

Module 2

Mechanism of crystallization: homogeneous and heterogeneous nuclei formation, under cooling, dendritic growth, grain boundary irregularity.

Effects of grain size, grain size distribution, grain shape, grain orientation on dislocation/strength and creep resistance - hall - petch theory, simple problems

Classification of crystal imperfections: - types of dislocation – effect of point defects on mechanical properties - forest of dislocation, role of surface defects on crack initiation.

Burgers vector –dislocation source, significance of frank read source in metals deformation - correlation of dislocation density with strength and nano concept, applications.

Significance high and low angle grain boundaries on dislocation – driving force for grain growth and applications during heat treatment.

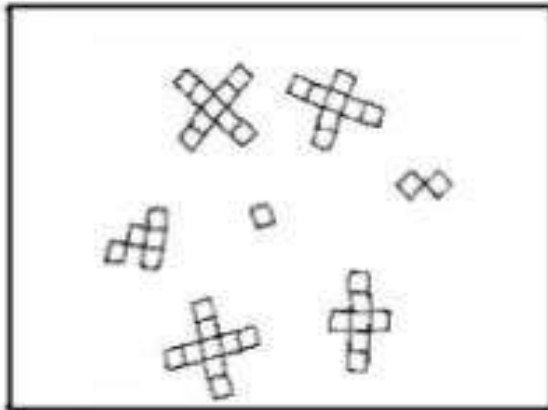
Polishing and etching to determine the microstructure and grain size. Fundamentals and crystal structure determination by X –ray diffraction, simple problems –SEM and TEM.

Diffusion in solids, fick's laws, mechanisms, applications of diffusion in mechanical engineering, simple problems.

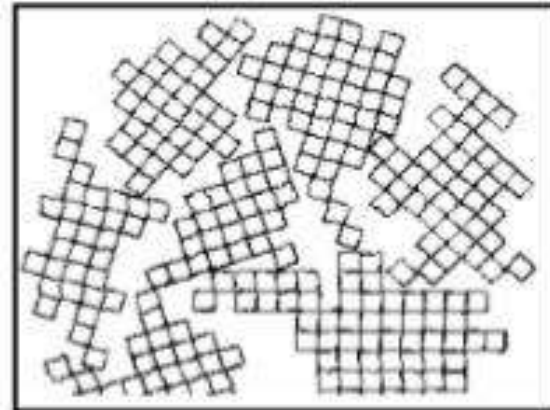
Solidification/Freezing

- Freezing, or **solidification**, is a phase change during which a liquid turns into a solid when its temperature is lowered below its freezing point.
- For most of the substances, the melting and freezing points are the same temperature; however, certain substances possess differing solid–liquid transition temperatures.
- The solidification of metallic, polymeric, and ceramic materials is an important process to study because of its effect on the properties of the materials involved.
- During solidification of molten/liquid crystalline materials, formation of crystals take place and the

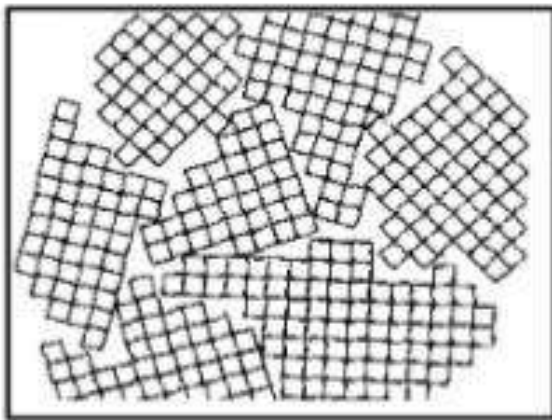
Solidification process



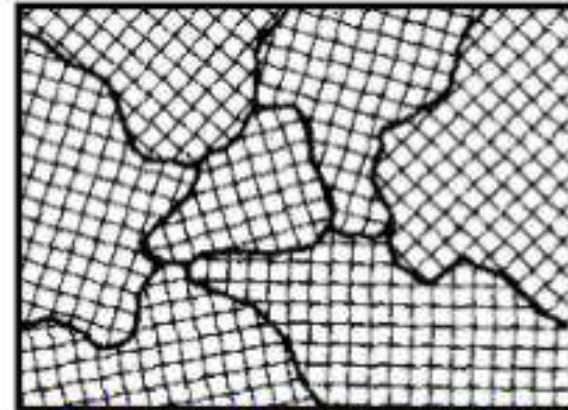
1. **Nucleation**: It begins at foreign particles in melt.



2. **Crystal growth**: Crystals begin to grow from each.



3. **Grain Formation**: Interface develops.



4. **Polycrystalline structure**: Grain growth is limited by another grain, creating a boundary between them

Importance of solidification/Freezing

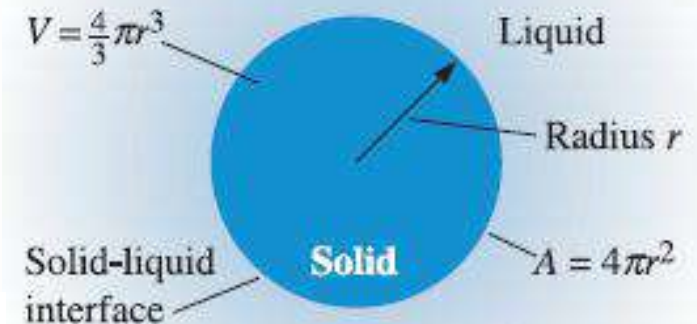
- Solidification is considered one of the most important manufacturing processes.
- Several million pounds of steel, aluminum alloys, copper, and zinc are being produced through the casting process.
- High-quality optical fibers and other materials, such as fiberglass, also are produced from the solidification of molten glasses.
- Many thermoplastic materials such as polyethylene, polyvinyl chloride (PVC), polypropylene, and the like are processed into useful shapes (i.e., fibers, tubes, bottles, toys, utensils, etc.) using a process that involves melting and solidification.

Crystallization

- Crystallization refers to the formation of solid crystals from a homogeneous **solution/melt**.
- Crystallization is the process through which the atoms, molecules or ions arrange themselves in a repeating pattern.
- Crystallization is the (natural or artificial) process of formation of solid crystals precipitating from a solution, melt or more rarely deposited directly from a gas.
- The crystallization process consists of two major events, **nucleation** and **crystal growth**
- The solubility of most compounds decreases as the temperature is lowered thus produce crystals and rapid cooling may cause the precipitation of amorphous solid or

Nucleation

- In the context of solidification, **the term nucleation refers to the formation of the first stable nanocrystallites from molten material.**
- In a broader sense, *the term nucleation refers to the initial stage of formation of one phase from another phase.*
- Aggregation of molecules/ions builds larger and larger and becomes a nucleus at some point
- The materials solidify as the liquid cools to just below its freezing (or melting) temperature, since the energy associated with the crystalline structure of the solid is then less than the energy of the liquid.
- This energy difference between the liquid and the solid is the free energy per unit volume ΔG_v and is *the driving force for solidification.*
- When the solid forms, a solid-liquid interface is created. A surface free energy σ_{sl} is associated with this interface.



Nucleation

- There are two types of nucleation: *homogeneous and heterogeneous*.
- *The distinction* between nucleation is 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.
- whereas for the heterogeneous type, nuclei form preferentially at structural inhomogeneities, such as container surfaces, insoluble impurities, grain boundaries, dislocations, and so on.

Undercooling/supercooling

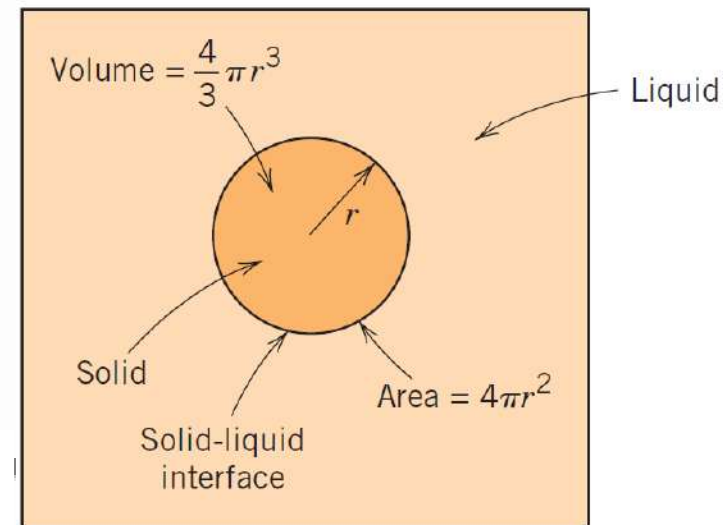
- Just below the melting point of the solid, *at freezing point*, atoms will cluster together called **embryos**, an equilibrium state of solid and liquid exist.
- At this stage embryos can form and dissolve.
- An appreciable nucleation rate (i.e., solidification) will begin only after the temperature, below the equilibrium solidification (or melting) temperature.
- This phenomenon is termed *supercooling* (or *undercooling*), and the degree of supercooling for homogeneous nucleation is significant.

Homogeneous nucleation

- At temperatures sufficiently below the solidification temperature, nucleation occurs by grouping of few atoms from the liquid.
- In homogeneous nucleation, nucleation originates at the time of undercooling.
- Homogeneous nucleation is uniform throughout the liquid.
- If the size of the nucleated atoms are sufficiently large enough to be stable then the cluster of atoms is called as nuclei.
- During the formation nuclei, the kinetic energy of the atoms in the liquid will be released as heat energy; which in turn increases the local heat surrounding the nuclei.
- This heat energy is compensated by the heat loss to the surrounding and freeze more and more atoms.
- Atoms can attach to existing nuclei or form their own nuclei.

- The theory of nucleation/Phase transformations involves a thermodynamic parameter called free energy (or *Gibbs free energy*), G .
- A transformation will occur spontaneously only when ΔG has a negative value.
- In solidification of a pure material, the nuclei of the solid phase form in the interior of the liquid as atoms cluster together to form a packing arrangement similar to that found in the solid phase.
- It is assumed that each nucleus is spherical in geometry and has a radius r .

The total free energy is contributed by the free energy difference between the solid and liquid phases, or the volume free energy, ΔG_v , its value is negative and energy associated with solid–liquid phase boundary or surface free energy γ .

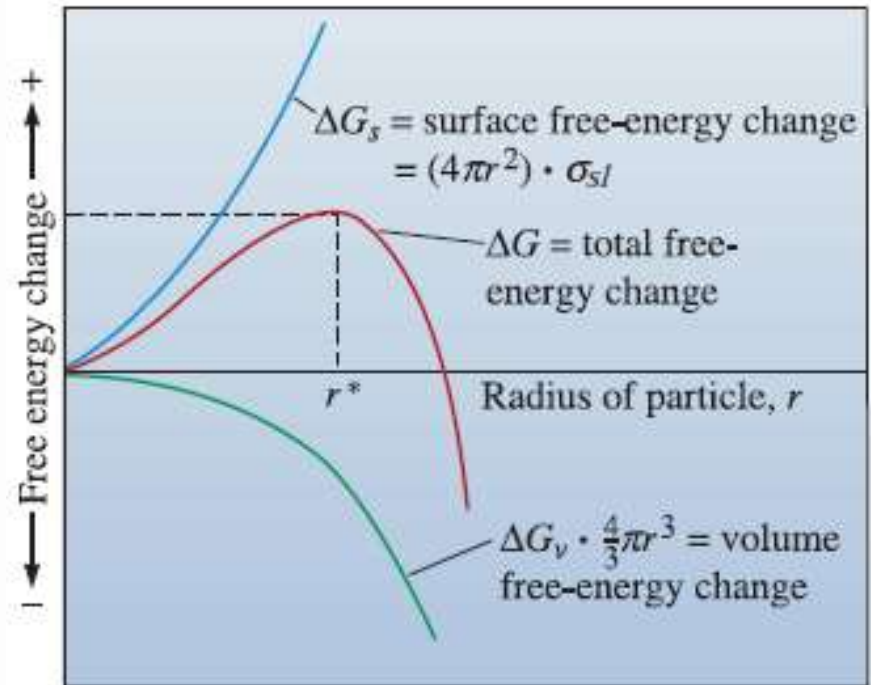


Nucleation

- The total change in energy G ,

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

- $\frac{4}{3} \pi r^3$ and $4\pi r^2$ are the volume and surface area of sphere with radius ' r '.
- ΔG_v is the free energy change per unit volume
- γ is the surface free energy of the solid-liquid interface



ΔG_v negative since the phase transformation is assumed to be thermodynamically feasible.

- As a solid particle begins to form as atoms in the liquid cluster together, its free energy first increases. If this cluster reaches a size corresponding to the critical radius r^* , *then growth will continue with the accompaniment of a decrease in free energy.*
- On the other hand, a cluster of radius less than the critical will shrink and redissolve. This subcritical particle is an *embryo*, whereas the particle of radius greater than r^* is termed a *nucleus*.
- *A critical free energy, ΔG^* , occurs at the critical radius and ΔG^* corresponds to an activation free energy, which is the free energy required for the formation of a stable nucleus.*
- It can be considered as an energy barrier to the nucleation process.
- Since r^* and ΔG^* appear at the maximum on the free energy-versus-radius curve

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

- Which leads to the result

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

- Substitution of this expression for r^* and results ΔG^*

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

- This volume free energy change ΔG_v is the driving force for the solidification transformation, and its magnitude is a function of temperature.
- At the temperature at which the solid and liquid phases are predicted to be in thermodynamic equilibrium (i.e., at the freezing temperature), the free energy of the solid phase and that of the liquid phase are equal ($\Delta G_v = 0$), *so the total free energy change (G) will be positive.*
- This means that with a lowering of temperature at temperatures below the equilibrium solidification temperature (T_m), *nucleation occurs more readily.*
- When the solid is very small with a radius less than the **critical radius** for nucleation (r^*), *further* growth causes the total free energy to increase.
- *The **critical radius** (r^*) is the minimum size of a crystal that must be*

Heterogeneous Nucleation

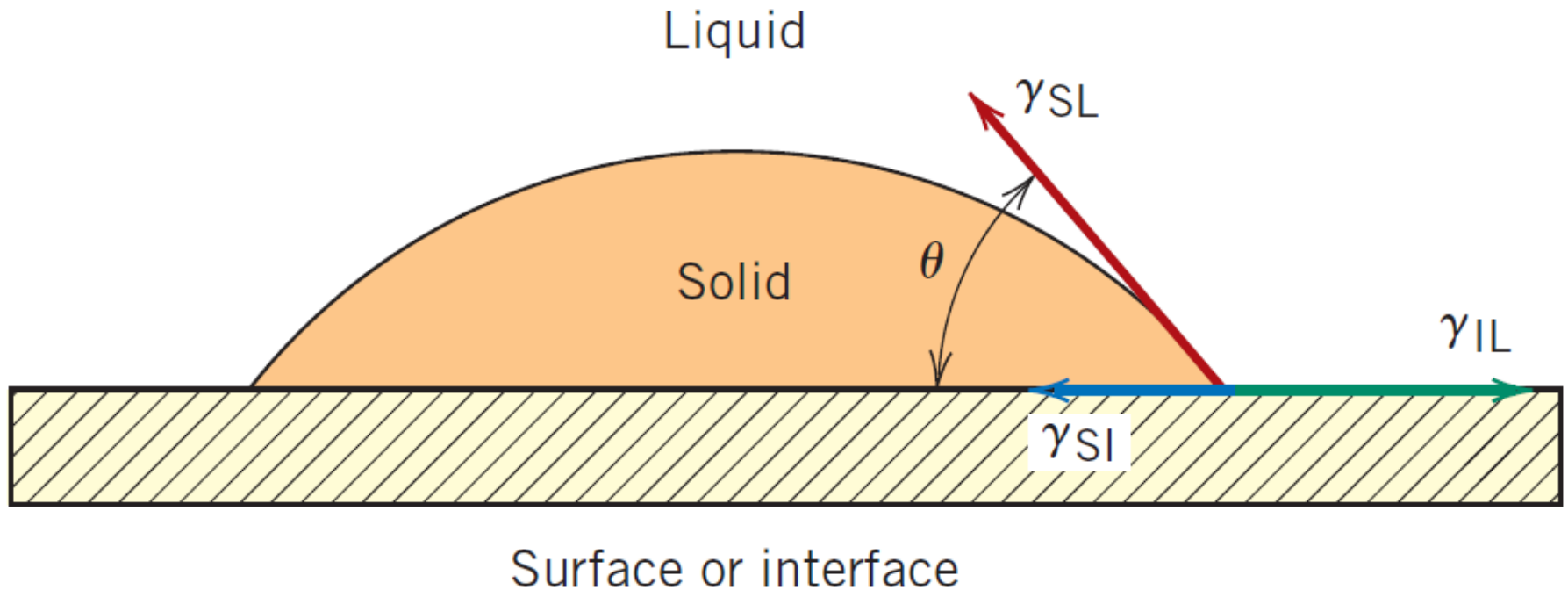
- The activation energy (i.e., energy barrier) for nucleation is lowered when nuclei form on preexisting surfaces or interfaces, since the surface free energy is reduced.
- In other words, it is easier for nucleation to occur at surfaces and interfaces than at other sites, this type of preferential nucleation is termed *heterogeneous nucleation*.
- A low level of undercooling is required to initiate this type of nucleation.
- Walls of the container promotes heterogeneous nucleation.
- Addition of grain refiner to molten metal produce fine grains, since the grain refiner solidifies faster and act as sites for heterogeneous nucleation thereby reducing the size

- In order to understand this phenomenon, let us consider the nucleation, on a flat surface, of a solid particle from a liquid phase.
- It is assumed that both the liquid and solid phases “wet” this flat surface, that is, both of these phases spread out and cover the surface.
- There are three interfacial energies (represented as vectors) that exist at two-phase boundaries— γ_{SL} , γ_{SI} and γ_{IL} —as well as the wetting angle (the angle between the and vectors).

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

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

$$\Delta G^* = \left(\frac{16\pi\gamma_{SL}^3}{3\Delta G_v^2} \right) S(\theta)$$

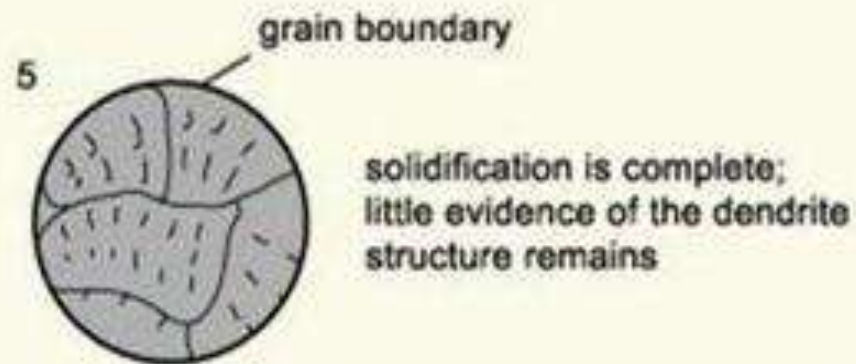
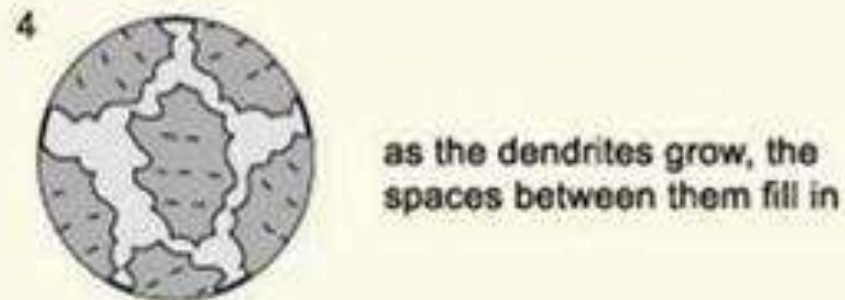
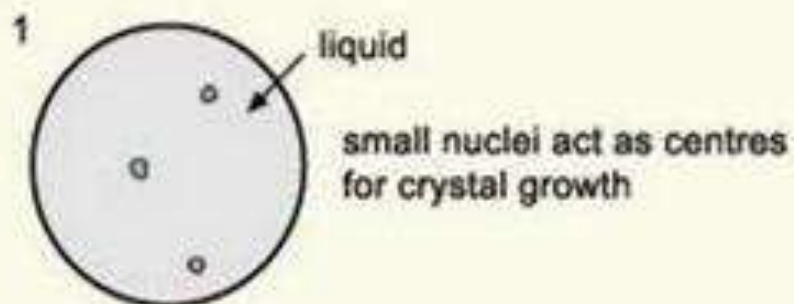


Heterogeneous nucleation of a solid from a liquid.

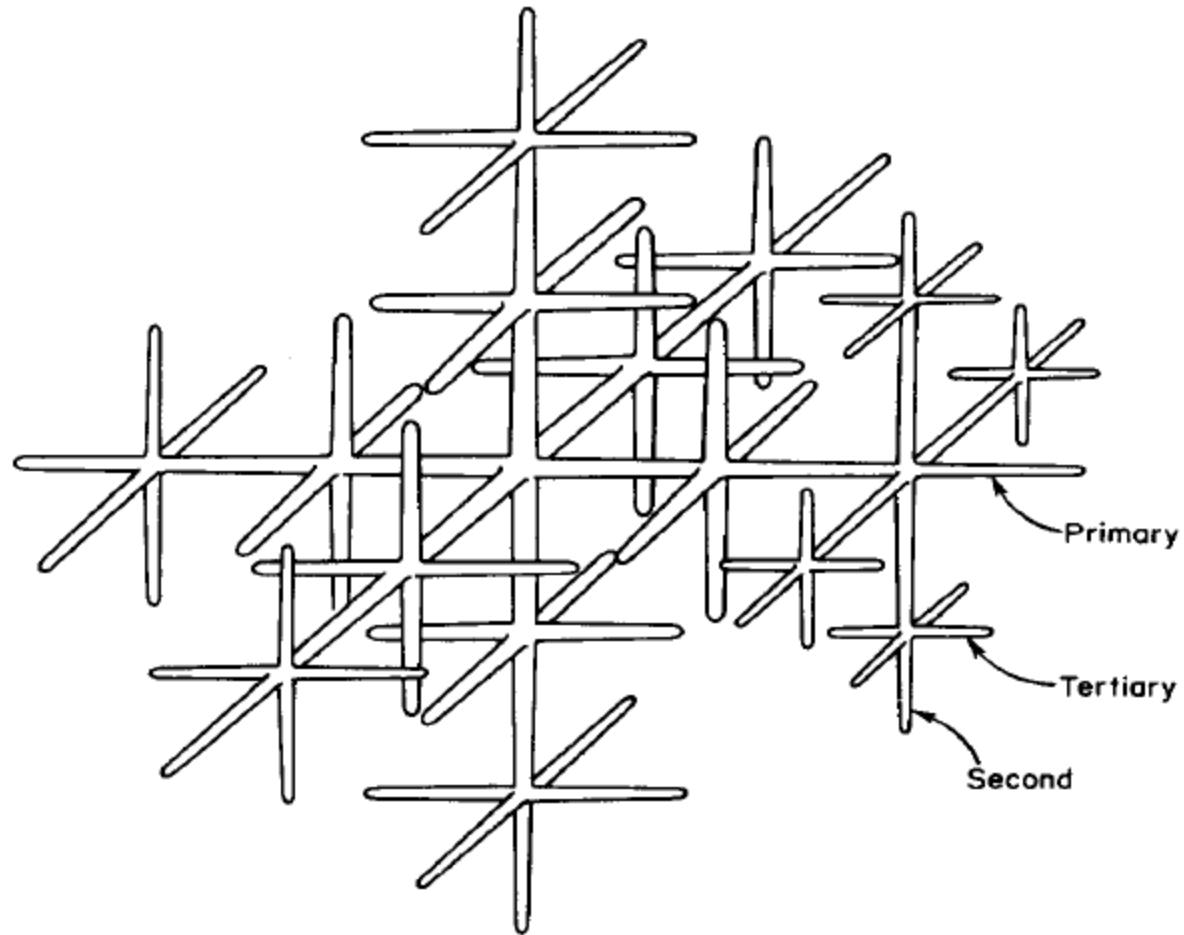
The solid-surface (γ_{SI}), solid-liquid (γ_{SL}), and liquid-surface (γ_{IL}), interfacial energies are represented by vectors. The wetting angle is also shown.

Dendritic growth

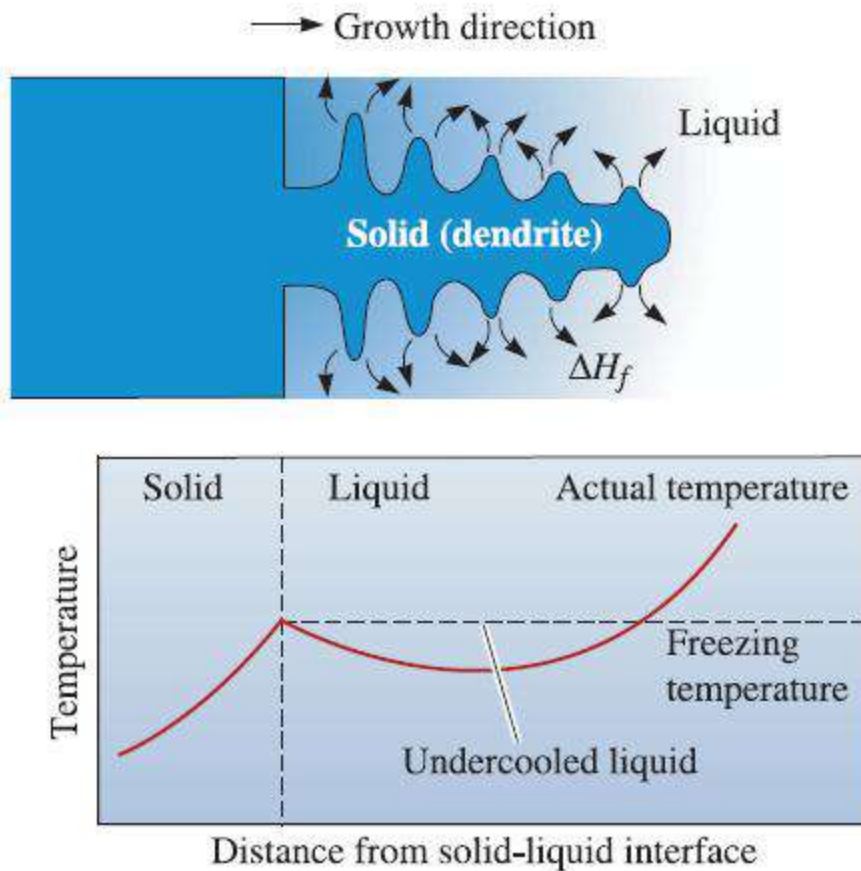
- If the nucleation in liquid is not initiated and the nucleation is poor, the liquid has to be undercooled before the solid forms.
- Under these conditions, a small solid protuberance called a **dendrite**, *which forms at the interface*, is encouraged to grow since the liquid ahead of the solidification front is undercooled.
- Under the aforesaid conditions, the solid nucleus are grown by attracting atoms from the liquid to form space lattice.
- As the crystal grows in three dimension, the attachment of atoms take place only in preferred directions, mainly along the axes of the crystal.
- The growth has tree like appearance *and it is called as dendritic growth*. (The word dendrite comes from the Greek word



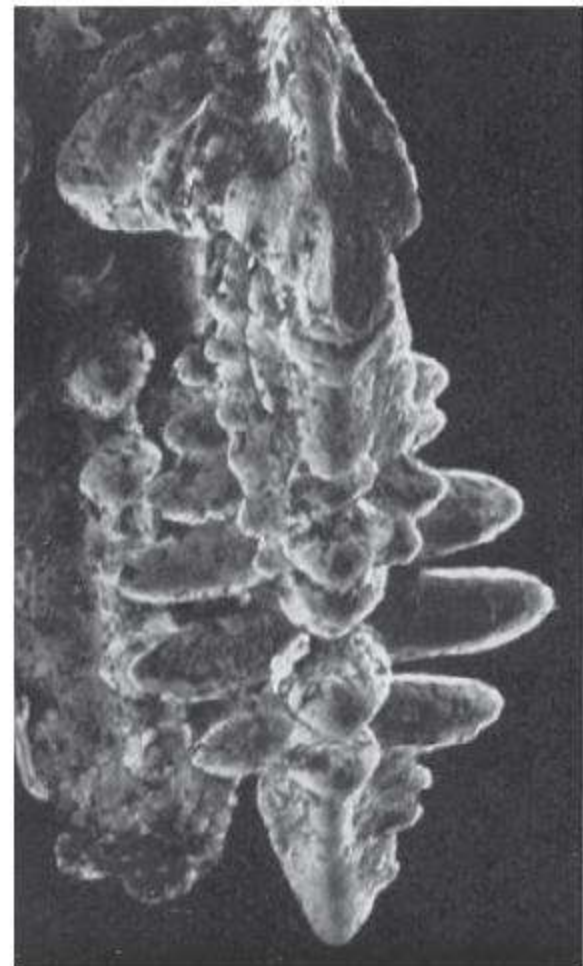
Dendritic growth in 3D



- The final shape of the dendrite is in the form of a skeleton, forms primary, secondary and tertiary arms, which will be similar to the branches and twigs growing from the trunk of a tree.
- *As the solid dendrite* grows, the latent heat of fusion is conducted into the undercooled liquid, raising the temperature of the liquid toward the freezing temperature. Secondary and tertiary dendrite arms can also form on the primary stalks to speed the evolution of the latent heat.
- Dendritic growth continues until the undercooled liquid warms to the freezing temperature.
- The dendritic arms can grow longer/thicker till the space between them is filled with solid.
- In pure metals, dendritic growth normally represents only a small fraction and there won't be any evidence of dendritic growth.



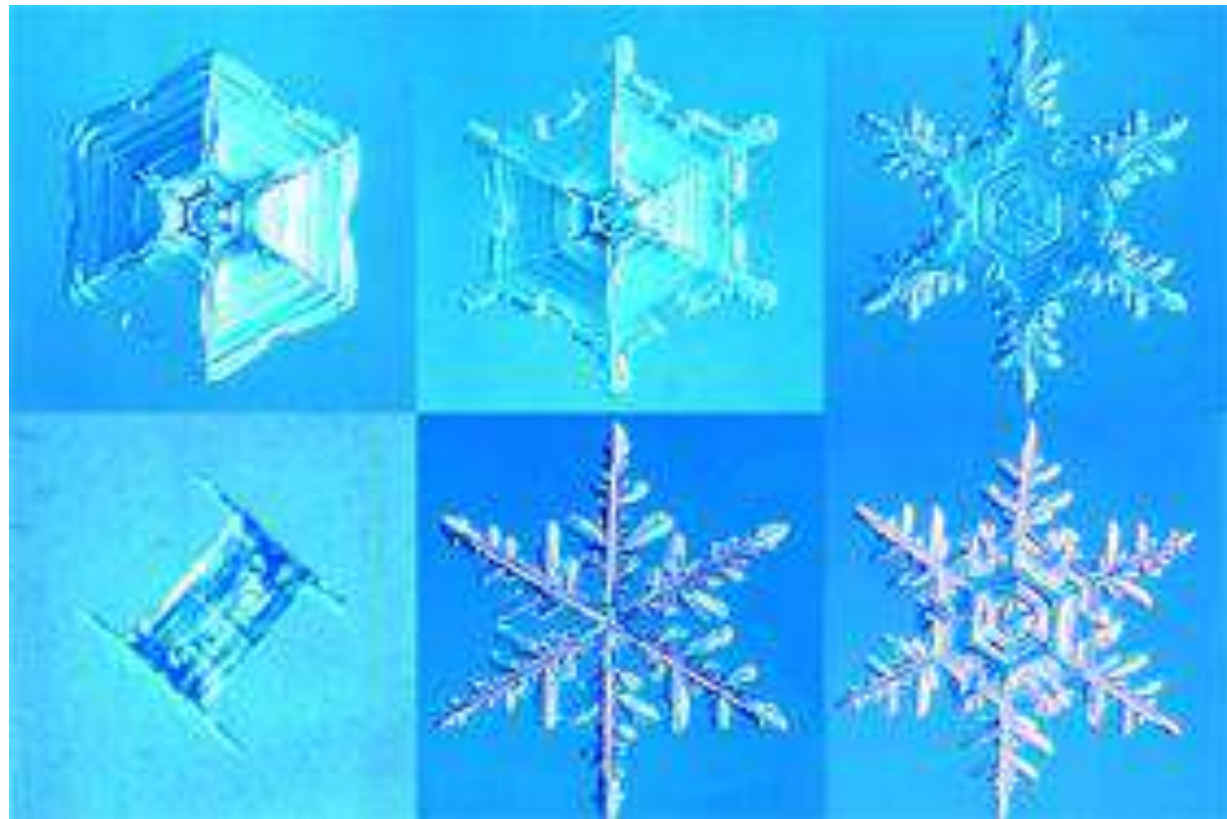
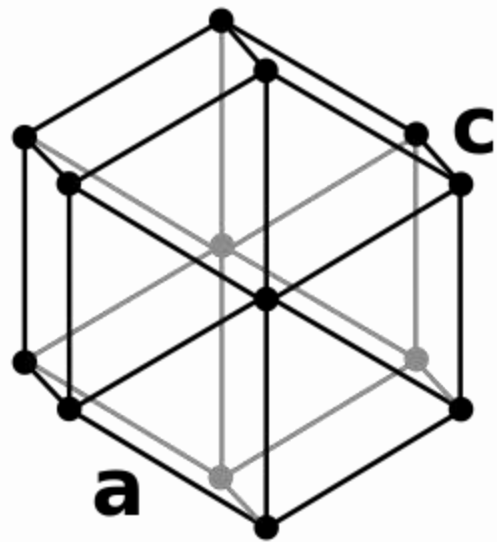
(a)



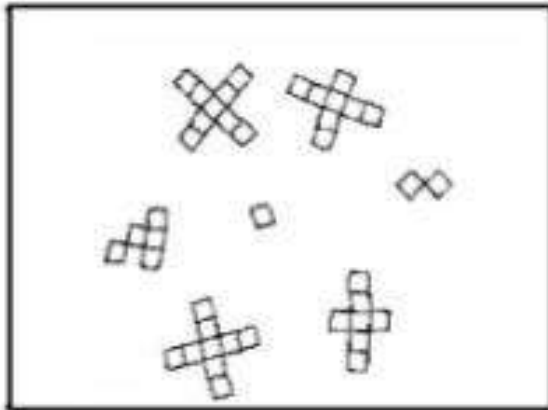
(b)

- (a) If the liquid is undercooled, a protuberance on the solid-liquid interface can grow rapidly as a dendrite. The latent heat of fusion is removed by

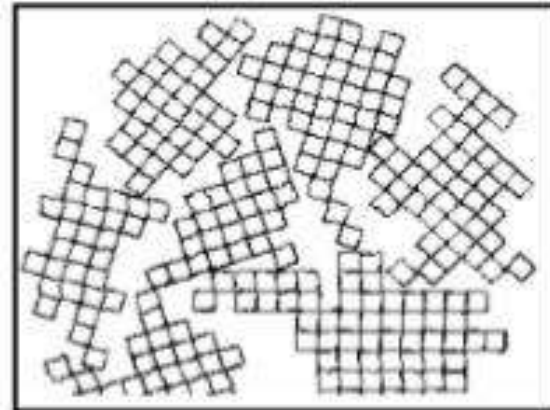
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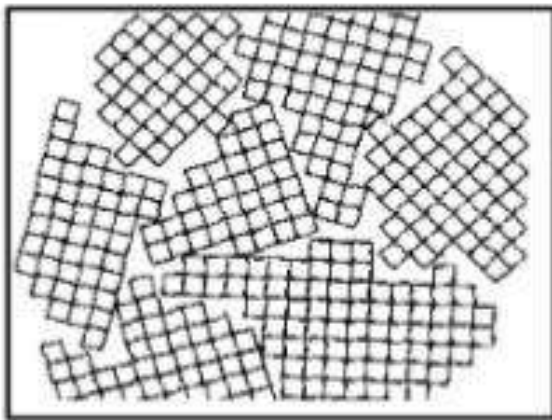
Grain boundary irregularity



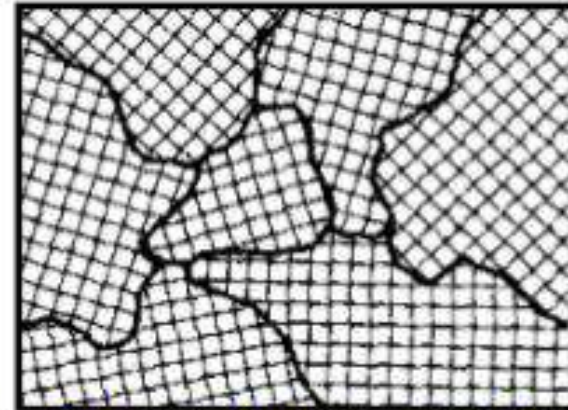
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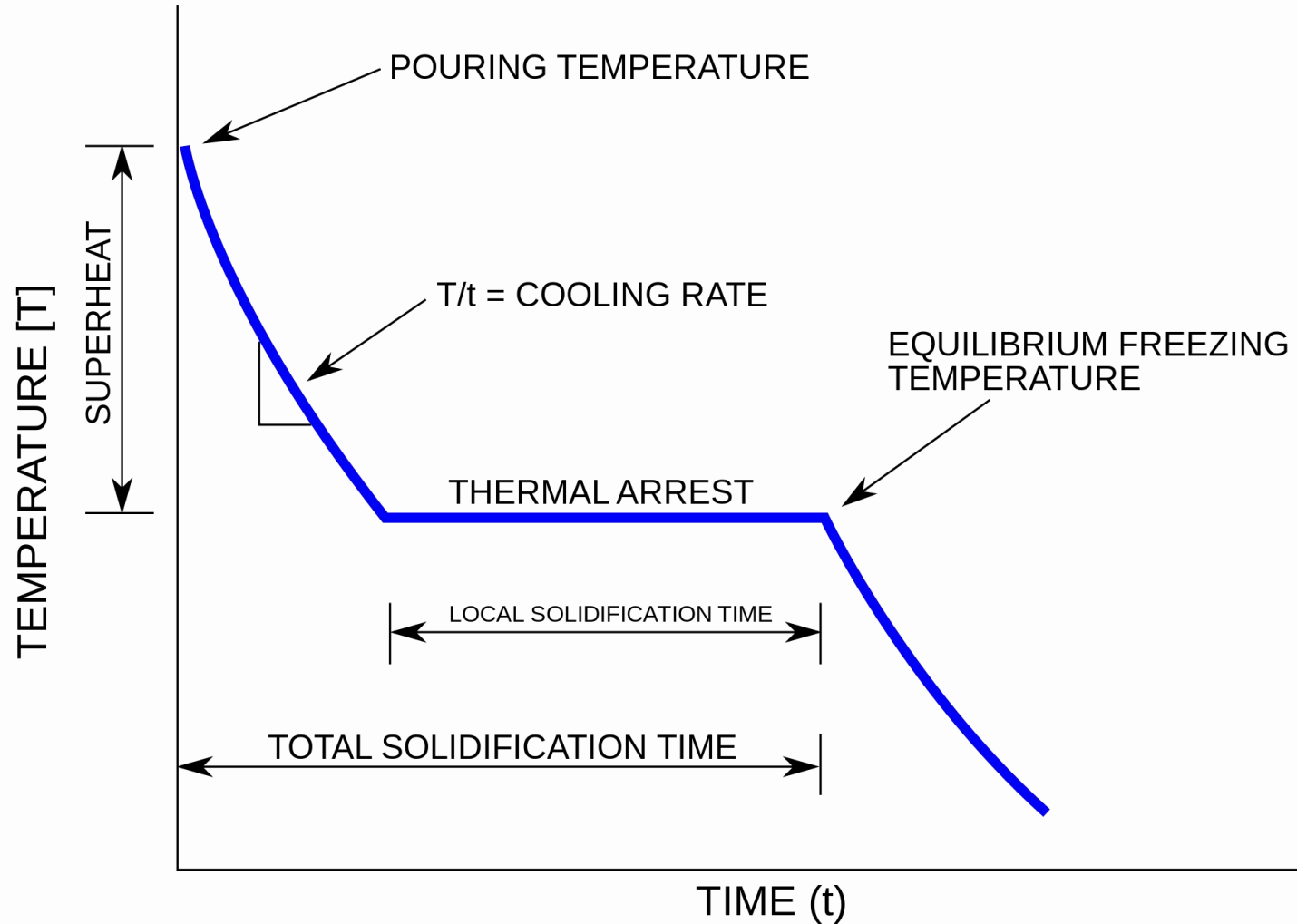


3. **Grain Formation**: Interface develops.



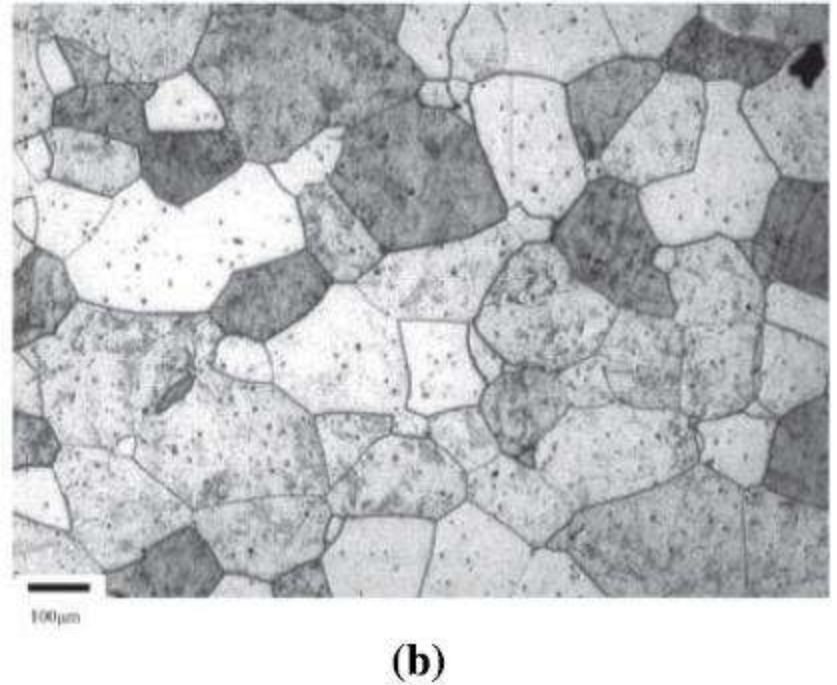
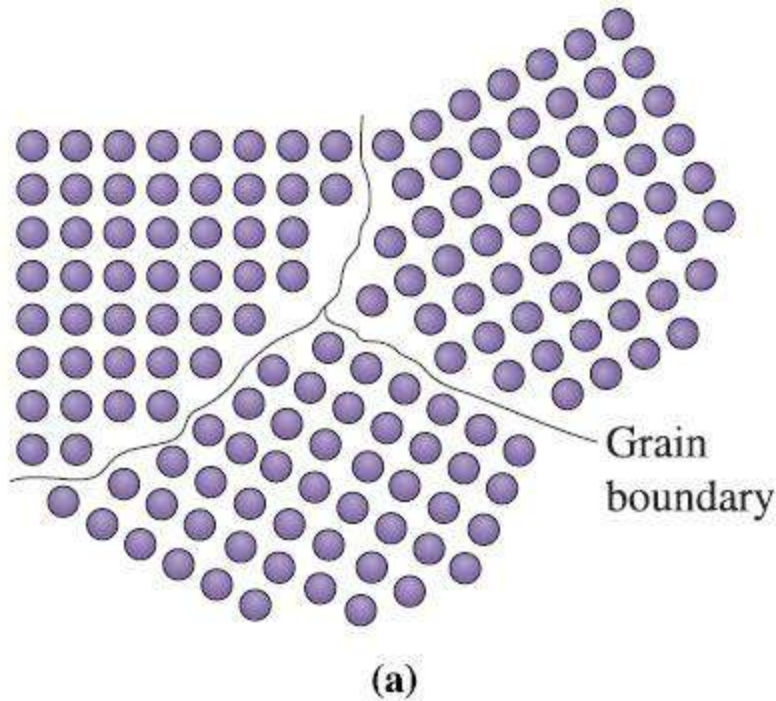
4. **Polycrystalline structure**: Grain growth is limited by another grain, creating a boundary between them

Cooling curve



Grain boundary irregularity

- During solidification of liquid metals, when crystals or grains with different atomic orientations meet each other, as the grains are formed from different nucleus.
- The atomic packing between the two adjacent grains will be distorted and the region can be considered as imperfection.
- The transition zone, where atoms are aligned neither of the neighboring grains are called grain boundary.
- Atoms at the grain boundary had more energy than the atoms at the interior of the grains.



- (a) The atoms near the boundaries of the three grains do not have an equilibrium spacing or arrangement.
- (b) Grains and grain boundaries in a stainless steel sample.

Grain size

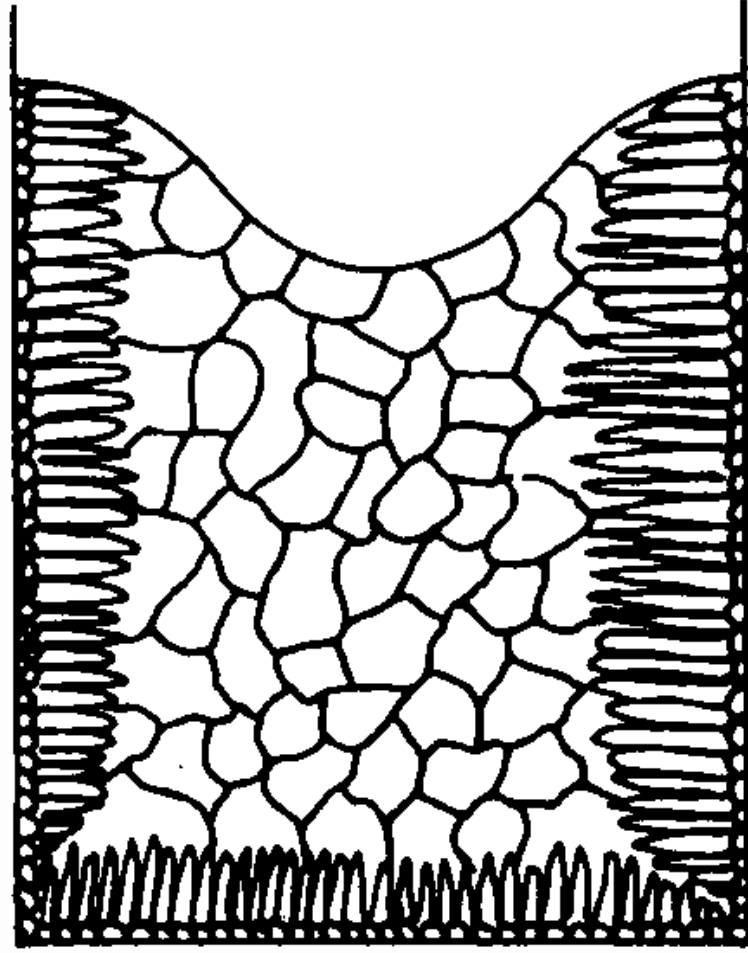
- The microstructure of single phase materials can be varied by changes in the size, shape and orientation of grains.
- The size and shape of the grains are associated with the prevailing conditions during grain growth.
- The rate of cooling of the molten material can affect the grain growth.
- If the cooling rate is too slow (small degree of undercooling), at the onset of nucleation, only a few nuclei will form and the growth commences only from those nuclei, and the resultant crystal sizes will be large.
- If the cooling rate is rapid (high degree of undercooling/supercooling) a large number of nuclei will form and the resulting crystal will be small.
- The grain sizes can be adjusted with the help of thermo-mechanical treatments.
- A well designed thermo mechanical process gives microstructure with preferred orientation gives tailored material properties.

Effect of grain size on material properties

- In a fine grained material, there are more grain boundaries within the bulk of material.
- Grain boundaries are obstructions to dislocation movements.
- Dislocations will pile-up at the grain boundaries.
- Therefore, more stress will be needed to deform such materials.
- Thus, A fine grain material has more strength and hardness.
- These materials will have poor ductility.

Grain shape

- The nature of the container in which the liquid metal cools also affect the shape and number of grains.
- Large number of fine grains will be formed at the contact point of the mold and the solidifying metal.
- when the molten metal first strike the mold create a chilling effect, which results in fine grained metal at the surface.
- As the mol is warmed, the chilling effect will reduce and the nuclei formation retards as the solidification progresses.



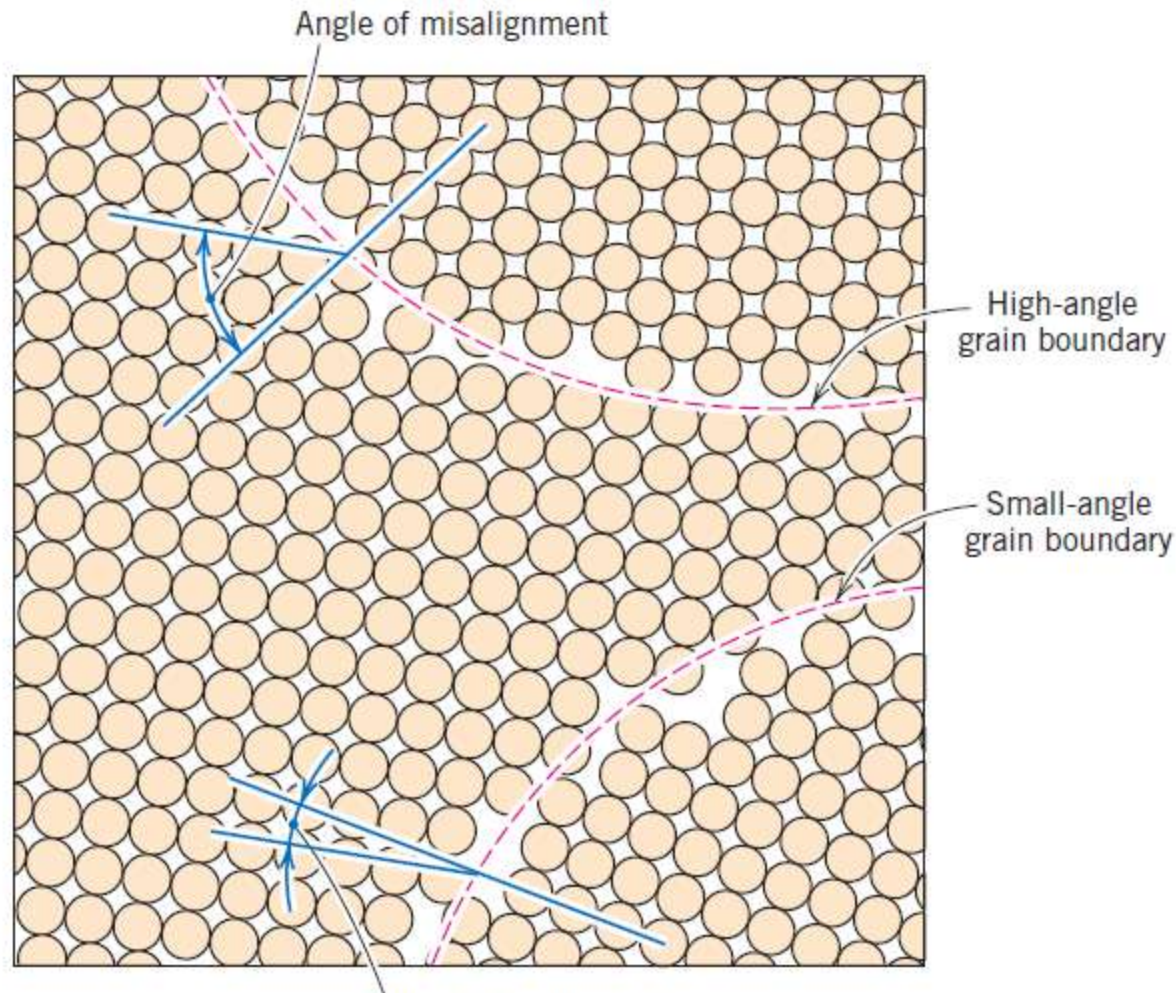
Grain shape.....

- In the intermediate portion nature of cooling is favorable to the formation of columnar grains.
 - At the centre of the mold equi-axed grains can be observed.
 - The distinguished grains will be observed in large molds, in narrow molds equi-axed grains will be absent.
 - A metallic mould can give fine grained structure and a sand mold can give a coarse grained structure.
- * *equi-axed means equal length in all the three dimensions*

Orientation of grains

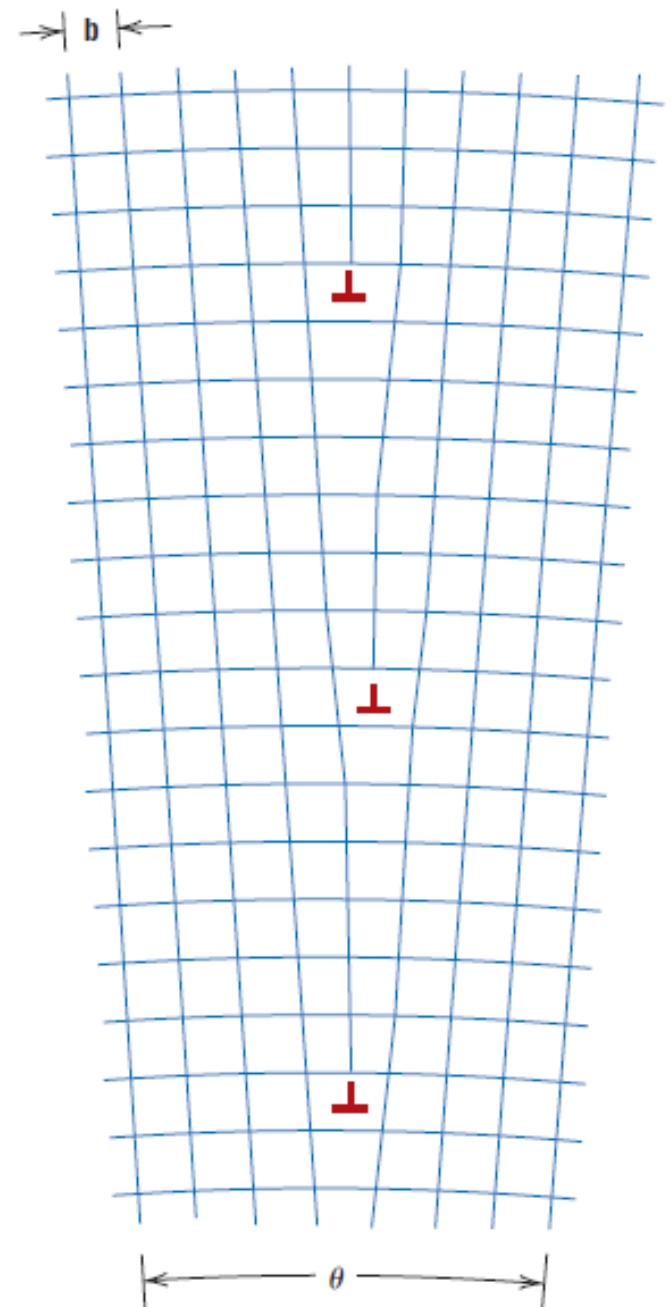
- Grains are formed are having random crystallographic orientation.
- Grains can be grown in specified directions using metallographic techniques.
- Grains of iron grown in $[100]$ direction have a higher magnetic permeability than any other orientation.

Effects of Grain size, shape and orientation on dislocation and creep



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- Various degrees of crystallographic misalignment between adjacent grains are possible.
- When this orientation mismatch is slight, on the order of a few degrees, then the term ***small- (or low-) angle grain boundary*** is used.
- One simple small angle grain boundary is formed when edge dislocations are aligned in the manner as in Figure, a regular array. This type is called a ***tilt boundary***.
- When the angle of misorientation is parallel to the boundary, a ***twist boundary results, which can be described by an array of screw***



- When this orientation mismatch is large, on the order of a appreciable degrees, then the term ***high angle grain boundary*** is used.
- As the angle of mismatch increases the density of grain boundary ledges will increase, and they are good sources of dislocation.
- Moving dislocations can pile up at the grain boundary and induce stress concentration ahead of the slip planes and can create dislocation in adjacent grains.
- If the slip planes are more at grain boundaries, hardness will be high at grain boundaries than the center.
- As the grain size reduces, the grain boundary behavior will be experienced at the center also, so grains will have uniform hardness.

- Small grains barriers dislocation mobility lead to higher strength and hardness.
- Strain hardening is greater in fine grained material than the coarse grained material.
- Grain boundary sliding observe at temperatures above $0.5 T_m$, this sliding is prominent with increasing temperature and the deformation caused by sliding of grain boundaries.
- This phenomenon is called as **creep** in materials.

Hall-Petch equation

- One method of controlling the properties of a material is by controlling the grain size. By reducing the grain size, we increase the number of grains and, hence, increase the amount of grain boundary area. Any dislocation moves only a short distance before encountering a grain boundary, and the strength of the metallic material is increased.
- The **Hall-Petch equation relates the grain size to the yield strength**,

$$\sigma_y = \sigma_0 + Kd^{-1/2}$$

- where σ_y is the yield strength (the level of stress necessary to cause a certain amount of permanent deformation), d is the average diameter of the grains, and σ_0 and K are constants for the metal.
- The Hall-Petch equation is not valid for materials with

The yield strength of mild steel with an average grain size of 0.05 mm is 20,000 psi. The yield stress of the same steel with a grain size of 0.007 mm is 40,000 psi. What will be the average grain size of the same steel with a yield stress of 30,000 psi? Assume the Hall-Petch equation is valid and that changes in the observed yield stress are due to changes in grain size.

$$\sigma_y = \sigma_0 + Kd^{-1/2}$$

Thus, for a grain size of 0.05 mm, the yield stress is

$$20,000 \text{ psi (6.895 MPa)/(1000 psi)} = 137.9 \text{ MPa}$$

(Note: 1000 psi = 6.895 MPa). Using the Hall-Petch equation

$$137.9 = \sigma_0 + \frac{K}{\sqrt{0.05}}$$

For the grain size of 0.007 mm, the yield stress is 40,000 psi (6.895 MPa)(1000 psi) = 275.8 MPa. Therefore, again using the Hall-Petch equation:

$$275.8 = \sigma_0 + \frac{K}{\sqrt{0.007}}$$

Solving these two equations, $K = 18.44 \text{ MPa} \cdot \text{mm}^{1/2}$, and $\sigma_0 = 55.5 \text{ MPa}$. Now we have the Hall-Petch equation as

$$\sigma_y = 55.5 + 18.44 d^{-1/2}$$

If we want a yield stress of 30,000 psi or 206.9 MPa, the grain size should be 0.0148 mm.

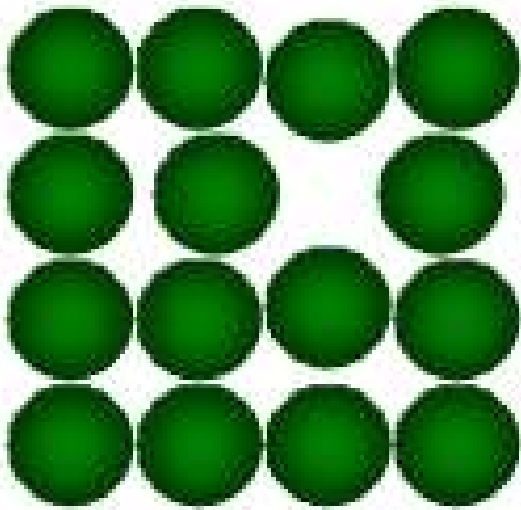
- The Hall-Petch constants of AZ31 Magnesium alloys are $K = 0.5 \text{ MPa}\cdot\text{m}^{1/2}$ and $\sigma_0 = 3 \text{ MPa}$, what is the yield strength of the if the grain size is $4 \text{ }\mu\text{m}$.

Crystal imperfections

- Point Defects or zero dimensional
 - Vacancy
 - Self interstitial or interstitialcy
 - Interstitial impurity
 - Substitutional Impurity
 - Frenkel defect
 - Schottky defect
- Line defects- or one dimensional defect
 - Edge dislocation
 - Screw dislocation
- Surface defects or two dimensional defect
 - Grain boundaries
 - Tilt boundaries
 - Twin boundaries
 - Stalking fault

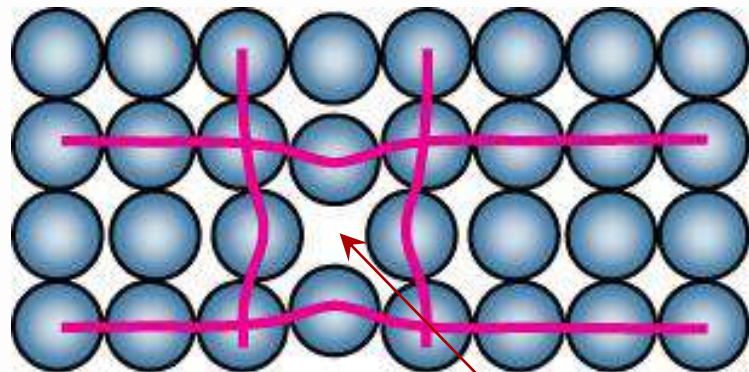
Vacancies

- If an atom is missing from the regular lattice site, then it is called as vacancy.
- This defect arises due to imperfect packing of atoms or by the thermal vibrations at high temperature.



Vacancy

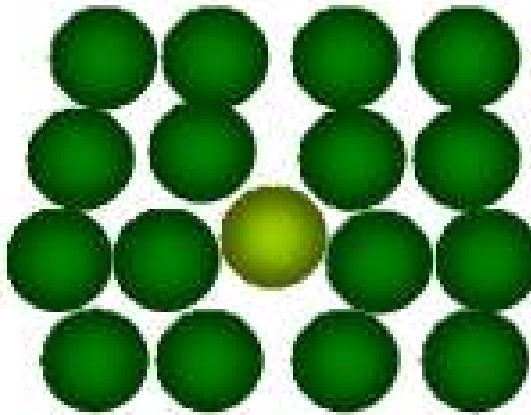
distortion
of planes



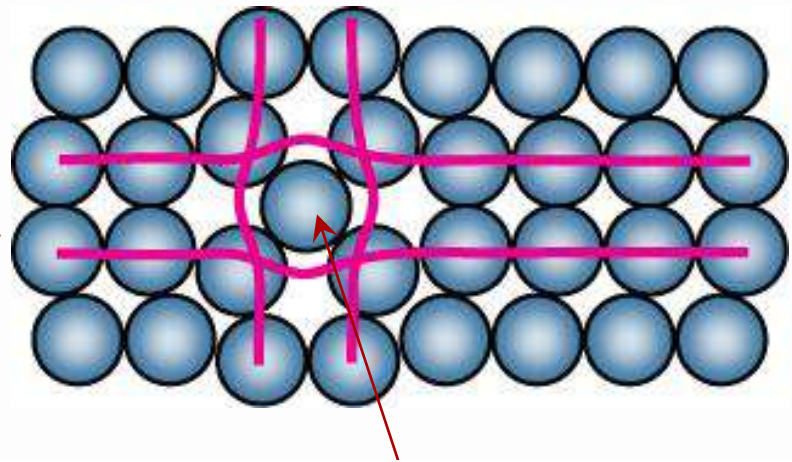
Vacancy

Self interstitial or interstitialcy

- This is the inverse of vacancy, where atom squeezes into the in the space between the normal lattice positions.
- Interstitial spaces are very small and such interstitial produces greater distortions to the surrounding lattice than a vacancy.



distortion
of planes

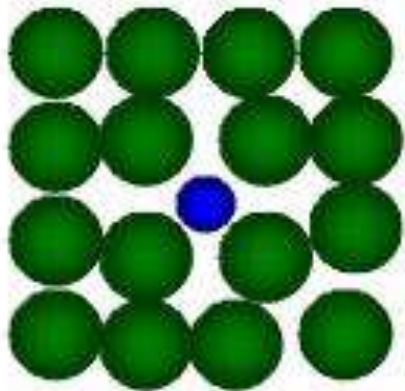


Impurities

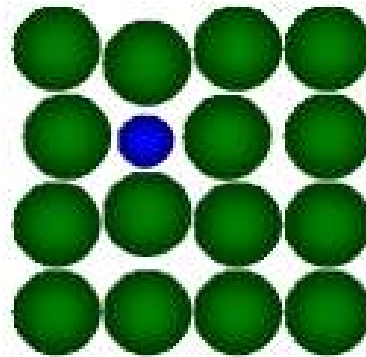
- Impurities are atoms of a foreign material.

A **substitutional impurity** refers to a foreign atom substitutes/replaces a foreign atom in a regular crystal site.

An **Interstitial impurity** is a small sized atom occupying the void space between the parent atoms on regular sites.



Interstitial impurity



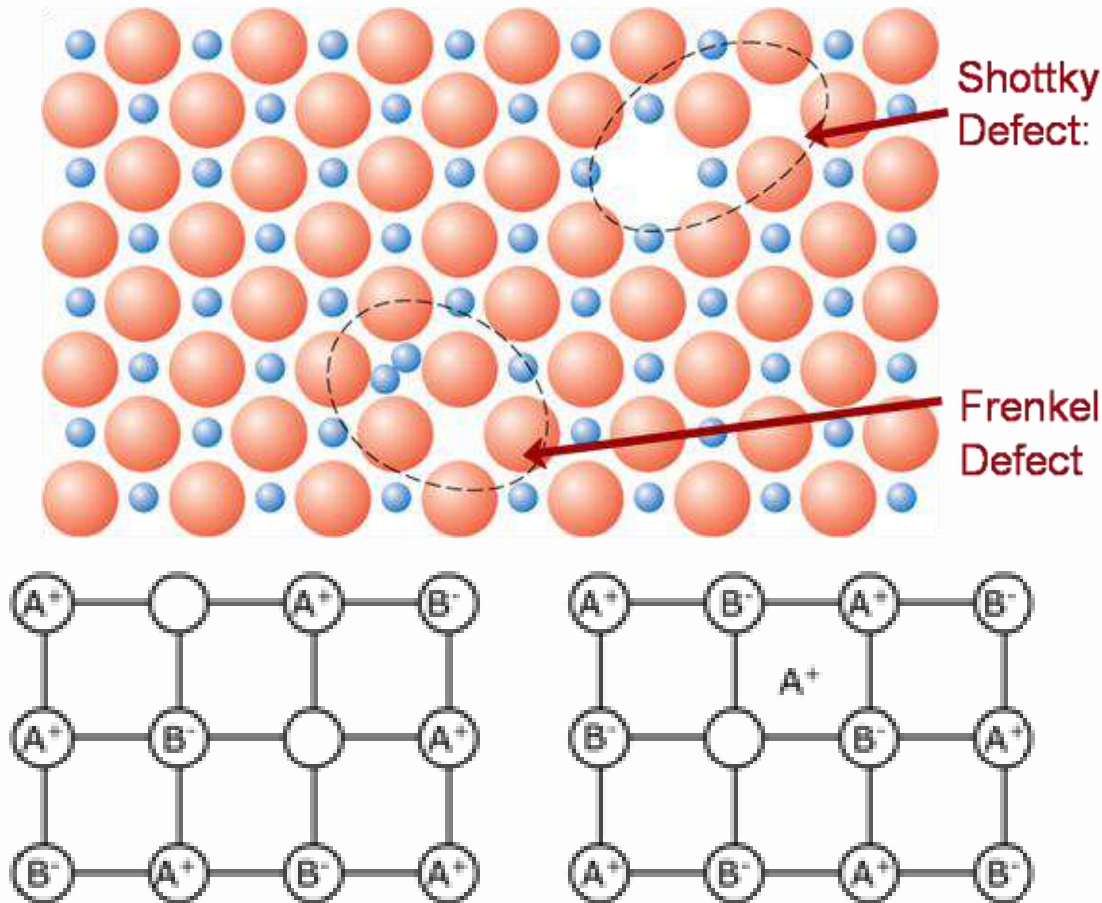
Substitution impurity

Frenkel defect

- This defect is present in ionic crystal.
- In ionic crystals, even if the defects are present overall electrical neutrality should be maintained.
- When an ion is displaced from a regular site to another, then it is called as frenkel defect.
- The cations are smaller ions, therefore it is possible for them to get displaced into the void spaces.
- Anions can't occupy the void space, since the voids or interstitial sites are too small to accomodate them.

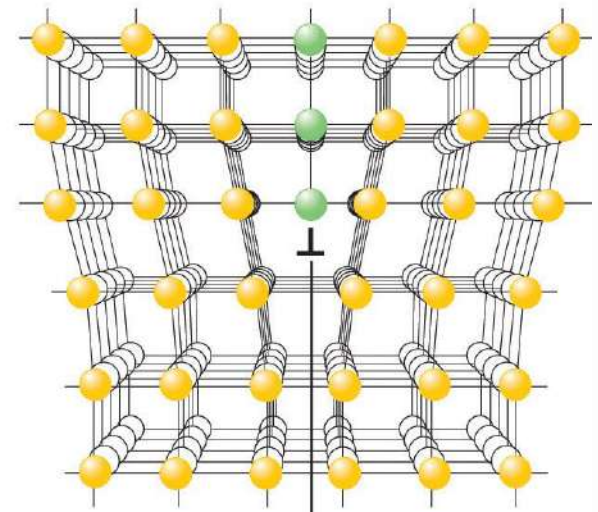
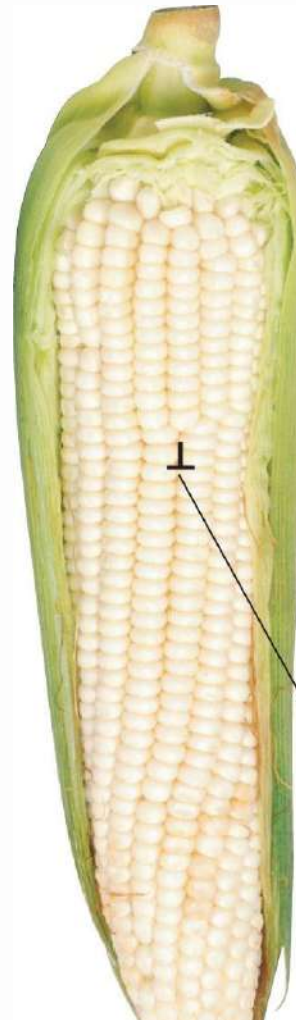
Schottky defect

- When a pair of cation anion is missing from the lattice of a ionic crystal, the defect is known as Schottky defect.
- Schittky defect is similar to vacncy in normal crystals.



Types of Dislocation

- The linear disturbances of atomic arrangements are called line defects or dislocations
- Edge dislocation
- Screw dislocation



Origin of edge dislocation

Effect of point defects on mechanical properties -



forest of dislocation,

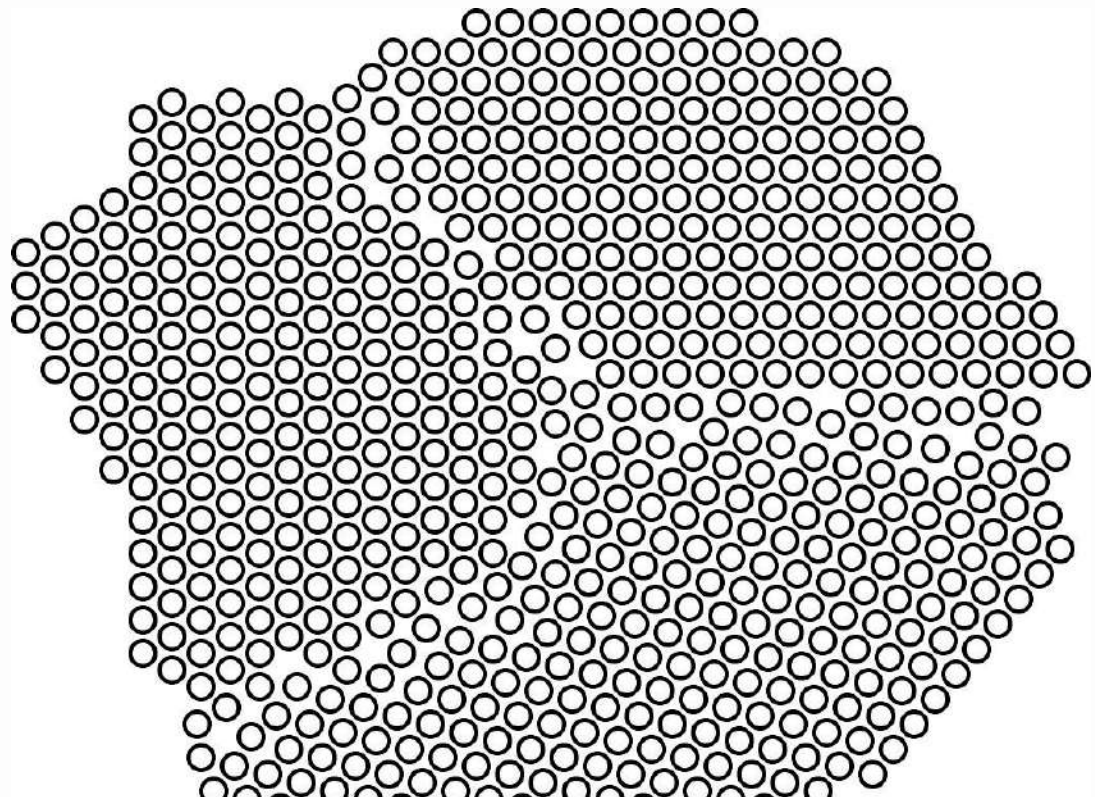
Role Of Surface Defects On Crack Initiation.



Driving force for grain growth and applications during heat treatment

- If the metal specimen is kept at the elevated temperature, the grains will grow and the resultant grains become coarse.
- This phenomenon is called **grain growth**.
- Larger grains have lower free energy and it will result in the reduction in amount of grain boundary.
- The lowest energy of the metal would be as that of a single crystal.
- The **driving force for grain growth is the reduction in energy**.
- The *force opposing this driving force is the rigidity of the lattice and it will decrease as the*

- For any given temperature, there is maximum grain size at which these forces are at equilibrium.
- The factors which favors slow nucleation can result in rapid growth and it will result in a coarse grained material.



Factors that govern grain growth

1. Degree of prior deformation

- Amount of prior deformation favors nucleation and decreases the final grain size.
- At critical deformation, the grain will grow to a very large size upon annealing.
- If the deformation is low the lesser will be the distorted region that can act as nucleation sites.
- Only a few few grains will be formed during crystallization, resulting a coarse grained structure.
- With the increase in deformation, the number of nucleationsites will be more and there by the number of grains.

- **Time at temperature**

- Increasing the time at any temperature above the recrystallization temperature favors the grain growth and increases the final grain size.

- **Annealing temperature.**

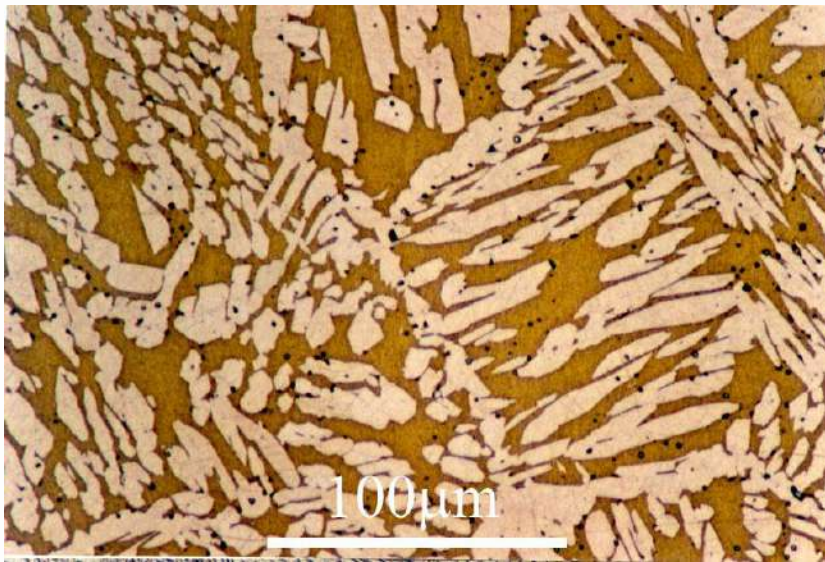
- The lower the grain size above the recrystallization temperature, the finer will be the grain size.
- At low temperature diffusion rate will be slower thereby grain growth.

- **Insoluble impurities**

- Greater the amount and finer the distribution of dissolvable impurities, finer the grain size
- They not only act as nucleation sites, but also act as barriers to grain boundary movements, results in finers grains

Determination of microstructure

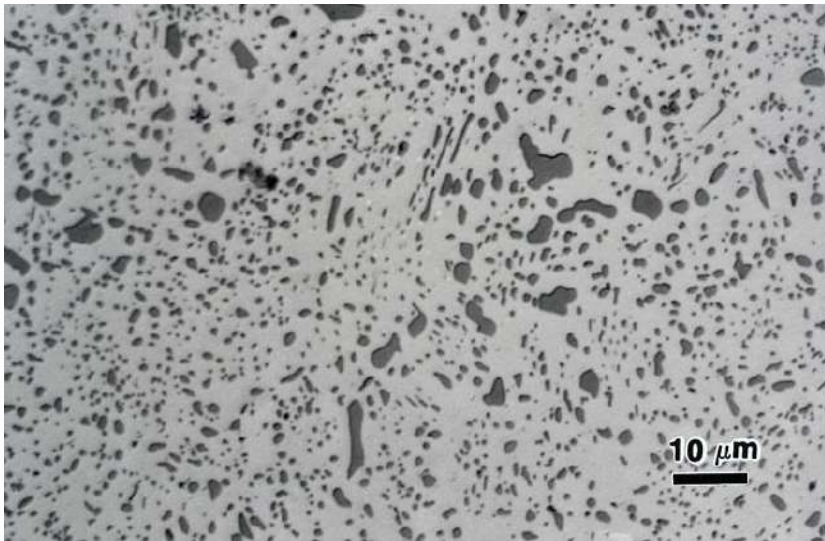
- **Metallography** is the part of metallurgy related to the study of metals by microscopic examination using optical or electron microscope.
- Metallographic examination reveals the structure of grains, grain boundaries, presence of microphases, line defects and surface defects.
- **Optical microscope** is used to study the features and internal make up of the material at microscopic level.
- The magnification level of optical microscope is **2000x**.
- For this purpose, the surface of the small sample is



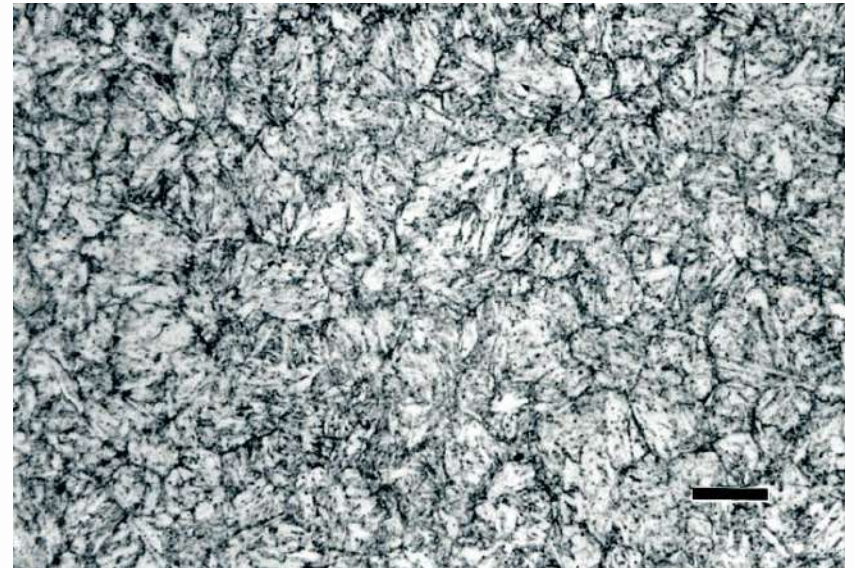
Cu-Ni Alloy



Steel



Tool Steel

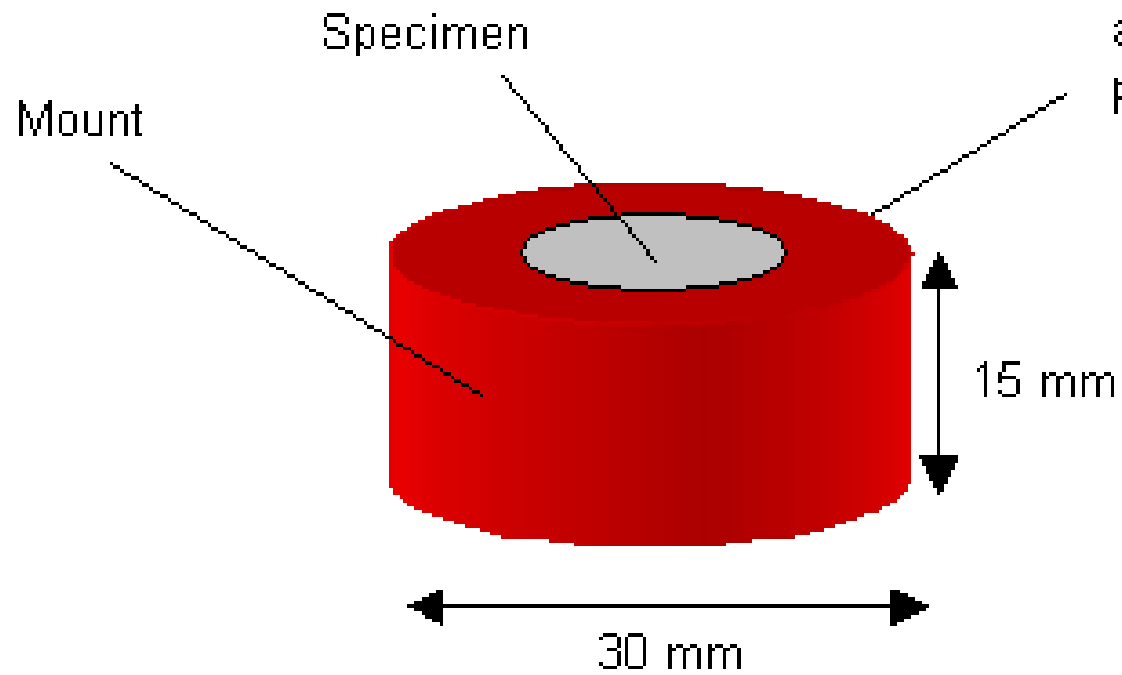


Heat treated Steel

Selecting and cutting the specimen

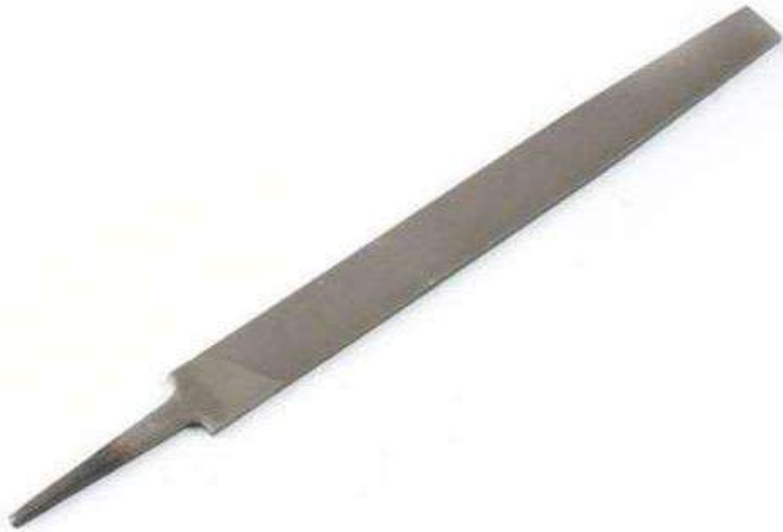
- The specimen selected for the study should be a true representative of the material being studied.
- In the case of casting, welding, case hardening etc., the structure and composition of the material varies considerably within a single component. In such cases, specimens should be chosen from the area of interest.
- After selecting the particular region from the mass, the specimen has to cut carefully using a saw or abrasive wheel.
- While cutting the specimen should not be heated to avoid the further change in the microstructure.
- Specimens of sizes 10-15mm in diameter or square is preferred and smaller samples should be mounted using thermoplastic resin.

Edges of mounted sample
are rounded using coarse
paper



Rough grinding

- First step in grinding is to make the surface absolutely flat.
- It can be done using a file, rotating grinding wheel or a motor driven emery belt.
- It is preferred to keep the file stationary and rub the specimen against it.
- Again care must be taken to avoid heating.
- The specimen should be washed to remove the coarse filings and abrasive particles.



Intermediate and fine grinding

- This is carried out by emery papers of progressively smaller grit sizes.

	Grit		Application
	40-80	Coarse	Material removal
	100-150	Medium	Leveling
	180-500	Fine	Finishing
	600-1500	Micro	Fine sanding

- The emery paper is kept on a flat surface, such as glass and the specimen is rubbed against it in a single direction.
- Once the grinding is completed, the specimen should

Intermediate and fine grinding

- If the specimen is first ground with emery paper with a grit size of 220, the new scratches should be at 90° to the previous grinding.
- The process should repeat with subsequent grit papers, 320, 400, 600 etc...
- While transferring the grinding papers, the specimen should be turned 90°.
- The grinding should be continued till all the scratches from the previous grinding disappear.
- Machine grinding is also possible by fixing the emery paper on a rotating wheel.
- Fine grinding is done in a manner similar to the previous grit sizes and the emery papers will be designated as 1/0, 2/0, 3/0, 4/0.

Polishing

- During fine grinding a series of parallel grooves will be left on the sample surface by the last emery paper employed.
- Polishing is meant to remove these grooves.
- Polishing is done by a polishing cloth pad impregnated with suitable polishing medium.
- The cloth is wetted with distilled water and a small quantity of polishing powder or paste is applied.
- The specimen is pressed against the rotating wheel and moved opposite to the direction of rotation.
- Harder specimens (Steel/iron) are generally given two stage polishing.
- Diamond powder in the form of paste or slurry or alumina



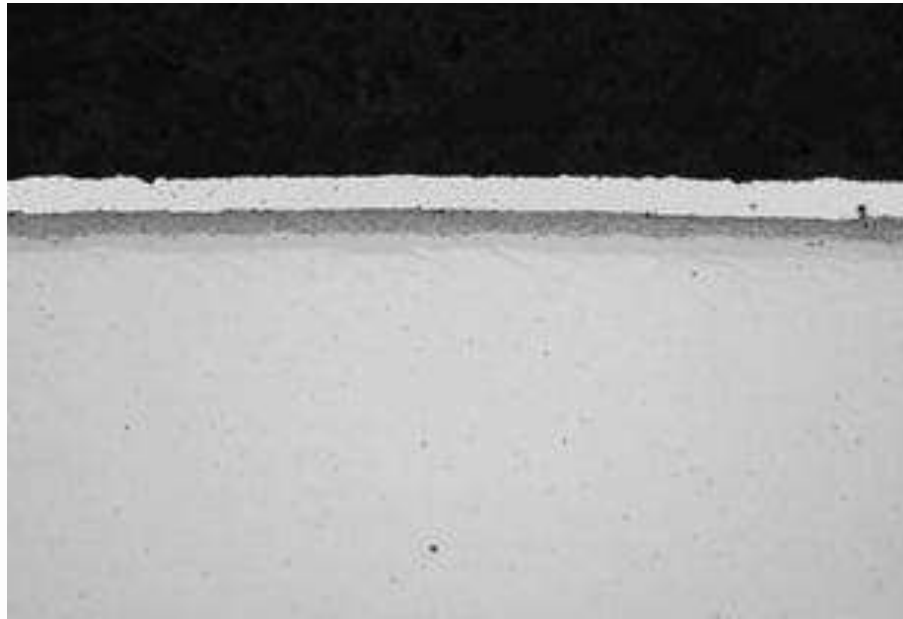
Polishing...

- At the end of the polishing, the surface should be scratch free with perfectly shining appearance.
- The surface should appear as a mirror.
- When the sample, after cleaning, is examined under optical microscope at 100x, the surface should be scratch free.

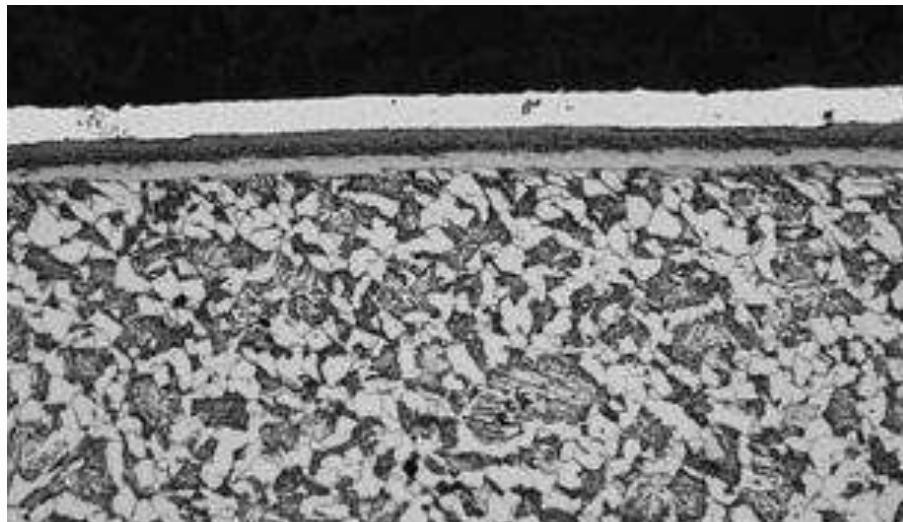
Etching

- Before etching the specimen can be checked for inclusions, slags, flakes etc.
- The mechanism of polishing is such that it leaves an amorphous metal on the surface and true structure will not be revealed.
- An etchant is used to dissolve this amorphous layer so as to observe the microstructural features under the microscope.
- In alloys, preferential etching is required to dissolve the one or more phases.
- Etching is different for different phases, because of

- Before etching the surface of the specimen should be thoroughly cleaned.
- Surface can be cleaned by dipping the sample in boiling alcohol.
- Once the sample is cleaned, the specimen is etched by dipping the specimen into the etching reagent and agitated for several seconds.
- Once the sample is treated with etchants, the specimen is very quickly transferred to water wash away the etchant.
- During etching, the bright appearance of the sample may be lost and it becomes dull and in some materials grain structure may be visible.



Before etching

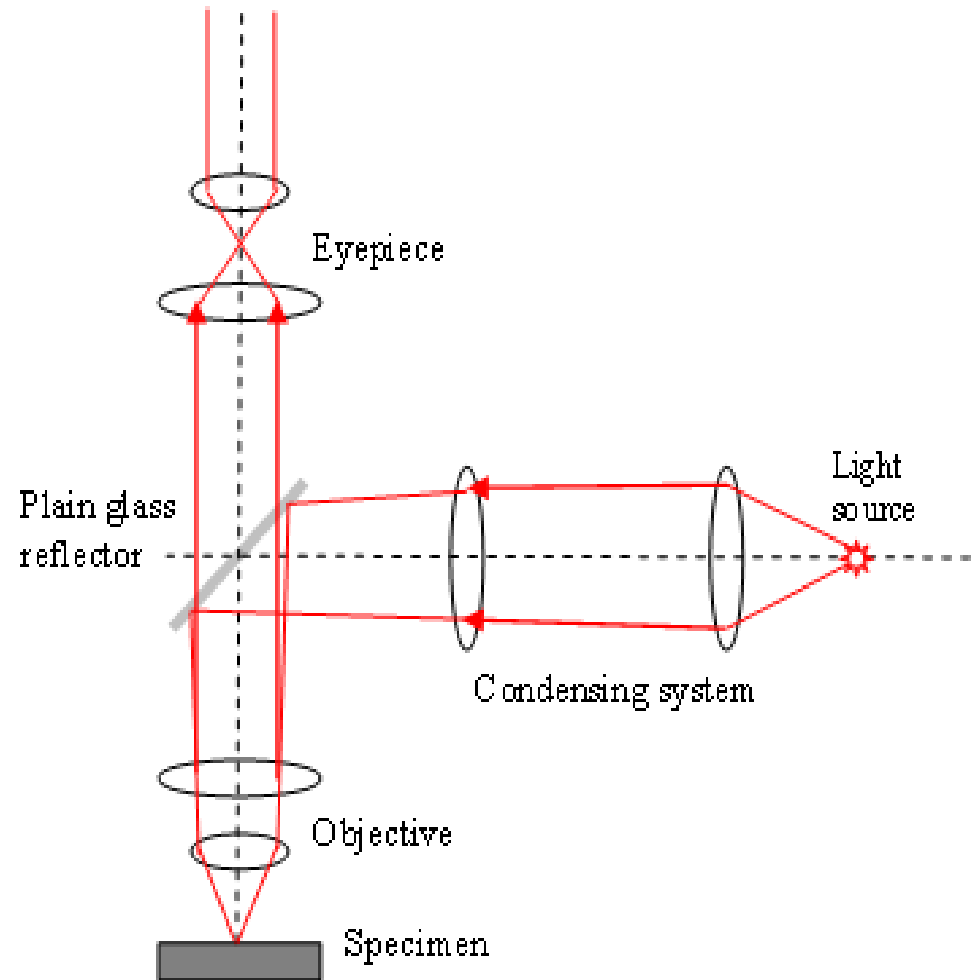
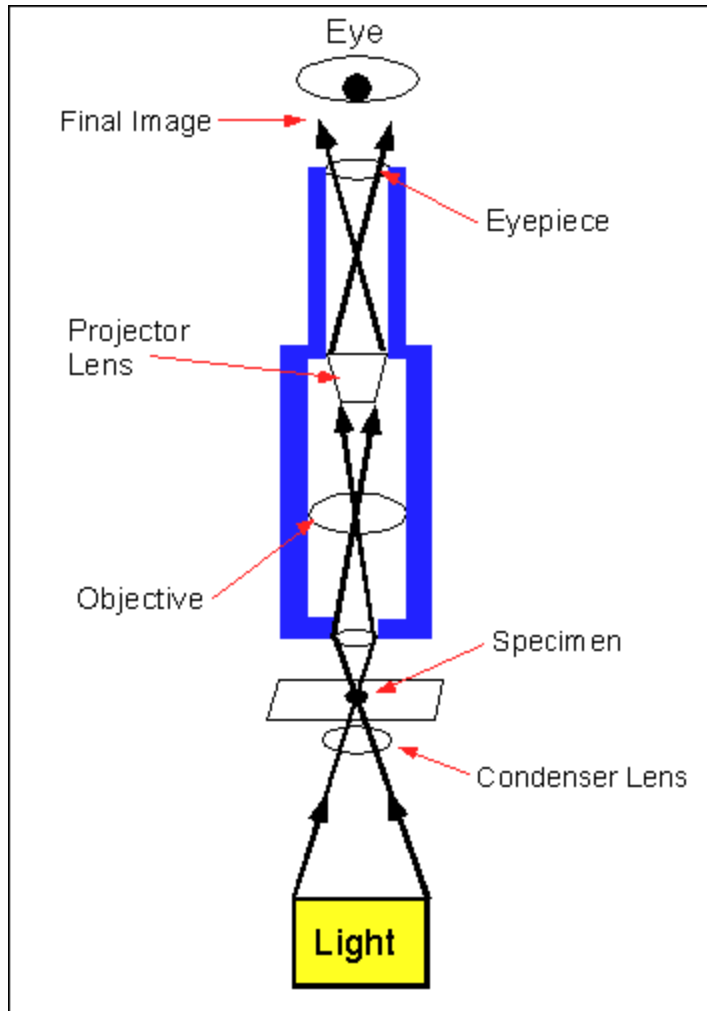


After etching

Common etchants

chant	Composition	Conc.	Conditions	Comments
Adler Etchant	Copper ammonium chloride Hydrochloric acid Ferric chloride, hydrated DI Water	9 grams 150 ml 45 grams 75 ml	Immersion is recommended for several seconds	For etching 300 series stainless steel and Hastelloy superalloys
Kalling's No. 2	CuCl ₂ Hydrochloric acid Ethanol	5 grams 100 ml 100 ml	Immersion or swabbing etch at 20 degrees Celsius	For etching duplex and 400 series stainless steels and Ni-Cu alloys and superalloys.
Kellers Etch	Distilled water Nitric acid Hydrochloric acid Hydrofluoric acid	190 ml 5 ml 3 ml 2 ml	10-30 second immersion. Use only fresh etchant	Excellent for aluminum and titanium alloys.
Kroll's Reagent	Distilled water Nitric acid Hydrofluoric acid	92 ml 6 ml 2 ml	Swab specimen up to 20 seconds	Excellent for titanium and alloys.
Nital	Ethanol Nitric acid	100 ml 1-10 ml	Immersion up to a few minutes.	Most common etchant for Fe, carbon and alloys steels and cast iron - Immerse sample up from seconds to minutes; Mn-Fe, MnNi, Mn-Cu, Mn-Co alloys.
Marble's Reagent	CuSO ₄ Hydrochloric acid Water	10 grams 50 ml 50 ml	Immerse or swab for 5-60 seconds.	For etching Ni, Ni-Cu and Ni-Fe alloys and superalloys. Add a few drops of H ₂ SO ₄ to increase activity.
Murakami's	K ₃ Fe(CN) ₆ KOH Water	10 grams 10 grams 100 ml	Pre-mix KOH and water before adding K ₃ Fe(CN) ₆	Cr and alloys (use fresh and immerse); iron and steels reveals carbides; Mo and alloys uses fresh and immerse; Ni-Cu alloys for alpha phases use at 75 Celcius; W and alloys use fresh and immerse; WC-Co and complex sintered carbides.
Picral	Ethanol Picric acid	100 ml 2-4 grams	Seconds to minutes Do not let etchant crystallize or dry –explosive	Recommended for microstructures containing ferrite, carbide, pearlite, martensite and bainite. Also useful for magnetic alloys, cast iron, high alloy stainless steels and magnesium.

Optical microscope

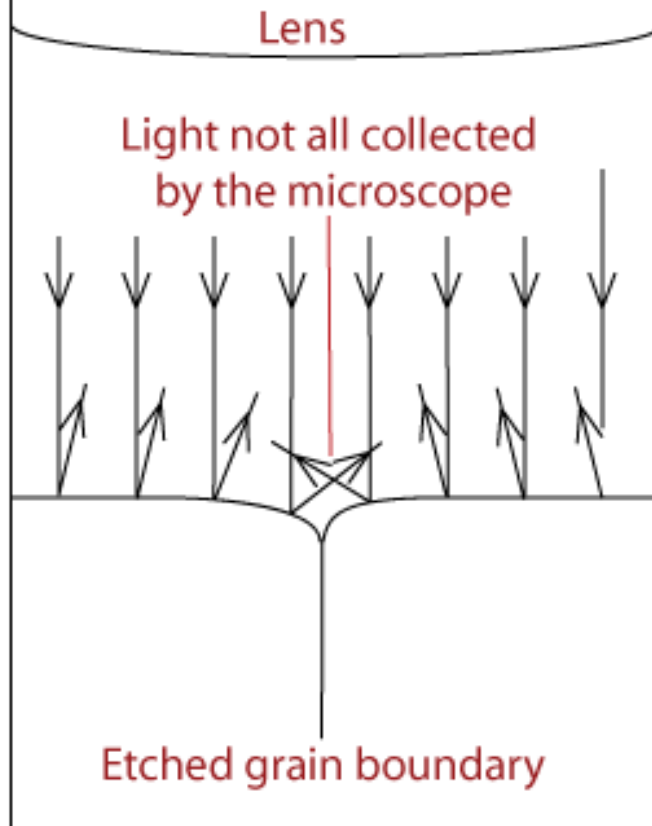


Optical microscope

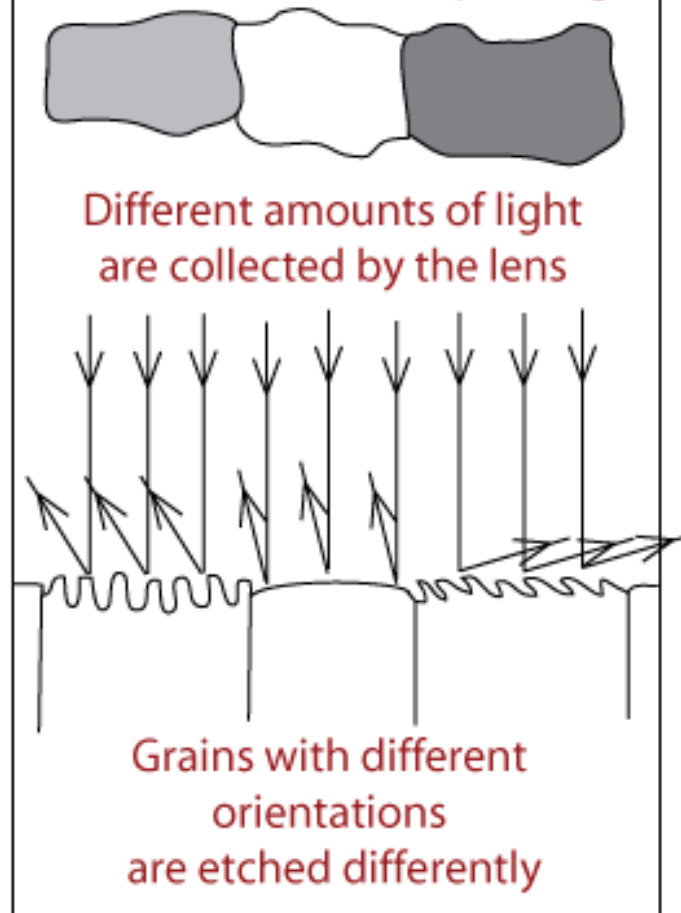
- Study of microstructure is carried out using reflected light, as the light cannot penetrae the system.
- The major parts of the microscope are;
 - Illuminating system
 - Objective lens
 - Eyepiece lens
- The maximum possible magnification is 2000x
- The objective lens convert the refleced light frm the surface to an image, it also magnifies the image.
- In eyepiece the observer views the magnified image.

Optical microscope-Grains

Examples of how contrast can arise



Schematic of microscope image:

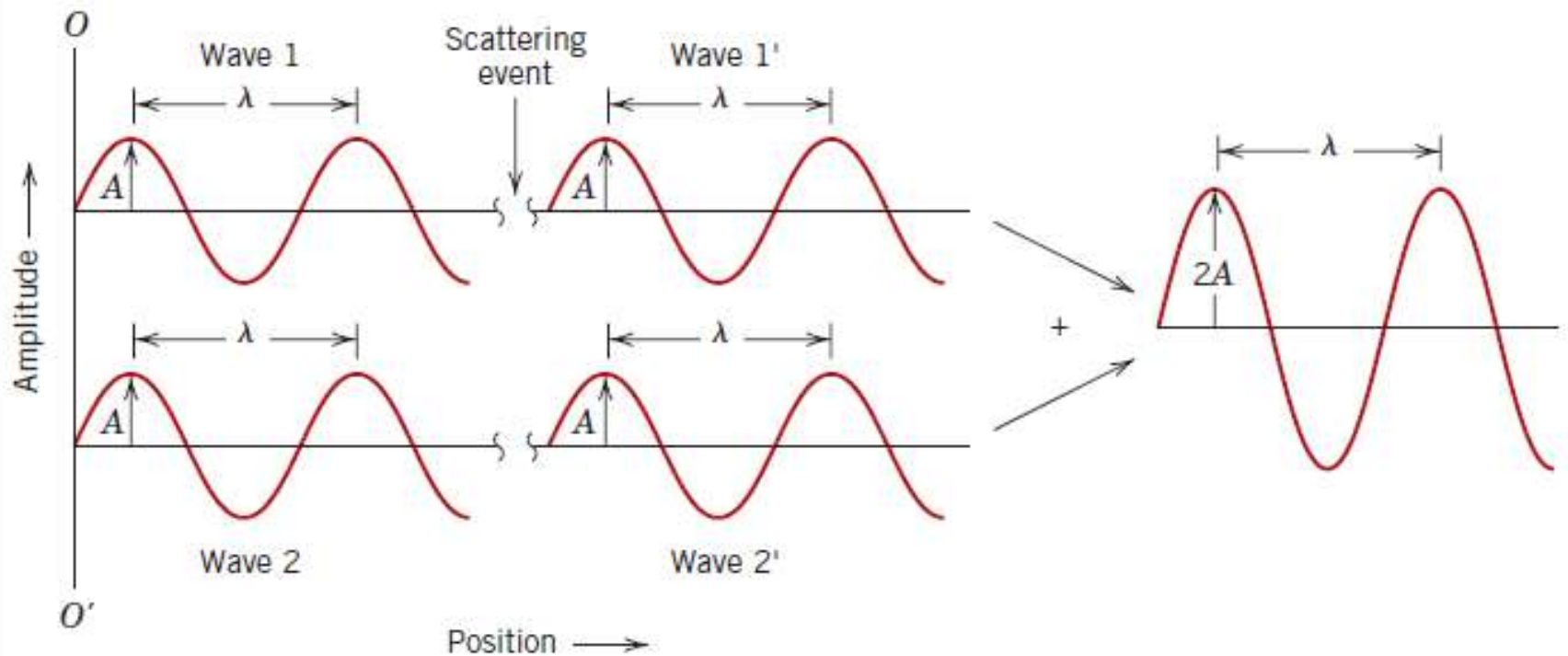


X-ray Diffraction: Determination of Crystal Structures

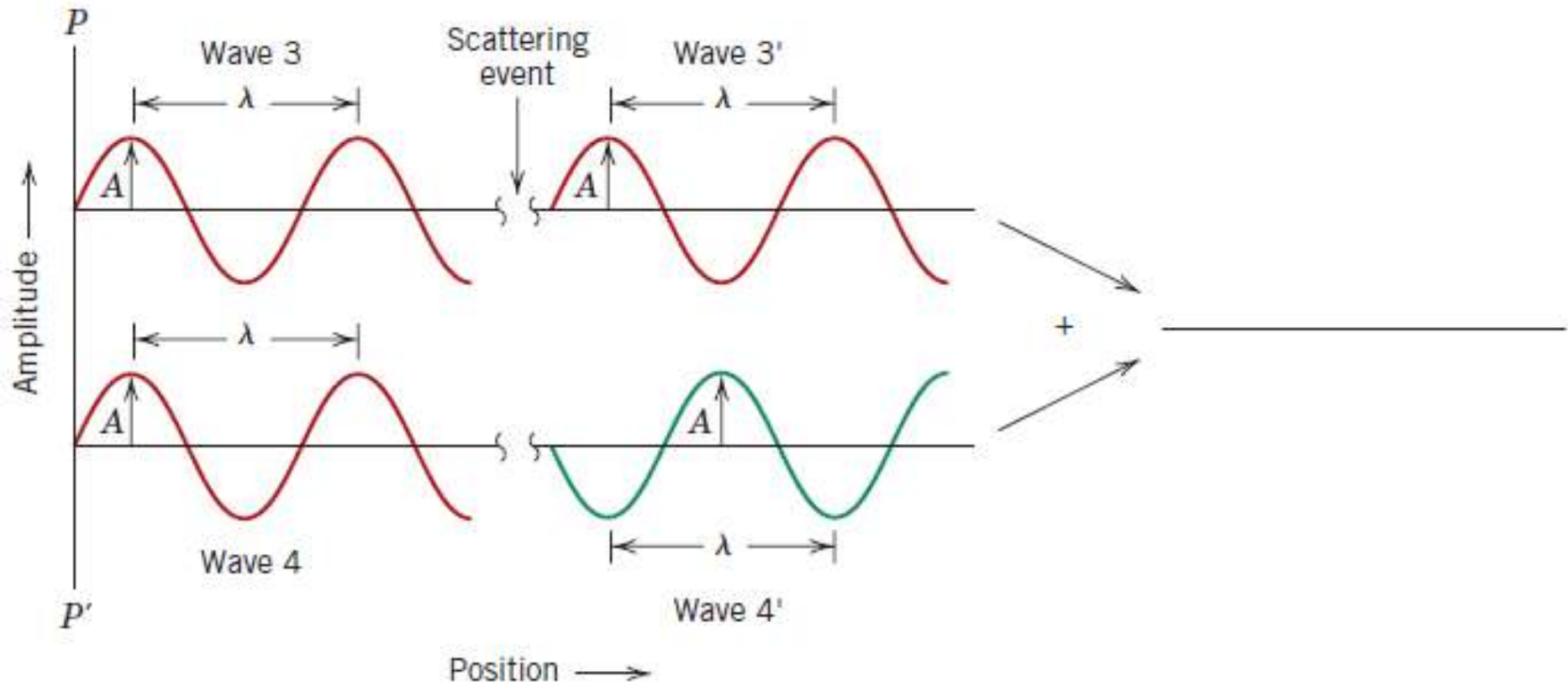
DIFFRACTION

- Diffraction occurs when a wave encounters a series of regularly spaced obstacles that (1) are capable of scattering the wave, and (2) have spacings that are comparable in magnitude to the wavelength.
- Furthermore, diffraction is a consequence of specific phase relationships established between two or more waves that have been scattered by the obstacles.

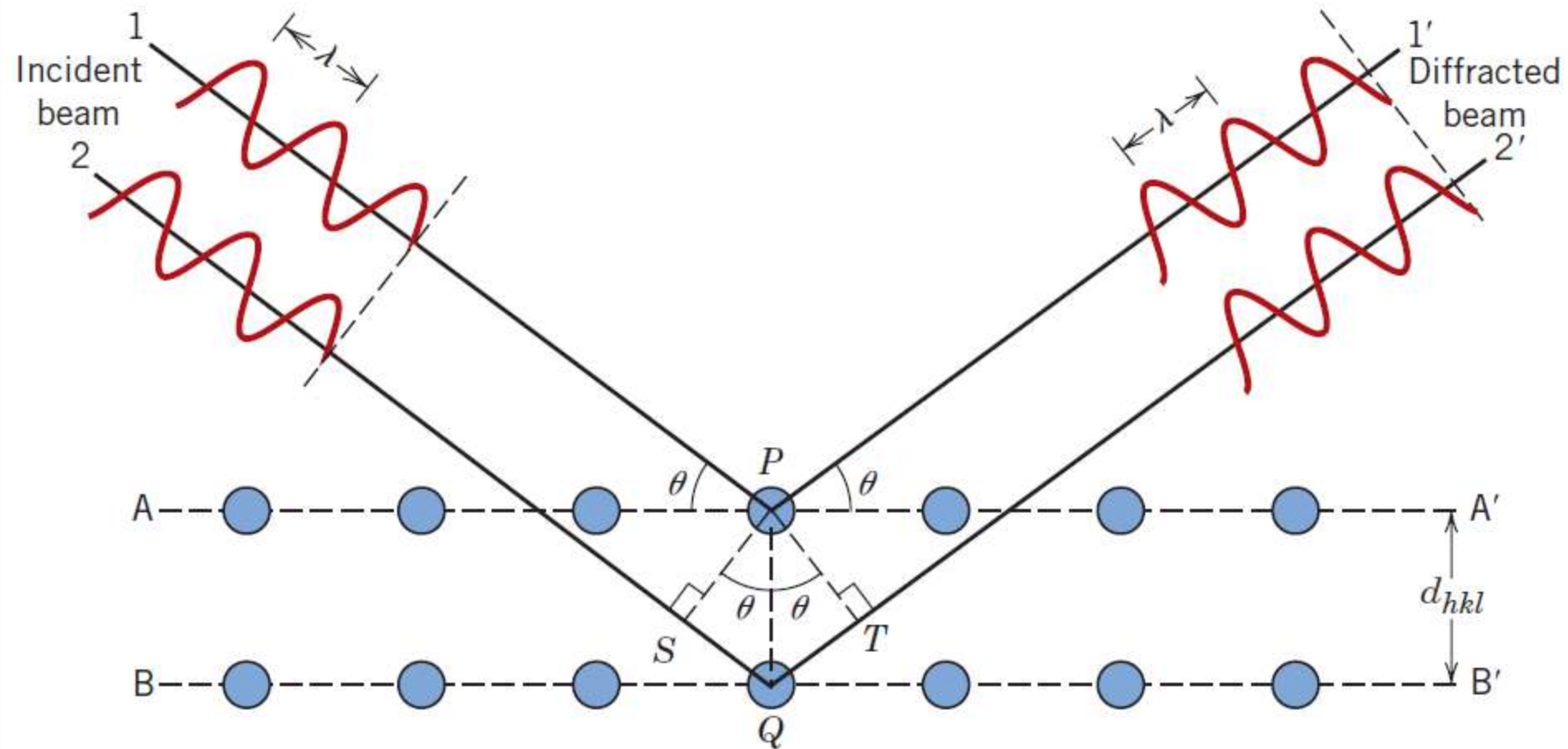
- Waves 1 and 2 with *the same wavelength* are in phase.
- If both waves are scattered in such a way that they traverse different paths.
- The scattered waves, have a difference in path length which will be an integral number of wavelengths and they will mutually reinforce or constructively interfere with one another; and amplitudes are added.



- Other phase relationships are possible between scattered waves that will not lead to this mutual reinforcement. The other extreme is *wherein the path length difference after scattering is some integral number of half wavelengths*.
- *The scattered waves are out of phase—that is, corresponding amplitudes cancel or annul one another, or destructively interfere (i.e., the resultant wave has zero amplitude).*



X-Ray Diffraction and Bragg's Law



X-Ray Diffraction and Bragg's Law

- X-rays are a form of electromagnetic radiation that have high energies and short wavelengths—wavelengths on the order of the atomic spacings for solids.
- When a beam of x-rays impinges on a solid material, a portion of this beam will be scattered in all directions by the electrons associated with each atom or ion that lies within the beam's path.

Necessary conditions for diffraction of x-rays by a periodic arrangement of atoms.

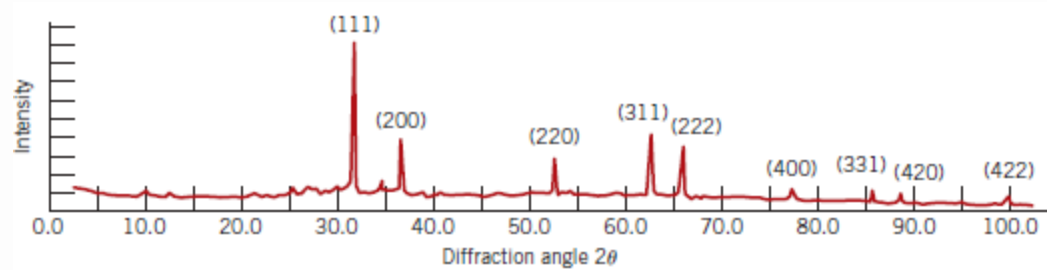
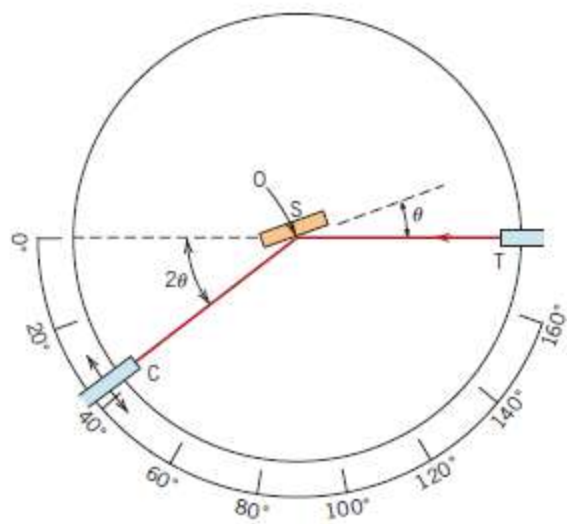
- Consider the two parallel planes of atoms A-A' and B-B' in Figure, which have the same h, k , and l Miller indices and are separated by the interplanar spacing d_{hkl} .
- Now assume that a parallel, monochromatic, and coherent (in-phase) beam of x-rays of wavelength is incident on these two planes at an angle θ .
- Two rays in this beam, labeled 1 and 2, are scattered by atoms P and Q .
- *Constructive interference* of the scattered rays 1' and 2' occurs also at an angle θ to the planes, if the path length difference between 1-P-1 and 2-Q-2 (i.e., $\overline{SQ} + \overline{QT}$) is equal to whole number, n , of wavelengths.
- That is, the condition for diffraction is

$$n\lambda = \overline{SQ} + \overline{QT}$$

$$n\lambda = d_{hkl} \sin \theta + d_{hkl} \sin \theta$$

$$n\lambda = 2d_{hkl} \sin \theta$$

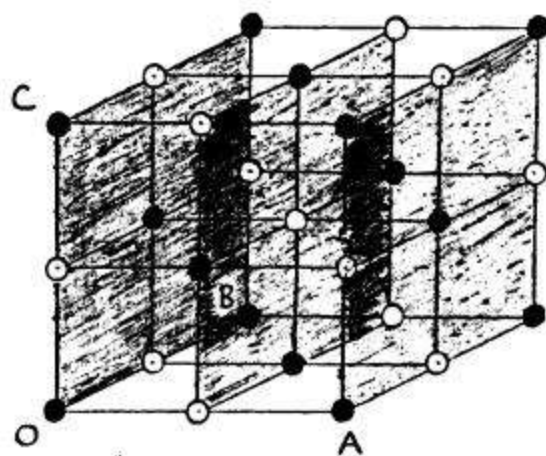
- This equation is known as **Bragg's law**; also, **n is the order of reflection, which**



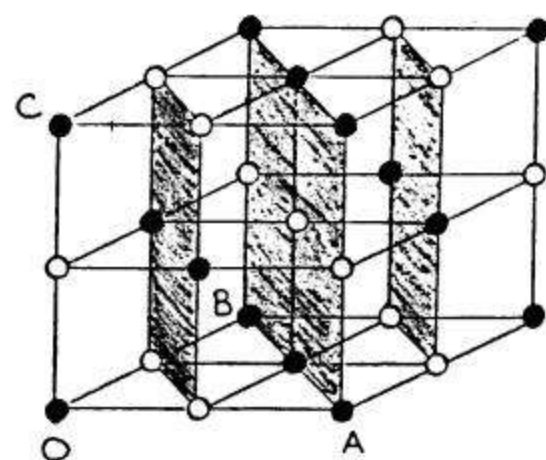
For BCC iron, compute (a) the interplanar spacing, and (b) the diffraction angle for the (220) set of planes. The lattice parameter for Fe is 0.2866 nm. Also, assume that monochromatic radiation having a wavelength of 0.1790 nm is used, and the order of reflection is 1.

Determine the expected diffraction angle for the first-order reflection from the (310) set of planes for BCC chromium when monochromatic radiation of wavelength 0.0711 nm is used.

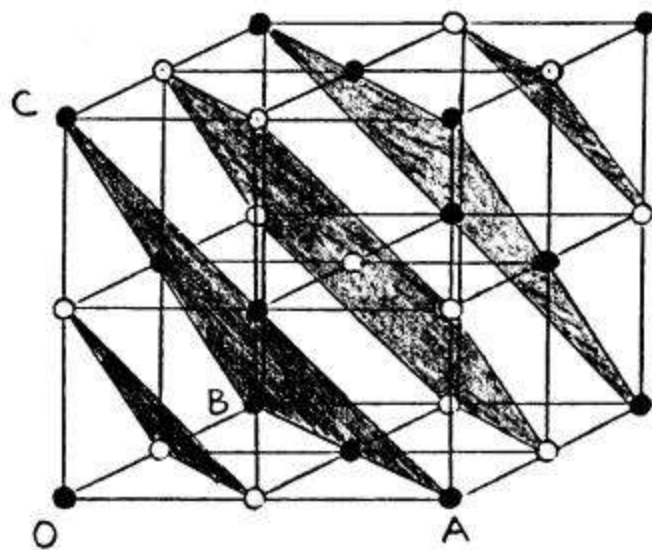
The metal niobium has a BCC crystal structure. If the angle of diffraction for the (211) set of planes occurs at 75.99° (first-order reflection) when monochromatic x-radiation having a wavelength of 0.1659 nm is used, compute (a) the interplanar spacing for this set of planes, and (b) the atomic radius for the niobium atom.



a) (200)



b) (220)



X-ray Diffraction Techniques

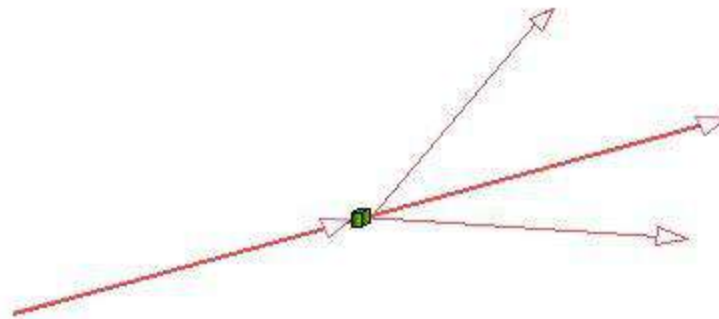
- Laue method
 - A single crystal is held stationary on the path of the beam, where θ is kept constant.
 - A white radiation is directed to the crystal so that numerous values of the wavelength are available.
 - The right combination lead to proper diffraction condition

Rotating crystal method

- A monochromated X-ray beam is made to fall on a single crystal of the material.
- The single crystal is rotated about an axis so that various sets of lattice planes come successively into reflecting positions.
- At some point the condition for diffraction will be satisfied.

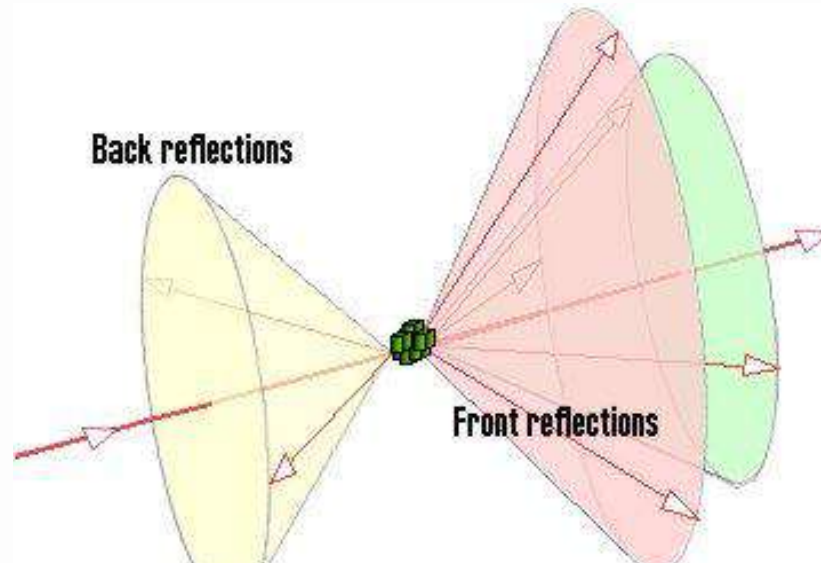
Powder method

- The powder method is used to determine the value of the lattice
- If a monochromatic x-ray beam is directed at a single crystal, then only one or two diffracted beams may result. parameters accurately.



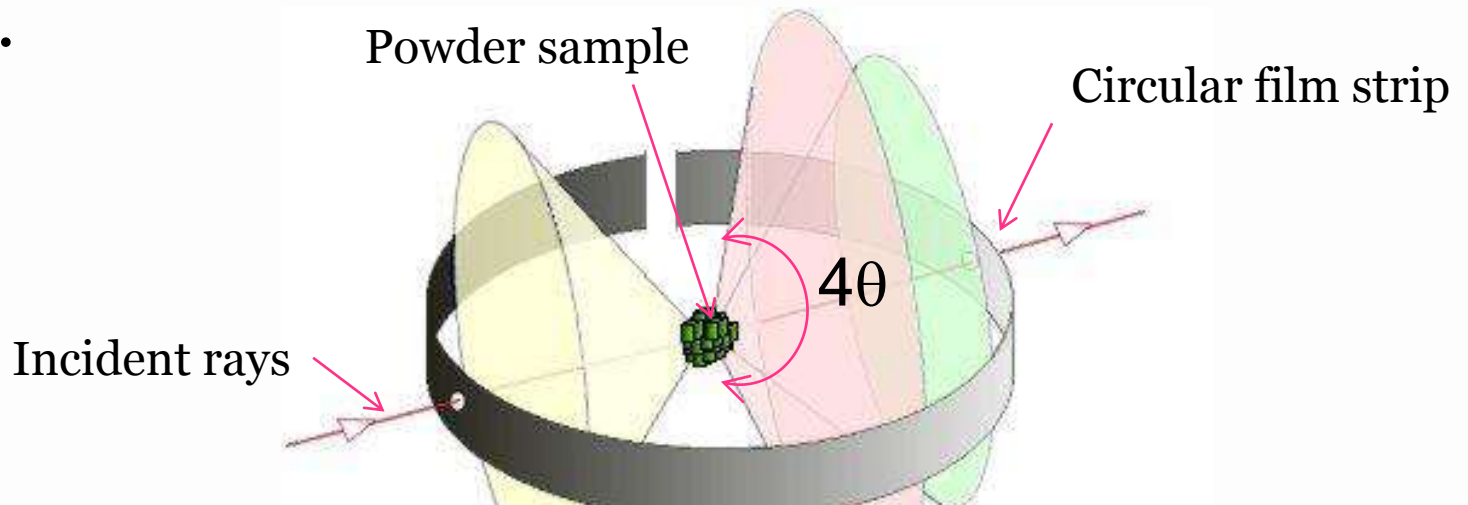
Powder method

- If the sample consists of some tens of randomly orientated single crystals, the diffracted beams are seen to lie on the surface of several cones. The cones may emerge in all directions, forwards and backwards.



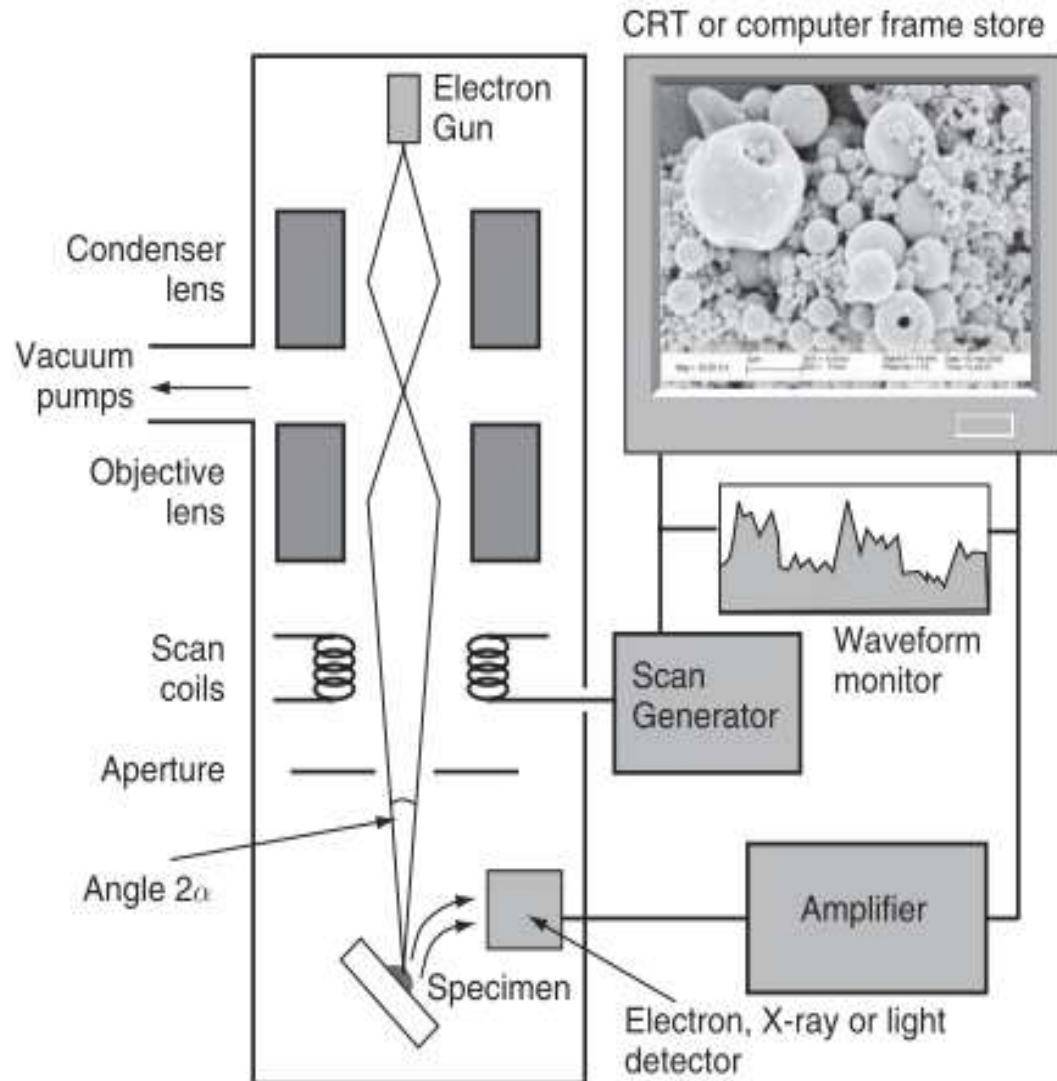
Powder method

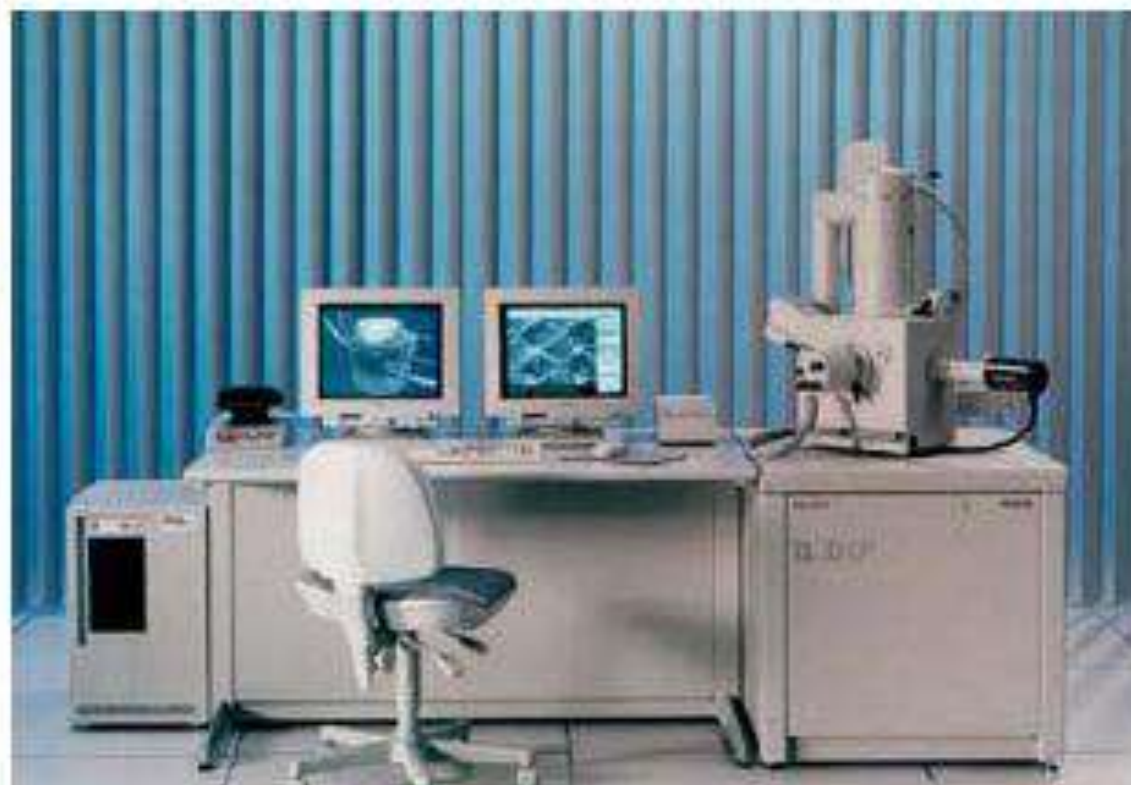
- A sample of some hundreds of crystals (i.e. a powdered sample) show that the diffracted beams form continuous cones.
- A circle of film is used to record the diffraction pattern as shown. Each cone intersects the film giving diffraction lines. The lines are seen as arcs on the film.



- The distance $S=R \times 4\theta$
- The camera radius $= 1\text{rad} = 57.3^\circ$

Scanning electron microscope





- In SEM, the surface of a specimen to be examined is scanned with an electron beam, and the reflected (or back-scattered) beam of electrons is collected, and then displayed at the same scanning rate on a cathode ray tube (similar to a CRT television screen).
- The image on the screen, which may be photographed, represents the surface features of the specimen.
- The surface may or may not be polished and etched, but it must be electrically conductive; a very thin metallic surface coating must be applied to nonconductive materials.
- Magnifications ranging from 10 to 50,000 times are possible.
- Accessory equipment permits qualitative and semi-

Characteristic Information: SEM

Topography

**The surface features of an object or "how it looks", its texture;
direct relation between these features and materials properties**

Morphology

**The shape and size of the particles making up the object; direct
relation between these structures and materials properties**

Composition

**The elements and compounds that the object is composed of
and the relative amounts of them; direct relationship between
composition and materials properties**

Crystallographic Information

**How the atoms are arranged in the object; direct relation
between these arrangements and material properties**

Three types of electron source:

- Tungsten filament,
- Lanthanum hexboride (LaB_6) emitter
- Field emission emitter (FEG)

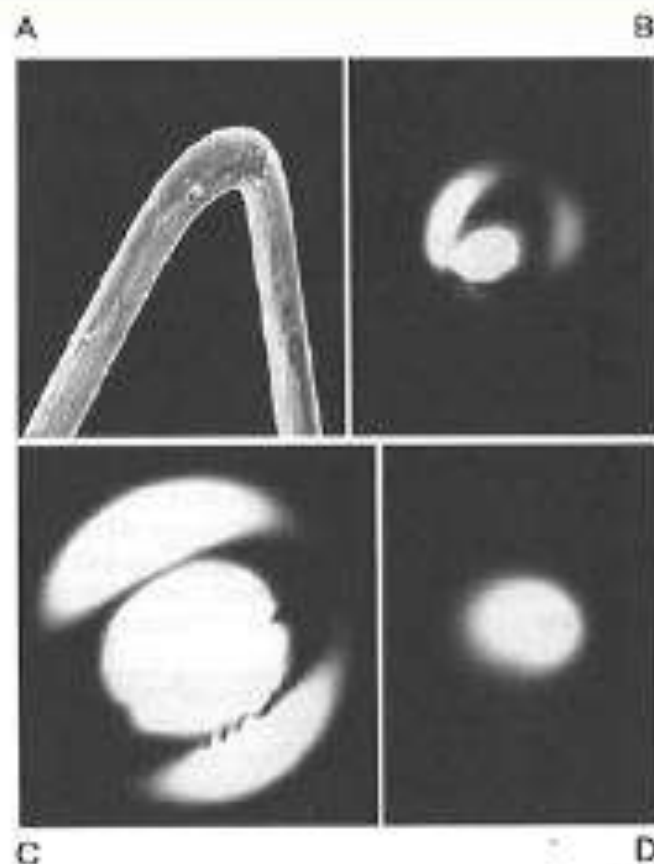


Figure 5.2. (A) The tip of a tungsten harpin filament; and the distribution of electrons when the filament is (B) underexposed and misaligned, (C) underexposed and aligned, and (D) saturated.

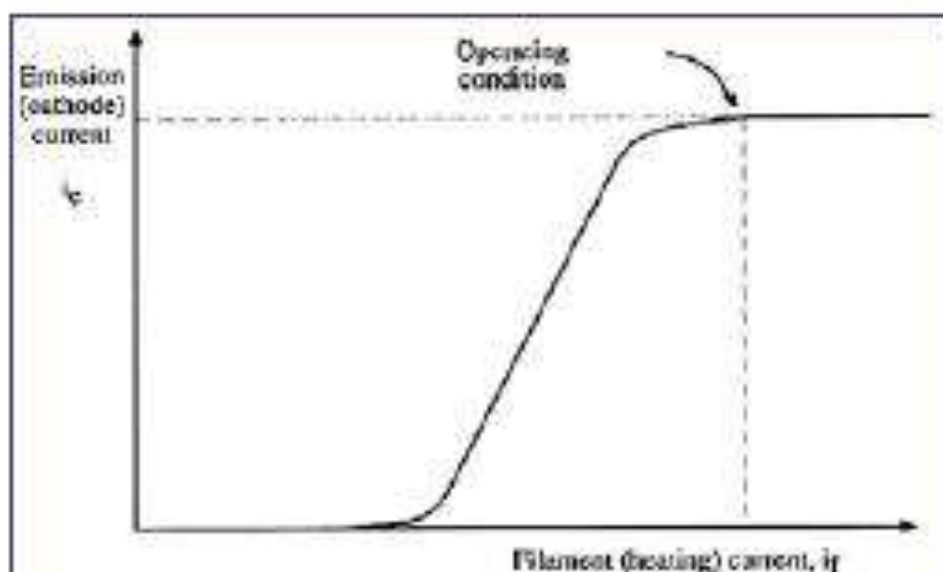
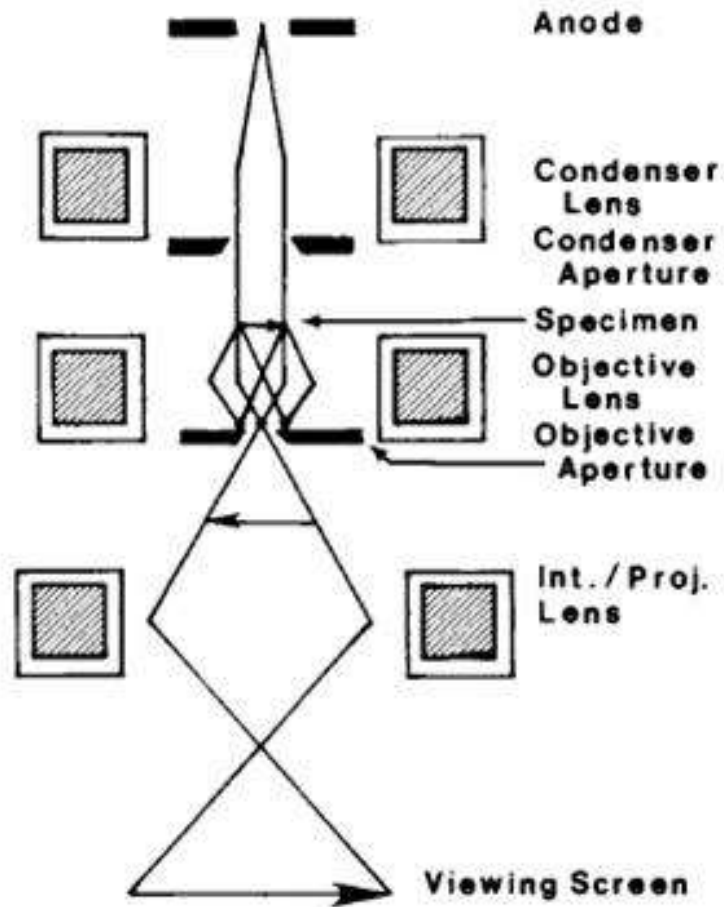


Figure 5.3. The relationship between the current emitted by the electron source (i_e) and the filament heating current (i_f) for a self-biasing gun. Increasing the filament current results in a maximum emission current termed saturation.

Transmission electron microscope



- The image seen with a transmission electron microscope (TEM) is formed by an electron beam that passes through the specimen.
- Details of internal microstructural features are accessible to observation; contrasts in the image are produced by differences in beam scattering or diffraction produced between various elements of the microstructure or defect.
- Since solid materials are highly absorptive to electron beams, a specimen to be examined must be prepared in the form of a very thin foil; this ensures transmission through the specimen of an appreciable fraction of the incident beam.
- The transmitted beam is projected onto a fluorescent screen or a photographic film so that the image may be viewed. Magnifications approaching $1,000,000\times$ are

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- Replicas of materials made with polymer were used in TEM earlier.
- Presently, the thin films of the material itself is used for the analysis, wafers of 250 μm were cut from the bulk material using diamond cutter and then thinning is done using grinding. Final thinning is done by electrochemical process or ion milling.
- The features like dislocation, stacking fault, formation of subgrains without crystallization etc., can be only observed in TEM.

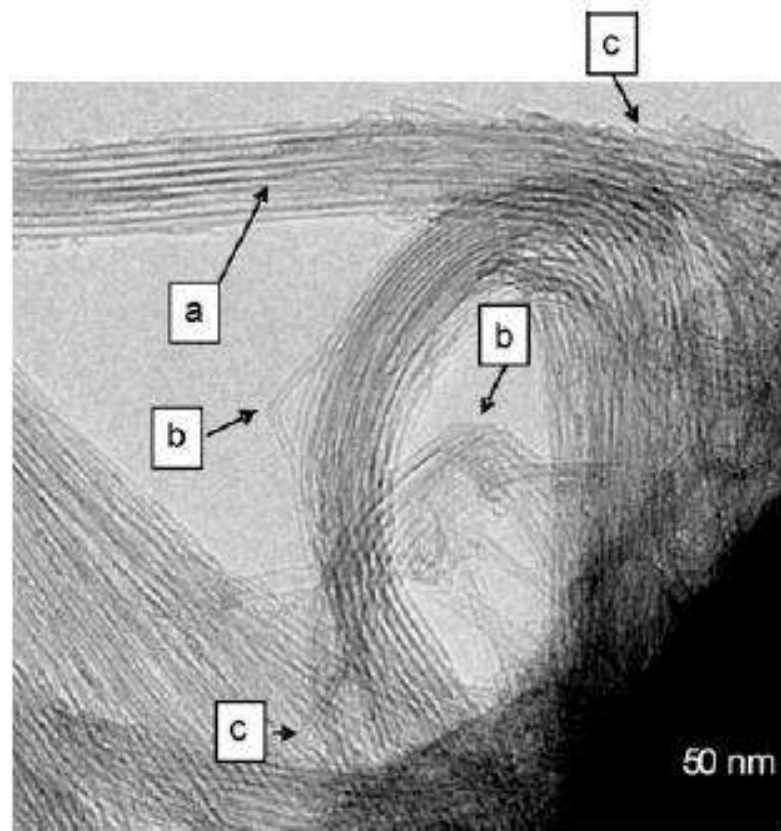


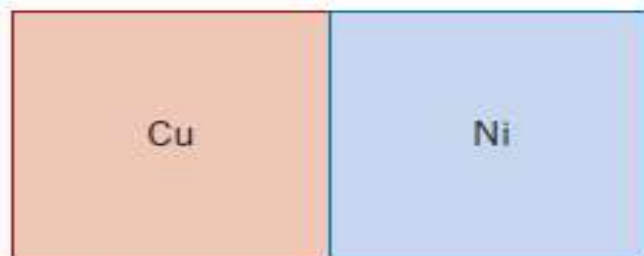
Fig. 2. TEM image of purified SWNTs: a) seemingly endless rope, b) isolated SWNT forming a knee, c) isolated SWNT end

Diffusion

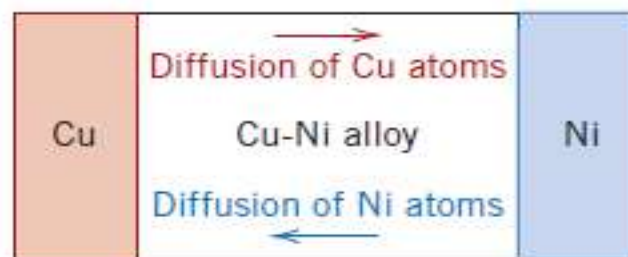
- **Diffusion** is the phenomenon of material transport by atomic motion.
- It is the process of mass flow by which atoms change their position relative to their neighbors under the influence of thermal energy and a gradient.
- This process, whereby atoms of one metal diffuse into another, is termed **interdiffusion**, or **impurity diffusion**.
- Diffusion also occurs for pure metals, but all atoms exchanging positions are of the same type; this is termed **self-diffusion**. In self-diffusion, normally, no compositional and property changes are observed.

Diffusion in solids

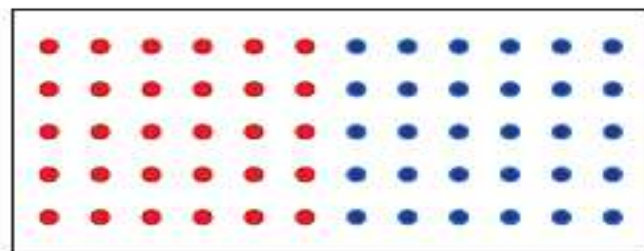
- The phenomenon of diffusion may be demonstrated with the use of a *diffusion couple*, which is formed by joining bars of two different metals together so that there is intimate contact between the two faces;
- If the diffusion couple is heated for an extended period at an elevated temperature (but below the melting temperature of both metals), and then cooled to room temperature.
- Chemical analysis will reveal that the concentrations of both metals vary with position.
- This result indicates that copper atoms have migrated or diffused into the nickel, and that nickel has diffused into copper.
- This process, whereby atoms of one metal diffuse into



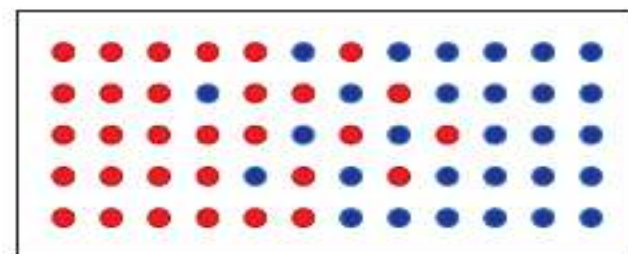
(a)



(a)



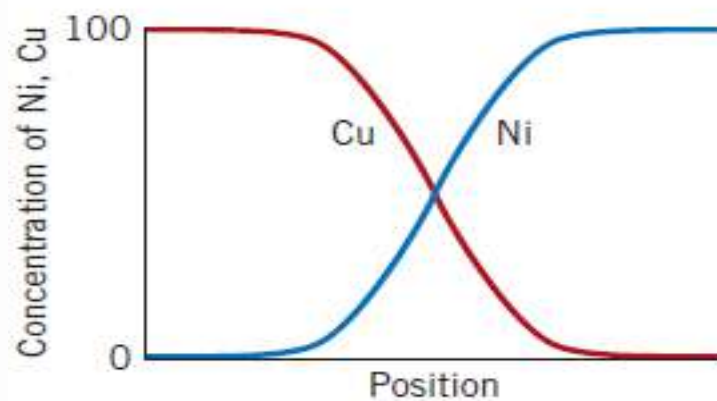
(b)



(b)



(c)

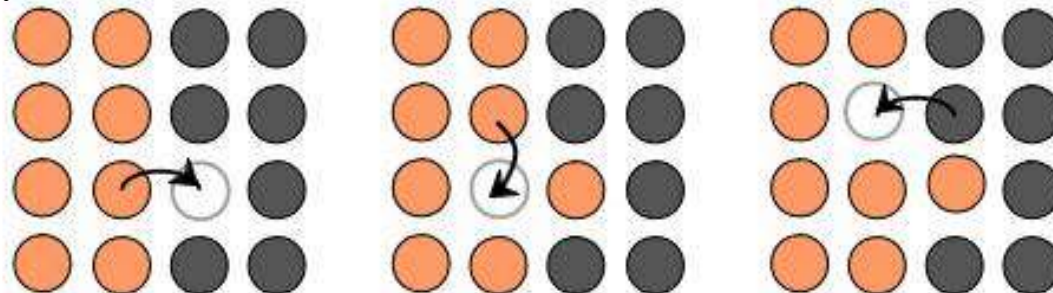


Mechanism of Diffusion

- From an atomic perspective, diffusion is just the stepwise migration of atoms from lattice site to lattice site.
- For an atom to diffuse, two conditions must be met:
 - There must be an empty adjacent site
 - The atom must have sufficient energy to break bonds with its neighbor atoms and then cause some lattice distortion during the displacement.
- The energy is vibrational in nature. At a specific temperature some small fraction of the total number of atoms is capable of diffusive motion, by virtue of the magnitudes of their vibrational energies. This fraction increases with rising temperature.
- Several different models for this atomic motion have been proposed; there are two dominating models for metallic

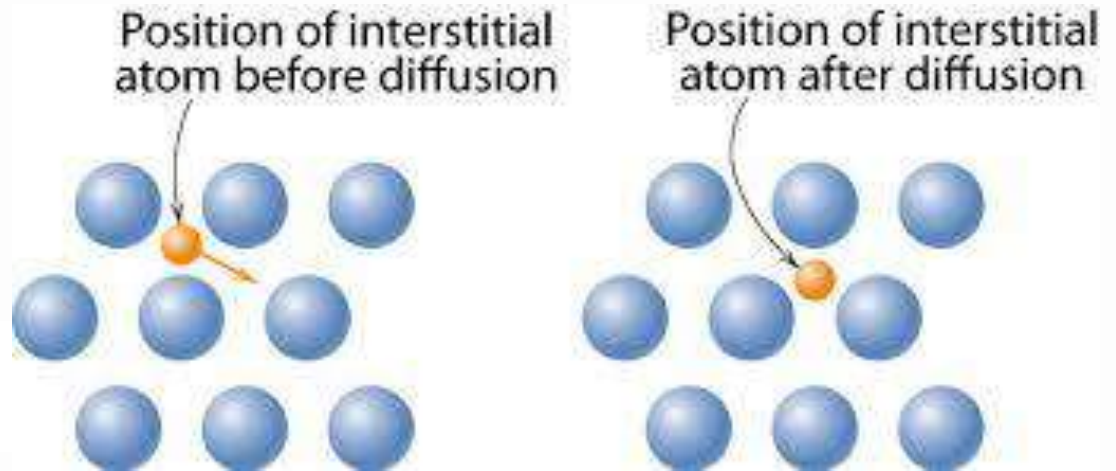
Vacancy Diffusion

- This mechanism involves the interchange of an atom from a normal lattice position to an adjacent vacant lattice site or vacancy and the mechanism is termed vacancy diffusion.
- This process necessitates the presence of vacancies, and the extent to which vacancy diffusion can occur is a function of the number of these defects that are present.
- Since diffusing atoms and vacancies exchange positions, the diffusion of atoms in one direction results in the motion of vacancies in the opposite direction.
- Both self-diffusion and inter-diffusion occur by this mechanism; for the inter-diffusion, the impurity atoms must substitute for host atoms.



Interstitial Diffusion

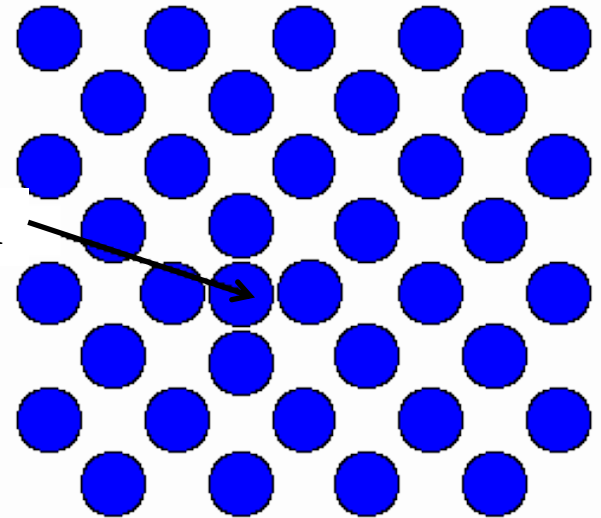
- The second type of diffusion involves atoms that migrate from an interstitial position to a neighboring one that is empty.
- Impurities such as hydrogen, carbon, nitrogen, and oxygen, which have atoms that are small enough to fit into the interstitial positions.
- Host or substitutional impurity atoms rarely form interstitials and do not normally diffuse via this mechanism.
- In most metal alloys, interstitial diffusion occurs much more rapidly than diffusion by the vacancy mode, since the interstitial atoms are smaller and thus more mobile.
- Furthermore, there are more empty interstitial positions than vacancies; hence, the chances of interstitial atomic movement are greater than for vacancy diffusion.



Interstitialcy (Self interstitial) Diffusion

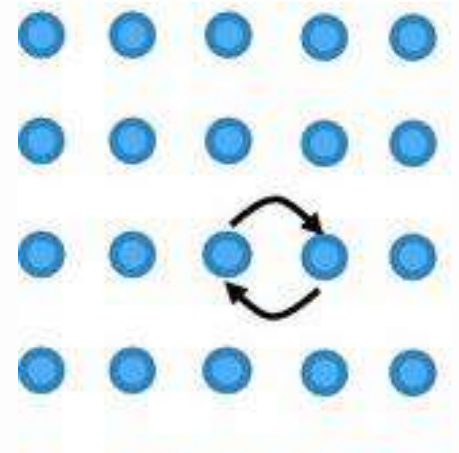
- In this mechanism an atom occupying an interstitial site forces a regular atom to leave its site to an interstitial site.
- Continuation of this results in interstitial diffusion.

Interstitialcy Diffusion



Direct Interchange Diffusion

- In this case two or more adjacent atoms jump past each other and exchange positions.
- This may take place between two, three or four atoms.
- When four atoms are involved, it is also known as ring diffusion or Zenner ring diffusion.
- This mechanism results in severe local lattice distortion, requiring much more energy for the atoms to jump



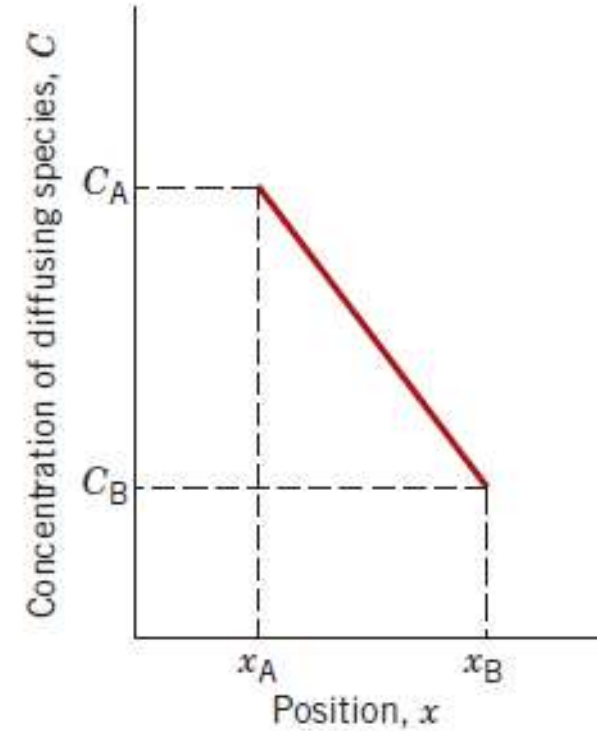
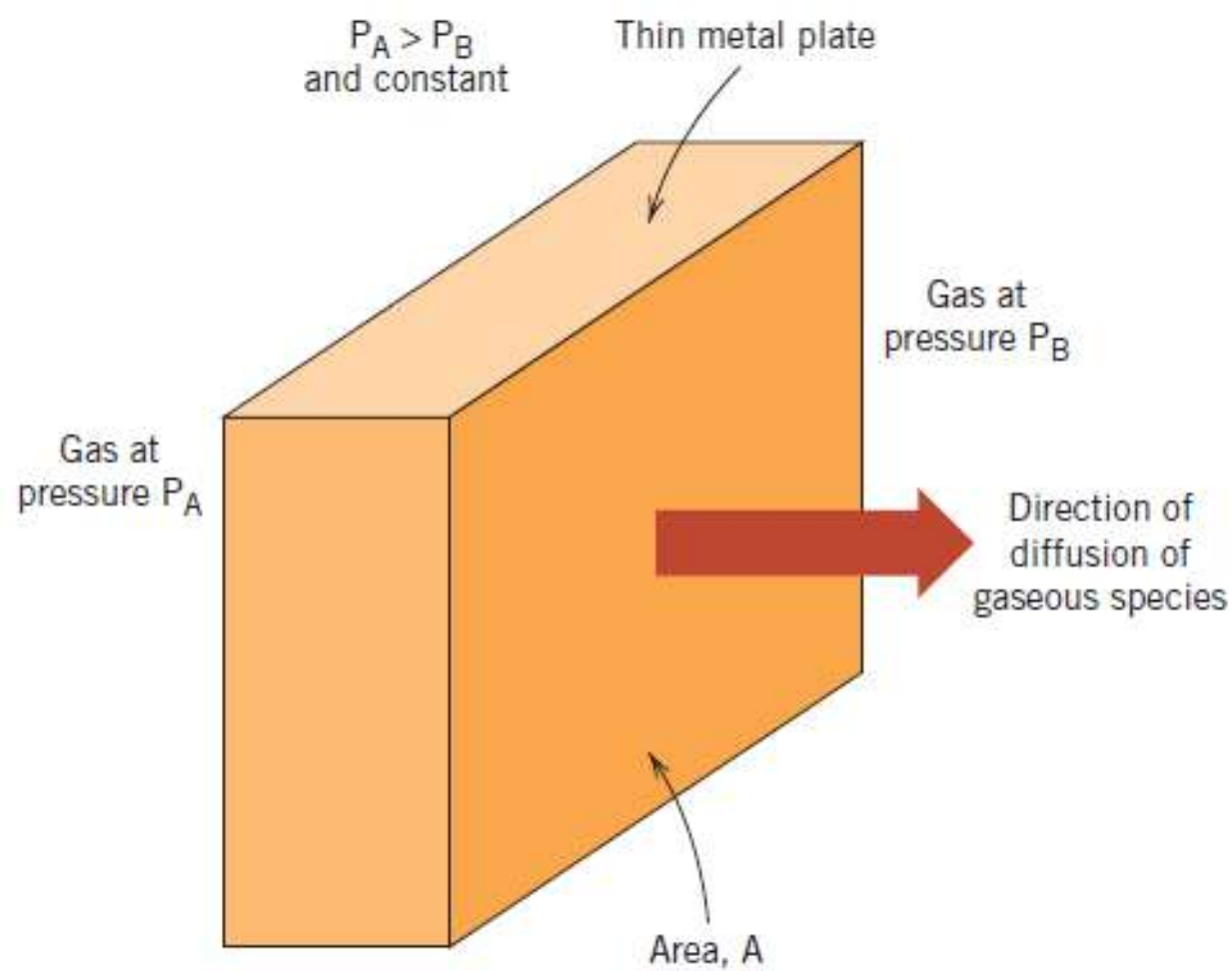
Kirkendall Effect

- In a binary solution of A and B, the rates at which A and B are not necessarily equal.
- Usually, the lower melting component diffuses much faster than the other.
- Inert markers (thin rods of a high melting point substances which is insoluble in the diffusion matrix) are placed at the weld joint of the couple, prior to the diffusion anneal.
- These markers are found to shift during the anneal in the slower moving species. The extent of this shift is found to be proportional to the square root of the diffusion time.
- The kind of movement indicates that the net mass flow due to the difference in diffusivities is being compensated by a bulk flow of matter in the opposite direction within the

Fick's Laws

Fick's First Law of diffusion- steady-state diffusion

- Diffusion is a time-dependent process; i.e., the quantity of an element that is transported within another is a function of time.
- This is necessary to know how fast diffusion occurs, or the rate of mass transfer.
- The rate of mass transfer is frequently known as **diffusion flux** (J); defined as the mass (or, equivalently, the number of atoms) M diffusing through and perpendicular to a unit cross-sectional area of solid per unit of time.
- In mathematical form, this may be represented as,
$$J = \frac{1}{A} \frac{dM}{dt}$$
- The units for J are kilograms or atoms per meter squared per second (kg/m²-s or atoms/m²-s).
- If the diffusion flux does not change with time, a steady-state condition exists. One common example of steady-state diffusion is the diffusion of atoms of a gas through a plate of metal for which the concentrations (or



- When concentration C is plotted versus position (or distance) within the solid x , the resulting curve is termed the **concentration profile**; the slope at a particular point on

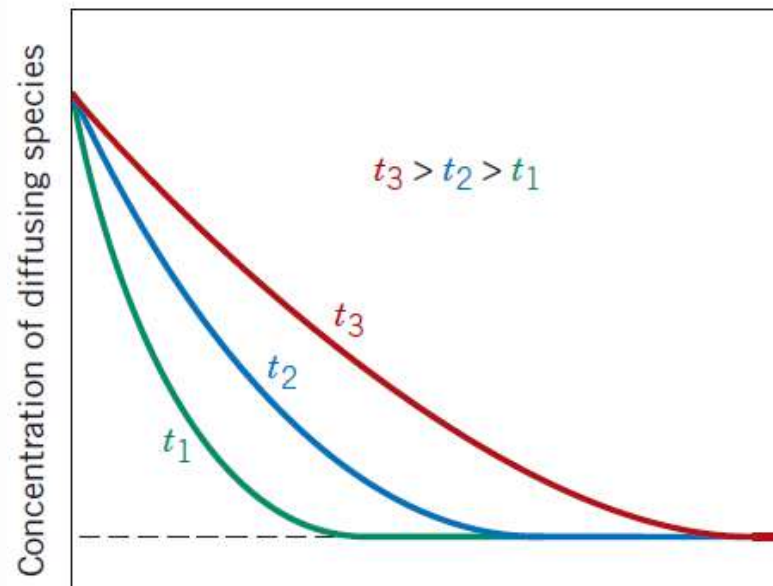
- **Fick's first law** states that, for a steady-state diffusion process in a single (x) direction, the flux is proportional to the concentration gradient.

$$J \propto \frac{\partial C}{\partial x} \quad \text{or} \quad J = -D \frac{\partial C}{\partial x}$$

- The constant of proportionality D is called the *diffusion coefficient*, which is expressed in square meters per second. The negative sign in this expression indicates that the direction of diffusion is from a high to a low concentration.
- One example of steady-state diffusion is found in the purification of hydrogen gas. One side of a thin sheet of palladium metal is exposed to the impure gas composed of hydrogen and other gaseous species such as nitrogen, oxygen, and water vapor.
- The hydrogen selectively diffuses through the sheet to the opposite side, which is maintained at a constant and lower

Fick's second Law of diffusion- Non-steady-state diffusion

- Most practical diffusion situations are nonsteady-state ones.
- That is, the diffusion flux and the concentration gradient at some particular point in a solid vary with time, with a net increase or reduction of the diffusing species.



- Consider an elemental volume of length Δx along the diffusion direction and a unit cross sectional area.
- The rate of accumulation or depletion of the diffusing species is $\frac{\partial C}{\partial t} \Delta x$

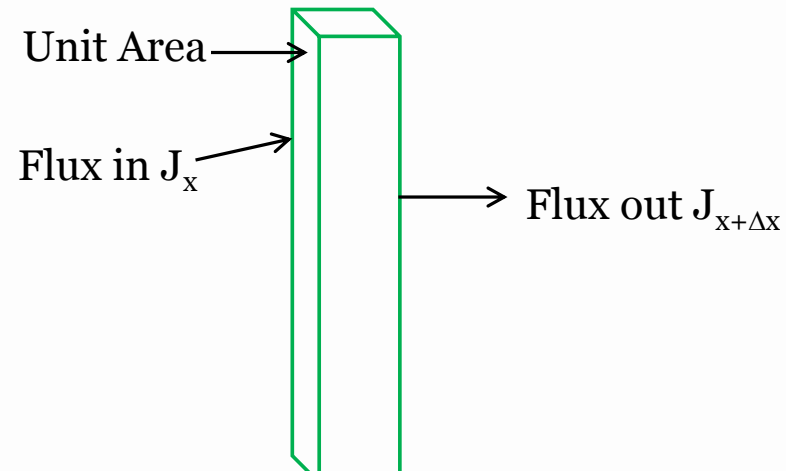
- The difference in flux in and out of the slab is;

$$\left[\frac{\partial C}{\partial t} \right] \Delta x = J_x - J_{x+\Delta x} = J_x - \left[J_x + \frac{\partial J}{\partial x} \Delta x \right]$$

$$\left[\frac{\partial C}{\partial t} \right] \Delta x = -\frac{\partial J}{\partial x} \Delta x \quad \text{or} \quad \frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x}$$

- Using first law;

$$J = -D \frac{dC}{dx}$$



$$\frac{\partial C}{\partial t} = -\frac{\partial}{\partial x} \left[-D \frac{\partial C}{\partial x} \right] = D \frac{\partial^2 C}{\partial x^2}$$

$$\text{or} \quad \frac{\partial C_x}{\partial t} = D \frac{\partial^2 C_x}{\partial x^2}$$

- C_x concentration of the diffusing species at some distance x from the surface.
- The diffusivity D , is independent of concentration eventhough in actual situations D varies with concentration.

Applications of Diffusion

Determination of diffusion coefficient

- The diffusion coefficient D can be determined experimentally using a diffusion couple (two bars of metals placed very close to each other Cu and Ni). At room temperature the thermal energy is insufficient to cause an appreciable diffusion. If the couple is heated to a higher temperature, near melting point, the diffusion of species start from bar 1 to bar 2 and vice versa. The effect of this diffusion is first at the interface, and it then proceed interior to the bars.

Corrosion resistance in duralumin

- Duralumin is an alloy of aluminium with 4% copper. In the properly heat treated condition, the alloy has the strength which is several times more than that of aluminium and light in weight. Thus, it is widely used in aircraft industries. The corrosion resistance of duralumin is poor compared to that of aluminium, hence the sheets of duralumin is sandwiched between thin sheets of pure aluminium and rolled to improve the corrosion resistance. This sandwich like material is called **alclad**. This material is heated to 550°C for giving the appropriate heat treatment to increase the strength. The copper from duralumin can diffuse into pure aluminium sheets and damage its

Carburization of steel

- Surface hardening of steel objects (gears, cams etc.) to improve their resistance against wear, indentation etc. is done by carburizing and nitriding. When the steel object is annealed at an elevated temperature in the carburizing medium, carbon diffuses into the steel from the surface under a concentration gradient.

Decarburization of steel

- The opposite of carburization is decarburization. Here, the carbon is lost from the surface layers of the steel, due to an oxidizing atmosphere that reacts with carbon to produce CO and CO₂. The fatigue resistance in steel is lowered due to decarburization. The extent of decarburizing can be estimated from the diffusion equation and post-machining operations can be undertaken to remove the decarburized layer.

Doping in semiconductors

- Semiconductor devices are doped with small controlled quantities of impurities for obtaining the desired electrical characteristics. The dopant atoms may be diffused into the pure semiconductor crystal from a gaseous atmosphere. The depth of penetration and the amount of dopant in the crystal can be estimated following the same procedure as

Melting and Casting

- This is a widely used technique for the production of metals, alloys, plastics and glasses.
- Diffusion plays an important role in the solidification of metals and alloys,

Sintering

- Refractory materials like ceramics and some metals are processed to useful shapes by compacting the small powdered particles, followed by heating at high temperature. During heating diffusion takes place and the cavities between the particles disappear.

Oxidation of aluminium

- Aluminium oxide acts as a very thin protective coating on the surface of aluminium. The oxide layer protects against the diffusion of oxygen and thus prevents further oxidation.

Beverage bottles

- PET bottles used for carbonated beverages are suitable to minimize the escape of CO_2 by diffusion
- This ensures that the beverages will not lose their fizz for a reasonable