MS31007: Materials Science

Chapter 4:
Solidification & Imperfections in SOLIDS

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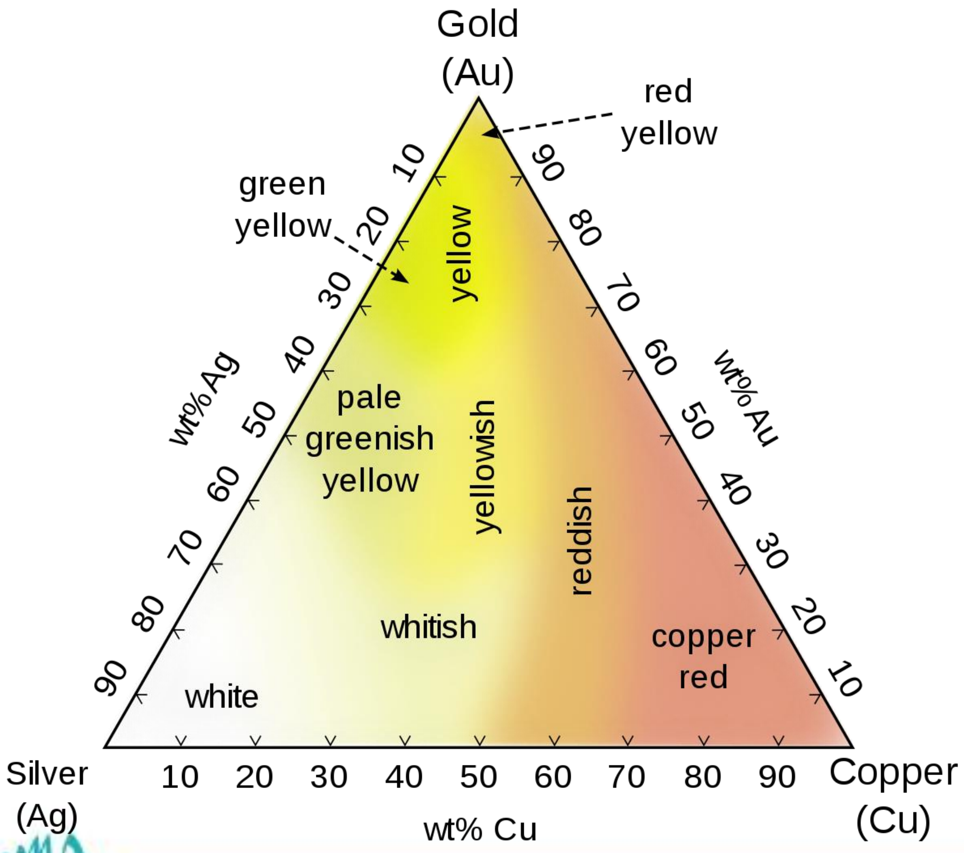
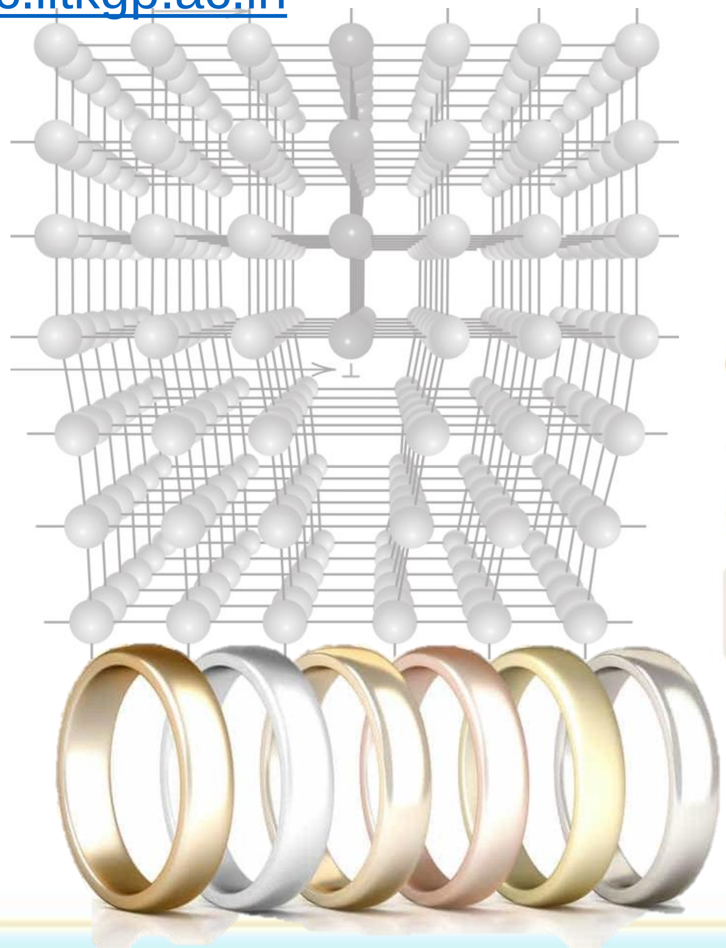




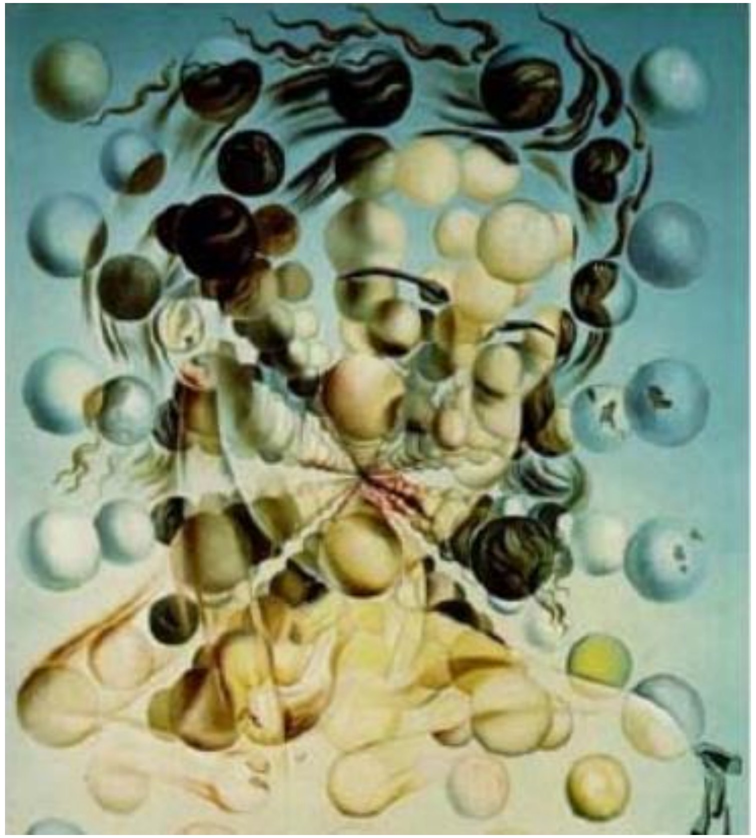
Imperfections in Solids

Real crystals are never perfect,
there are always defects

There is no such thing as a perfect crystal.

- What are these imperfections?
- Why are they important?

Many of the important properties of materials are due to the presence of imperfections.



"Crystals are like people, it is the defects in them which tend to make them interesting!"
- Colin Humphreys.

Why are defects important?

Bonding

+

Crystal Structure

+

Defects → **Properties**

Defects have a profound impact on the various properties of materials:

Production of advanced semiconductor devices require not only a rather perfect Si crystal as starting material, but also involve introduction of specific defects in small areas of the sample.

Defects are responsible for **color** (& price) of a **diamond crystal**.

Forging a metal tool introduces defects … and increases strength of the tool.

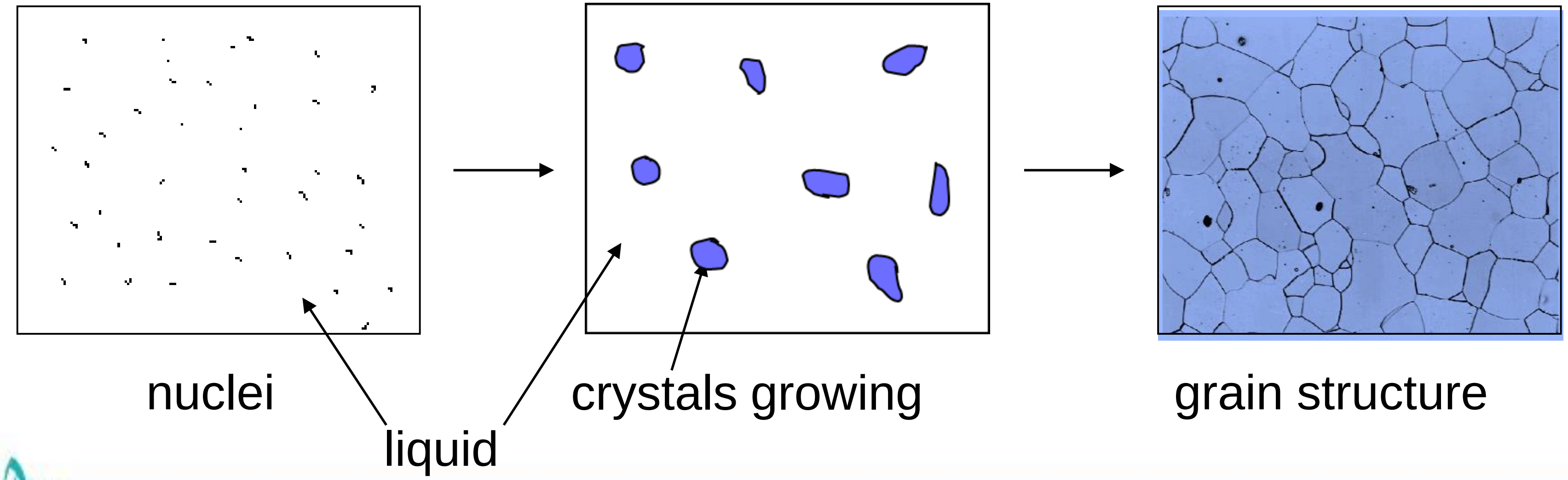
Objectives

- Describe the process of the solidification of metals distinguishing between homogeneous and heterogeneous nucleation.
- Describe the two energies involved in the solidification process of a pure metal, and write the equation for the total free-energy change associated with the transformation of the liquid state to solid nucleus.
- Distinguish between equiaxed and columnar grains and the advantage of the former over the latter.
- Distinguish between single crystal and polycrystalline materials
- Classify various types of crystalline imperfections and explain the role of defects on the mechanical and electrical properties of crystalline materials.
- Determine the ASTM grain size number and average grain size diameter and describe the importance of grain size and grain boundary density on the behavior of crystalline materials.
- Learn how and why optical microscopy, SEM, TEM, HRTEM, AFM, and STM techniques are used to understand more about the internal and surface structures of materials at various magnifications.
- Explain, in general terms, why alloys are preferred materials over pure metals for structural applications.

1. **Solidification** process for metals

Most metals are melted and then cast into semifinished or finished shape.

Solidification of a metal can be divided into the following steps:
- Formation of a stable nucleus
- Growth of a stable nucleus.



Al Ingot

Crystals grow until they meet each other

Formation of Stable Nuclei: Nucleation

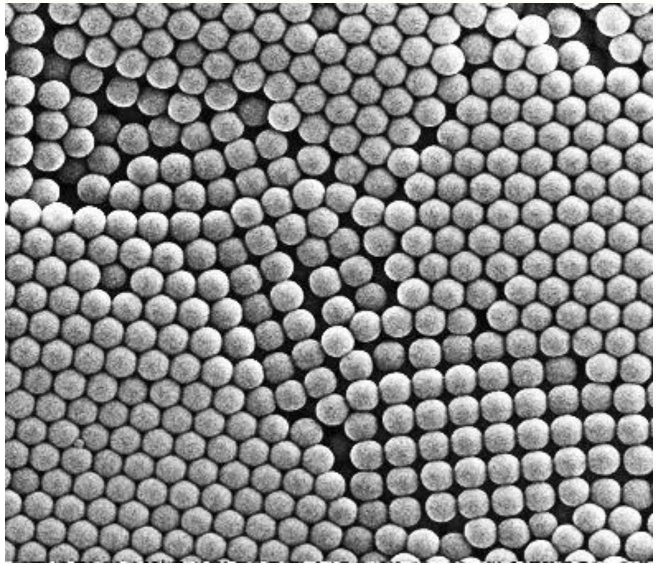
Nucleation is the process whereby nuclei (seeds) act as templates for crystal growth.

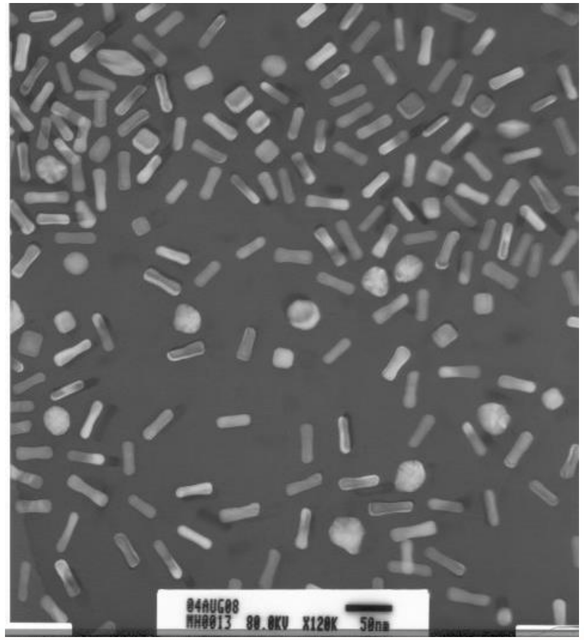
- formation of small clusters (~10’s –100’s of atoms) of the new phase
- Growth – little clusters get bigger

❑Homogeneous nucleation - nuclei form uniformly throughout the parent phase; requires considerable supercooling (typically 80-300°C).

❑Heterogeneous nucleation - form at structural inhomogeneities (container surfaces, impurities, grain boundaries, dislocations) in liquid phase much easier since stable “nucleating surface” is already present; requires slight supercooling (0.1-10ºC).

The energetics (and hence kinetics) of these processes are typically different

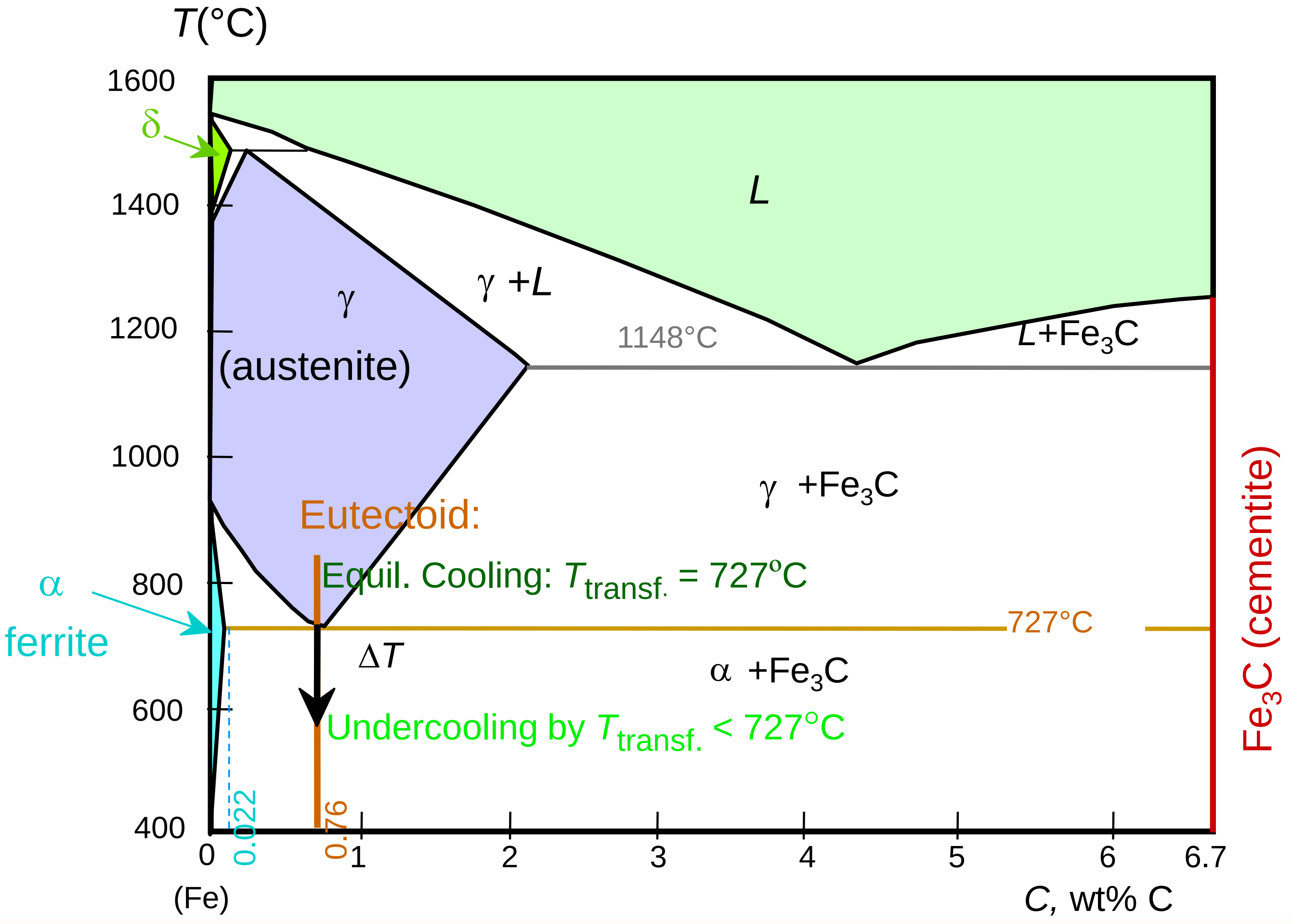




Supercooling

- During the cooling of a liquid, solidification (nucleation) will begin only after the temperature has been lowered below the equilibrium solidification (or melting) temperature T_m. This phenomenon is termed supercooling (or undercooling).

- The driving force to nucleate increases as ΔT increases
- Small supercooling → slow nucleation rate
  - few nuclei
  - large crystals
- Large supercooling → rapid nucleation rate
  - many nuclei
  - small crystals



Homogeneous Nucleation:
Nucleation of a spherical solid particle in a liquid

The discussion of energetics will use free energies

Remember the Gibbs free energy ΔG?

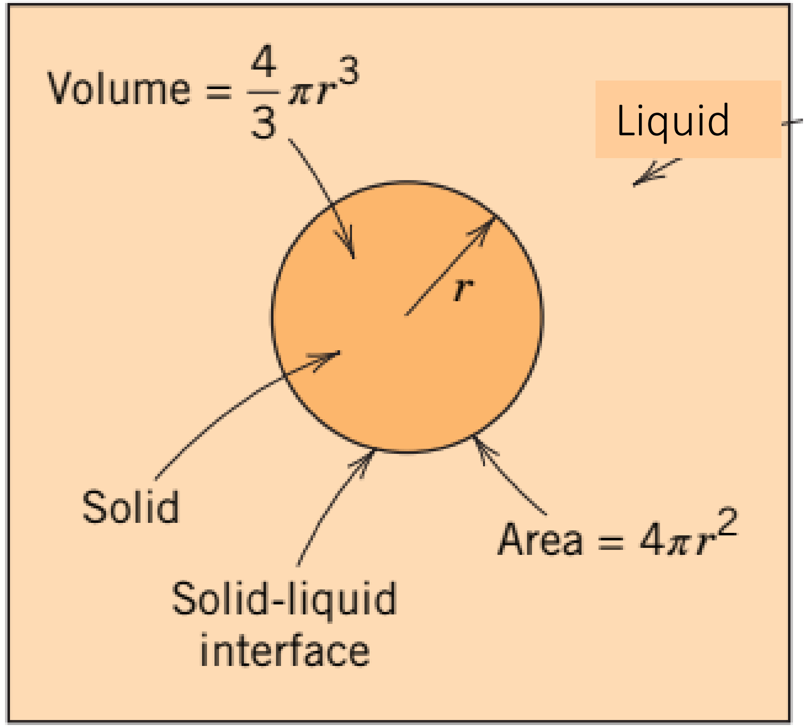
$\Delta G < 0$ for transformation occur spontaneously

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

- The change in free energy ΔG (a function of the internal energy and enthalpy of the system) must be negative for a transformation to occur.

- Assume that nuclei of the solid phase form in the interior of the liquid as atoms cluster together-similar to the packing in the solid phase.

- Also, each nucleus is spherical and has a radius r.



Energies involved in homogenous nucleation

Free energy changes as a result of a solidification transformation

1. Volume free energy, G_v

- Released by liquid to solid transformation.
- ΔG_v is change in free energy per unit volume between liquid and solid.
- Free energy change for a spherical nucleus of radius r is given by

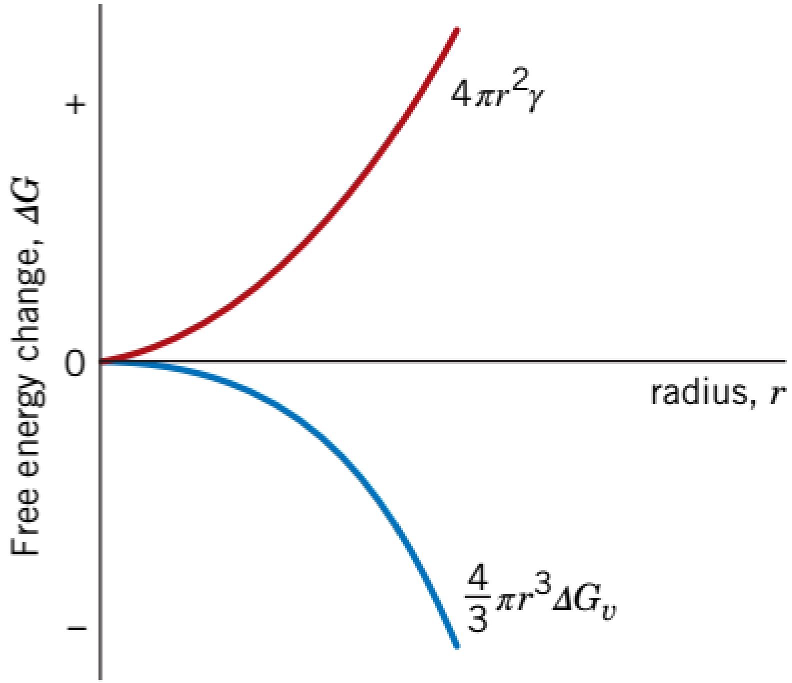
$$\Delta G_V = \frac{4}{3}\pi r^3 \Delta G_\upsilon$$

2. Surface energy, Gs

- Required to form new solid surface
- ΔG_s is energy needed to create a surface.
- γ is specific surface free energy.

ΔG_s is retarding energy.

$$\Delta G_S = 4\pi r^2 \gamma$$



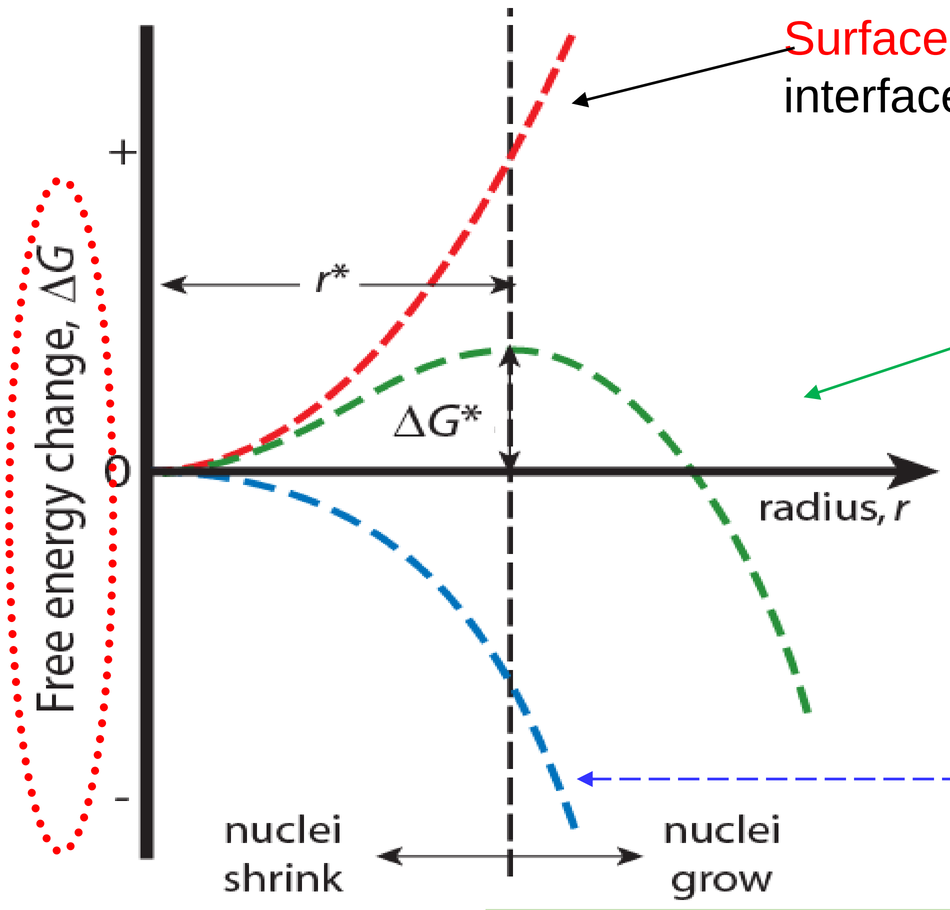
ΔG = Total Free Energy

$$\Delta G = \Delta G_S + \Delta G_V$$

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

Few points: 1) ΔG_v is negative if $T < T_{solidification}$
2) The surface free energy γ is always +ve

Homogeneous Nucleation & Energy Effects



Energy lowered by **redissolving**

Energy lowered by growing into crystals

Surface Free Energy- destabilizes the nuclei (it takes energy to make an interface) $\Delta G_S = 4\pi r^2 \gamma$

$\Delta G^* = \Delta G_S + \Delta G_V$

$$\Delta G^* = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

- There is a clear maximum in ΔG as a function of *r*
- This size r^* has physical meaning
- Particles smaller than this will not lead to nuclei
- Particles this size or larger will grow (they are called nuclei)
- ΔG^* can be thought of as an energy barrier to nucleation
- What is the value of ΔG^* ?

Volume (Bulk) Free Energy – stabilizes the nuclei (releases energy)

$$\Delta G_V = \frac{4}{3}\pi r^3 \Delta G_\upsilon$$

*r** = critical nucleus:
for *r* < *r** nuclei shrink; embryo
for *r* >*r** nuclei grow (to reduce energy)

Homogeneous Nucleation & Energy Effects

Homogeneous nucleation – ΔG^*, r^*

Take derivative of ΔG with respect to r and set it equal to zero, because r^* and ΔG^* appear at the maximum!

$$\Delta G^* = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

Eq (1)

$$\frac{d(\Delta G)}{dr} = \frac{d}{dr}\left(\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma\right) = 0$$

$$4\pi r^2 \Delta G_v + 8\pi r \gamma = 0$$

$$r^* = \frac{-2\gamma}{\Delta G_v}$$

Sub into eqn (1)

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2}$$

Some observations – ΔG_v is the driving force for nucleation (solidification)

It is a function of temperature!

At the equilibrium melting temperature T_m its value is zero!

Can I relate this to enthalpies (H) ? Of course!

$G = H - TS$

where $H = U + pV$ is the enthalpy, T is the temperature, and S is the entropy.

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

Equilibrium occurs when the temperature is equal to the melting point (Tm) so that

$$\Delta G = \Delta H_f - T_m \Delta S = 0 \quad \Rightarrow \quad \Delta S = \frac{\Delta H_f}{T_m}$$

It can be shown that ΔG_v is a function of temperature as

$$\Delta G_v = \frac{\Delta H_f (T_m - T)}{T_m}$$

$$r^* = \frac{2\gamma T_m}{\Delta H_f \Delta T}$$

ΔH_f is the latent heat of fusion (i.e., the heat given up during solidification)

Heterogeneous Nucleation

Although levels of supercooling for homogeneous nucleation may be significant (~100s of ^{o}C), in practical situations they are often on the order of only several ^{o}C.

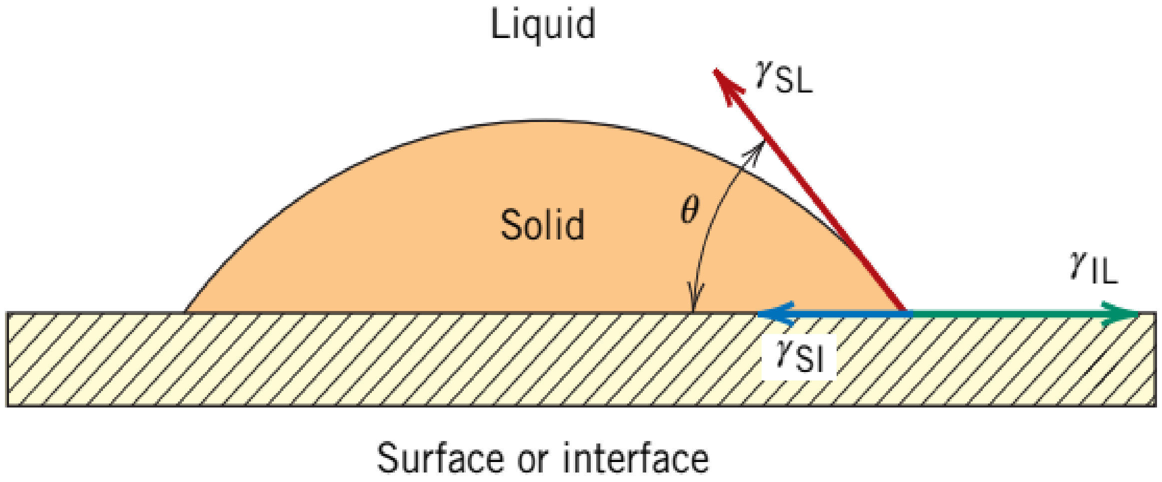
- **Activation energy for nucleation (ΔG^*) is lowered when nuclei form on preexisting surfaces or interfaces, because the surface free energy (γ) is reduced.**

It is easier for nucleation to occur at surfaces and interfaces than at other sites. This type of nucleation is termed *heterogeneous*.

Consider a flat surface or interface and a solid particle that nucleates off it

Now there are three interfacial energy terms

- Interface-liquid (γ_{IL}), solid-liquid (γ_{SL}), solid-interface (γ_{SI})
- If you write a force balance for the surface tension in the plane of the surface you get

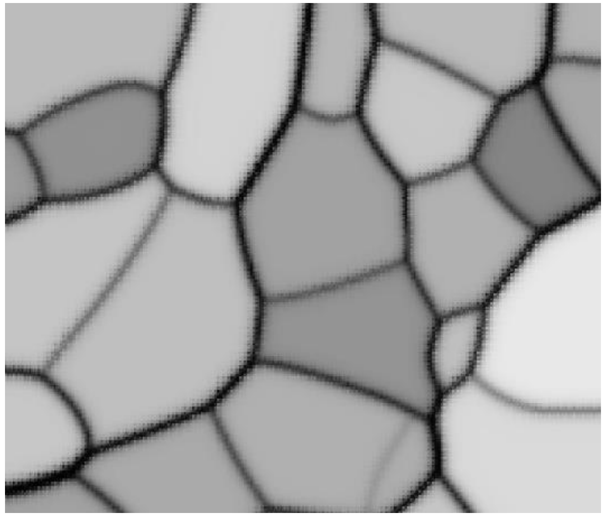


$$\gamma_{IL} = \gamma_{SI} + \gamma_{SL} \cos\theta$$

Growth of Crystals and Formation of Grain Structures

Nucleus grow into crystals in different orientations

- Crystal boundaries are formed when crystals join together at complete solidification.



- Crystals in solidified metals are called grains.
- Grains are separated by grain boundaries.
- The more the number of nucleation sites available, more the number of grains formed.
- The number of nucleation sites will affect the structure of the solid metal produced.
- If relative few nucleation sites are available, a coarse or large- grain structure will be produced.
- If many nucleation sites are available, a fine-grain structure will result.

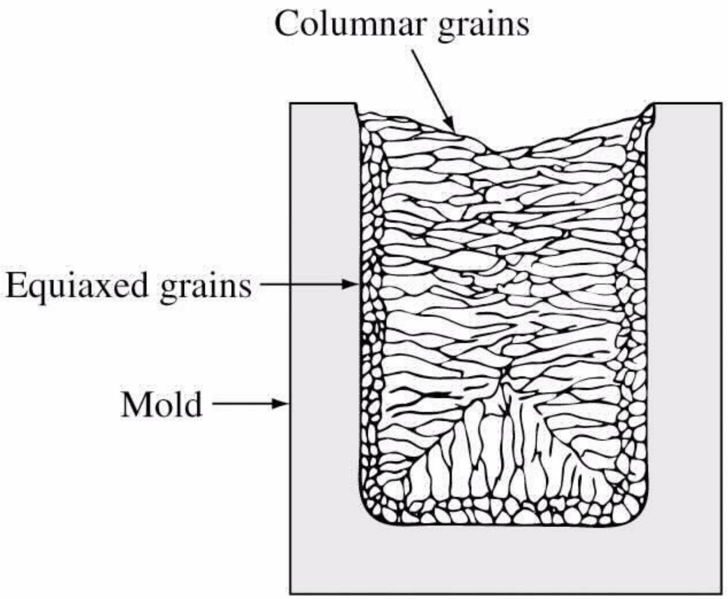
TYPES OF GRAINS

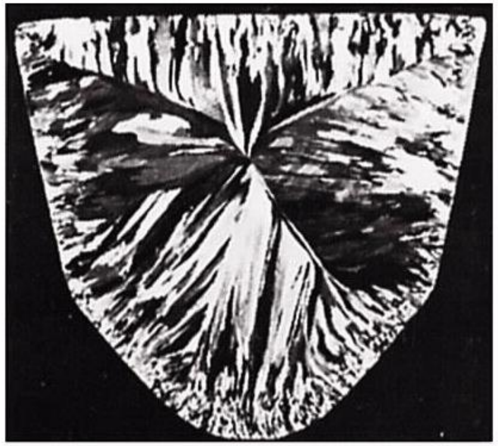
Grains can be

- Equiaxed (roughly same size in all directions)
- Columnar (elongated grains)

- **Equiaxed Grains:**
  - Crystals, smaller in size, grow equally in all directions.
  - Formed at the sites of high concentration of the nuclei.
  - Example:- Cold mold wall

- **Columnar Grains:**
  - Long thin and coarse.
  - Grow predominantly in one direction.
  - Formed at the sites of slow cooling and steep temperature gradient.
  - Example:- Grains that are away from the mold wall.



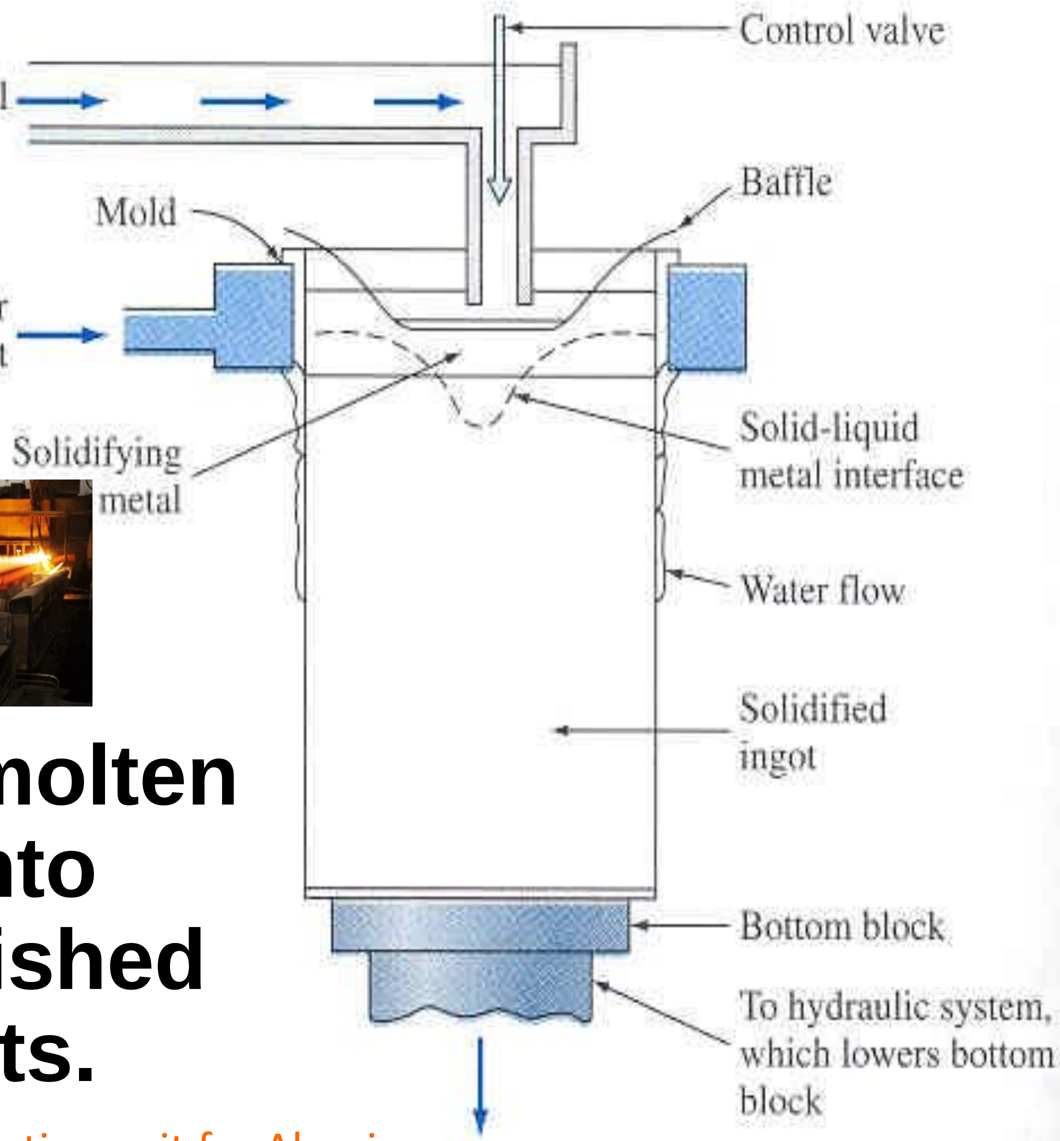


Schematic drawing of a solidified metal grain structure produced by using a cold mold Transverse section of an Al alloy ingot 1100 (99 % Al)

CASTING IN INDUSTRIES

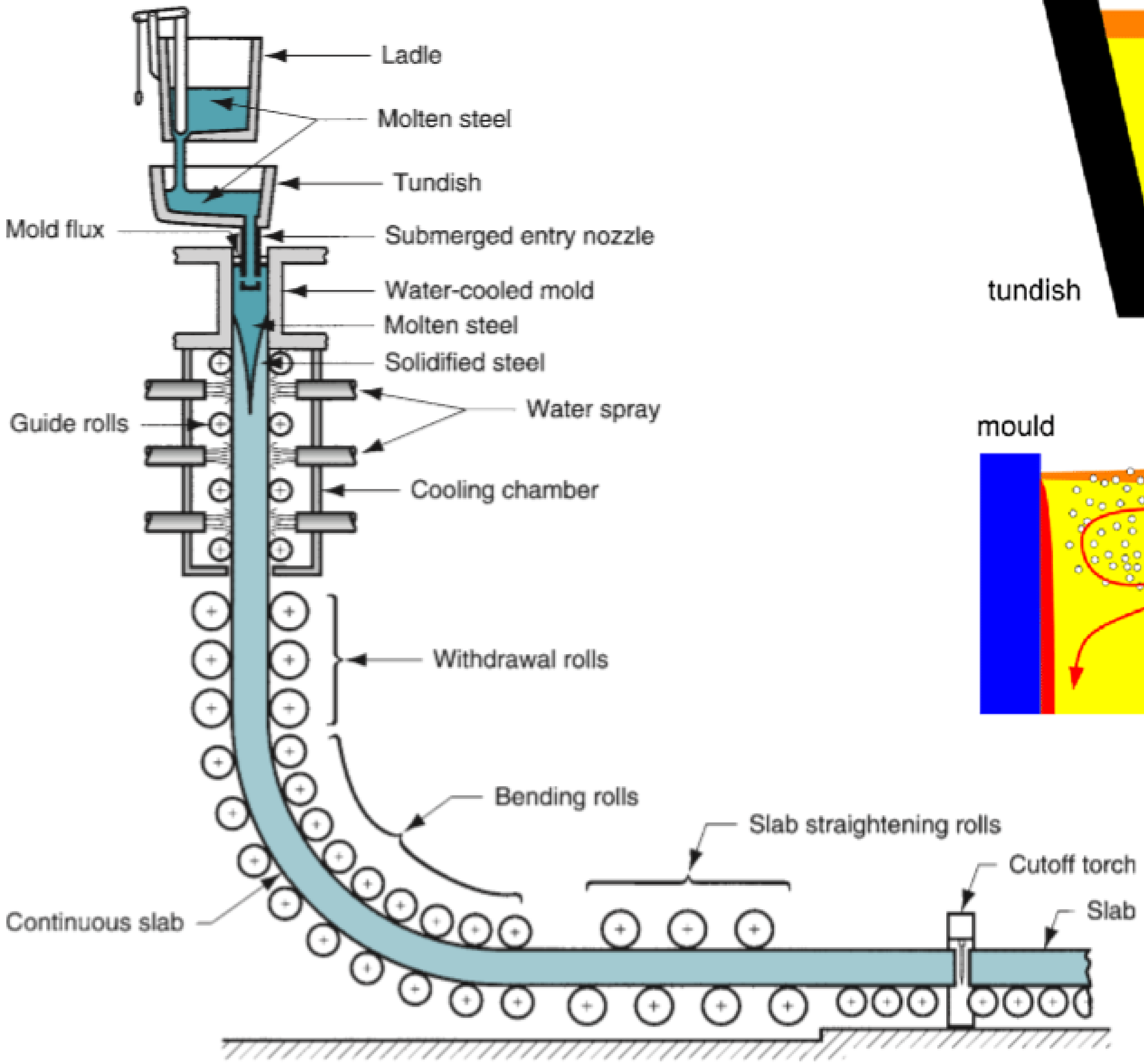
*An ingot is a material, usually metal, that is cast into a shape suitable for further processing.

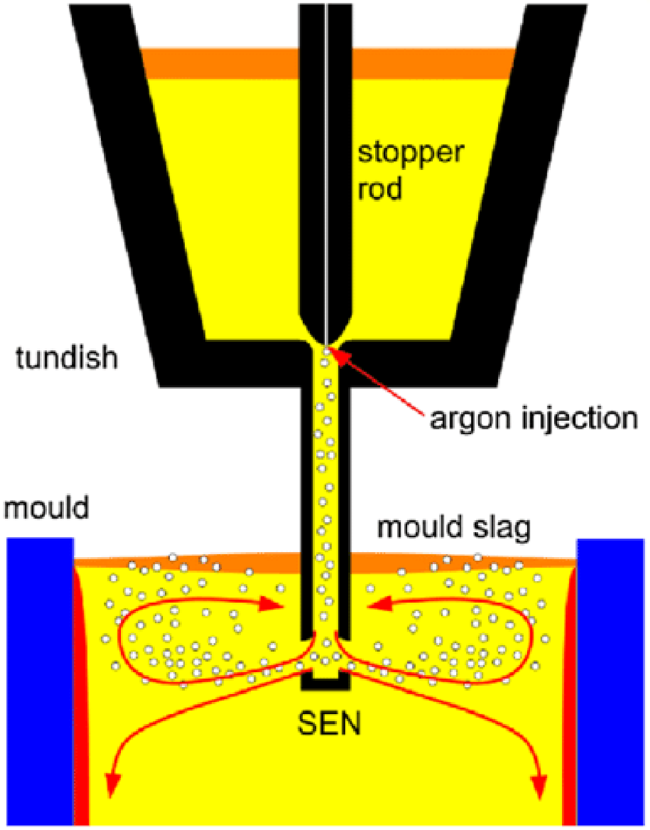
In industries, molten metal is cast into either semi finished or finished parts.

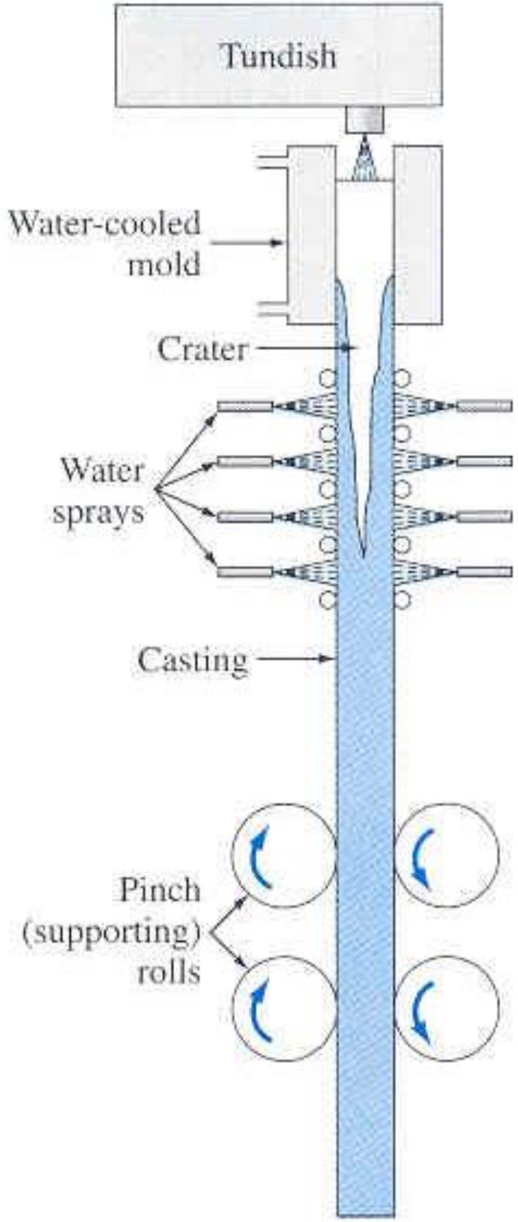


Direct-Chill Semicontinuous Casting unit for Aluminum

Continuous Casting of Steel Ingots



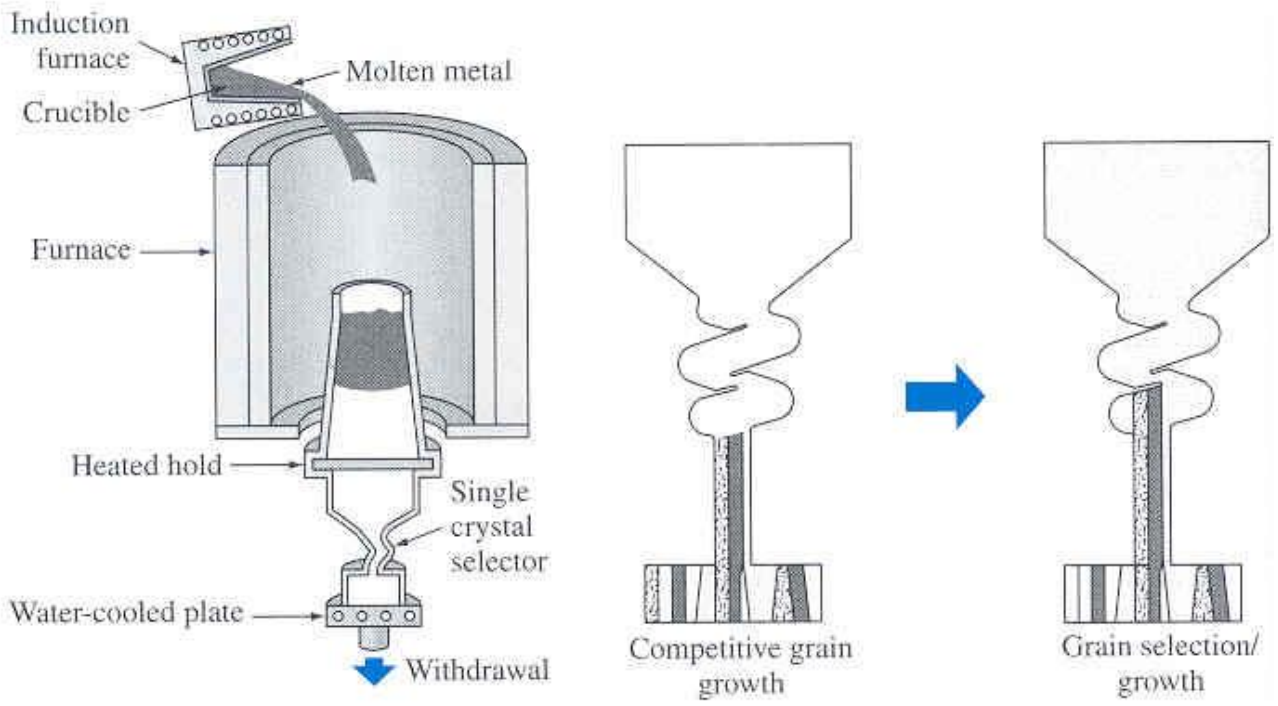




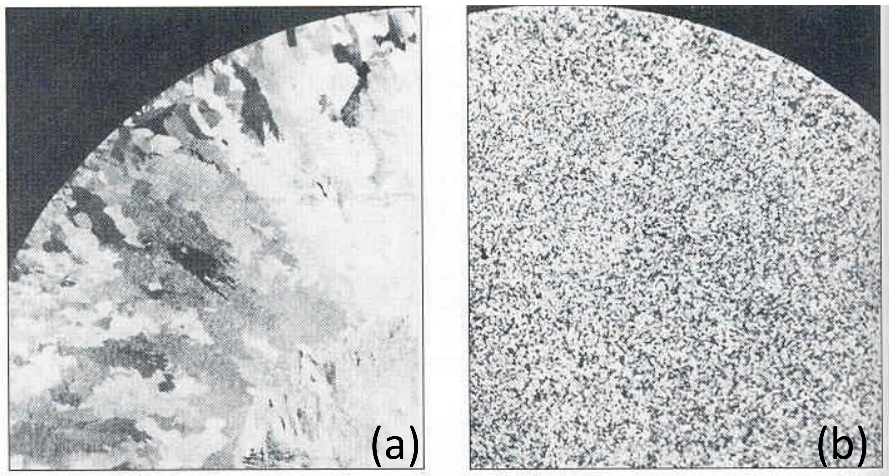
SOLIDIFICATION OF SINGLE CRYSTAL

- For some applications (Eg: Gas turbine blades-high temperature environment), single crystals are needed.
- Single crystals have high temperature creep resistance.
- Latent head of solidification is conducted through solidifying crystal to grow single crystal.
- Growth rate is kept slow so that temperature at solid-liquid interface is slightly below melting point.

Growth of single crystal for turbine airfoil.

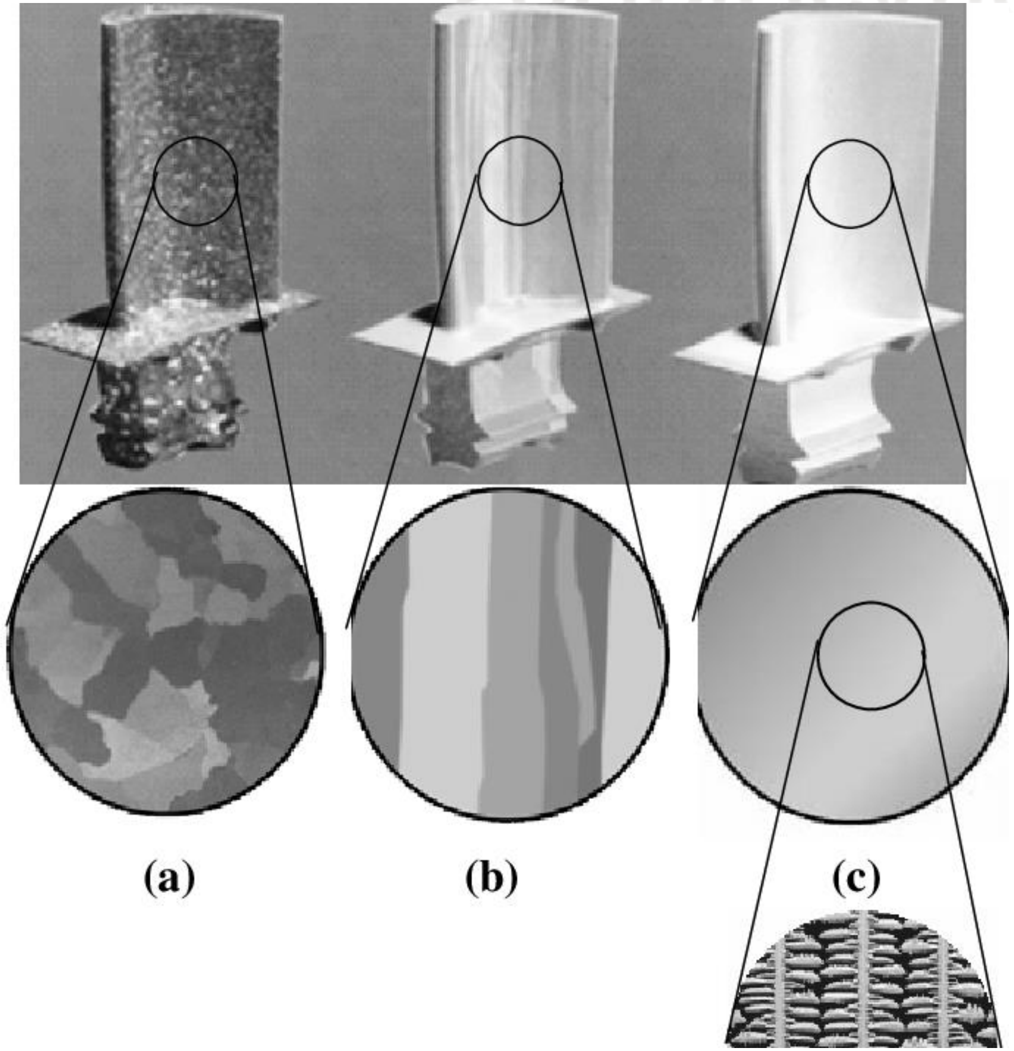


- **To produce cast ingots with fine grain size, *grain refiners* are added.**
- **Example:- For aluminum alloy, small amount of Titanium, Boron or Zirconium is added.**



Grain structure of Aluminum cast with (b) and without (a) grain refiners.

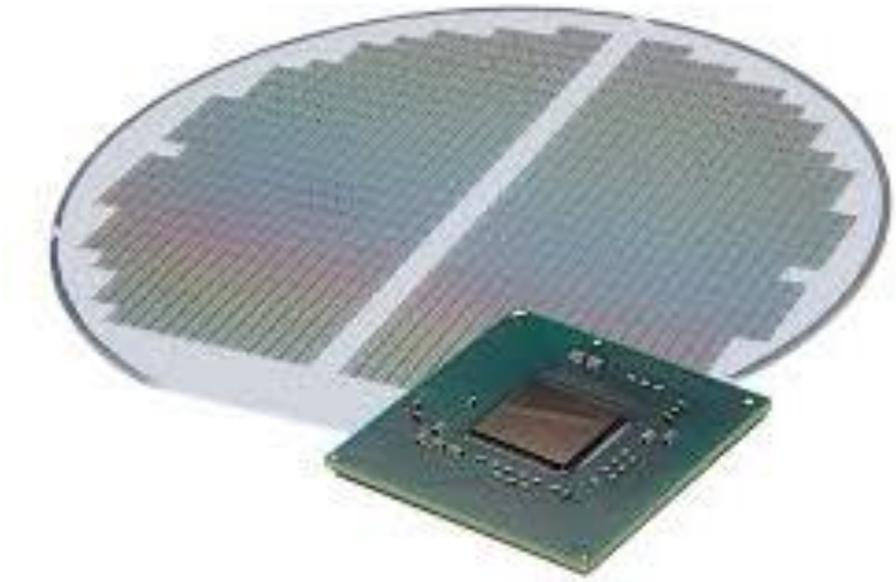
SOLIDIFICATION OF SINGLE CRYSTAL



Different grain structures of gas turbine airfoil blades: Polycrystal Equiaxed , (b) Polycrystal Columnar, and (c) Single Crystal

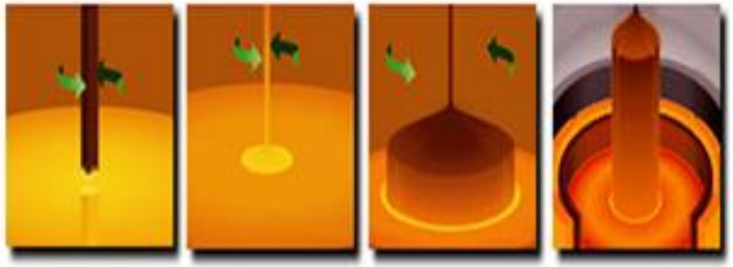
Solidification of Single Crystal

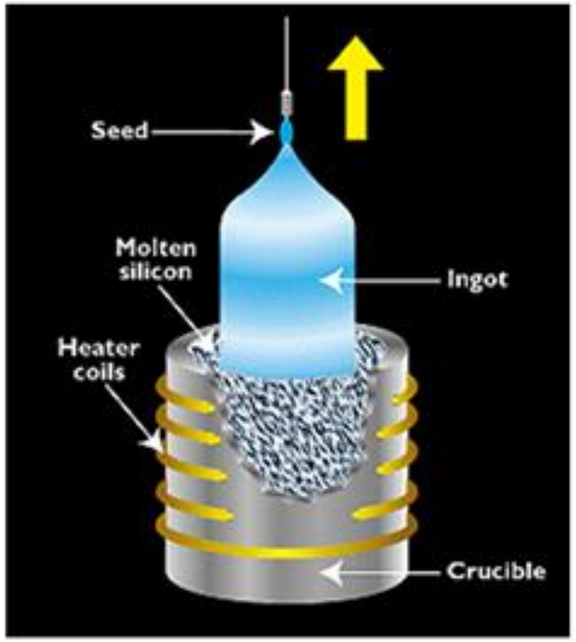
- Silicon single crystal is another example of industrial use of single crystal.
- Silicon single crystals are sliced into wafers for solid-state electronic integrated circuit chips.
- Single crystals are necessary for this application since grain boundaries would disrupt the flow of electrons in the device made from semiconductor silicon.

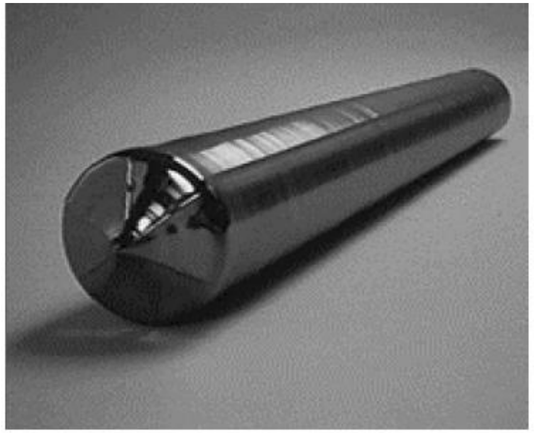


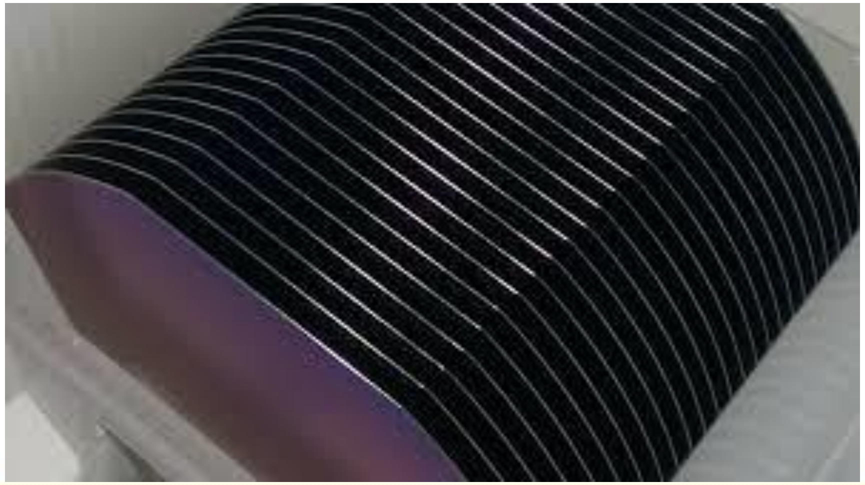
CZOCHRALSKI PROCESS

- This method is used to produce single crystal of silicon for electronic wafers.
- A seed crystal is dipped in molten silicon and rotated.
- The seed crystal is withdrawn slowly while silicon adheres to seed crystal and grows as a single crystal.

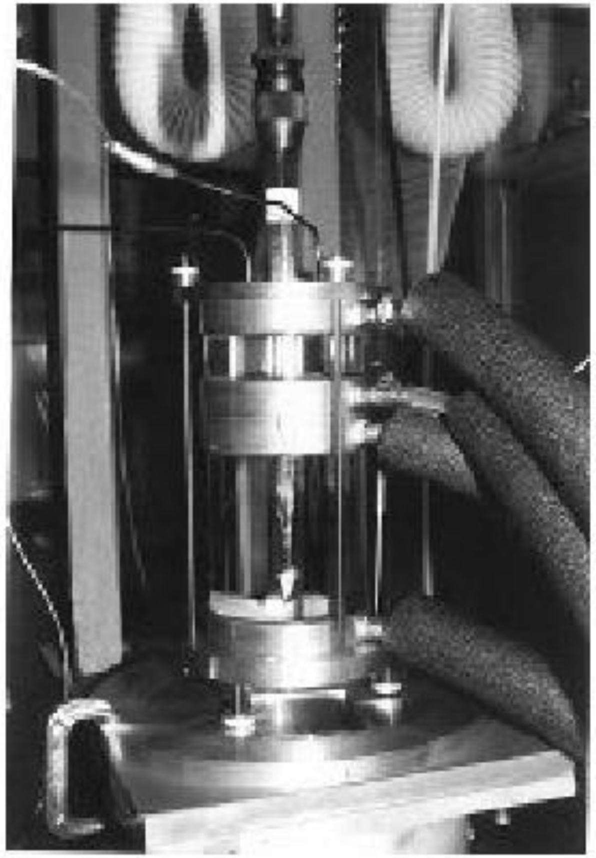








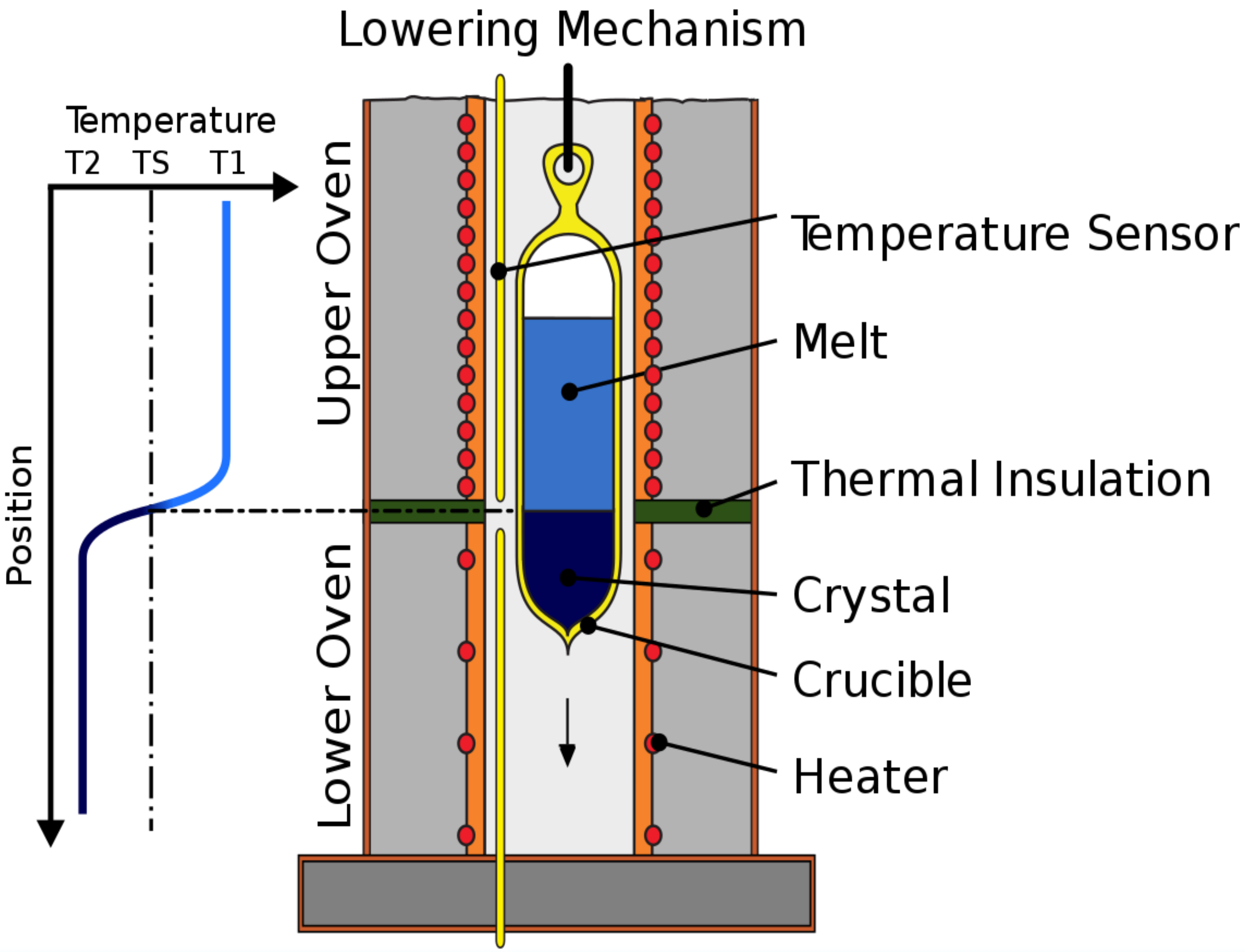
Silicon single crystal via Bridgman technique



Bridgman technique : The methods involve heating polycrystalline material above its melting point and slowly cooling it from one end of its container, where a seed crystal is located. A single crystal of the same crystallographic orientation as the seed material is grown on the seed and is progressively formed along the length of the container.

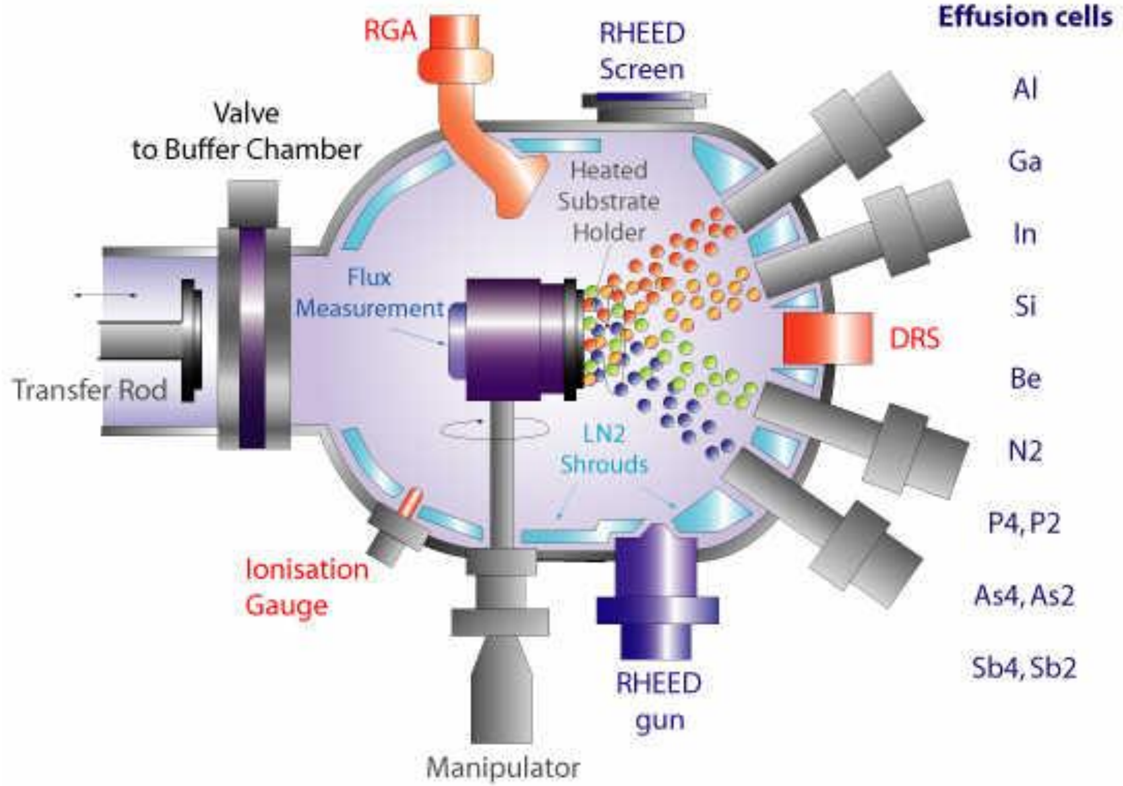
The process can be carried out in a horizontal or vertical orientation, and usually involves a rotating crucible/ampoule

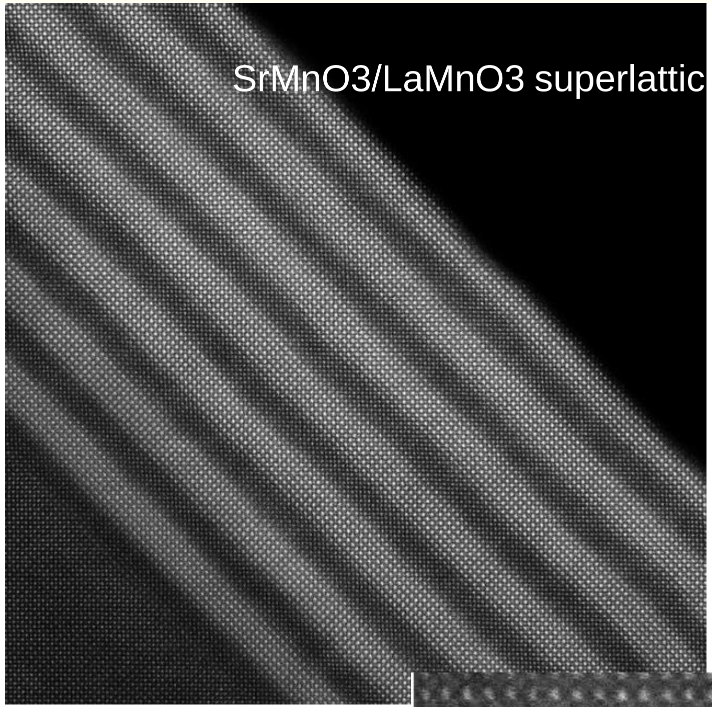
to stir the melt.

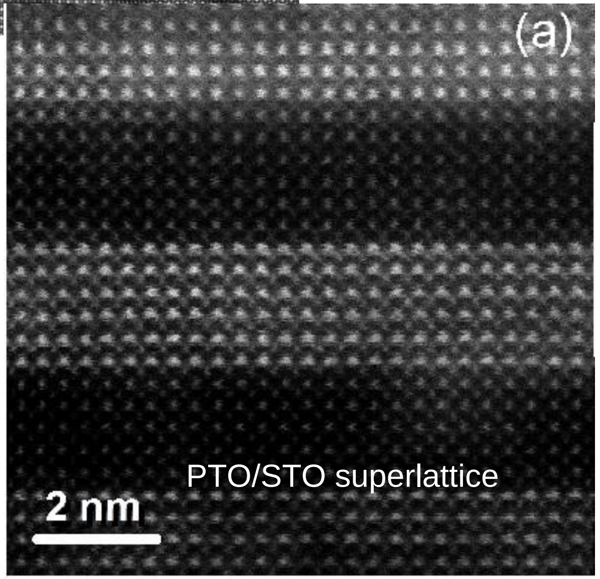


The Bridgman method is a popular way of producing certain semiconductor crystals such as GaAs, for which the Czochralski method is more difficult.

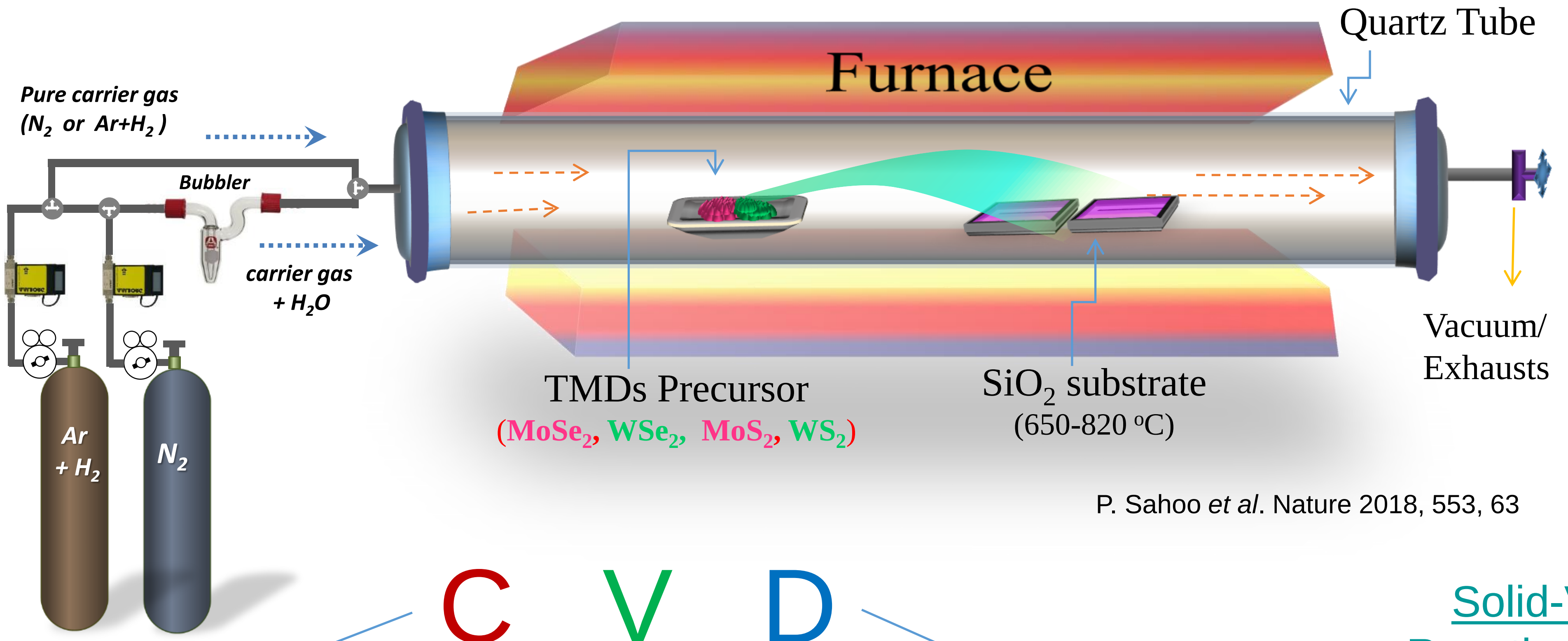
Different Types of Epitaxial Growth Techniques : Molecular Beam epitaxy







Chemical Vapor Deposition of Single 2D Crystals via edged epitaxy: 2D materials



P. Sahoo *et al*. Nature 2018, 553, 63

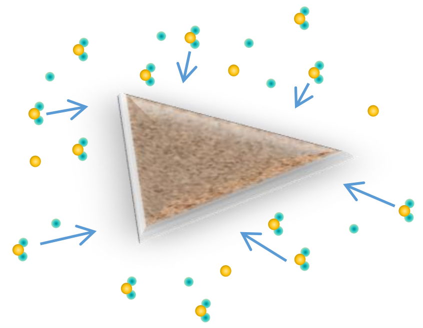
C V D

A chemical reaction occurs. Standard chemical concept apply: thermodynamics, kinetics

Precursor react in gas /vapor phase
Gas concepts, vacuum technology, evaporation rate

A solid product is formed on the substrate. Deposition rates, substrate effects: epitaxy, catalysis, roughness

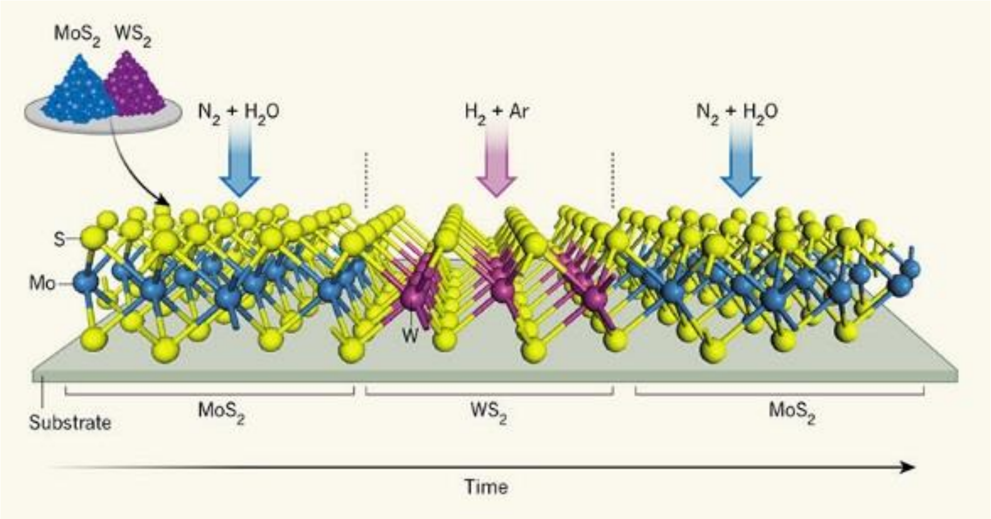
Solid-Vapor Reaction growth



Why CVD: Large varieties of films, Scalable, low-cost, stoichiometry control

Selective growth of MoS_2 - WS_2 Single crystal Heterostructure : Edged epitaxy

Achieved simply by controlling the carrier gas environment.



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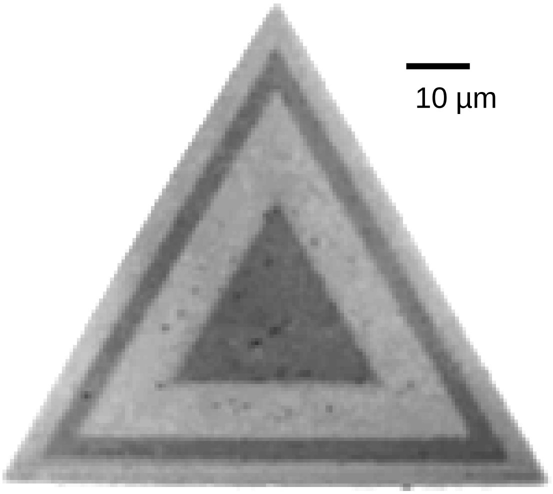
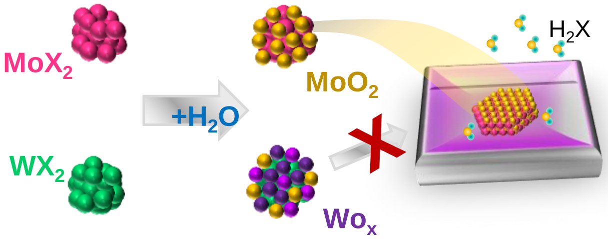
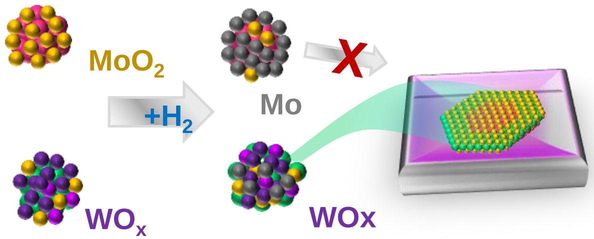


P. Sahoo *et al.* ACS Nano 2019

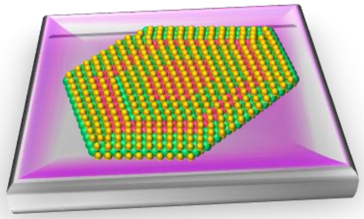
Stage 1: Growth of only MoX_2
Oxidation Step (H_2O vapor)



Stage 2: Growth of only WX_2
Reduction Step (H_2 gas)

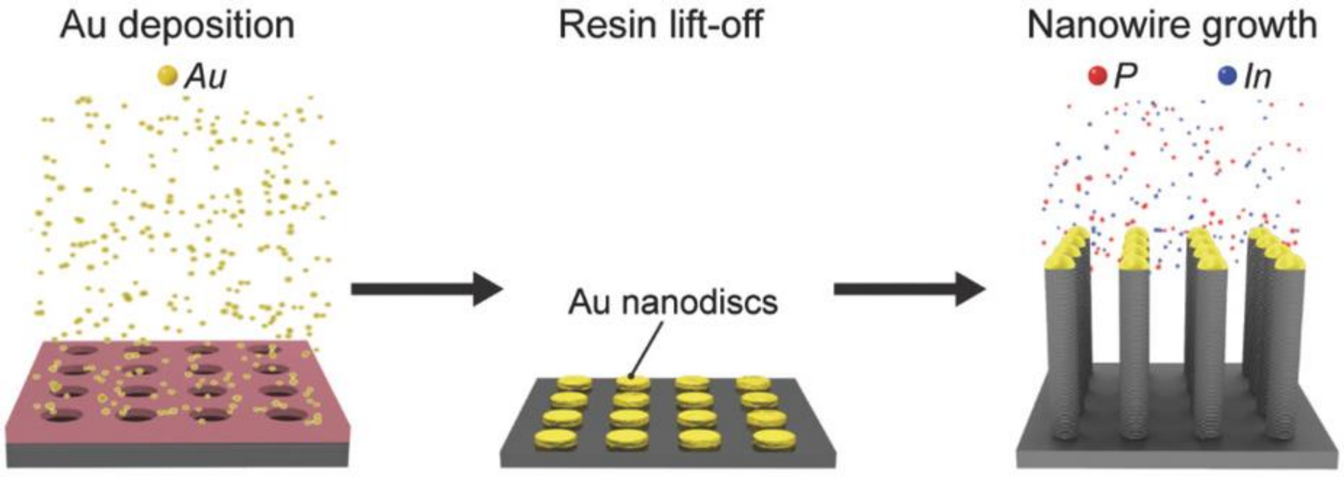


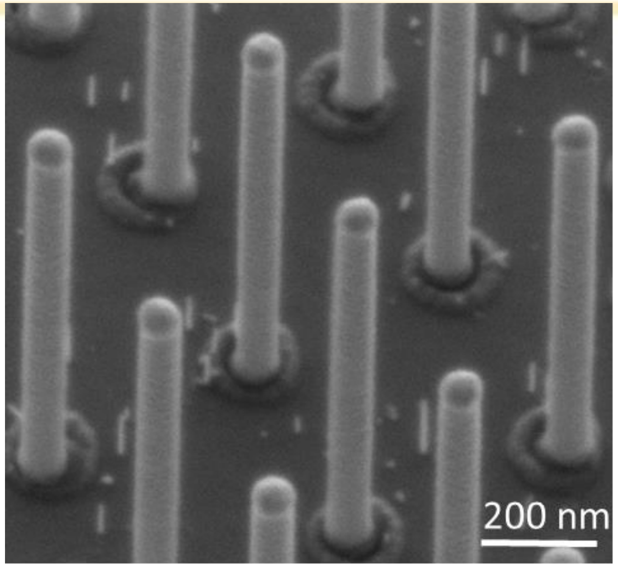
Sequential repetition of Stage 1 and Stage 2



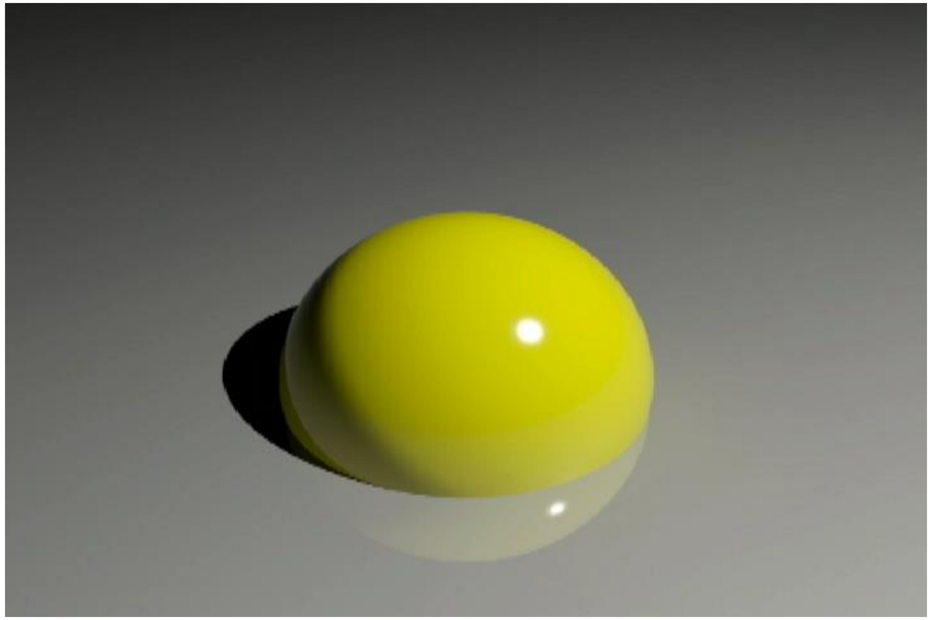
Vapor-Liquid-Solid growth: One dimensional single crystal / Nanowire

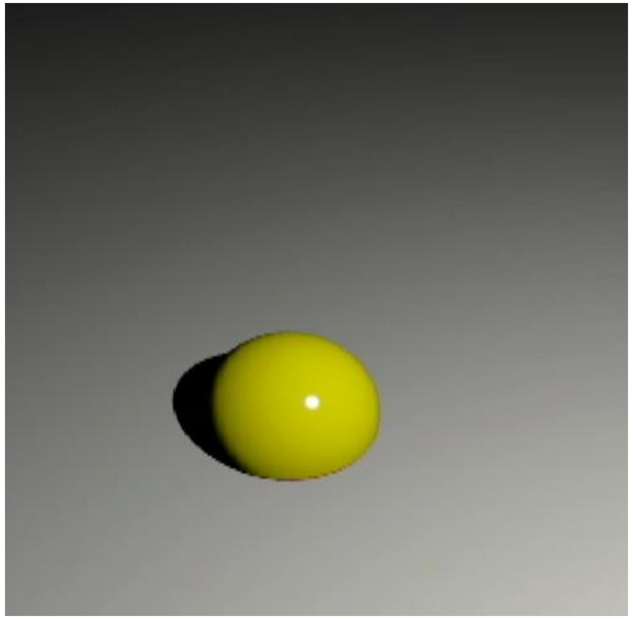
P. Sahoo et al. Nano Letters 2016 and 2017

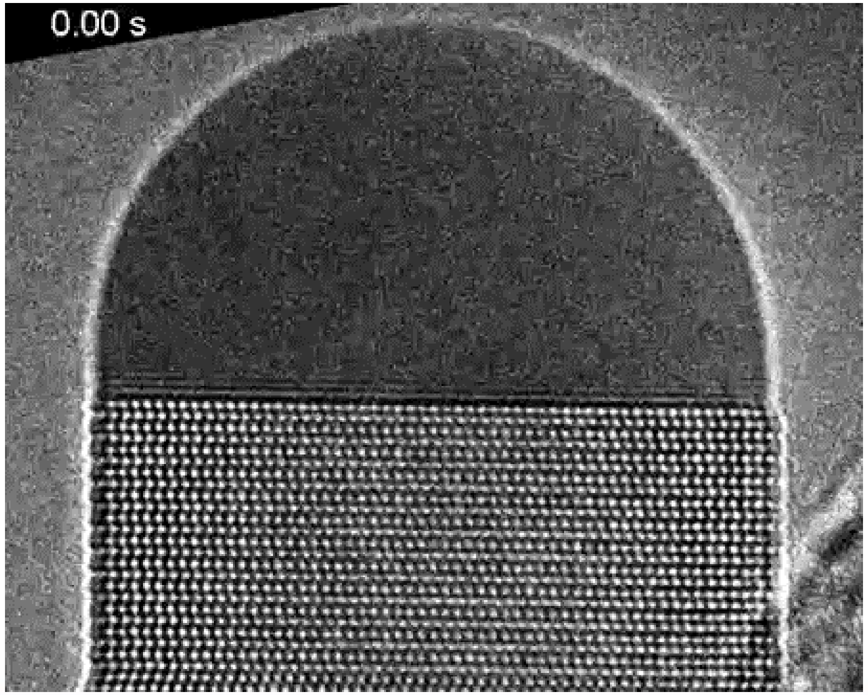




InP Semiconductor nanowire







METALLIC SOLID SOLUTIONS

- Few metals that are used in pure or nearly pure state are like high purity copper in electronic wire and high-purity aluminum used for bright metallic surface.
- Alloys are used in most engineering applications.
- Alloy is an mixture of two or more metals and nonmetals.
- Example:
  - Cartridge brass is binary alloy of 70% Cu and 30% Zinc.
  - Iconel is a nickel based superalloy with about 10 elements.

- Solid solution is a simple type of alloy in which elements are dispersed in a single phase.
- There are two types of solid solutions: substitutional and interstitial