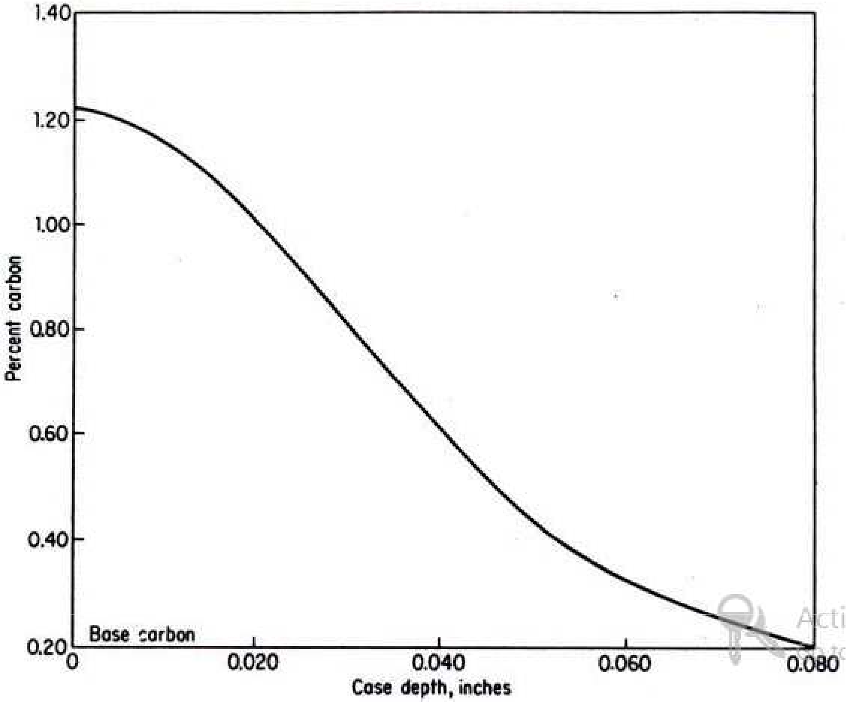


TREATMENT	CASE	CORE
A – best adapted to fine grained steels	Refined; Excess carbide not dissolved	Unrefined; soft and machinable
B-best adapted to fine grained steels	Slightly coarsened; some solution of excess carbide	Partially refined; stronger and tougher than A
C-best adapted to fine grained steels	Somewhat coarsened; solution of excess carbide favored; austenite retention promoted in highly alloyed steels.	Refined: maximum core strength and hardness; better combination of strength and ductility than B
D-best treatment for coarse grained steels	Refined solution of excess carbide favored; austenite retention minimized	Refined; soft and machinable; maximum toughness and resistance to impact
E-adapted to fine grained steels only	Unrefined with excess carbide dissolved; austenite retained; distortion minimized	Unrefined but hardened
F-adapted to fine grained steels only	Refined; solution of excess carbide favored; austenite retention minimized	Unrefined; fair toughness

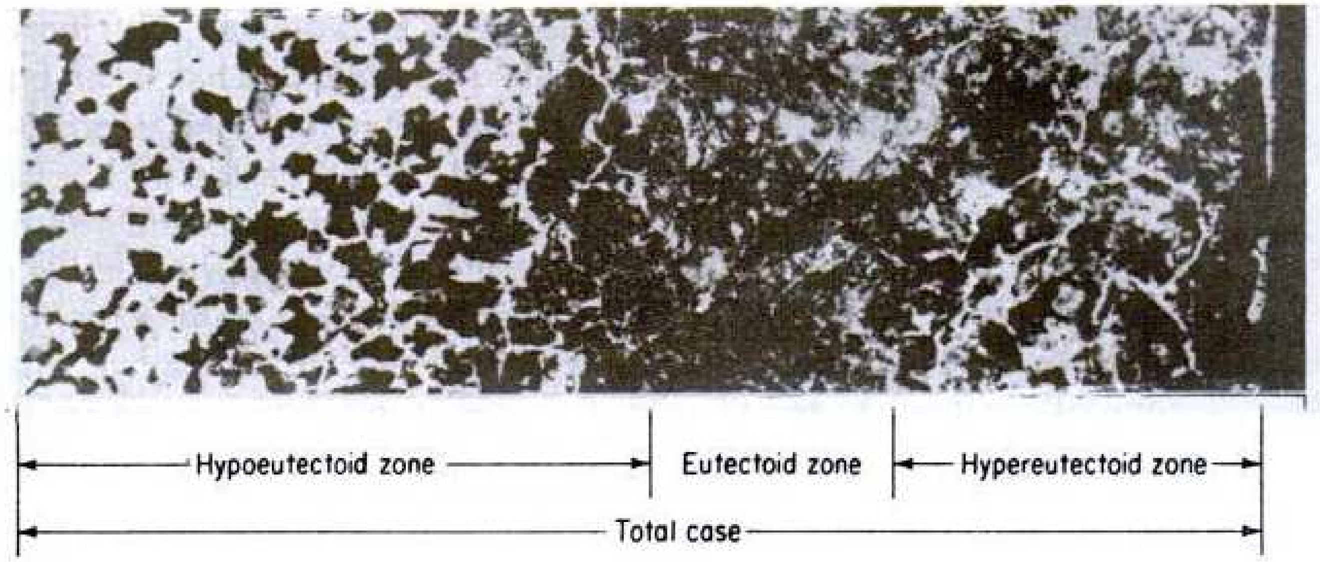
Carburizing

Relation of time and temperature to case depth





Carbon-concentration gradient in a carburized steel



Cyaniding and Carbonitriding

- ☐ In this case that contain both carbon and nitrogen are produced in liquid salt baths (cyaniding) or by use of gas atmospheres (carbonitriding). The temperatures used are generally lower than those used in carburizing, being between 750-900°C.
- ☐ Exposure is for a shorter time, and thinner cases are produced, up to 0.010in. For cyaniding and up to 0.030in. For carbonitriding.
- ☐ In Cyaniding is done in a liquid bath of NaCN, with the concentration varying between 30 and 97%. Both carbon and nitrogen enter the steel via the following reactions:

$$2NaCN + O_2 \longrightarrow 2NaCNO$$

$$3NaCNO \longrightarrow NaCN + Na_2CO_3 + C + 2N$$

- ☐ The temperature used for cyaniding is lower than that for carburizing and in the range of 800-870°C. the time of cyaniding is 0.5-3 hour to produce a case depth of 0.25 mm or less.

Cyaniding and Carbonitriding

- Carbonitriding is a case-hardening process in which a steel is heated in a gaseous atmosphere of such composition that carbon and nitrogen are absorbed simultaneously.
- This process is also known as dry cyaniding or gas cyaniding. It is the gas carburizing process modified by the addition of anhydrous ammonia.
- The decomposition of ammonia provides the nitrogen, which enters the steel along with carbon.
- A typical gas mixture consists of 15% $NH_{3,}$ $CH_{4,}$ and 80% of neutral carrier gas. The temperature used is 750-900°C. With increasing temperature, a greater proportion of carbon enters the steel.
- The presence of nitrogen in the austenite accounts for the major differences between carbonitriding and carburizing. Carbon-nitrogen austenite is stable at lower temperatures than plain-carbon austenite and transforms more slowly on cooling. Carbonitriding therefore can be carried out at lower temperatures and permits slower cooling rates than carburizing in the hardening operation

Nitriding

- ☐ In contrast to the processes described before, nitriding is carried out in the ferrite region. Consequently, no phase change occurs after nitriding .
- ☐ This part to be nitrided should possess the required core properties prior to nitriding. Pure ammonia decomposes to yield nitrogen which enters the steel:

$$2NH_3 \longrightarrow 2N + 3H_2$$

- ☐ The solubility of nitrogen in ferrite is small. Most of the nitrogen that enters the steel forms hard nitrides (e.g. Fe_3N). A typical nitriding steel contains alloying elements of 1%Al, 1.5%Cr and 0.2%Mo. Al, Cr, and Mo form very hard and wear resistant nitrides.
- ☐ The temperature of nitriding is 500-590°C. the time for a case depth of 0.02mm is about 2 hour. In addition with wear resistance, it also increases the resistance of a carbon steel to corrosion in moist atmospheres.
- ☐ A common problem encountered in nitriding is the formation of γ' nitride (Fe_4N) on the outer layers of the case , known as the “white layer”, as it looks white under the microscope. This layer is very brittle and tends to crack. It must be removed by final grinding operation. Its formation can be minimized by maintaining the correct ratio of NH_3/ H_2 in the gas mixture during the heat treatment.

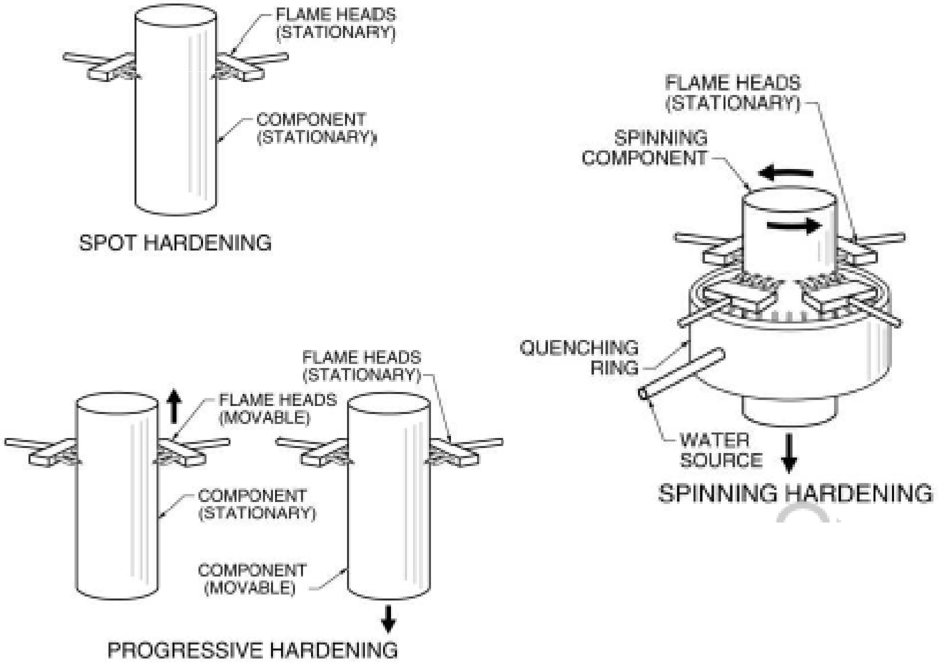
Thermal Energy Treatments

Flame Hardening

❑ For large work pieces, such as mill rolls, large gears and complicated cross sections, in such cases, flame hardening is done by means of an oxyacetylene torch. Heating should be done rapidly by the torch and the surface quenched, before appreciable heat transfer to the core occurs.

❑ Four methods are generally use for Flame Hardening

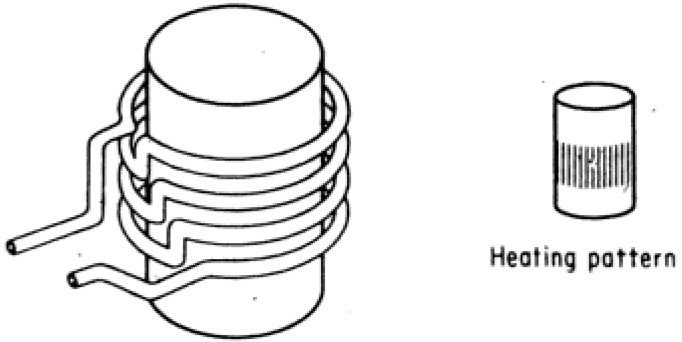
- ✓ Stationary (Spot): Torch and work is stationary
- ✓ Progressive: Torch moves over a work piece
- ✓ Spinning: Torch is stationary while work piece rotates
- ✓ Progressive-spinning: Torch moves over a rotating work piece.



Induction Hardening

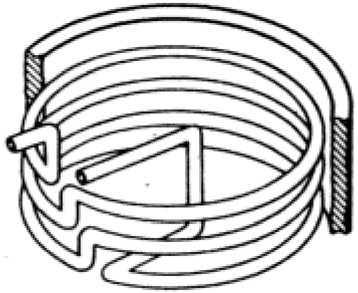
- ☐ Here, an alternating current of high frequency passes through an induction coil enclosing the steel part to be heat treated. The induced emf heats the steel. the depth up to which the heat penetrates and rises the temperature above A_{c3} is inversely proportional to the square root of the AC frequency.
- ☐ Correspondingly, the hardened depth decreases with increasing frequency in induction hardening, the heating time is usually a few seconds. Immediately after heating water jets are activated to quench the surface . Martensite is produced at the surface, making it hard and wear resistant. The microstructure of the core remains unaltered. Induction hardening is suitable for mass production of articles of uniform cross section

Five basic designs of work coils with the heat patterns developed by each are shown below

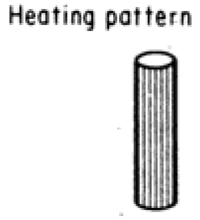


A Simple Solenoid for external heating

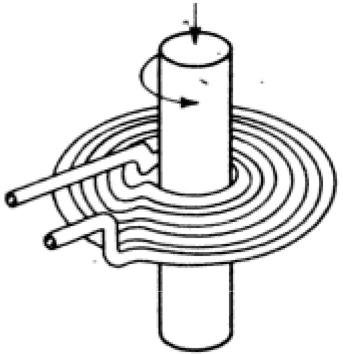
Induction Hardening

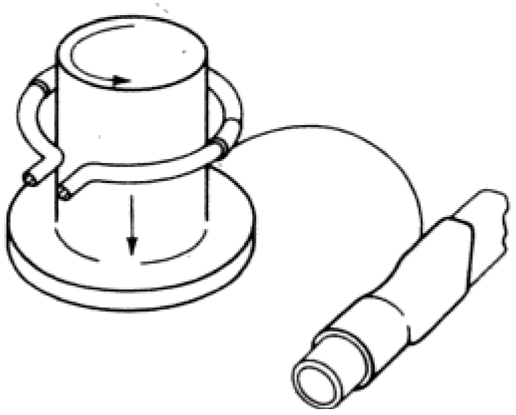


A coil to be used internally for heating bores



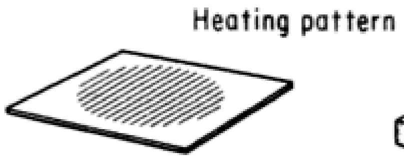
A “pie-plate” type of coil designed to provide high current densities in a narrow band for scanning applications.

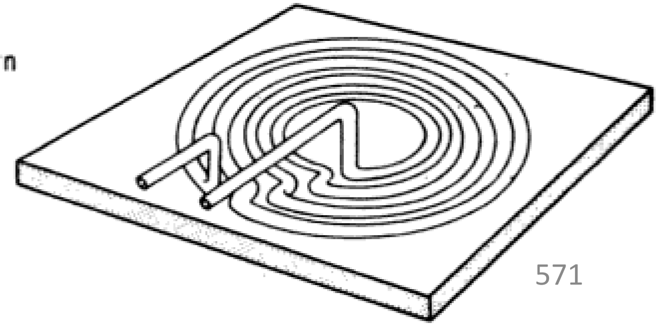




A Single turn coil for scanning a rotating surface, provided with a contoured half turn that will aid in heating the fillet

A ‘Pancake’ coil for spot heating.





Laser Hardening

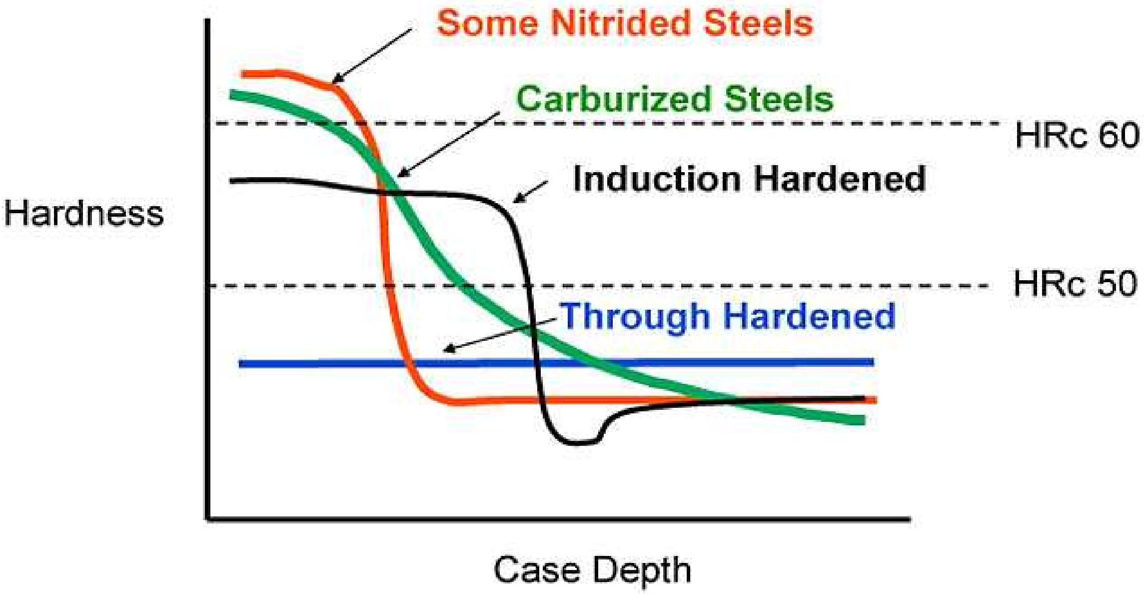
- Laser hardening treatment is widely used to harden localized areas of steel and cast iron machine components. This process is sometimes referred to as laser transformation hardening to differentiate it from laser surface melting phenomena.
- There is no chemistry change produced by laser transformation hardening, and the process, like induction and flame hardening, provides an effective technique to harden ferrous materials selectively.
- As laser beams are of high intensity, a lens is used to reduce the intensity by producing a defocused spot of size ranging from 0.5 to 25 mm. proper control of energy input is necessary to avoid melting.
- Laser transformation hardening produces thin surface zones that are heated and cooled very rapidly, resulting in very fine Martensitic microstructures, even in steels with relatively low hardenability. High hardness and good wear resistance with less distortion result from this process.
- Laser hardening has the advantage of precise control over the area to be hardened, an ability to harden reentrant surfaces, very high speed of hardening and no separate quenching step (the quench is effected by the mass of the unheated material).
- The disadvantage is that the hardening is shallower than in induction and flame hardening.

Electron Beam (EB) Hardening

- Electron Beam (EB) hardening is like laser treatment, is used to harden the surfaces of steels. The EB heat treating process uses a concentrated beam of high-velocity electrons as an energy source to heat selected surface areas of ferrous parts. Electrons are accelerated and are formed into a directed beam by an EB gun.
- After exiting the gun, the beam passes through a focus coil, which precisely controls beam density levels (spot size) at the work piece surface and then passes through a deflection coil.
- To produce an electron beam, a high vacuum of 10^{-5} torr is needed in the region where the electrons are emitted and accelerated. This vacuum environment protects the emitter from oxidizing and avoids scattering of the electrons while they are still traveling at a relatively low velocity.
- Like laser beam hardening, the EB process eliminates the need for quenchants but requires a sufficient work piece mass to permit self quenching.
- A mass of up to eight times that of the volume to be EB hardened is required around and beneath the heated surfaces. Electron beam hardening does not require energy absorbing coatings, as does laser beam hardening.

Relative benefits of common surface-hardening processes

PROCESS	BENEFITS
Carburizing	Hard, highly wear-resistant surface (medium case depths); excellent capacity for contact load; good bending fatigue strength; good resistance to seizure; excellent freedom from quench cracking; low-to-medium cost steels required; high capital investment required
Nitriding	Hard, highly wear-resistant surface (shallow case depths); fair capacity for contact load; good bending fatigue strength; excellent resistance to seizure; excellent dimensional control possible; good freedom from quench cracking (during pretreatment); medium-to-high-cost steels required; medium capital investment required; improved salt corrosion resistance
Induction hardening	Hard, highly wear-resistant surface (deep case depths); good capacity for contact load; good bending fatigue strength; fair resistance to seizure; fair dimensional control possible; fair freedom from quench cracking; low-cost steels usually satisfactory; medium capital investment required
Flame hardening	Hard, highly wear-resistant surface (deep case depths); good capacity for contact load; good bending fatigue strength; fair resistance to seizure; fair dimensional control possible; fair freedom from quench cracking; low-cost steels usually satisfactory; low capital investment required



Residual Stresses

- ❑ These are stresses that remain in the part after the force has disappeared. Residual stresses always arise from a nonuniform plastic deformation.
- ❑ In the case of heat treatment, this nonuniform plastic deformation may be caused by the temperature gradient or the phase change or usually a combination of both factors during cooling.
- ❑ Residual stresses are a very serious problem in heat treatment, since they often result in distortion or cracking and in some cases in premature failure of the part in service.
- ❑ Consider the effect of temperature gradient alone . It was shown earlier, under the effect of size and mass, that during quenching the surface is cooled more rapidly than the inside.
- ❑ *Almost all solids expand as they are heated and contract as they are cooled.* This means that at the end of 10 s (for example) the surface, since it is at a much lower temperature, should have contracted much more than inside.
- ❑ However since the outside and inside are attached to each other, the inside, being longer, will prevent the outside from contracting as much as it should. It will therefore elongates the outside layer, putting them in tension while the inside in turn will be in compression.

Residual Stresses

- Thermal stresses may by calculated from the following formula:

$$S = \alpha \, . E \, . \Delta T$$

Where S = Thermal stress, psi

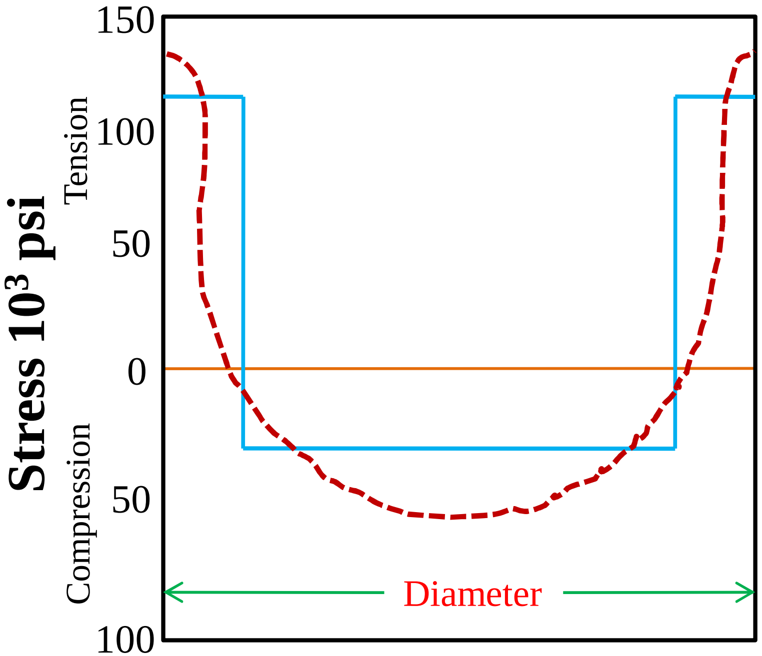
α = Coefficient of linear expansion in./(in.)(°F)

E = Modulus of elasticity, psi

ΔT = Difference in temperature, °F

The stress distribution is plotted schematically in below figure.

The stress distribution across the dia. Due to temperature gradient. Dotted curve indicates a truer representation of the stress distribution.



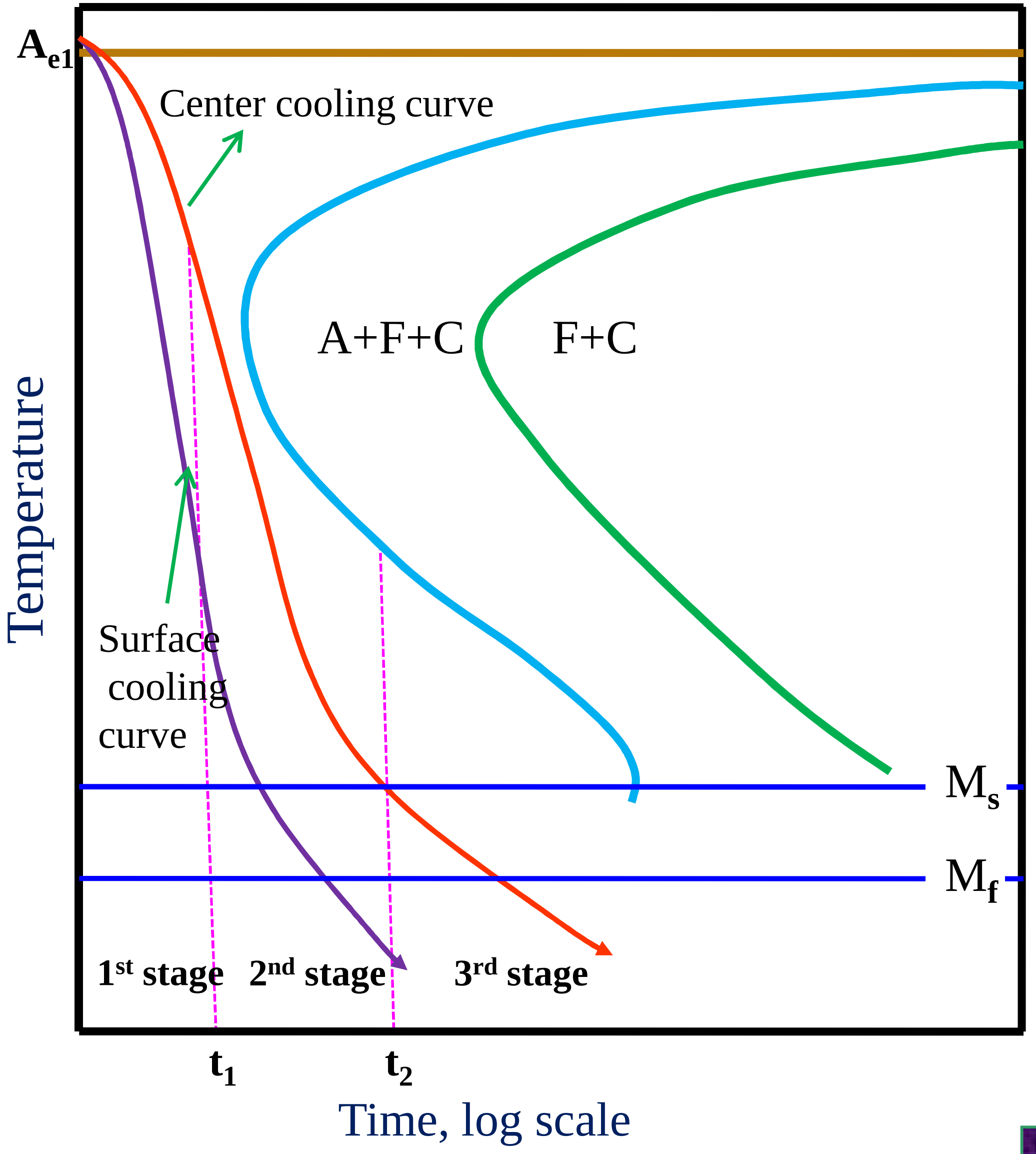
The area in tension must balance the area in compression in order for the stresses to be in equilibrium across the cross section

Residual Stresses

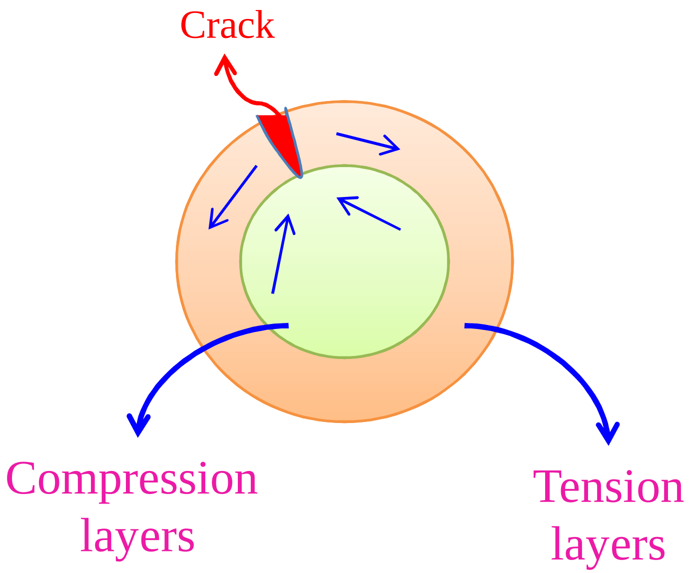
- ❑ In general, the tensile stress on the surface may reach a very high value. If this stress exceeds the ultimate strength of the material, cracking will occur.
- ❑ In the case of steel, however, thermal stresses alone very rarely lead to cracking. If the stress is below the yield strength of the steel, the stress will be borne elastically.
- ❑ When the entire piece has reached room temperature, $\Delta T = 0$, and therefore, since the thermal stress will be zero, there will be no distortion.
- ❑ If the stress exceeds the yield strength, the surface layer will be plastically deformed or permanently elongated. At room temperature the surface will have residual compressive stress and the inside, residual tensile stress.
- ❑ Let us consider the combined effect of temperature gradient and phase change for two possibilities: (1) *Through-Hardened steel and* (2) *Shallow-Hardened steel*
- ❑ The next two slides shows the surface- and center- cooling curves superimposed on the I-T diagram for the *through hardened steel* and *shallow hardened steel*.
- ❑ In many applications, the tensile stress developed by the external force is maximum at or near the surface. For these applications, shallow hardened or case-hardened parts are preferred.

Residual Stresses

Through-Hardened Condition



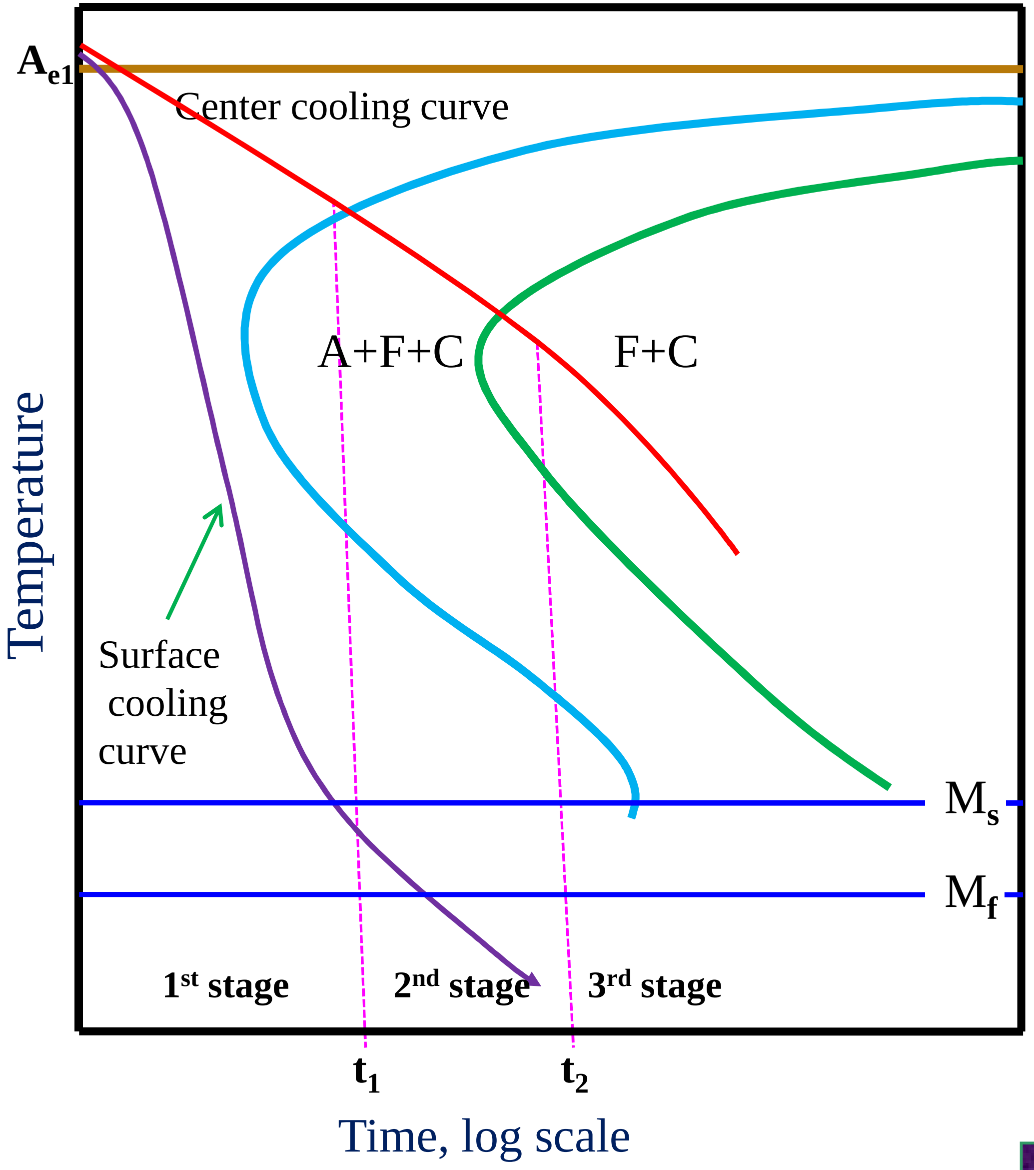
STAGE	STRESS CONDITION	
	SURFACE	CENTER
First Temperature gradient	Tension	Compression
Second A →M of surface	Compression	Tension
Third A→M of center	Tension	Compression



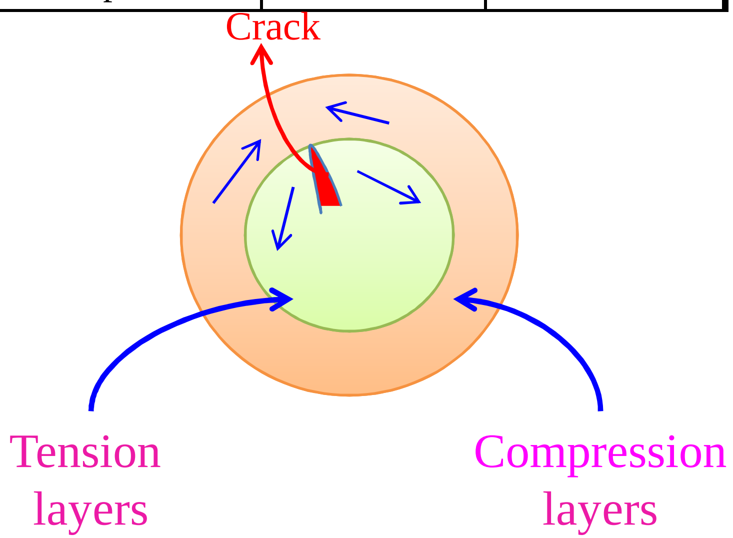
Possible fracture in Through-Hardened steel

Residual Stresses

Shallow-Hardened Condition

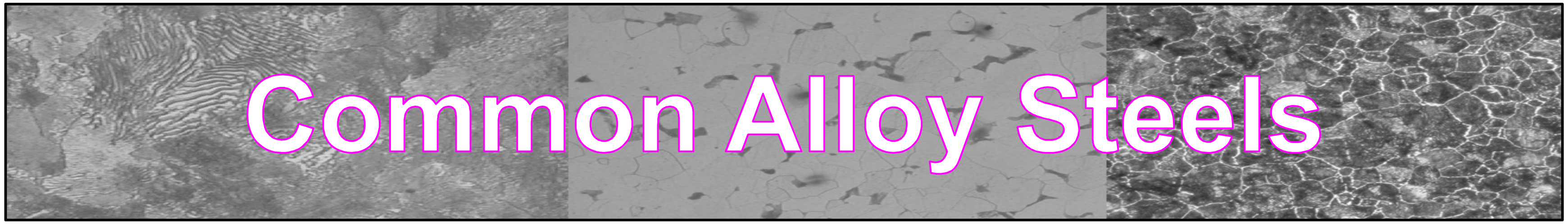


STAGE	STRESS CONDITION	
	SURFACE	CENTER
First Temperature gradient	Tension	Compression
Second A →M of surface A→P of center	Compression	Tension
Third Cooling of center to room temperature	Greater Compression	Greater Tension



Possible fracture in Shallow-Hardened steel

Common Alloy Steels



Avala Lava Kumar* : Suneeti Purohit : Gautam Behera

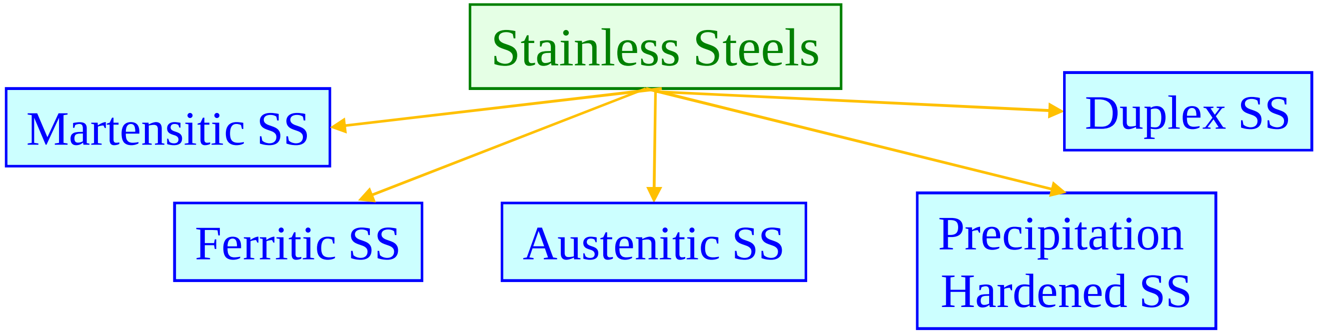
Department of Metallurgical & Materials Engineering (MME)

Veer Surendra Sai University of Technology (VSSUT), Burla -768018

**E-mail : lavakumar.vssut@gmail.com*

Stainless Steels

- Stainless Steels are a large group of special alloys developed primarily to withstand corrosion. These steels contain chromium in excess of 12% by weight which imparts “stainless” characteristics to iron alloys.
- Types of stainless steels:



Stainless Steels

Martensitic SS

Ferritic SS

Austenitic SS

Precipitation Hardened SS

Duplex SS

- AISI Grades of stainless steels:

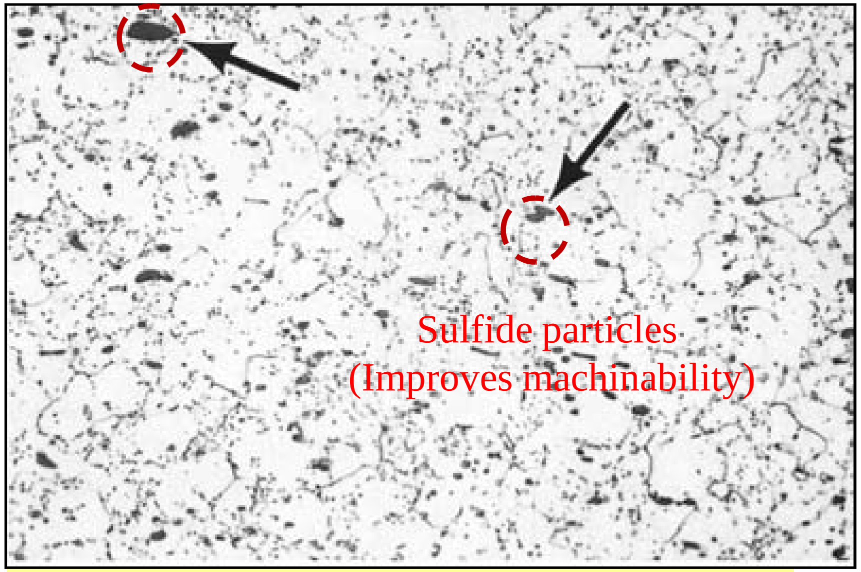
Series Designation	Groups
2xx	Chromium-Nickel-Manganese; Nonhardenable, Austenitic, Nonmagnetic
3xx	Chromium-Nickel; Nonhardenable, Austenitic, Nonmagnetic
4xx	Chromium; Hardenable, Martensitic, Magnetic
4xx	Chromium; Nonhardenable, Ferritic, Magnetic
5xx	Chromium; Low chromium; Heat-Resisting

Martensitic Stainless Steel

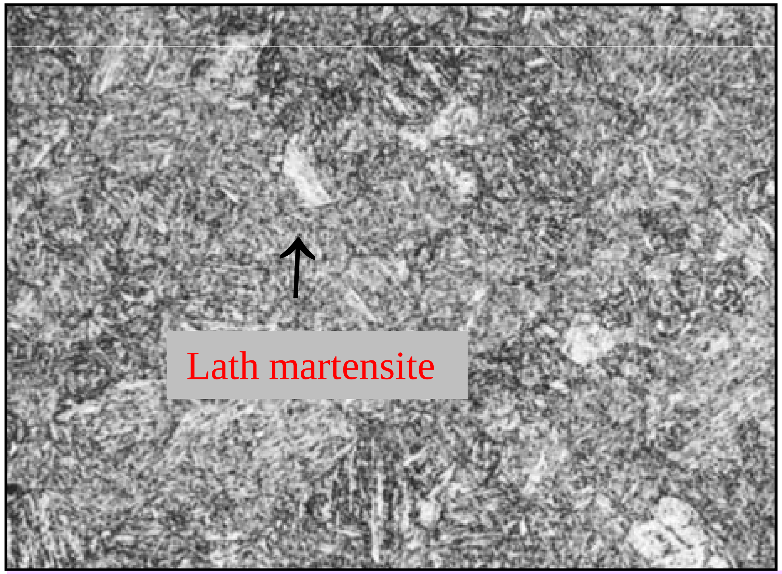
- ☐ These are primarily straight chromium steels with 11.5 to 18% Cr, 0.15% C, 1.25% Mn, and 1%Si.
- ☐ Common examples are 403, 410, 416, 420, 440A, 501 & 502 (AISI grades).
- ☐ Used for turbine blades and corrosion resistant applications

Heat Treatment

- ✓ Process Annealing → 650 - 760 °C, ↑ ductility and machinability
- ✓ Austenitizing → 925 -1065 °C followed by oil quenching or air cooling, ↑ corrosion resistance and strength



Microstructure of annealed 416 stainless steel etched with Vilella's reagant



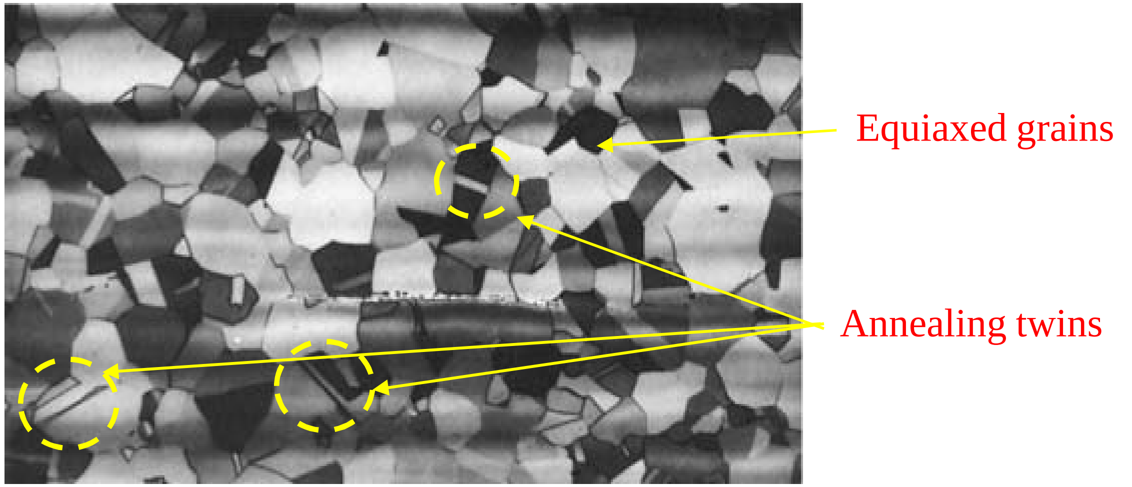
Microstructure of hardened type 403 stainless steel etched with 4% picral-HCl

Austenitic Stainless Steel

- ☐ These are chrome-nickel (3xx type) or chrome -nickel- manganese(2xx type) alloys.
- ☐ Total content of Ni and Cr is at least 23%.
- ☐ Difficult to machine but can be improved by addition of selenium of sulfur.
- ☐ Best high temperature strength and scaling resistance. Hence shows best corrosion resistance
- ☐ Used in chemical industry and for household and sanitary fittings.

Heat Treatment

- ✓ Cold working causes work hardening but hot working can easily be done.
- ✓ Annealing at high temperatures → Recrystallization and carbide solution
- ✓ Solution treatment → Dissolution of chromium carbides



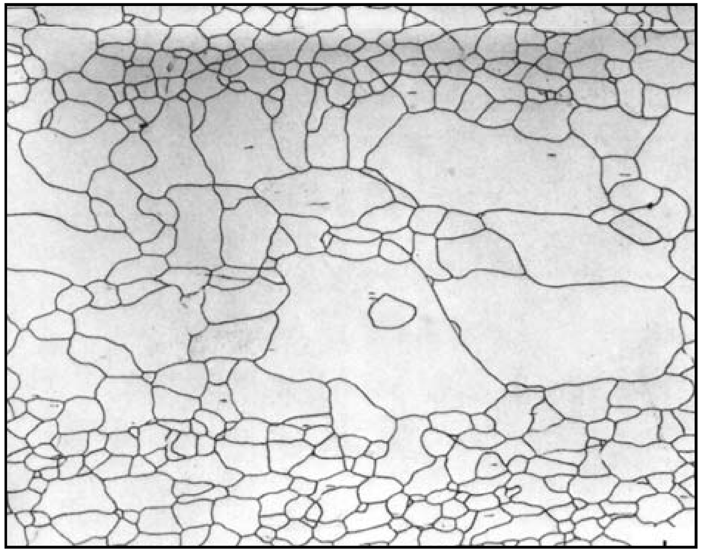
Microstructure of annealed type 316L austenitic stainless steel etched in 20% HCl, 2% NH4FHF, 0.8% PMP

Ferritic Stainless Steel

- These are primarily straight chromium steels with 14 to 27% Cr. Carbon is restricted both to maintain high toughness and ductility and to prevent austenite formation (As carbon expands the gamma loop)
- These steels can be cold formed easily and hence are used for deep drawn parts such as vessels for food and chemical industries and for architectural and automotive trim.

Heat Treatment

- ✓ Can be cold or hot worked.
- ✓ Annealing → 760 - 966°C, Recrystallization of cold-worked structures → achieves maximum softness, ductility and corrosion resistance.



Single-phase microstructure of an annealed ferritic stainless steel

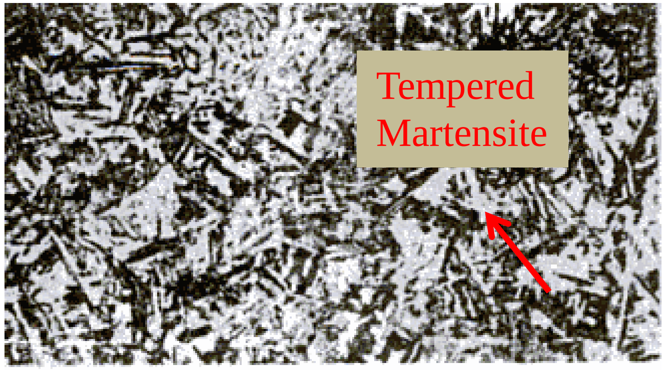
Microstructure of annealed ferritic stainless steel containing 26% Cr and 1% Mo, etched electrolytically in 60% HNO_3-H_2O

Precipitation Hardened Stainless Steel

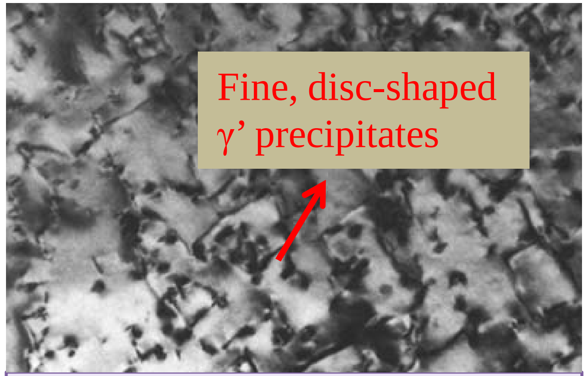
- Contains Mo, Nb, Ti or Al in addition to basic composition. Ni content is generally less to reduce the stability of austenite.
- Common Grades are: 630/17-4 PH (17% Cr, 4%), 631/17-7 PH,15-5 PH etc.
- Provides high strength and toughness while maintaining the corrosion resistance of stainless steels. Also shows excellent elevated-temperature performance and are widely used in the aerospace industry.
- Strengthening is accomplished by the precipitation of intermetallic compounds such as Ni_3Al in austenitic or ductile low-carbon martensitic matrices.

Heat Treatment

- ✓ These steels are usually solution – annealed followed by air cooling with the resultant transformation of austenite to martensite. After forming ageing (480-620 ^{o} C) is carried out to cause precipitation effect.
- ✓ More is the ageing temperature, better is the ductility, toughness and resistance to stress corrosion.


Tempered Martensite

Microstructure of 17-4PH alloy solution treated at1038 ^{o} C and aged at 495 ^{o} C


Fine, disc-shaped γ' precipitates

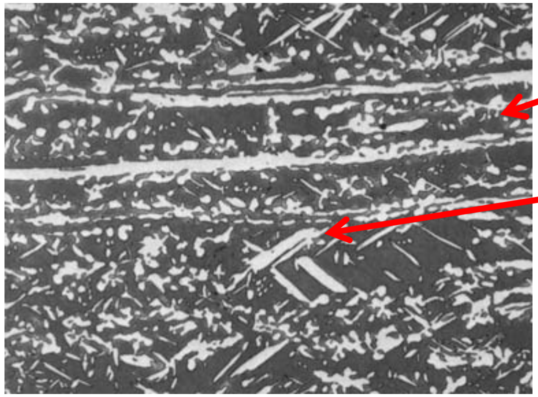
Microstructure of an aged austenitic precipitation-hardening stainless steel

Duplex Stainless Steel

- Duplex stainless steels by design have nearly balanced amounts of ferrite and austenite.
- Compositions of duplex stainless steels range from 17 to 30% Cr and 3 to 13% Ni. Molybdenum, a ferrite stabilizer, is also typically present.
- Shows higher strength and better resistance to stress corrosion. Decrease in ductility at low temperature is compensated by increased rates of strain hardening due to strain-induced transformation of austenite to martensite
- Used in petrochemical industry (for handling wet an dry CO_2, sour gas and oil products), heat exchanges (welded tubing), chemical, industries etc.

Heat Treatment

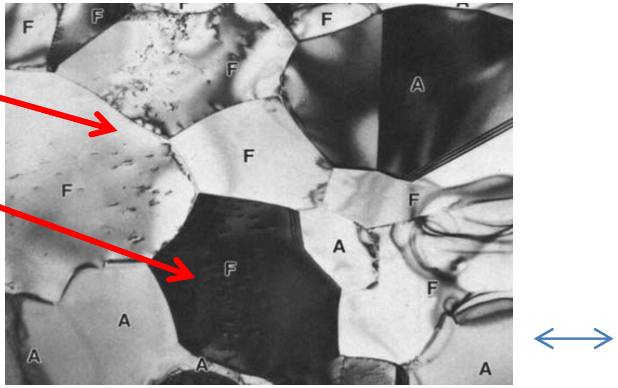
- ✓ Thermomechanical processing is accomplished in the two-phase ferrite austenite fields.
- ✓ Amounts of ferrite and austenite formed during hot working or annealing are a function of temperature. Higher temperatures produce larger amounts of ferrite. Hence, hot working temperatures must be kept between 1000 - 1200 °C



Microstructure of duplex stainless steel 7Mo-Plus

Ferrite

Austenite



Microstructure of cold worked and annealed duplex stainless steel Al 2205

Tool Steel

- ☐ Tool steel refers to a variety of carbon and alloy steels that are particularly well-suited to be made into tools.
- ☐ Characteristics include high hardness, resistance to abrasion (excellent wear), an ability to hold a cutting edge, resistance to deformation at elevated temperatures (red-hardness).
- ☐ Tool steel are generally used in a heat-treated state.

AISI-SAE tool steel grades		
Defining property	AISI-SAE grade	Significant characteristics
Water-hardening	W	
Cold-working	O	Oil-hardening
	A	Air-hardening; medium alloy
	D	High carbon; high chromium
Shock resisting	S	
High speed	T	Tungsten base
	M	Molybdenum base
Hot-working	H	H1-H19: chromium base H20-H39: tungsten base H40-H59: molybdenum base
Plastic mold	P	
Special purpose	L	Low alloy
	F	Carbon tungsten

Tool Steel and their Uses

- ☐ Shock resisting tool steels → Intended for applications requiring toughness and resistance to shock-loading such as hammers, chisels, punches, driver bits and others.
- ☐ Water hardening tool steels → Shallow hardened and relatively low resistance to softening. They are suitable for woodworking tools, hand-metal cutting tools such as taps and reamers and cutlery.

Steels for Room Temperature Use (Classified according to their quenching media)

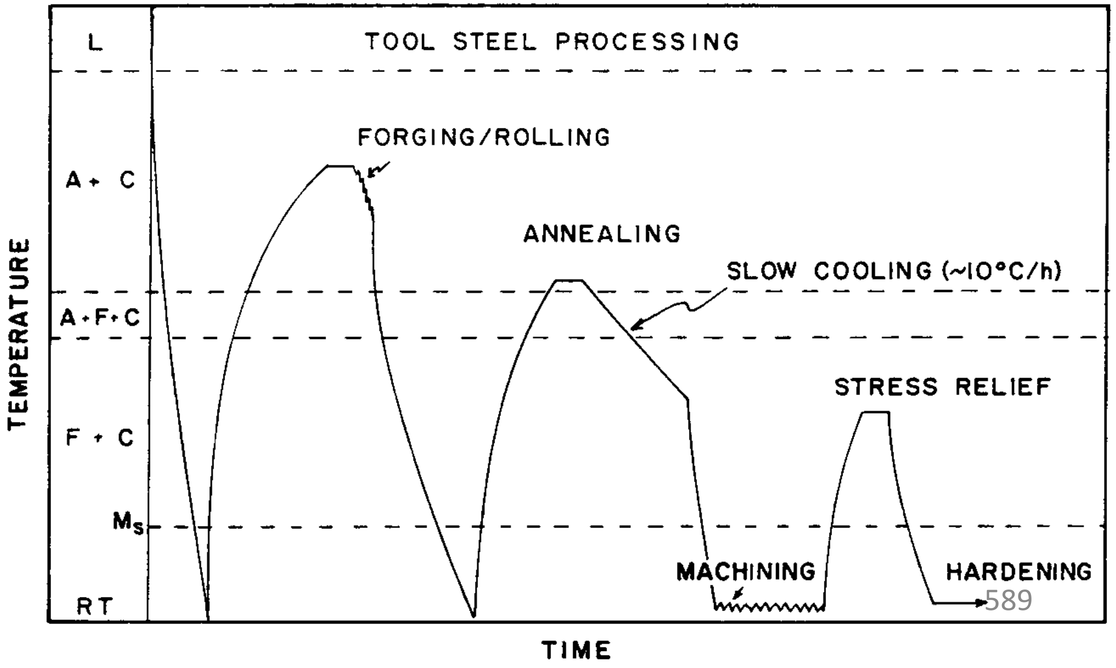
- ☐ Water hardened grades (W) → Plain carbon steels with 0.6-1.0 %C. These have a low hardenability, ie., martensite only to a depth of 0.5 in. V can be added (forms V_4C_3)to improve the hardness and wear resistance of these steels.
- ☐ Shock resistant grades (S) → Contain small amounts of Cr or Mo and are quenched in oil. They have lower C contents (0.5%) to improve impact strength.
- ☐ Oil hardened grades (O) → Small percentages of Cr and W with 0.9 %C. The have medium hardness and are used to short run cold forming dies.
- ☐ Air hardening grades (A) → Greater amounts of Cr and Mo and 1 %C. Used for complicated shapes and thread rolling. Mo and W are relatively expensive so they are only added in small amounts to give much improved hardenability.
- ☐ High carbon, high Cr grades (D grade) → 12 %Cr and 1.5-2.25 %C are extremely wear resistant and used for long run dies and for gauges. Chromium is a relatively low cost addition for increasing hardenability with the excess Cr, $Cr_{23}C_6$ is also formed, which improves wear resistance.

Tool Steel

- Chromium hot working steels (H grades) → 5-7 % Cr, 0.4-1.0% V, 1.5-7.0% W, 1.5% Mo, 0.35% C. Medium hot working for Mg and Al extrusion die-casting dies.
- Tungsten hot working steels (H) → 9.5-12 % W, 3.5-12.0 % Cr, 0.35 % C. Hot working, extrusion and forging dies for brass, nickel and steel.
- Tungsten high speed steel (T) → 12-18 % W, 4.0 % Cr, 1-5 % V, 0.7-1.5 % C. Original high speed (HS) cutting steel with excellent HT wear resistance.
- Molybdenum HS steel (M) → 3.5-8.0 % Mo, 1.5-6.0 % W, 4.0 % Cr, 1-5 % V, 5 % Co, 0.8-1.5 % C. Used for 85% of US cutting steels before the advent of ceramic cutting tools.

Heat Treatment Processes

Schematic diagram of tool steel processing up to the final hardening heat treatment



High Speed Steel (HSS)

- ❑ HSS is a subset of tool steel, commonly used in tool bits and cutting tools. It is often used in power saw blades and drill bits.
- ❑ They are characterized by high carbon contents, sometimes up to 1.5%, and major additions of strong carbide forming elements such as chromium, molybdenum, tungsten and vanadium. Up to 12% Co is also included in some of the more complex grades.
- ❑ It can withstand higher temperatures without losing its temper (hardness) which allows it to cut faster than high carbon steel, hence the name.
- ❑ Other characteristics include high hardness, resistance to abrasion (excellent wear), an ability to hold a cutting edge, resistance to deformation at elevated temperatures (red-hardness).
- ❑ Modulus Of elasticity: 221GPa, Density : 8767 kg/m^3 (↑ durability & hardness), Thermal Conductivity: 21W/m/K
- ❑ HSS are mainly of two types: Tungsten based ones (T grades), Molybdenum based ones (M grades)

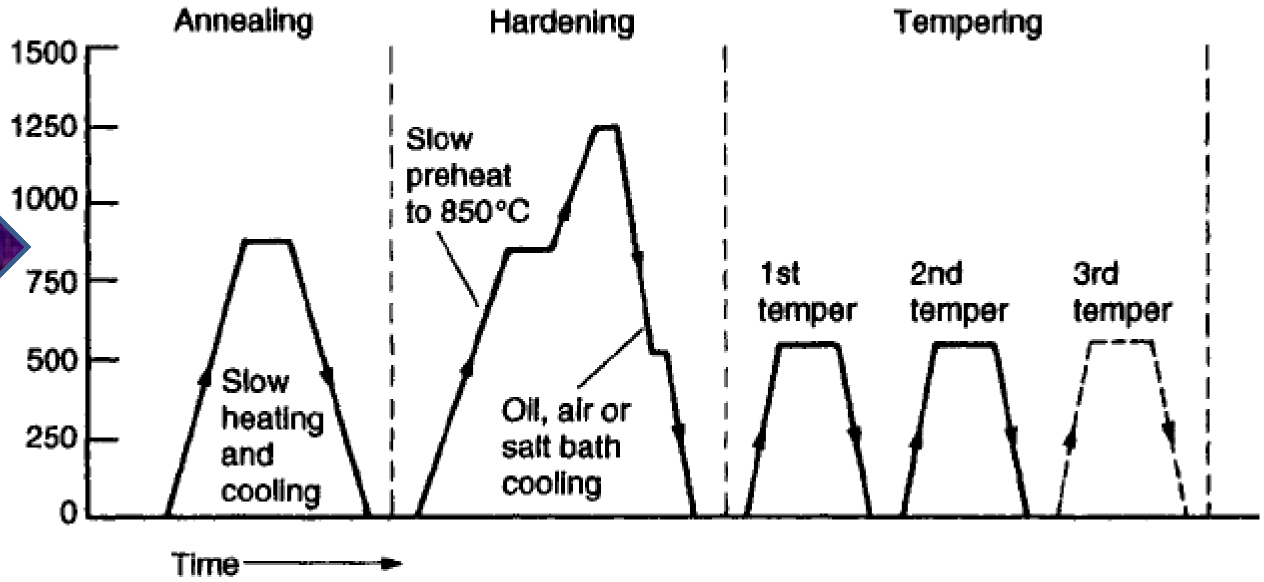
Three popular grades of high-speed steel

AISI-SAE grade	*C%*	*W%*	*Mo%*	*Cr%*	*V%*
T1	0.75	18		4	1
M1	0.8	2	8	4	1
M2	0.85	6	5	4	2

High Speed Steel (HSS)

Heat Treatment

Schematic diagram of the heat treatment of High Speed Steel



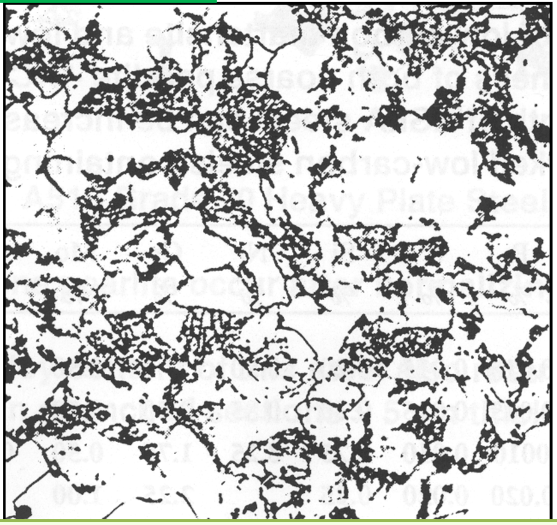
Microstructure of KMnO4 etched M2 high-speed steel showing Feathery, MC eutectics (M, maybe Fe, Mn, Cr with a little W, Mo, V).

High Strength Low Alloy Steel (HSLA)

- HSLA steels are low carbon steels that contain up to 10 % alloying additions of the strong carbide- or nitride-forming elements niobium, titanium or vanadium, separately or together.
- The alloying elements enable martensite and bainite to form during quenching and increases strength and impact toughness.

ASTM Grade	C%	Mn%	P%	S%	Ni%	Cr%	Mo%	V%	Zr %	B%	Cu %
A533 grade B	0.22	1.25	0.015	0.015	0.20		0.50				
A517 grade F	0.15	0.80	0.015	0.015	0.20	0.50	0.50		0.1	0.002	0.3
A543 class 1	0.15	0.35	0.010	0.010	0.25	1.75	0.50	0.02			
A542 class 1	0.12	0.45	1.020	1.020	0.25	2.25	1.00				
A 203 grade D	0.12	0.45	0.015	0.015	0.25						
A553 type 1	0.10	0.65	0.010	0.010	0.25						

High Strength Low Alloy Steel (HSLA)



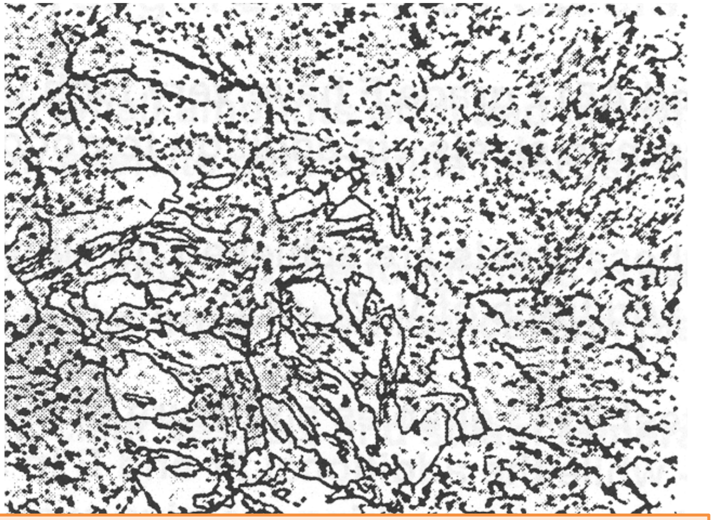
Microstructure of A533 grade B quenched from 900 ºC and tempered at 620 ºC showing ferrite and tempered bainite

A533 grade B

- ✓ Contains small amounts of Ni and Mo, ↑ hardenability, forms ferrite plus bainite microstructure on quenching.
- ✓ Tempering of bainite ↑ toughness, strength & similar ductility to the hot worked low-carbon plain-carbon steels.
- ✓ Used for nuclear vessels and steam generators

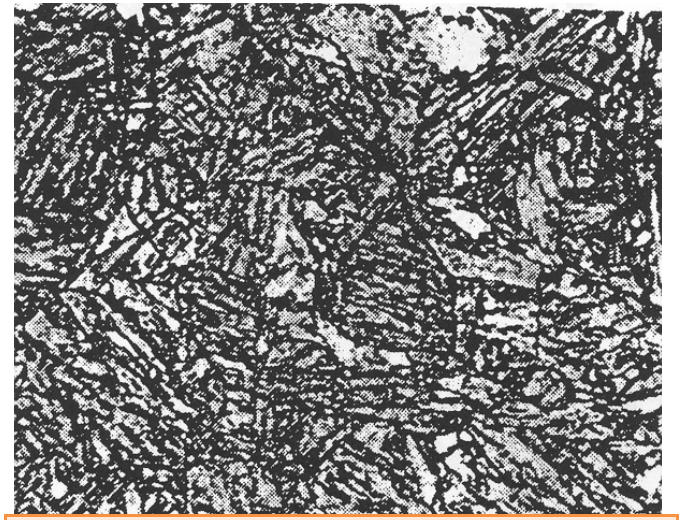
Grades A543 class 1 and A517 grade F

- ✓ Contains Ni, Cr, Mo with further additions of V, Zr, and B.
- ✓ Very high yield and tensile strengths in addition to good toughness
- ✓ Ni, Cr, Mo + V forms a mixture of martensite and bainite on quenching, while the additional Zr and B enables 100% martensite to form on quenching to give even greater strength.
- ✓ Zr + B → Forms precipitate at high temperatures, ↑ strength
- ✓ Tempering of bainite and martensite → 600-650 ºC, ↑ toughness
- ✓ Used in plates, shapes, forgings and for weld constructions including bridges and nuclear pressure vessels etc.



Microstructure of A543 class 1 quenched from 850 ^{o}C and tempered at 650 ^{o}C showing tempered bainite and martensite.

HSLA



Microstructure of A517 grade F quenched from 925 ^{o}C and tempered at 650 ^{o}C showing Tempered martensite.

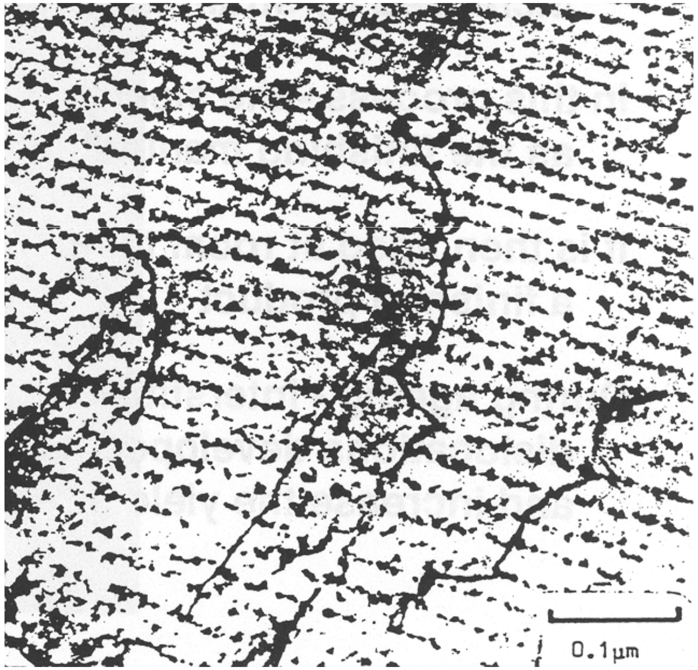
A203 grade D and A553 type 1

- ✓ Ni improves low temperature notch toughness.
- ✓ 3.5 %Ni in Steel A203 does not improve the strength but after tempering ductile-brittle transition temperature is lowered to below -20 ^{o}C.
- ✓ 9% Ni content of A533 improves the strength by “solid solution strengthening” up to the level of the Ni-Cr-Mo HSLA steel and also gives A533 a higher ductility so that its ductile to brittle transition temperature is lowered to below –200 ^{O}C.
- ✓ A 203 is used for a variety of relatively low-stress, low temperature applications and A533 is used for high-stress low-temperature applications such as pressure vessels and for the transport of liquified natural gas (-170 ^{o}C)

High Strength Low Alloy Steel (HSLA)

A542 class1

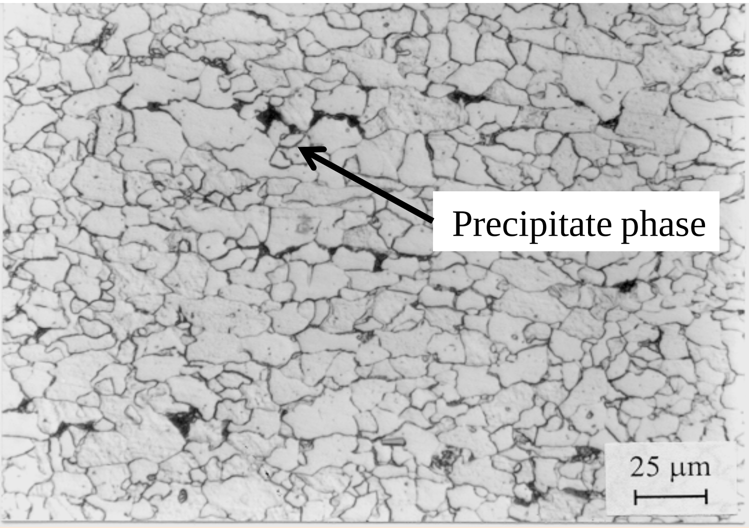
- ✓ Contains Cr and Mo which increases its resistance to high temperature creep (Due to interphase precipitation hardening) and corrosion resistance.
- ✓ Quenching and Tempering ↑ strength with good ductility similar to A543
- ✓ Used for high pressure chemical reactors and refinery vessels.



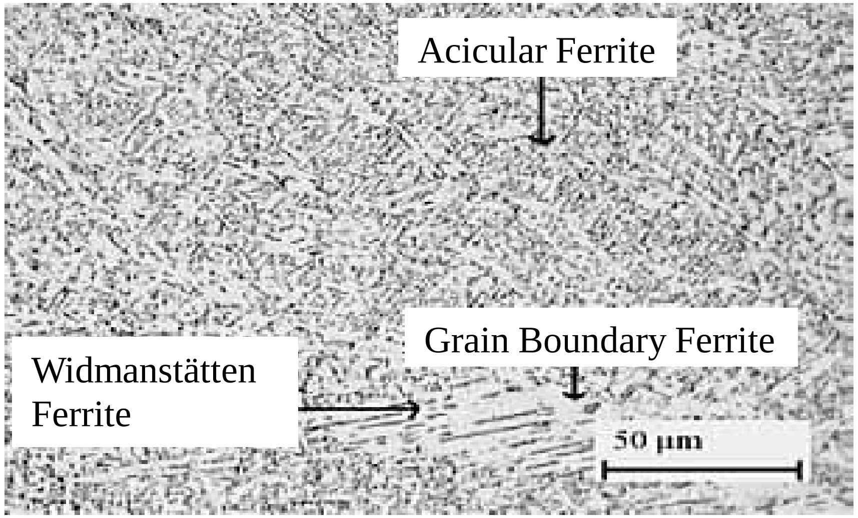
Microstructure of 0.15C–0.75V HSLA Steel showing interphase precipitation at the α/γ boundary

Microalloyed Steel

- Microalloyed steel → Contains small amounts (< 0.2%) of strong carbide forming elements such as niobium, vanadium, titanium, molybdenum, zirconium, boron, and rare earth metals → refines the grain microstructure (Grain size of ferrite ASTM 12-14) & facilitates precipitation hardening (by forming fine dispersion of alloy carbides).
- These steels have improved strength and excellent weldability compared to mild steel. In terms of performance and cost, these steels lie between carbon steel and low alloyed steel.
- Typical mechanical properties of Microalloyed steel are: Yield Strength → 400-500 Mpa, Tensile Strength → 600-650 Mpa, % Elongation → 20-22.
- Used in vehicles/transportation, tubular components, heavy equipment, rails, off-shore/platforms, bridges, suspension components, building structures etc.



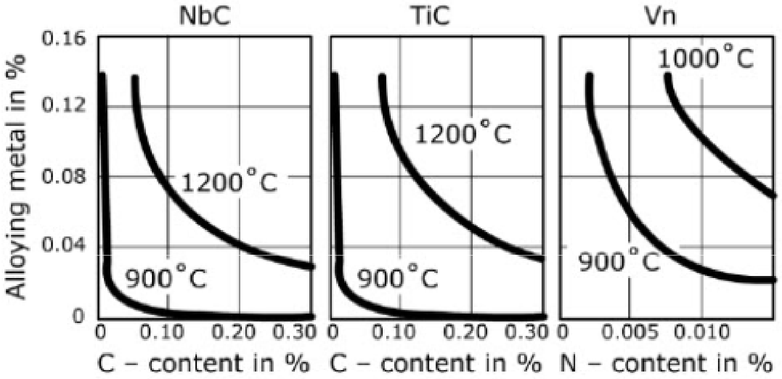
Microstructure of Nb-Ti steel obtained from plane strain compression tests after soaking at 1200°C



Microstructure of low carbon microalloyed steel produced by thermo-mechanical processing

Heat Treatment

- In order to realize the full strengthening potential of micro-alloying additions, it is necessary to use a soaking temperature prior to forging that is high enough to dissolve all vanadium-bearing precipitates. A soaking temperature above 1100°C is generally preferred.
- For Nb–Ti microalloyed steel the single step austenite reheating temperature at 1150°C provides better austenite conditioning than the higher reheating temperature at 1240°C.



- Finishing temperature for rolling also plays an important in determining the grain size and, hence the strength level.
- If rolling is done through the transformation into the completely ferritic condition, fine ferrite is seen in subgrain structures.
- Alternatively, If rolling is finished above the γ/α transformation, the nature of the transformation is altered by increasing the cooling rate. Slow rates of cooling obtained by coiling at a particular temperature will give lower strengths than rapid rates imposed by water spray cooling following rolling. Rapid cooling rate results in transformation of equi-axed ferrite to Widmanstätten ferrite with a much higher dislocation density.

Physical metallurgy of Common nonferrous alloys

Avala Lava Kumar* : Suneeti Purohit : Gautam Behera

Department of Metallurgical & Materials Engineering (MME)

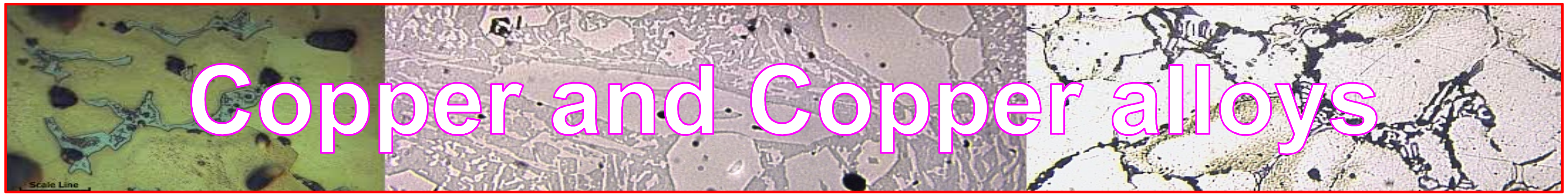
Veer Surendra Sai University of Technology (VSSUT), Burla -768018

**E-mail : lavakumar.vssut@gmail.com*

Introduction

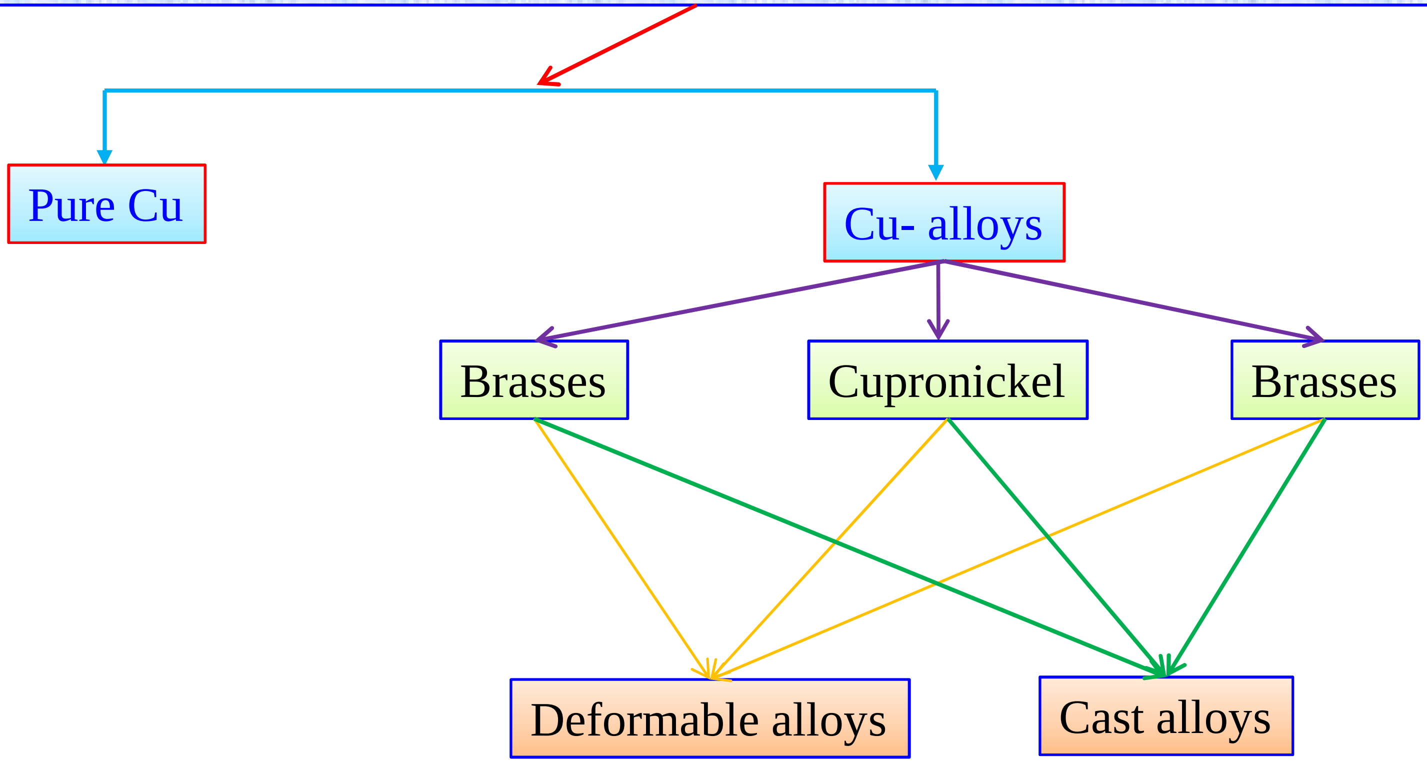
- Metallic materials, when considered in abroad sense, may be divided into two large groups, ferrous and non ferrous.
- The ferrous materials are iron-based, and the non ferrous materials have some element other than iron as the principle constituent .
- The bulk of the nonferrous materials is made up of the alloys of copper, aluminum, magnesium, nickel, tin, lead, titanium and zinc.
- Other nonferrous metals and alloys that are used to a lesser extent include cadmium, molybdenum, cobalt, zirconium, beryllium, tantalum, and the precious metals gold, silver and the platinum group.

  → *This chapter will be concerned with the more important nonferrous metals and alloys These are as follows.*
- Copper and copper alloys (Bronze and Brass)
- Aluminum and aluminum alloys



Copper and Copper alloys

Copper and Copper Alloys



Pure Cu

Cu- alloys

Brasses

Cupronickel

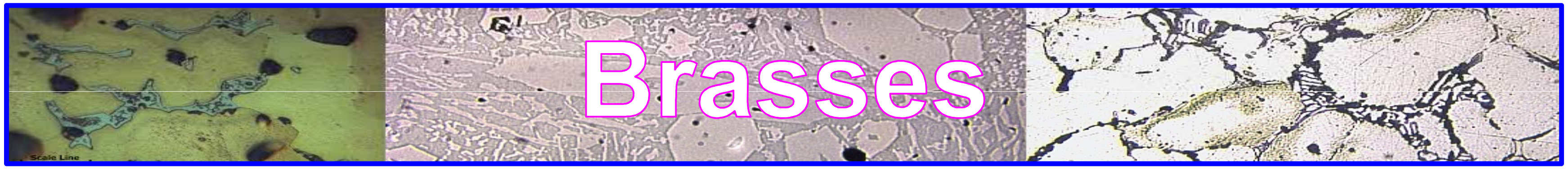
Brasses

Deformable alloys

Cast alloys

Introduction

- ☐ The properties of copper that are most important are high electrical and thermal conductivity, good corrosion resistance, machinability, strength, and easy fabrication.
- ☐ Most of the copper that is used for electrical conductors contains over 99.9 percent copper and is identified as electrolytic tough-pitch copper (ETP) or oxygen-free high-conductivity copper (OFHC).
- ☐ ETP copper contains from 0.02 to 0.05 percent oxygen, which is combined with copper as the compound cuprous oxide (Cu_2O). As cast, copper oxide and copper form an inter dendritic mixture. After working and annealing, the inter dendritic network is destroyed, and the strength is improved.
- ☐ Oxygen-free copper is used in electronic tubes or similar applications because it makes a perfect seal to glass.
- ☐ *Arsenical copper : 0.3 % arsenic has improved resistance to special corrosive conditions.*
- ☐ *Free cutting copper : 0.6 % tellurium excellent machining properties.*
- ☐ *Silver – bearing copper : 7 to 30 oz/ton. Silver raises the Recrystallization temperature of copper, thus preventing softening during soldering of commutators.*

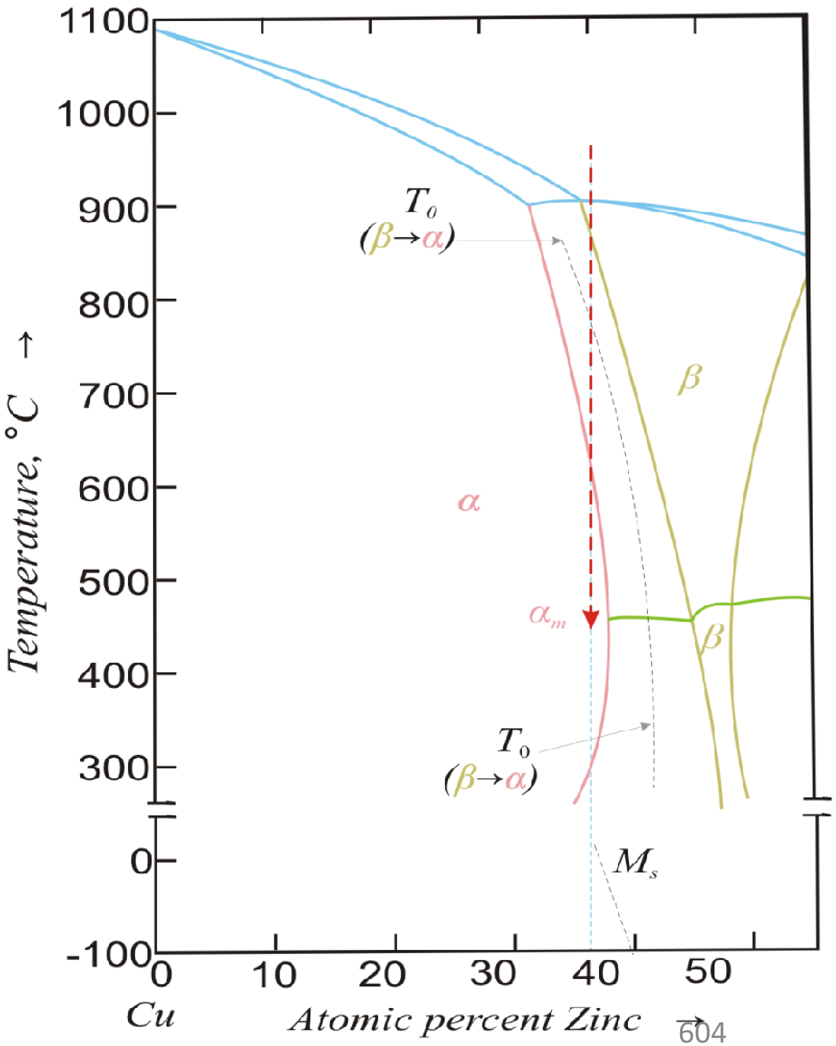


Brasses

Introduction

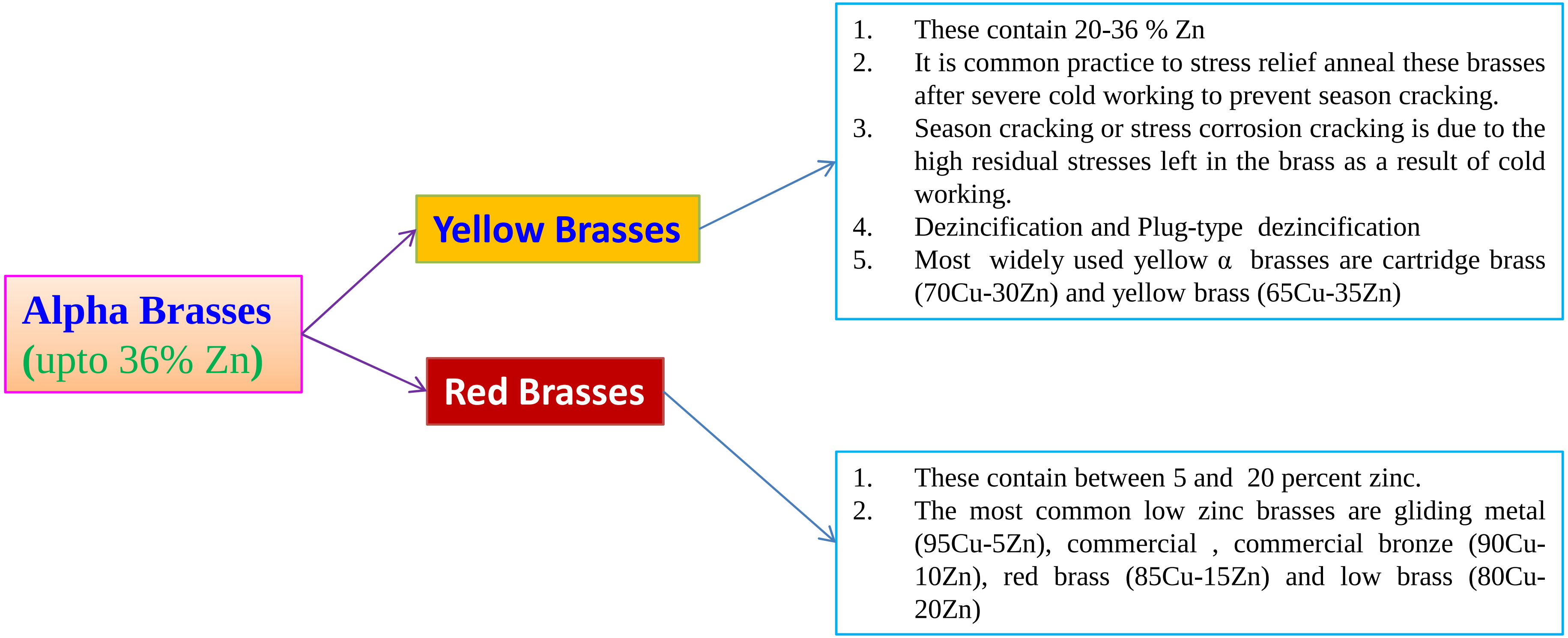
- Brasses are essentially *alloys of copper zinc*. Some of these alloys have small amounts of other elements such as lead, tin, or aluminum.

- The portion of the binary copper zinc phase diagram which is applicable to commercial alloys is shown in Fig.
- The solubility of zinc in the alpha (α) solid solution increases from 32.5 % at 910 ºC to about 39 % at 455 ºC.
- Since copper is F.C.C , the α solid solution is F.C.C the beta (β) phase is B.C.C electron compound and undergoes ordering, indicated by a dot-dash line, in the region of 455 to 470 ºC.
- On cooling in this temperature range the B.C.C β phase, with copper and zinc atoms randomly dispersed at lattice points, changes continuously to the ordered structure β’ , which is still B.C.C.



Alpha Brasses

- But with the copper atoms at the corners and zinc atoms at the centers of the unit cubes. The ordering reaction is so rapid that it cannot be retarded or prevented by quenching. The best combination of strength and ductility is obtained in 70Cu-30Zn brass.
- The commercial brasses may be divided into two groups, brasses for cold working (α brasses) and brasses for hot working (α plus β brasses)



Alpha Brasses
(upto 36% Zn)

Yellow Brasses

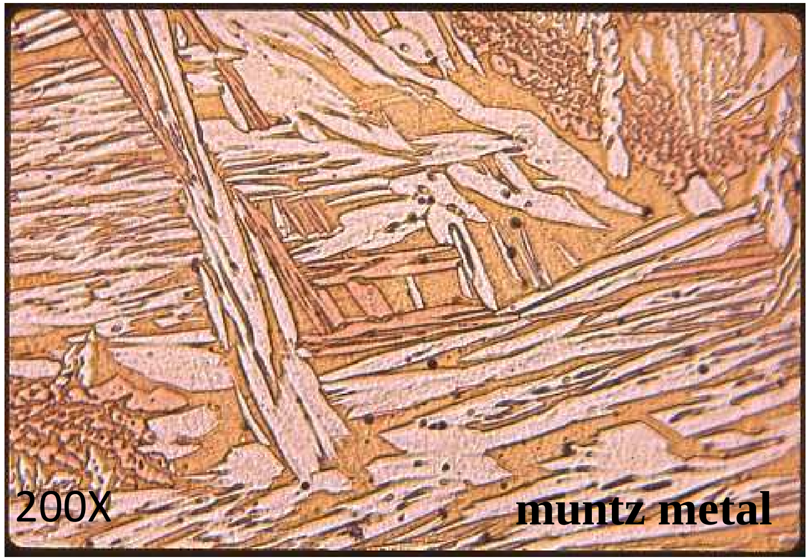
1. These contain 20-36 % Zn
2. It is common practice to stress relief anneal these brasses after severe cold working to prevent season cracking.
3. Season cracking or stress corrosion cracking is due to the high residual stresses left in the brass as a result of cold working.
4. Dezincification and Plug-type dezincification
5. Most widely used yellow α brasses are cartridge brass (70Cu-30Zn) and yellow brass (65Cu-35Zn)

Red Brasses

1. These contain between 5 and 20 percent zinc.
2. The most common low zinc brasses are gliding metal (95Cu-5Zn), commercial , commercial bronze (90Cu-10Zn), red brass (85Cu-15Zn) and low brass (80Cu-20Zn)

Alpha plus Beta Brasses

- ☐ These contain from 54 to 62 % copper. And this alloy consist of two phases, α and β'. The β' phase is harder and more brittle at room temperature than α; therefore, these alloys are more difficult to cold work than the α brasses.
- ☐ At elevated temperatures the β phase becomes very plastic, and since most of these alloys may be heated into the single phase β region, they have excellent hot-working properties.
- ☐ The most widely used α+β' brass is *muntz metal (60Cu-40Zn)*, which has high strength and excellent hot-working properties.



- ☐ Muntz metal is used in condenser heads, perforated metal and architectural work.

Alpha plus Beta Brasses

- Free-cutting brass (61.5Cu-35.5Zn-3Pb) has the best machinability of any brass combined with good mechanical and corrosion resistant properties.
- Forging brass (60Cu-38Zn-2Pb) has the best hot working properties of any brass and is used for hot forgings, hardware and plumbing parts.
- Architectural bronze (57Cu-40Zn-3Pb) has excellent forging and free matching properties.
- Naval brass (60Cu-39.25Zn-0.75Sn), also known as *tobin bronze*, has increased resistance to salt water corrosion and is used for condenser plates, welding rod, propeller shafts, piston rods, and valve systems.
- Manganese bronze (58.5Cu-39Zn-1.4Fe-1Sn-0.1Mn), really a high-zinc brass, has high strength combined with excellent wear resistance and is used for clutch disks, extruded shapes, forgings, pump rods, shafting rod, valve stems, and welding rod.
- Cast brasses The previous discussion was concerned primarily with wrought brasses, which are mainly binary alloys of copper and zinc. The cast brasses are similar in name to the wrought brasses but usually contain appreciable amounts of other alloying elements. Tin may be present from 1 to 6 percent and lead from 1 to 10 percent; some alloys may contain iron, manganese, nickel and aluminium.

Bronzes

Introduction

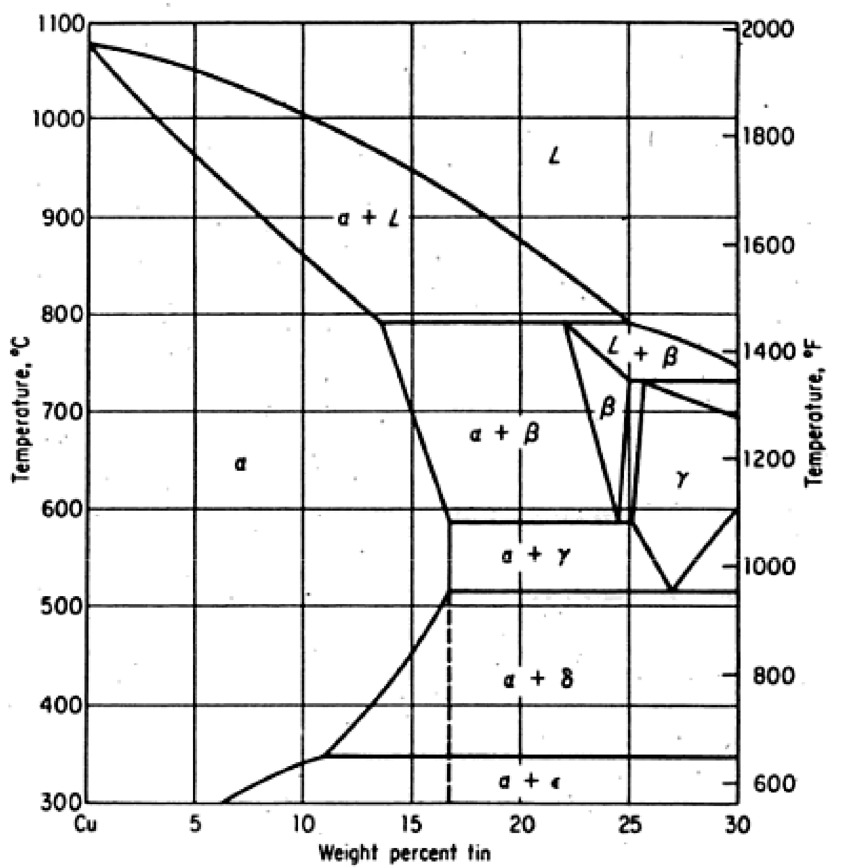
- ❑ The term bronze was originally applied to the copper-tin alloys; however, the term is now used for any copper alloy, with the exception of copper-zinc alloys, that contains up to approximately 12% of the principle alloying element.
- ❑ Bronze, as a name, conveys the idea of a higher-class alloy than brass, and it has been incorrectly applied to some alloys that are really special brasses
- ❑ Commercial bronzes are primarily alloys of copper and tin, aluminum, silicon, or beryllium. In addition, they may contain phosphorus, lead, zinc or nickel.

Tin Bronzes

- ❑ These are generally referred to as *phosphor bronzes* since phosphorous is always present as a deoxidizer in casting.
- ❑ The usual range of phosphorus content is between 0.01 and 0.5%, and of tin between 1 and 11 percent.
- ❑ The copper- rich portion of the copper-tin alloy system is shown in next page. The β phase forms as the result of a peritectic reaction at 798 ºC. At 586 ºC, the β phase undergoes a eutectoid reaction to form the eutectoid mixture (α+γ). At 520ºC, gamma (γ) also undergoes a eutectoid transformation to (α+δ).

Tin Bronzes

- The diagram also indicates the decomposition of the δ phase. This takes place by a eutectoid reaction at 350 ºC forming (α+ε). This reaction is so sluggish that in commercial alloys, the epsilon (ε) phase is nonexistent.
- The slope of the solvus line below 520 ºC shows a considerable decrease in the solubility of tin in the α phase.
- The precipitation of the δ and ε phase due to this change in solubility is slow that, for practical purposes, the solvus line is indicated by the vertical dotted line below 520 ºC.

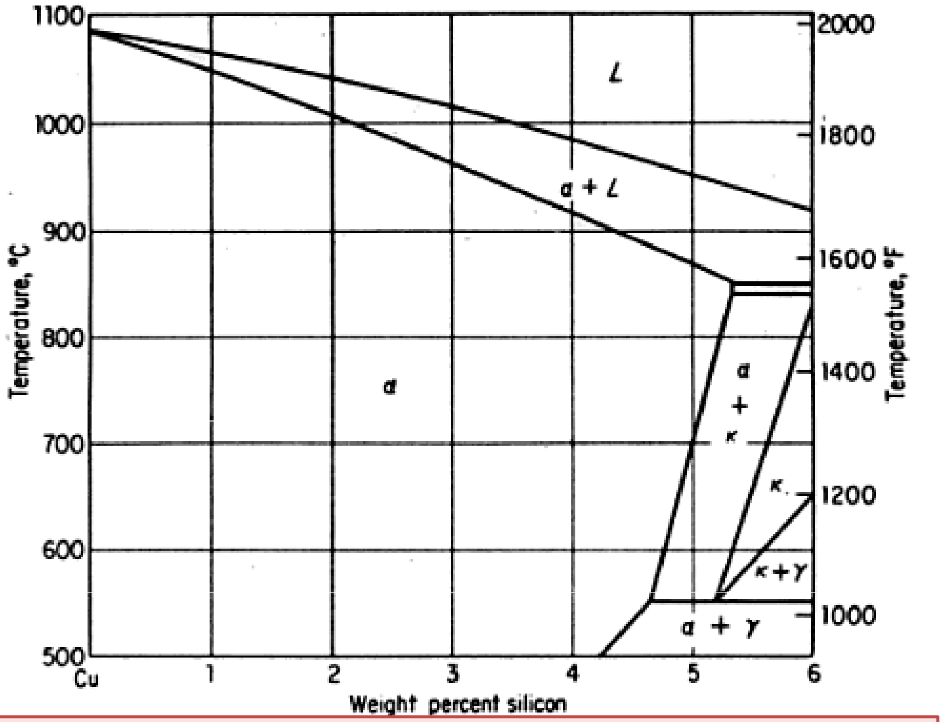


Copper-rich portion of the copper tin phase diagram

- For this reason, slow cooled cast tin bronzes containing below 7% tin generally show only a single phase, the α solid solution. There is some of the δ phase in most castings containing over 7 percent tin. *The phosphor bronzes are characterized by high strength, toughness, high corrosion resistance and freedom for season cracking .*

Silicon Bronzes

- The copper-rich portion of the copper-silicon alloy system is shown in Fig. The solubility of silicon in the α phase is 5.3% at 850ºC and decreases with temperature.
- The eutectoid reaction at 555ºC is very sluggish, so that commercial silicon bronzes, which generally contain less than 5% Si, are single phase alloys.

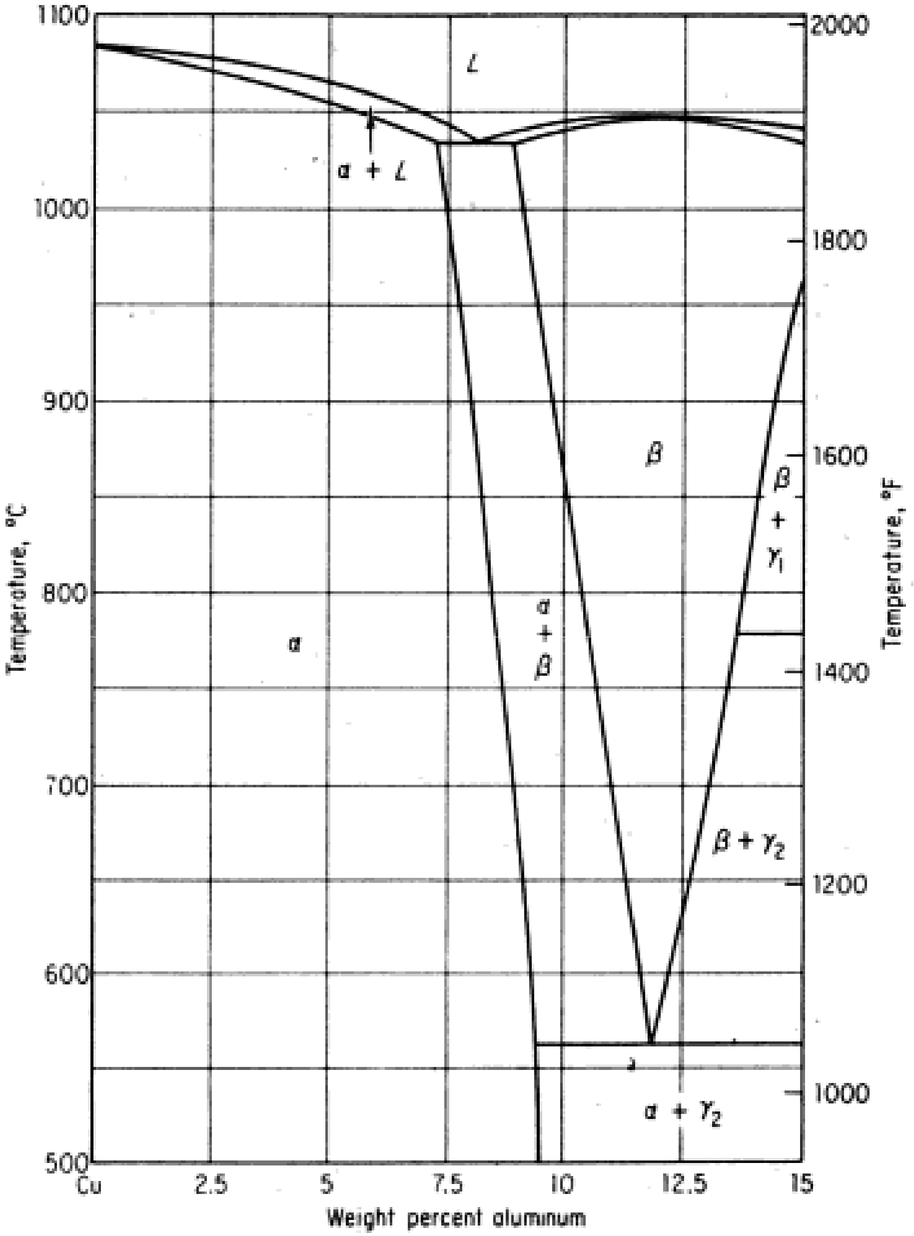


Copper-rich portion of the copper Silicon phase diagram

- Silicon bronzes are the strongest of the work-hardenable copper alloys. They have mechanical properties comparable to those of mild steel and corrosion resistance comparable to that of copper.
- They are used for tanks, pressure vessels, marine construction, and hydraulic pressure lines.

Aluminum Bronzes

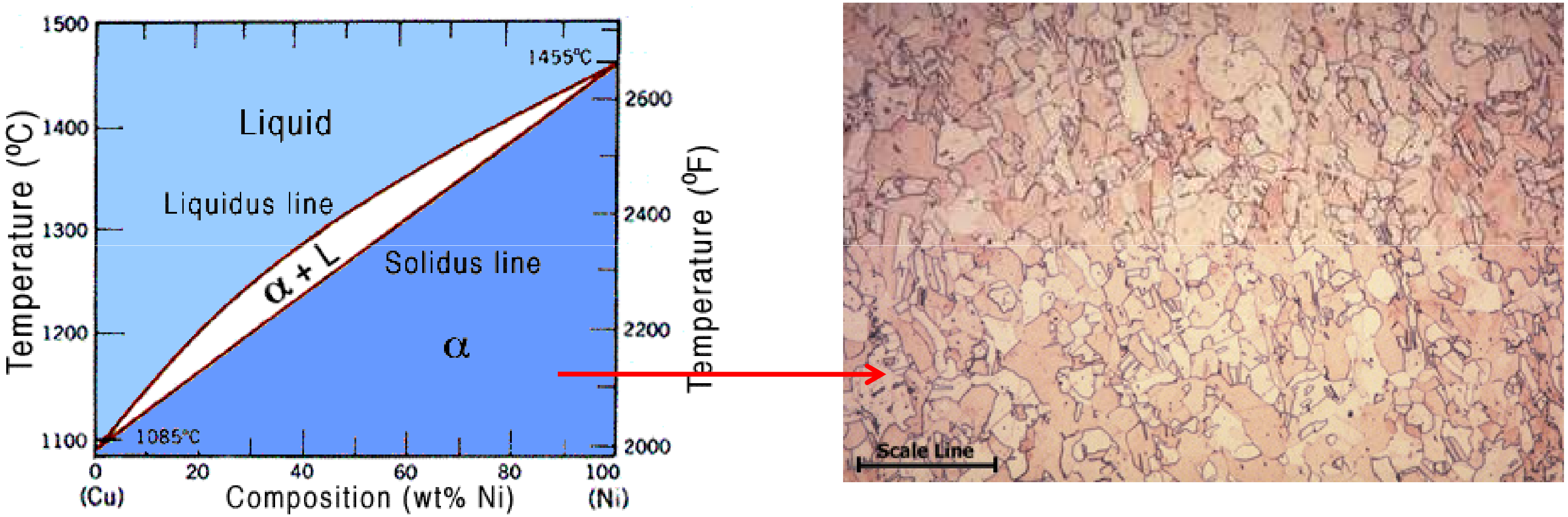
- The maximum solubility of aluminum in the α solid solution is approximately 9.5% at 565ºC to form the ($\alpha+\gamma_2$) mixture.
- Most commercial aluminum bronzes contain 4 and 11 percent aluminum. Those alloys containing up to 7.5% Al are generally single-phase alloys, while those containing between 7.5 and 11% aluminum are two phase alloys. Other elements such as iron, nickel, manganese, and silicon are frequently added to aluminum bronzes
- The single-phase aluminum bronzes show good cold working properties with good corrosion resistance to atmospheric and water attack.
- The α+β aluminum bronzes are interesting because they can be heat treated to obtain structures similar to those in steel.



Copper-rich portion of the copper aluminum phase diagram

Cupronickels

- These are copper-nickel alloys that contain up to 30% nickel. The copper-nickel binary phase diagram shows complete solubility, so that all cupronickels are single-phase alloys. They are not susceptible to heat treatment and may have their properties altered only by cold working.



- The cupronickel alloys have high resistance to corrosion fatigue and also high resistance to the corrosive and erosive action of rapidly moving sea water. They are widely used for condenser, distiller, evaporator and heat exchanger tubes for naval vessels and coastal power plants.

Aluminum alloys

“ Where ever weight is the enemy

Where ever appearance matters

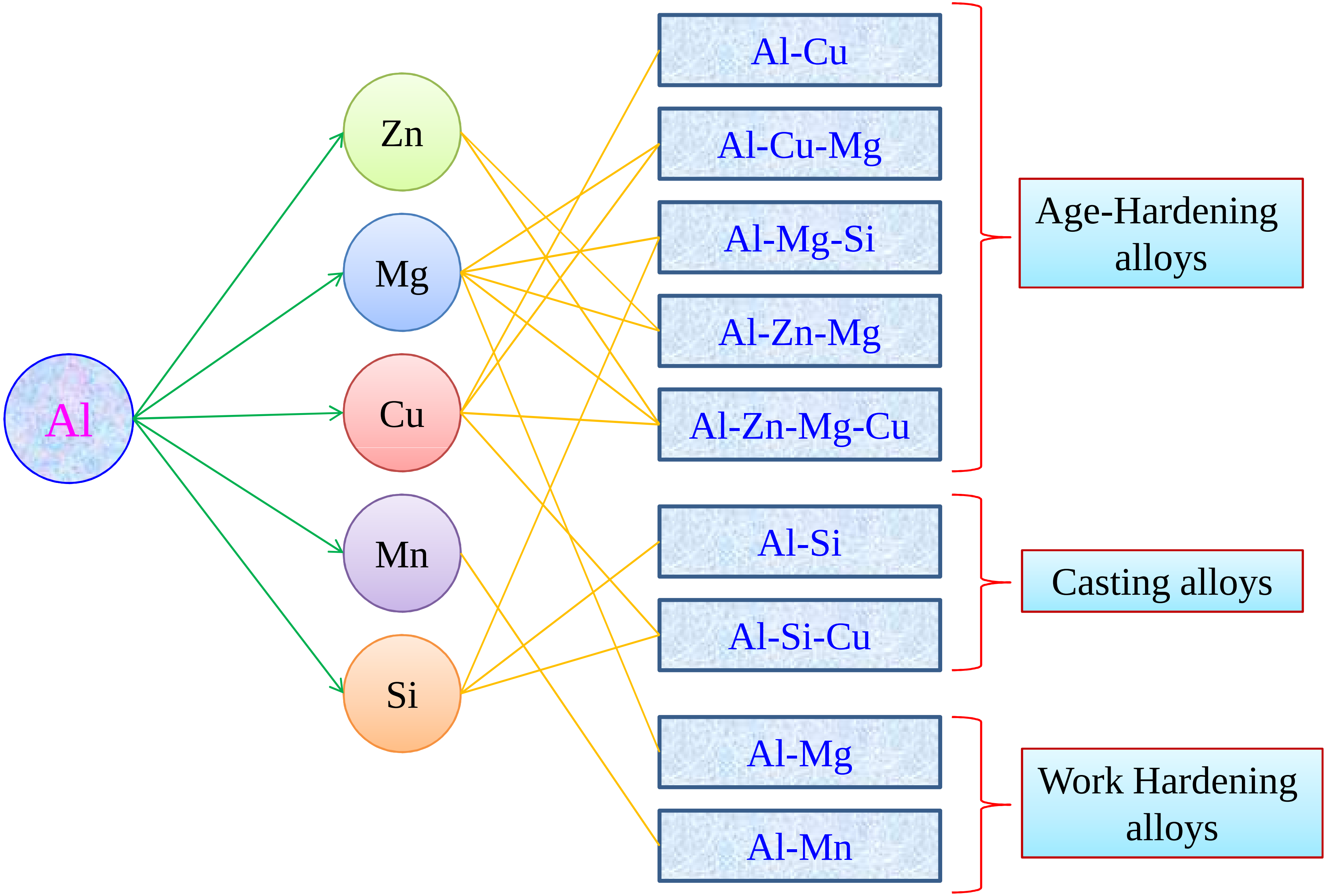
Where ever durability is required”

The answer is Aluminum & its alloys

Introduction

- Aluminum and its alloys possess many attractive characteristics including light weight, high thermal and electrical conductivities, a nonmagnetic nature, high reflectivity, high resistance to corrosion, reasonably high strength with good ductility and easy fabrication.
- Nevertheless, probably the most important characteristic of aluminum is its low density, which is about one-third that of steels and copper alloys. Because of this, certain aluminum alloys have a better strength-to-weight ratio than high-strength steels.
- Among the many alloying elements added to aluminum, the most widely used are copper, silicon, magnesium, zinc, and manganese. These are used in various combinations, and in many cases they are used together with other additions to produce classes of age hardening, casting, and work hardening alloys.
- All age hardening alloys contain alloying elements that dissolve in aluminum at elevated (solution treatment) temperatures and precipitate at lower (aging) temperatures. An example of an age hardening alloy is Al-Cu *(which will discussed in coming slides).*
- Most casting alloys contain silicon, which improves the fluidity and mold-filling capacity of aluminum alloys and reduces their susceptibility to hot cracking and the formation of shrinkage cavities during solidification. Work hardening alloys frequently contain Mn and Mg, which form a fine dispersion of inter metallic phases and/or impart solid-solution strengthening.

Major Aluminum alloy systems



Al

Zn

Mg

Cu

Mn

Si

Al-Cu

Al-Cu-Mg

Al-Mg-Si

Al-Zn-Mg

Al-Zn-Mg-Cu

Al-Si

Al-Si-Cu

Al-Mg

Al-Mn

Age-Hardening alloys

Casting alloys

Work Hardening alloys

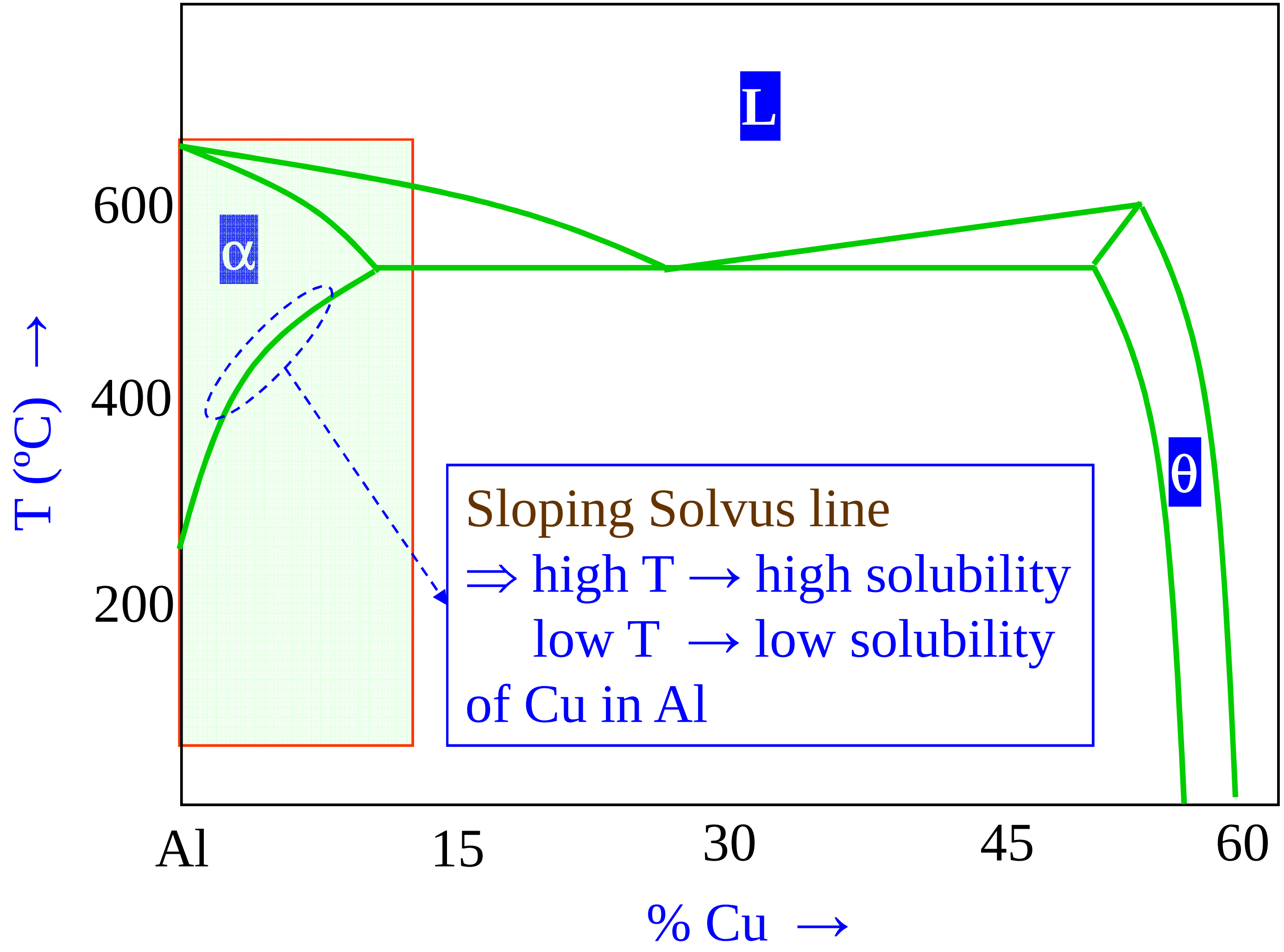
ALUMINIUM ALLOY DESIGNATION SYSTEM

ALLOY GROUP	MAJOR ALLOYING ELEMENTS	EXAMPLE
AA 1XXX	Min. 90% pure Al.	AA 1050
AA 2xxx	Copper	AA 2014, AA2024
AA 3XXX	Manganese	AA 3003
AA 4XXX	Silicon	AA 4030
AA 5XXX	Magnesium	AA 5083
AA 6XXX	Magnesium+Silicon	AA 6061
AA 7XXX	Zinc	AA 7075, AA 7175
AA 8XXX	Others	AA 8020

Heat treatment

- The most important heat treating process for non ferrous alloys is *age hardening*, or *precipitation hardening*.
- In order to apply this heat treatment, the equilibrium diagram must show partial solid solubility, and the slope of the solvus line must be such that there is greater solubility at a higher temperature than at a lower temperature.
- The purpose of precipitation hardening treatment is to improve strength of the materials. It can explained by with respect to dislocations.
- The presence of dislocation weakens the crystal → easy plastic deformation
- Putting hindrance to dislocation motion increases the strength of the crystal
- Fine precipitates dispersed in the matrix provide such an impediment.
- For example: Strength of Al → 100 MPa
  Strength of Duralumin (Al + 4% Cu + other alloying elements) → 500 Mpa
- Two stages are generally required in heat treatment to produce age hardening:
  - ✓ Solution treatment
  - ✓ Aging

Age-Hardening

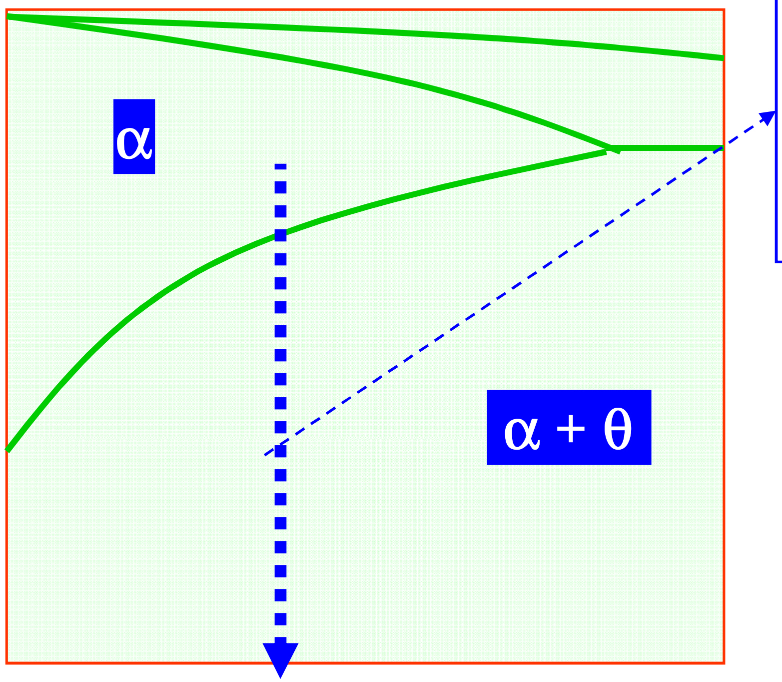


Sloping Solvus line
⇒ high T → high solubility
low T → low solubility
of Cu in Al

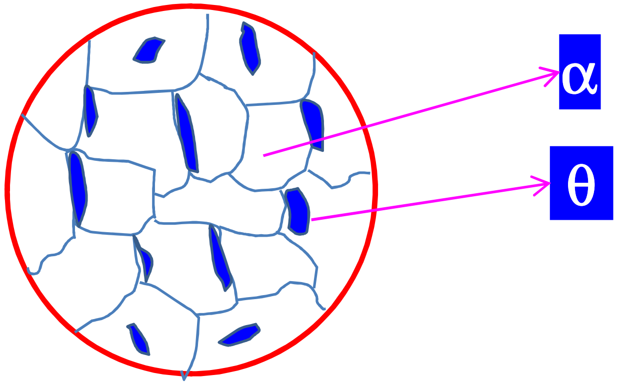
Al rich end of the Al-Cu phase diagram

Age-Hardening

On Equilibrium cooling



- $\alpha \rightarrow \alpha + \theta$
- Slow equilibrium cooling gives rise to coarse θ precipitates which is not good in impeding dislocation motion.*

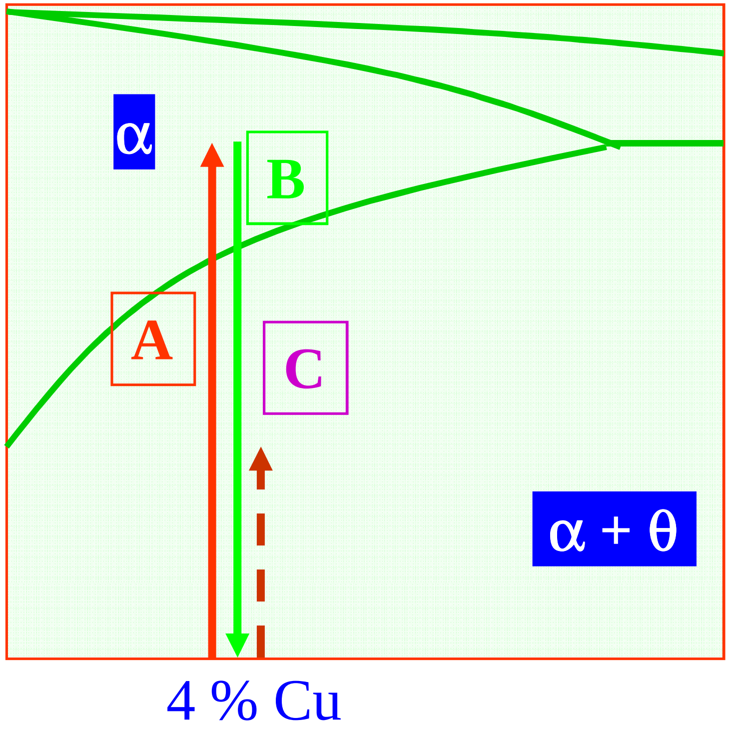


$$\begin{pmatrix}\alpha\,(FCC)\\ 4\,\%\,Cu\\ 550^{o}C\end{pmatrix} \xrightarrow{slow\ cool} \begin{pmatrix}\alpha\,(FCC)\\ 0.5\,\%\,Cu\\ RT\end{pmatrix} + \begin{pmatrix}\theta\ CuAl_2\,(Tetragonal)\\ 52\,\%\,Cu\\ RT\end{pmatrix}$$

Age-Hardening

To obtain a fine distribution of precipitates the cycle A → B → C is used

Solution treating at high temperature, then quenching (second phase is in solid solution) →Cycle A and B



A Heat (to 550°C) → solid solution α

B Quench (to RT) →

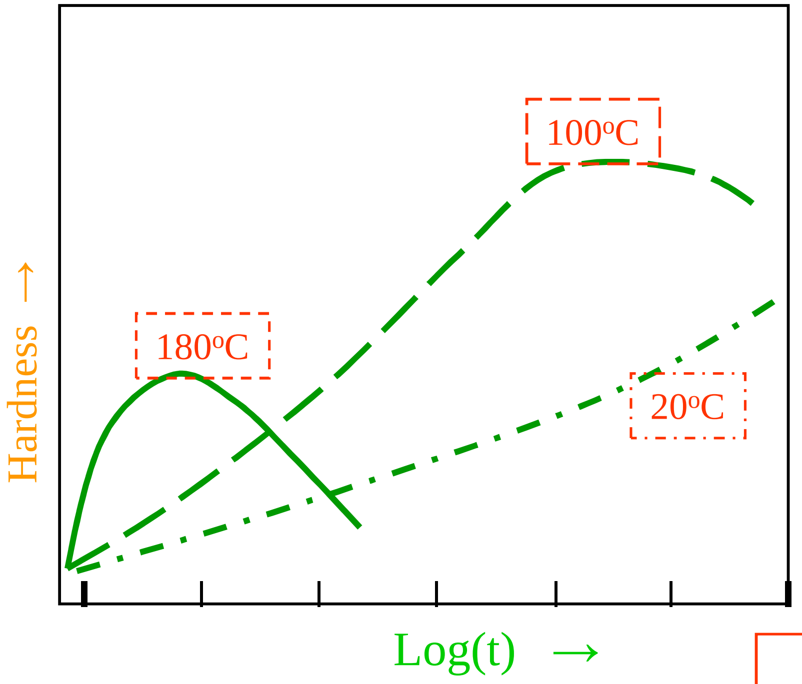
- supersaturated solution
- Increased vacancy concentration

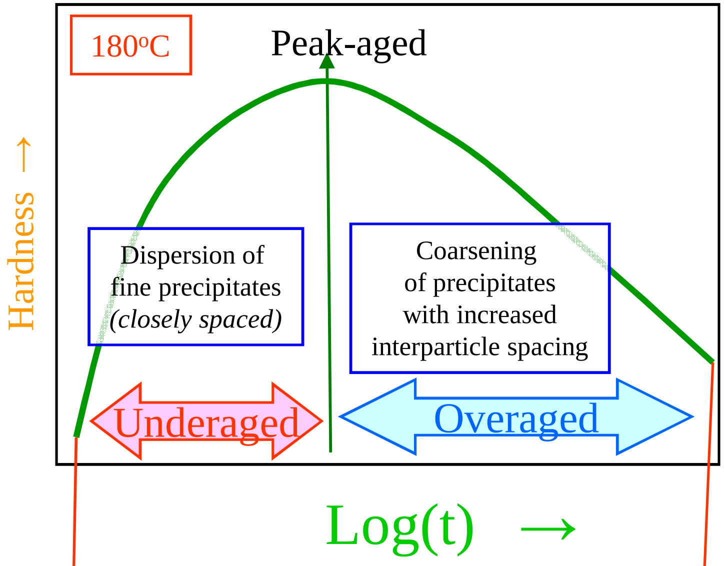
Ageing at room temperature or slightly higher temperature (Precipitation of second phase, giving strengthening effect) →Cycle C

C Age (*reheat* to 200°C) → fine precipitates

Note: Treatments A, B, C are for the same composition

Age-Hardening





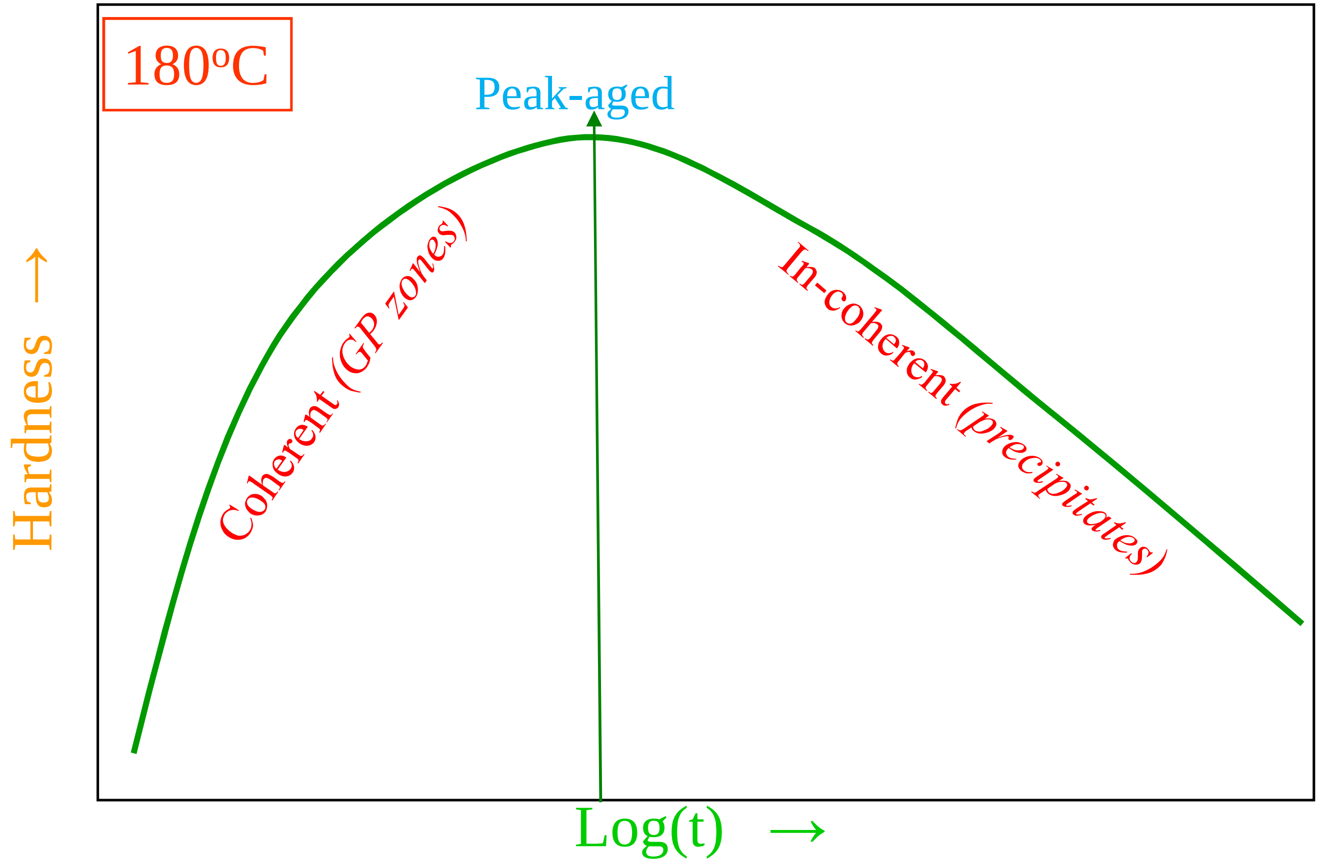
Region of solid solution strengthening *(no precipitation hardening)*

Region of precipitation hardening *(but little/some solid solution strengthening)*

- ❑ Higher temperature ⇒ less time of aging to obtain peak hardness
- ❑ Lower temperature ⇒ increased peak hardness

⇒ optimization between time and hardness required

A complex set of events are happening parallely/sequentially during the aging process
→ These are shown schematically in the figure below



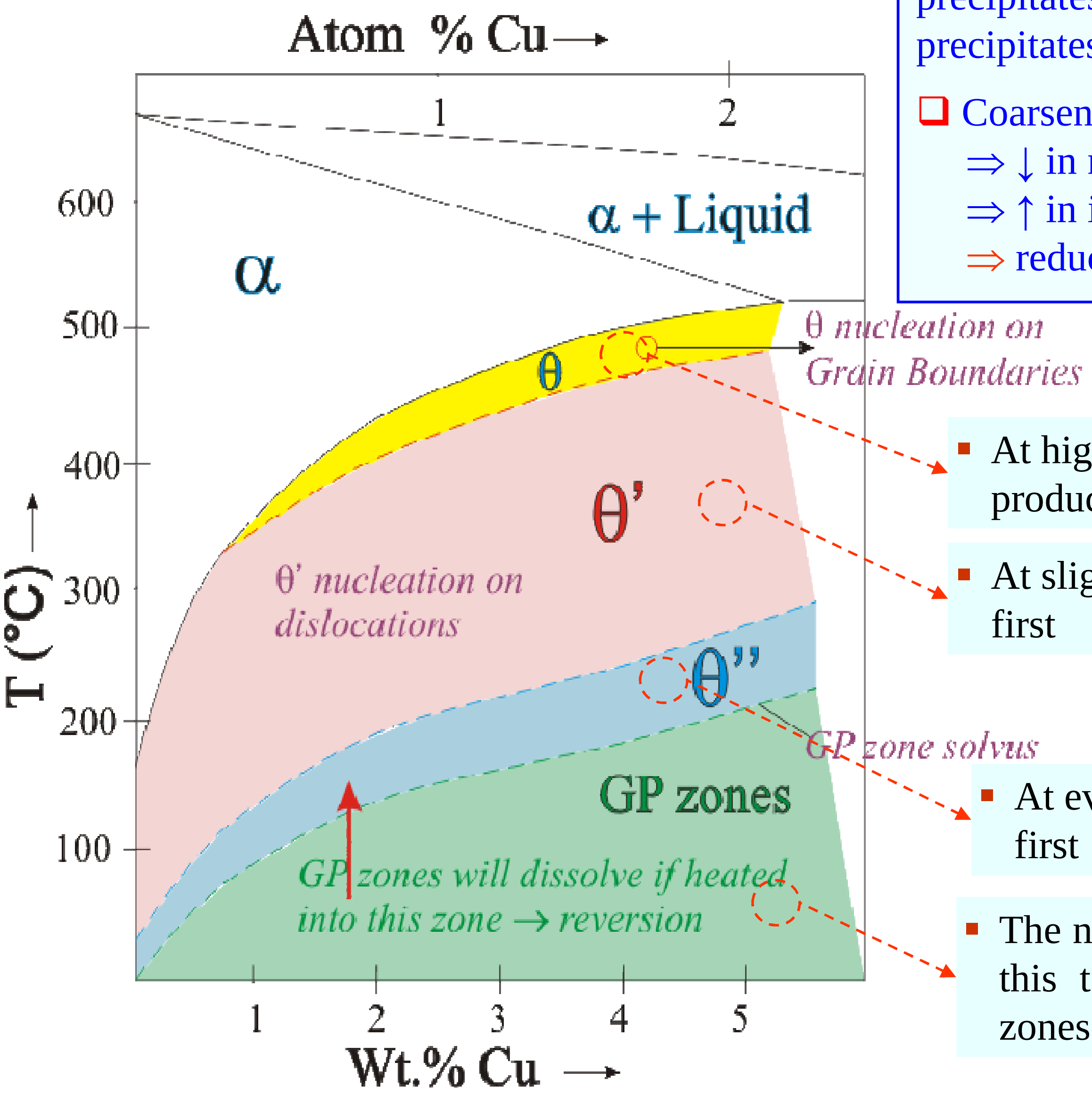
Increasing size of precipitates with increasing interparticle (inter-precipitate) spacing

Interface goes from coherent to semi-coherent to incoherent

Precipitate goes from GP zone → θ’’ → θ’ → θ

Age-Hardening

- Due to large surface to volume ratio the fine precipitates have a tendency to coarsen → small precipitates dissolve and large precipitates grow
- Coarsening
  - ⇒ ↓ in number of precipitate
  - ⇒ ↑ in interparticle (inter-precipitate) spacing
  - ⇒ reduced hindrance to dislocation motion



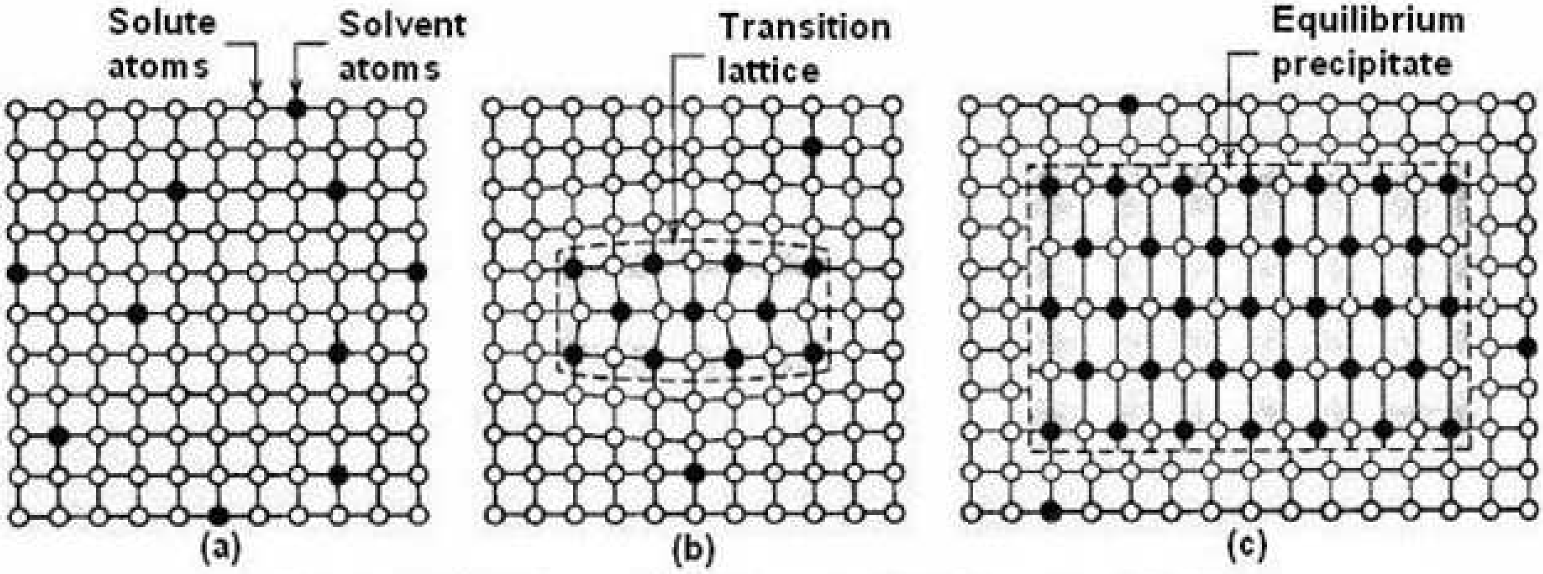
- At higher temperatures the stable θ phase is produced directly
- At slightly lower temperatures θ' is produced first
- At even lower temperatures θ'' is produced first
- The normal artificial aging is usually done in this temperature range to give rise to GP zones first

Coherent lattice theory

- The strengthening of a heat-treatable alloy by aging is not due merely to the presence of a precipitate. It is due to both the uniform distribution of a finely dispersed submicroscopic precipitate and the distortion of the lattice.
- There are several theories of precipitation hardening, to explain in what manner precipitate particles harden the matrix or solvent lattice, the most useful theory is *coherent lattice theory.*
- After solution treatment and quenching, the alloy is in a supersaturated condition, with the solute atoms distributed at random in the lattice structure (Fig A).
- During an incubation period, the excess solute atoms tend to migrate to certain crystallographic planes, forming clusters or embryos of the precipitate.
- During aging, these clusters form an intermediate crystal structure, or *transitional lattice*, maintaining registry (coherency) with the lattice structure of the matrix.
- The excess phase will have different lattice parameters from those of the solvent, and as a result of the atom matching (coherency), there will be considerably distortion of the matrix (Fig B).

Coherent lattice theory

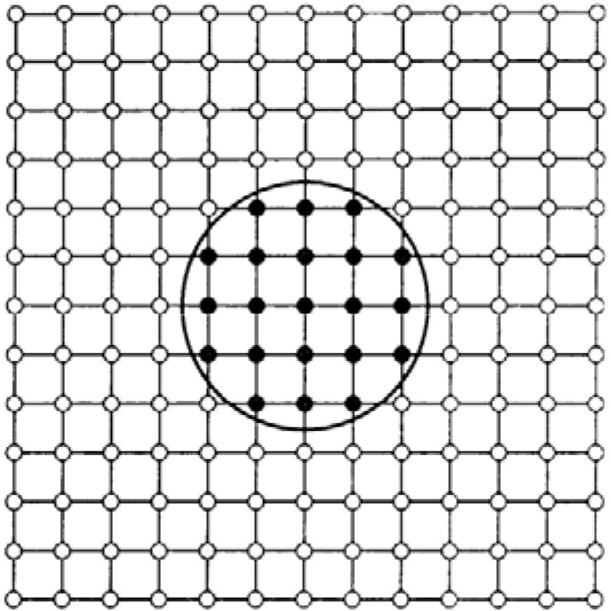
- ❑ The distortion of the matrix extends over a larger volume than would be the case if the excess phase were a discrete particle. Eventually the equilibrium excess phase is formed with its own lattice structure (Fig C).
- ❑ This causes a loss of coherency with the matrix and less distortion hardness and strength will decrease, and the alloy is ‘over-aged’. There will now be a boundary between the excess phase and the matrix so that the precipitated particle will be visible under the microscope.



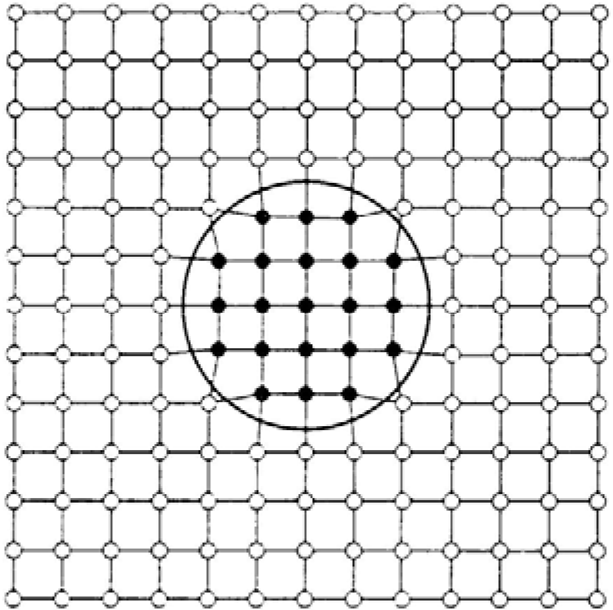
Stages in the formation of an equilibrium precipitate

Solid-Solid Interfaces

Consider an interface between two solid phases, α and θ, arising when θ nucleates and grows in α . *The interface can be of various types*:

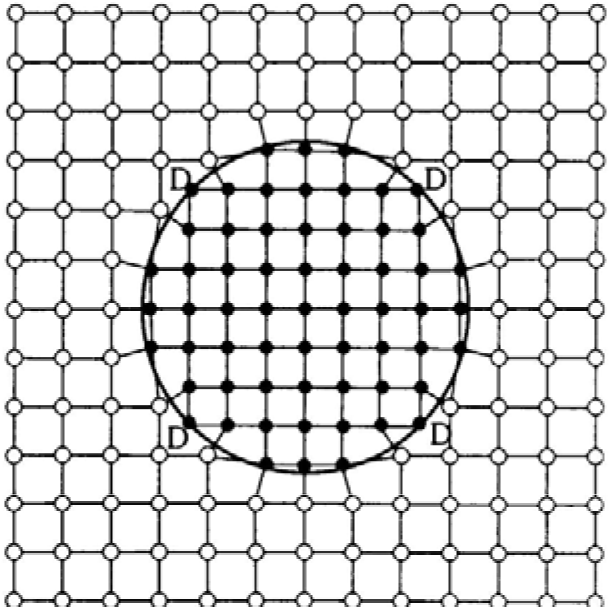


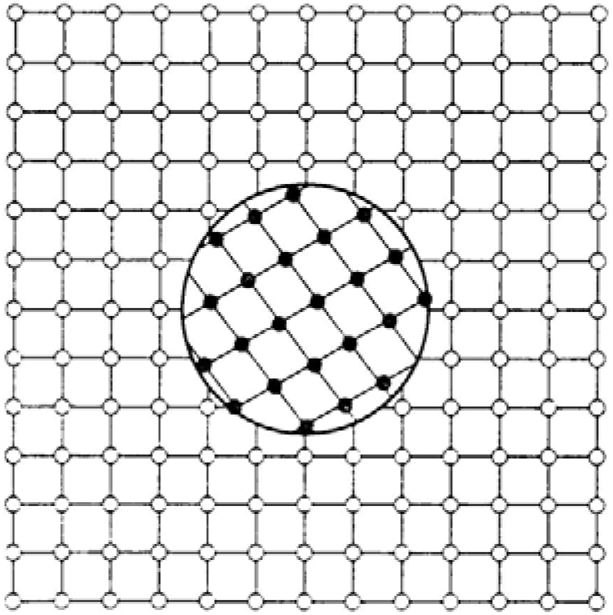
Coherent. There is perfect alignment of the lattices.



Coherent, with strain. It is likely that a coherent interface will have some elastic strain. The strain energy increases with the size of the growing particle and there will be a transition to a semi coherent interface.

Solid-Solid Interfaces

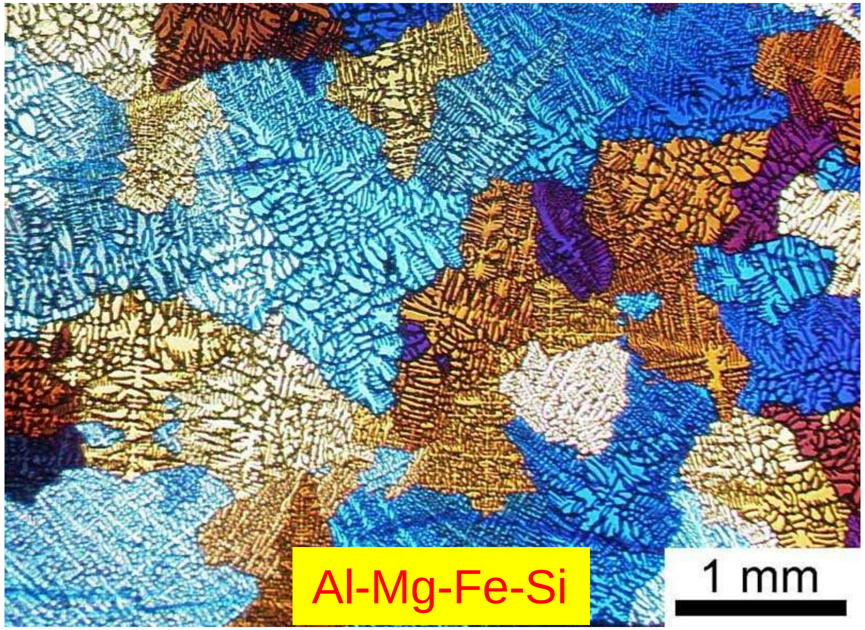


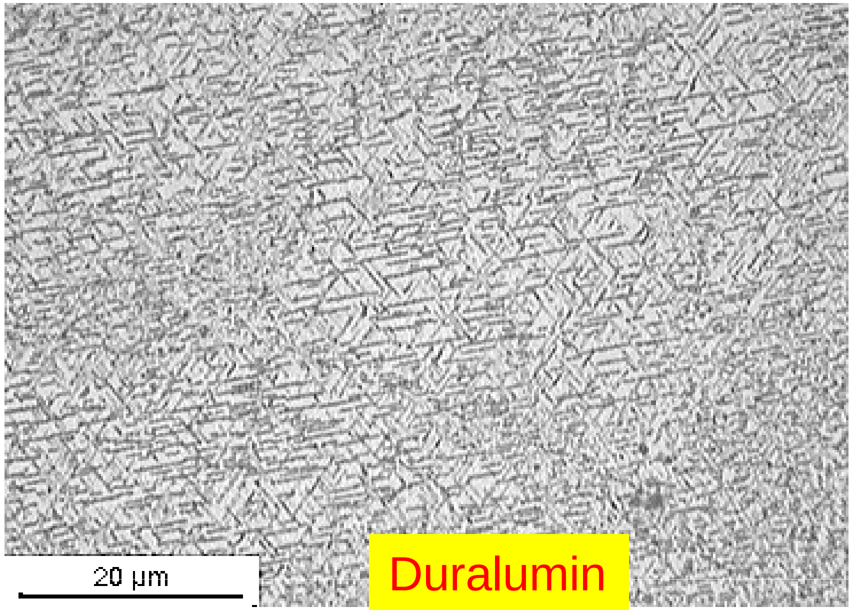


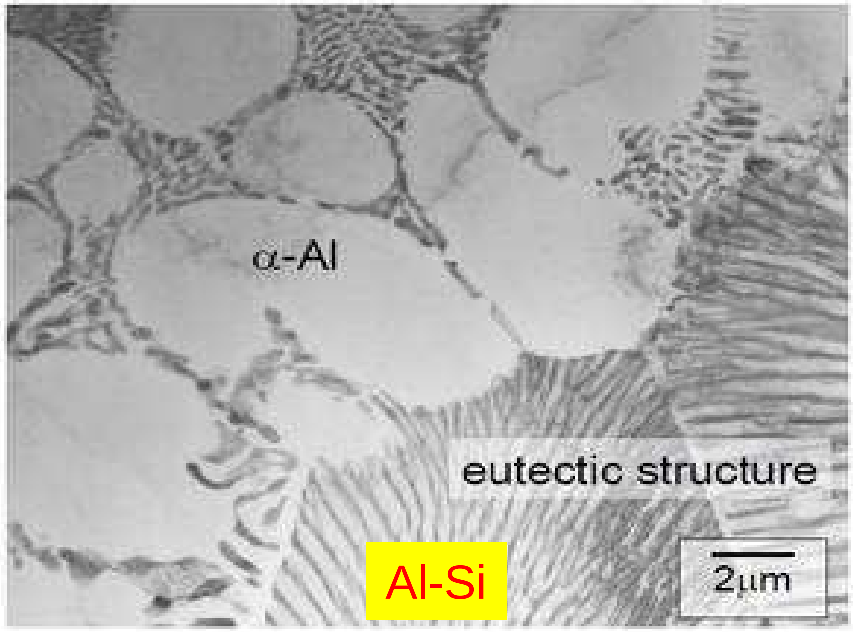
Semi-coherent. The introduction of dislocations (defects in the way the crystal is organized) reduces the overall elastic strain, although they themselves contribute to the energy of the system.

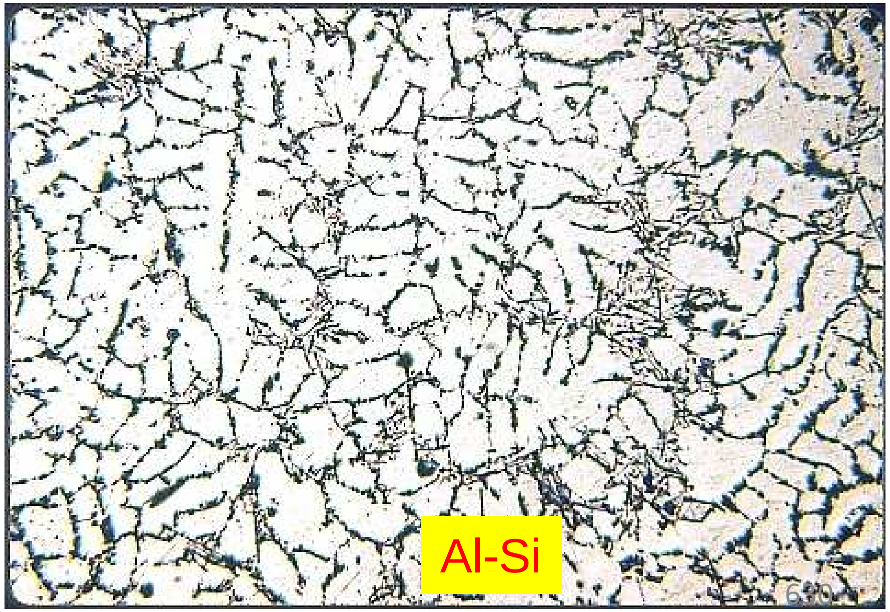
Incoherent. There is no matching at the interface

Microstructures of common aluminum alloys


Al-Mg-Fe-Si


Duralumin


Al-Si

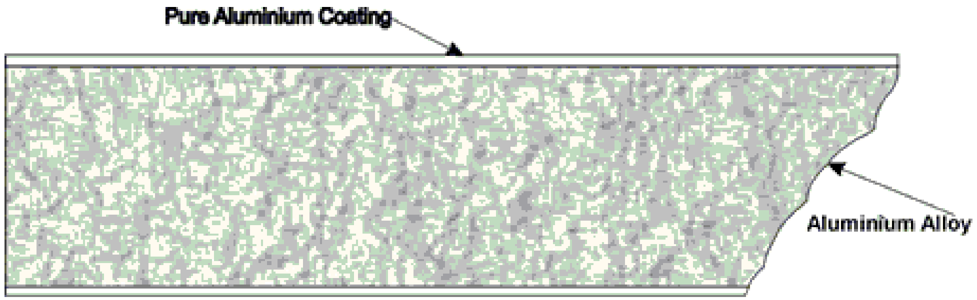

Al-Si

Corrosion Resistance of Al and Al-alloys

- ☐ The high corrosion resistance of aluminum is due to the self-protecting, thin, invisible oxide film that forms immediately on exposing surfaces to the atmosphere.
- ☐ This film protects the metal from further corrosion. If the oxide film is removed, in many environments, a new film will form immediately and the metal remains fully protected.
- ☐ In certain strongly acid or alkaline solutions, or in contact with moist corrosive materials that prevent access of oxygen to the aluminum surface, the protective film does not form readily. Therefore, the aluminum should be adequately protected or not used at all.
- ☐ A relatively thick oxide coating on aluminum and aluminum alloys may be produced by placing the metal into an aqueous solution containing 15 to 25% sulfuric acid. This process, known as *anodizing*, produces a clear, transparent coating containing submicroscopic pores that are usually sealed before use to prevent absorption and staining. Sealing may be accomplished by suitable heating in hot water.

Corrosion Resistance of Al and Al-alloys

- The corrosion resistance of Al-Cu alloys and Al-Zn alloys is satisfactory for most applications but is generally lower than that of the other aluminum alloys. Under certain corrosive conditions they are subject to intergranular corrosion.
- Therefore, these alloys in the form of sheet are usually clad with a high-purity alloy such as commercial aluminum or a magnesium-silicon alloy.
- The coating slabs are mechanically attached to the alloy core ingot, and the bonding is accomplished by hot rolling. The nominal cladding thickness per side is usually 1½ or 2½ percent of thickness of the base material.



- Alclad alloys are extensively used for aircraft applications because of the excellent combination of high strength and high resistance to corrosion.


Thank You!