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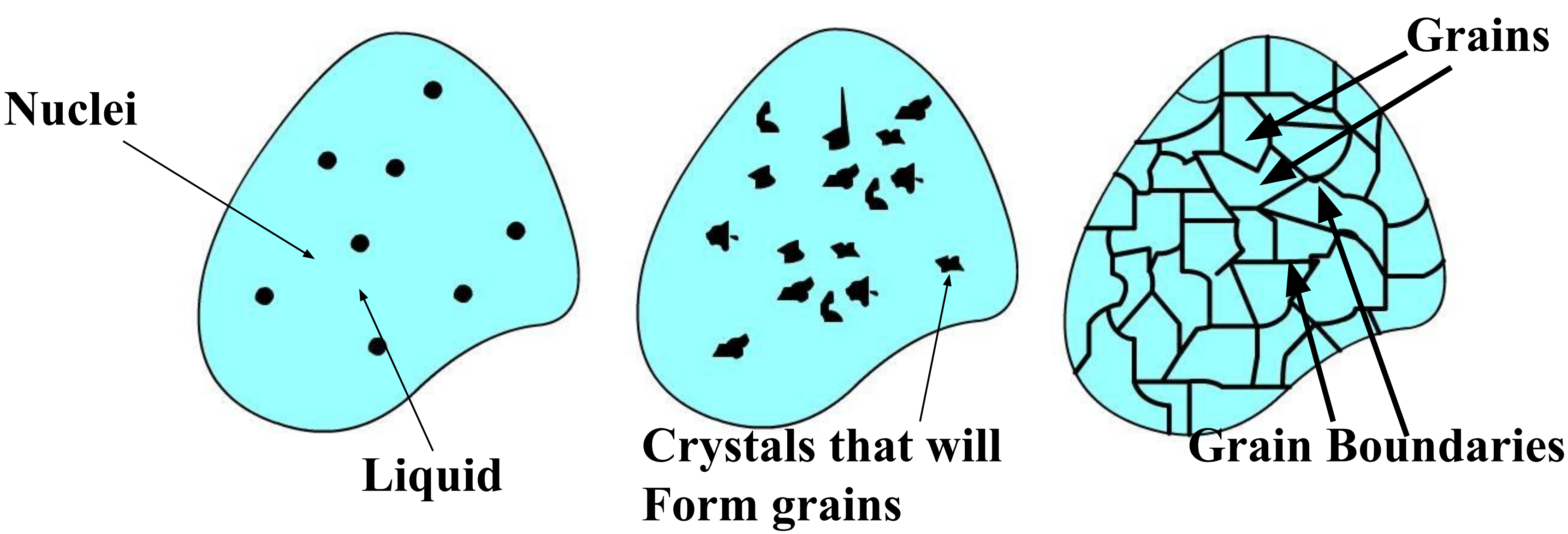
CHAPTER
4

Solidification
and
Crystalline Imperfections

Solidification of Metals

- Metals are melted to produce finished and semi-finished parts.
- Two steps of solidification
  - **Nucleation** : Formation of stable nuclei.
  - **Growth of nuclei :** Formation of grain structure.

- Thermal gradients define the shape of each grain.



Formation of Stable Nuclei

- Two main mechanisms: ***Homogenous*** and ***heterogeneous***.
- Homogenous Nucleation :
    - First and simplest case.
    - Metal itself will provide atoms to form nuclei.
    - Metal, when significantly undercooled, has several slow moving atoms which bond each other to form nuclei.
    - Cluster of atoms below ***critical size*** is called embryo.
    - If the cluster of atoms reach critical size, they grow into crystals. Else get dissolved.
    - Cluster of atoms that are grater than critical size are called nucleus.

Energies involved in homogenous nucleation.

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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

$$r = \frac{4}{3}\pi r^3 \Delta G_v$$

Surface energy Gs

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

Then $\Delta G_s = 4\pi r^2 \gamma$

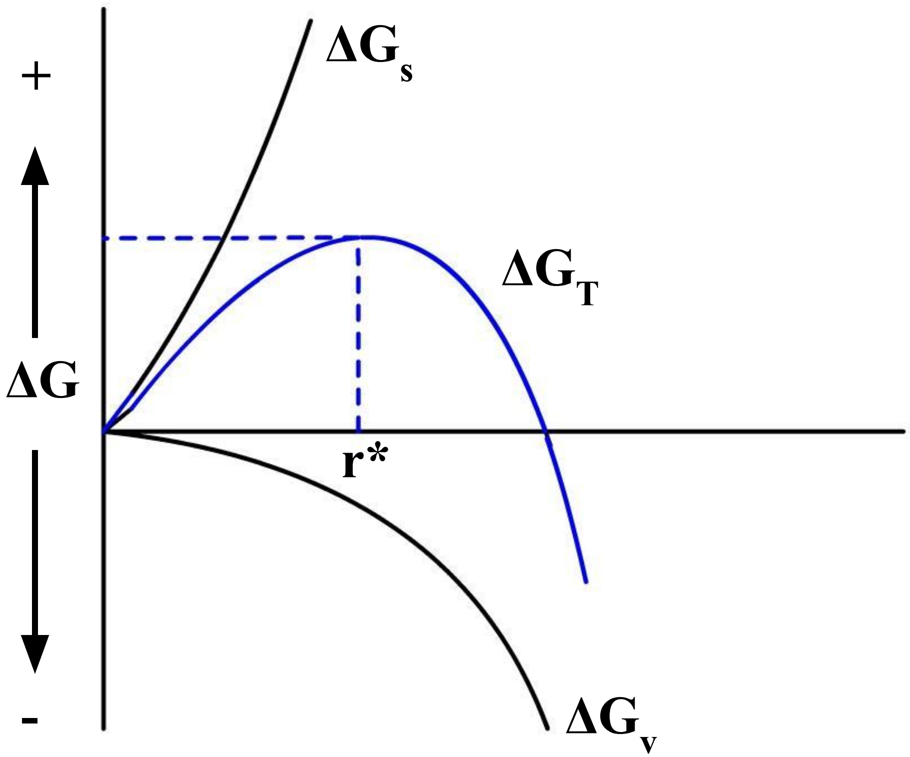
- ΔG_s is retarding energy.

Total Free Energy

- ***Total free energy*** is given by $$\Delta G_T = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

Since when r=r*, d(ΔG_T)/dr = 0

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



Nucleus

Above critical radius r* → **Energy lowered by growing into crystals**

Below critical radius r* → **Energy Lowered by redissolving**

Critical Radius Versus Undercooling

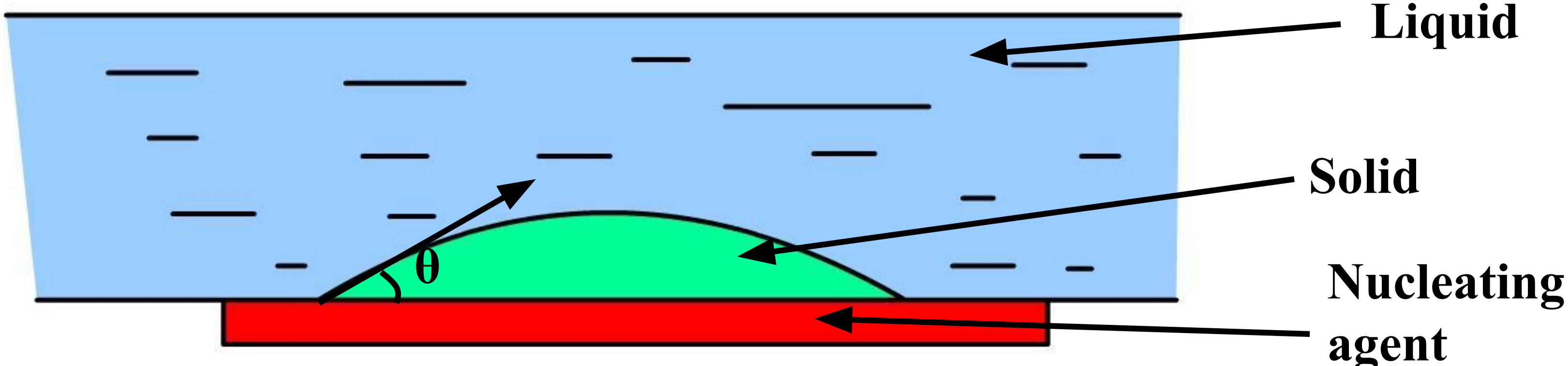
- Greater the degree of undercooling, greater the change in volume free energy ΔG_v
- ΔG_s does not change significantly.
- As the amount of *undercooling* ΔT increases, critical nucleus size decreases.
- Critical radius is related to undercooling by relation

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

r^* = critical radius of nucleus
γ = Surface free energy
ΔH_f = Latent heat of fusion
ΔT = Amount of undercooling.

Homogenous Nucleation

- Nucleation occurs in a liquid on the surfaces of structural material. Eg:- Insoluble impurities.
- These structures, called ***nucleating agents***, lower the free energy required to form stable nucleus.



- Nucleating agents also lower the critical size.
- Smaller amount of undercooling is required to solidify.
- Used excessively in industries.

Growth of Crystals and Formation of Grain Structure

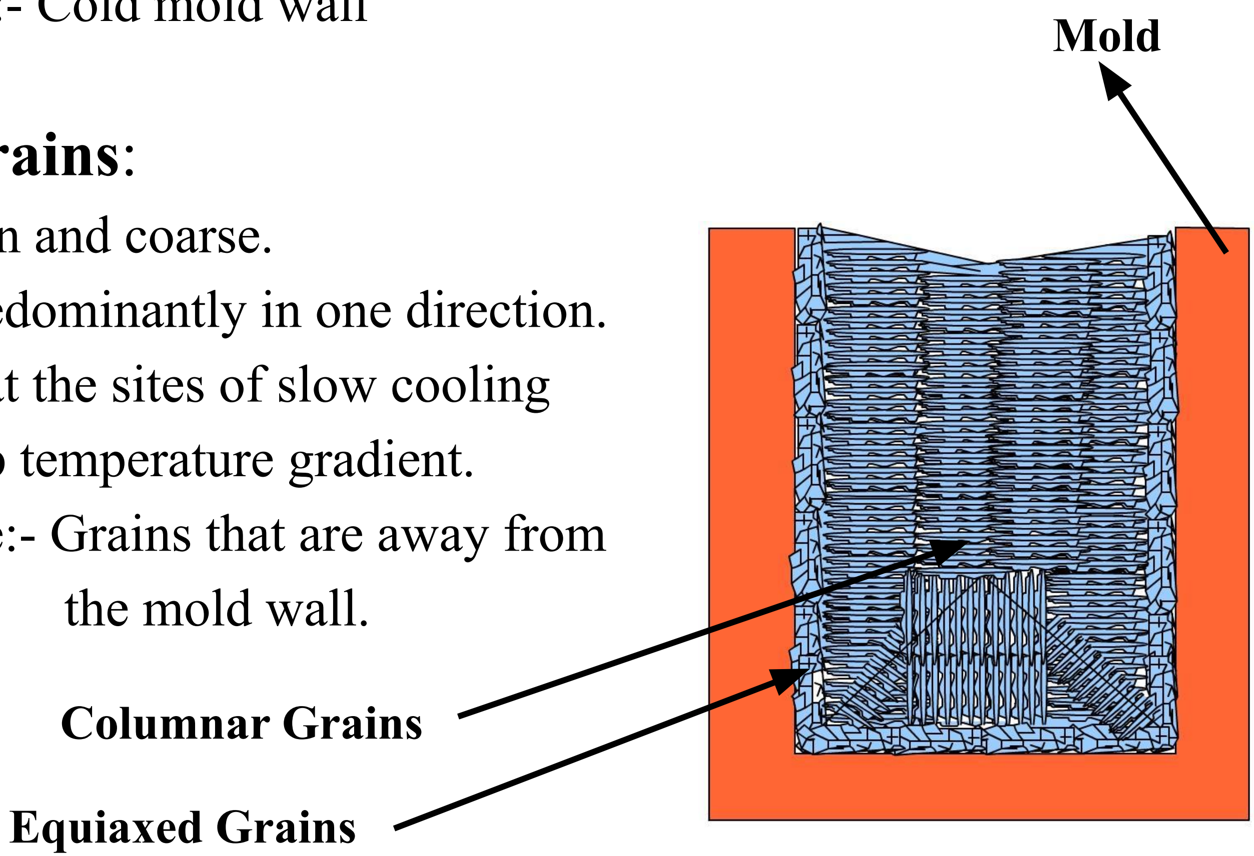
- Nucleus grow into crystals in different orientations.
- ***Crystal boundaries*** are formed when crystals join together at complete solidification.
- Crystals in solidified metals are called grains.
- Grains are separated by ***grain boundaries***.
- More the number of nucleation sites available, more the number of grains formed.

Nuclei growing into grains
Forming grain boundaries

Types of Grains

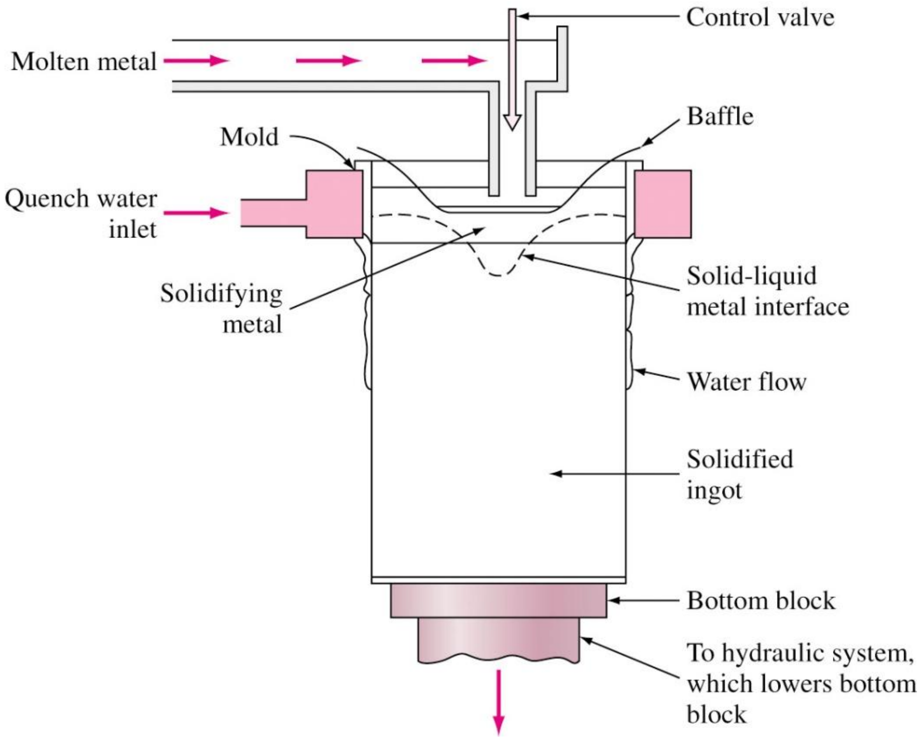
- **Equiaxed Grains:**
  - Crystals, smaller in size, grow equally in all directions.
  - Formed at the sites of high concentration of the nuclie.
  - Example:- Cold mold wall

- **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.

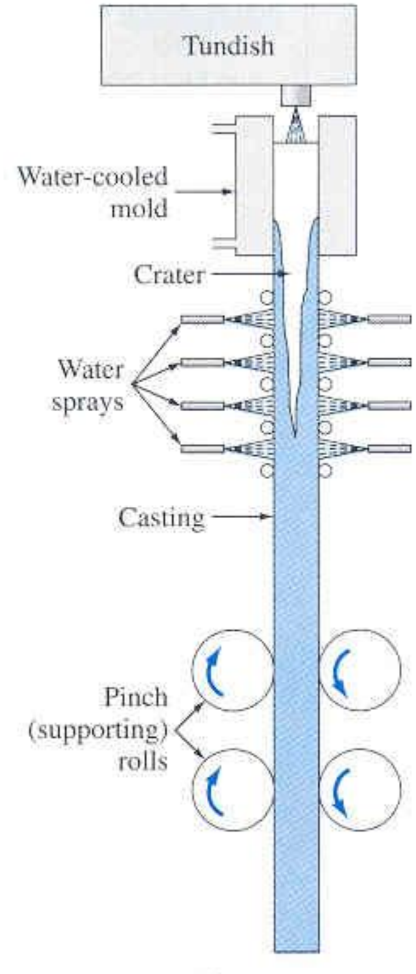


Casting in Industries

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



Direct-Chill semicontinuous Casting unit for aluminum



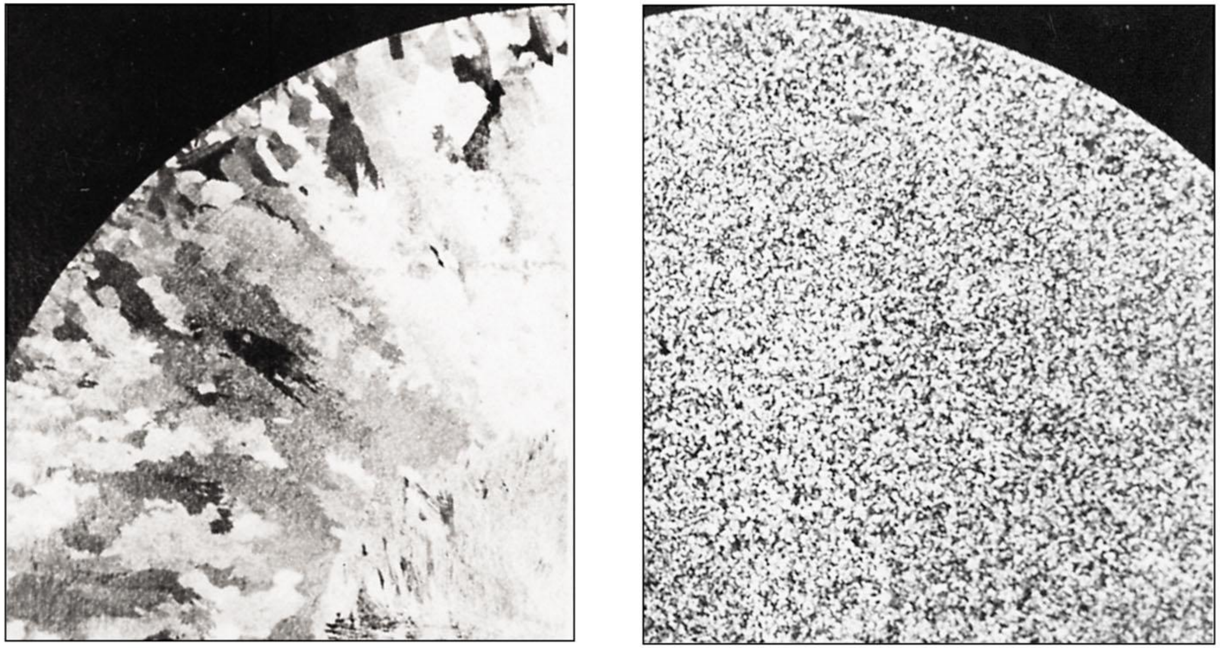
Continuous casting Of steel ingots

Iron Smelting: Video

- Please click on the following figure to open the video. (This video has voice).

Grain Structure in Industrial castings

- 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.

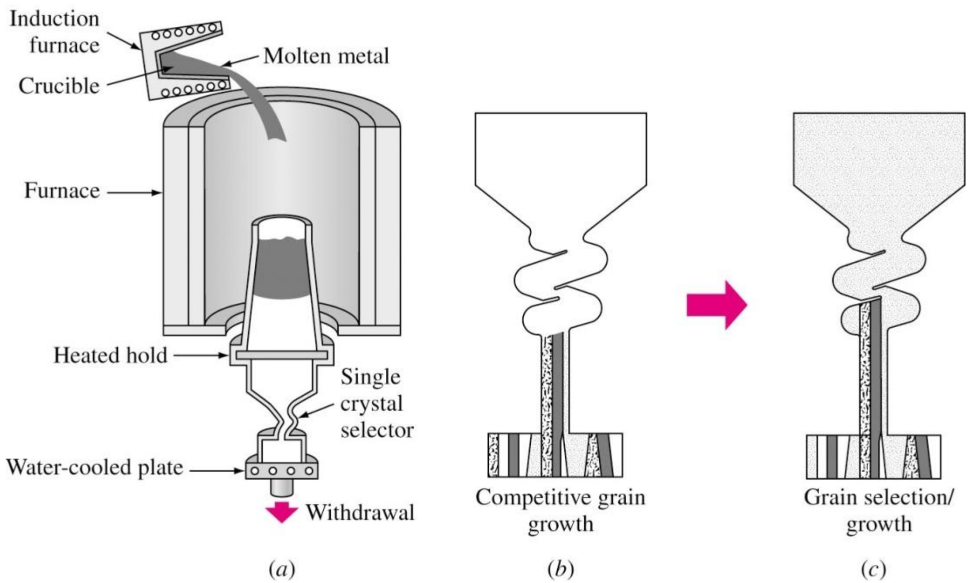


(a) (b)

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

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.

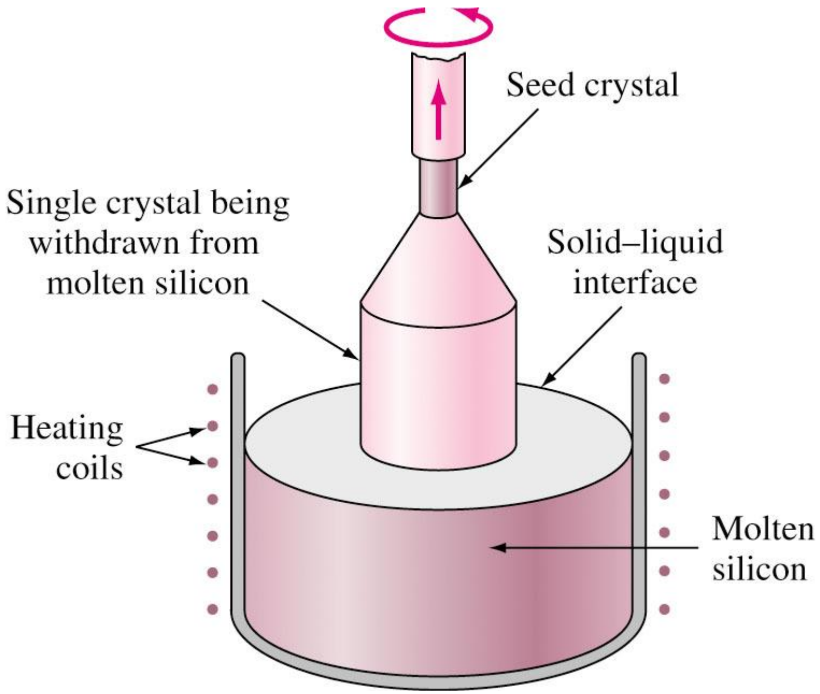


Growth of single crystal for turbine airfoil.

Foundations of Materials Science and Engineering, 5th Edn. Smith and Hashemi

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.



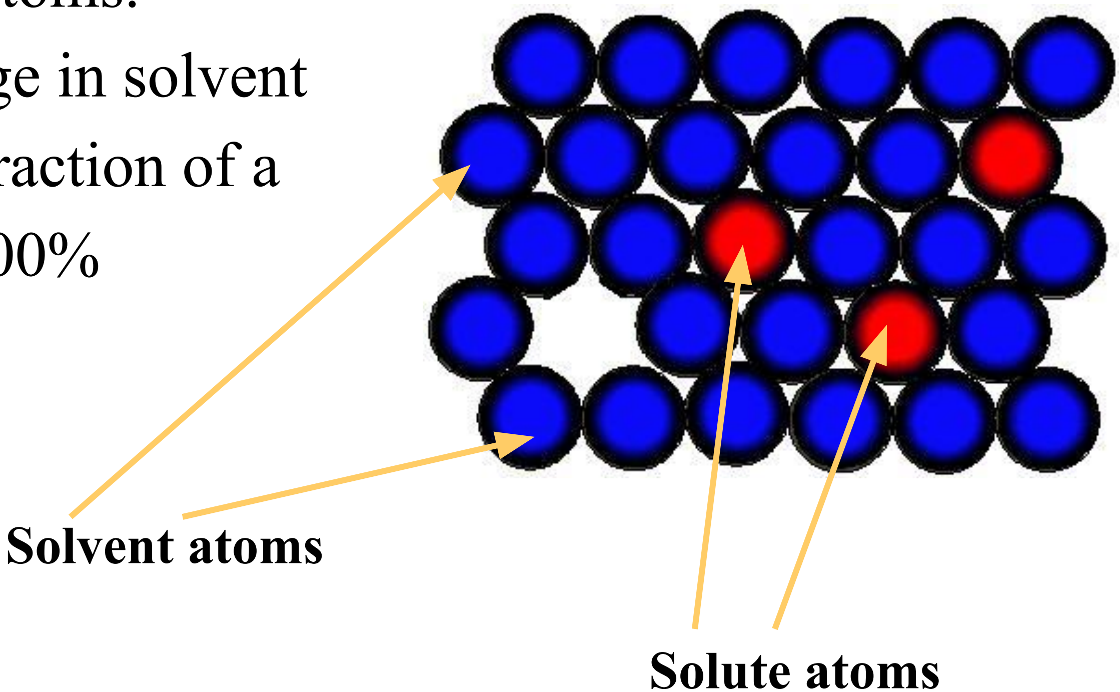
Metallic Solid Solutions

- 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.

Substitutional Solid Solution

- Solute atoms substitute for parent solvent atom in a crystal lattice.
- The structure remains unchanged.
- Lattice might get slightly distorted due to change in diameter of the atoms.
- Solute percentage in solvent can vary from fraction of a percentage to 100%



Substitutional Solid Solution (Cont..)

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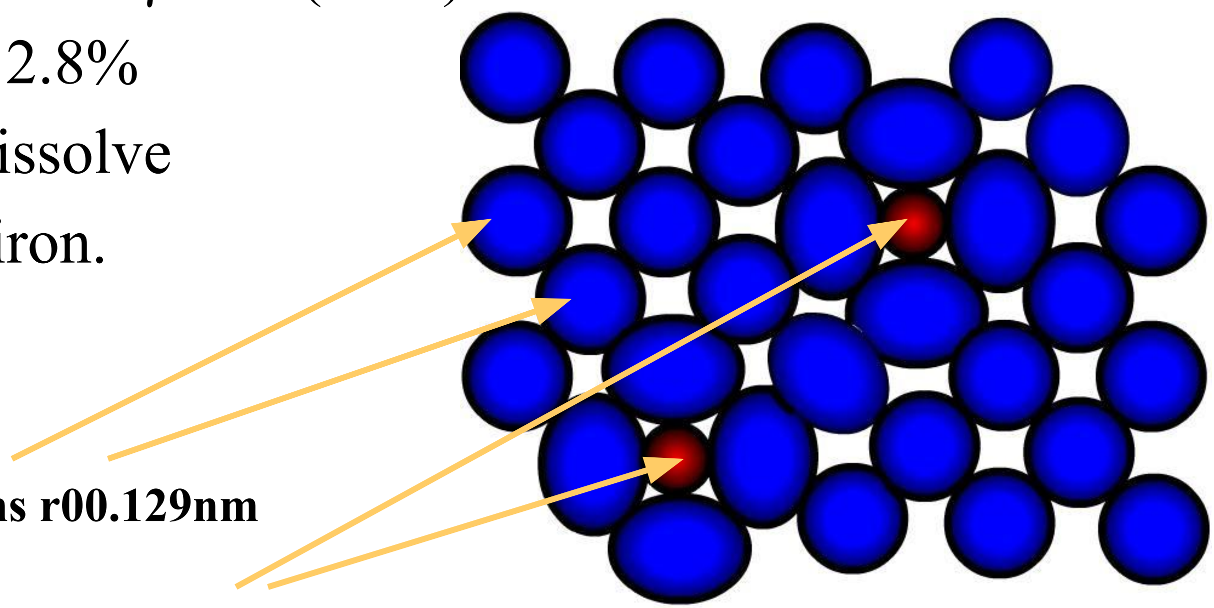
- The solubility of solids is greater if
  - The diameter of atoms not differ by more than 15%
  - Crystal structures are similar.
  - No much difference in electronegativity (else compounds will be formed).
  - Have some valence.

- Examples:-

System	Atomic radius Difference	Electron-e gativity difference	Solid Solibility
Cu-Zn	3.9%	0.1	38.3%
Cu-Pb	36.7%	0.2	0.17%
Cu-Ni	2.3%	0	100%

Interstitial Solid Solution

- Solute atoms fit in between the voids (interstices) of solvent atoms.
- Solvent atoms in this case should be much larger than solute atoms.
- Example:- between 912 and 1394^{0}C, interstitial solid solution of carbon in γ iron (FCC) is formed.
- A maximum of 2.8% of carbon can dissolve interstitially in iron.



Iron atoms r00.129nm

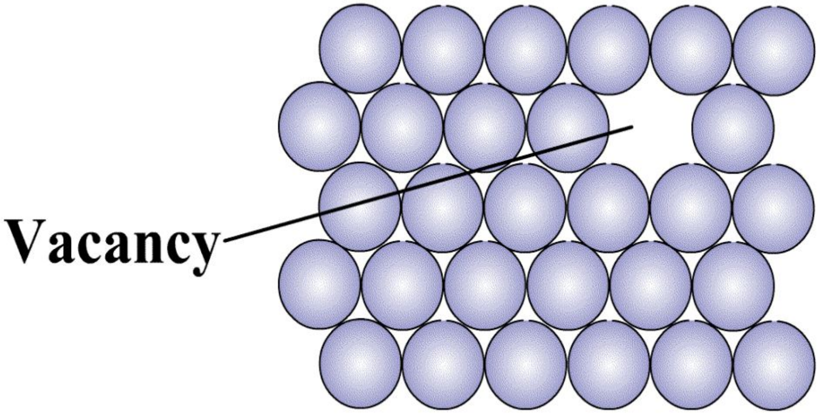
Carbon atoms r=0.075nm

Crystalline Imperfections

- No crystal is perfect.
- Imperfections affect mechanical properties, chemical properties and electrical properties.
- Imperfections can be classified as
  - Zero dimension point deffects.
  - One dimension / line deffects (dislocations).
  - Two dimension deffects.
  - Three dimension deffects (cracks).

Point Defects – Vacancy

- Vacancy is formed due to a missing atom.
- Vacancy is formed (one in 10000 atoms) during crystallization or mobility of atoms.
- Energy of formation is 1 ev.
- Mobility of vacancy results in cluster of vacancies.
- Also caused due to plastic defor--mation, rapid cooling or particle bombardment.



Vacancies moving to form vacancy cluster

Point Defects - Interstitially

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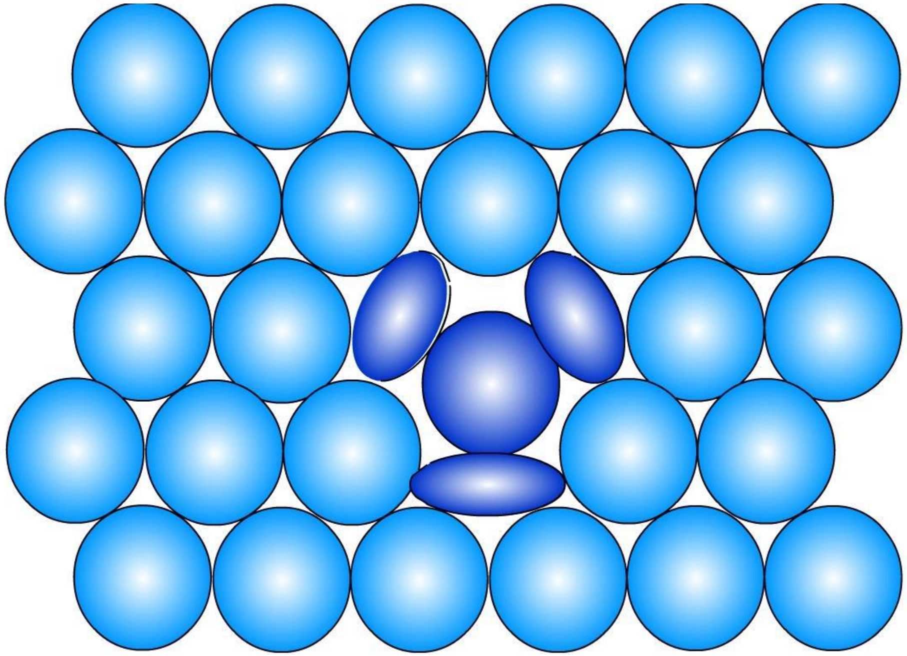
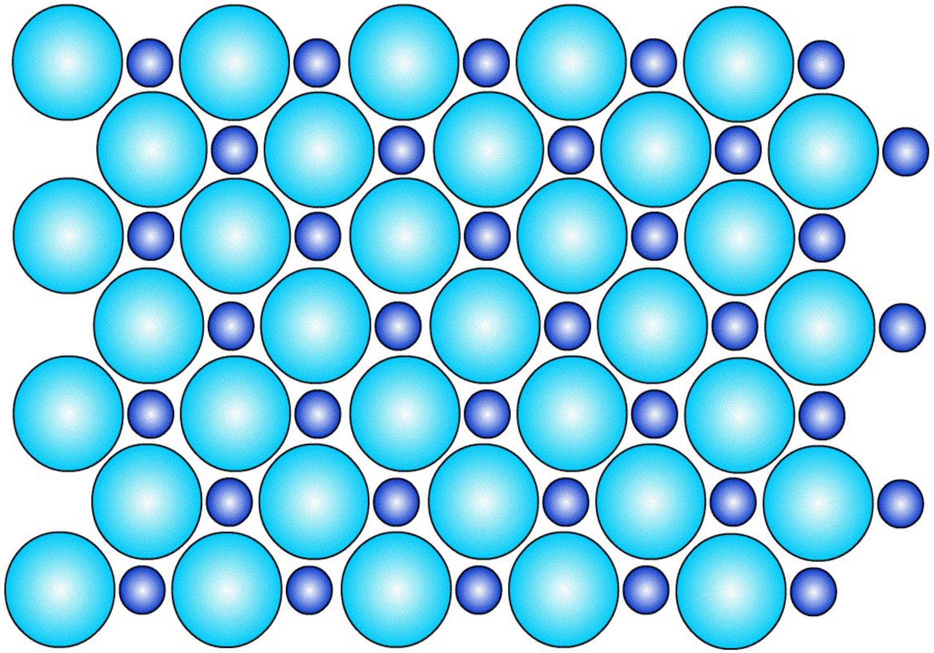
- Atom in a crystal, sometimes, occupies interstitial site.
- This does not occur naturally.
- Can be induced by irradiation.
- This defects caused structural distortion.



Point Defects in Ionic Crystals

- Complex as electric neutrality has to be maintained.
- If two appositely charged particles are missing, cation-anion divacancy is created. This is scohttky imperfection.
- Frenkel imperfection is created when cation moves to interstitial site.
- Impurity atoms are also considered as point defects.

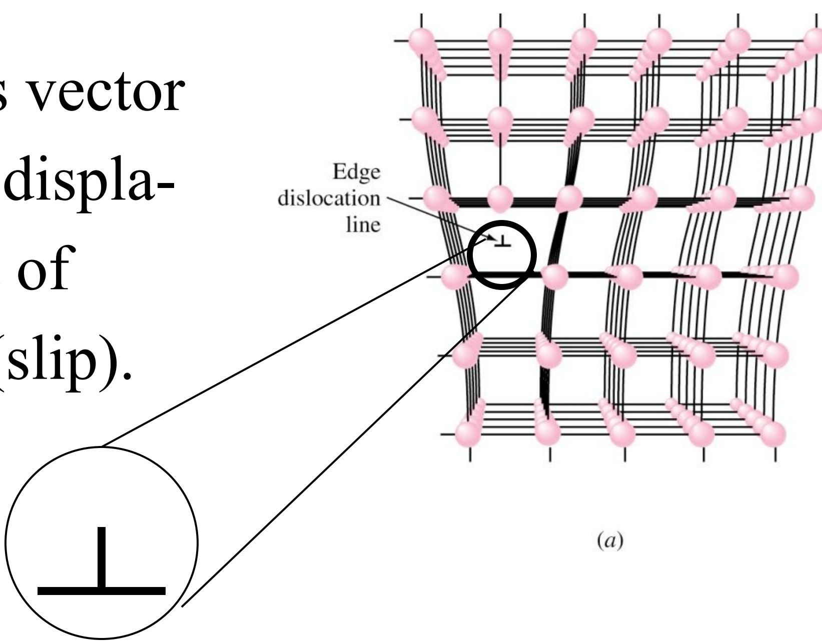


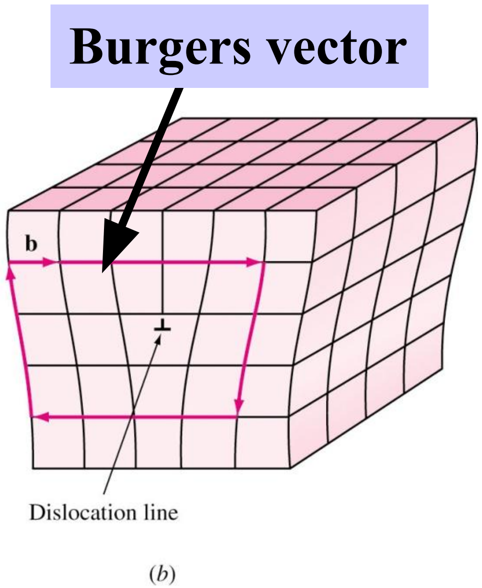
Line Defects – (Dislocations)

- Lattice distortions are centered around a line.
- Formed during
  - Solidification
  - Permanent Deformation
  - Vacancy condensation
- Different types of line defects are
  - Edge dislocation
  - Screw dislocation
  - Mixed dislocation

Edge Dislocation

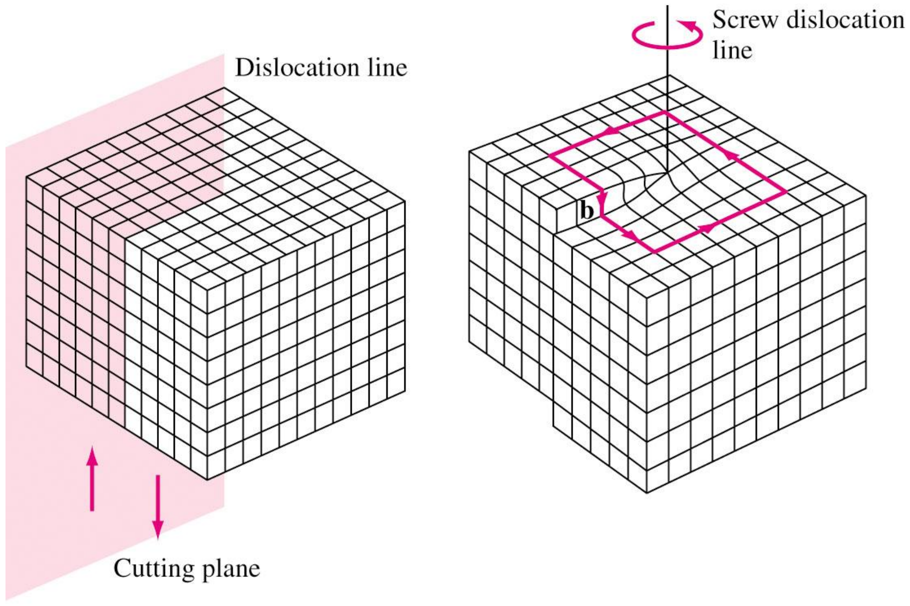
- Created by insertion of extra half planes of atoms.
- $\perp$ → Positive edge dislocation
- $\top$ → Negative edge dislocation
- Burgers vector
  Shows displa-
  cement of
  atoms (slip).





Screw Dislocation

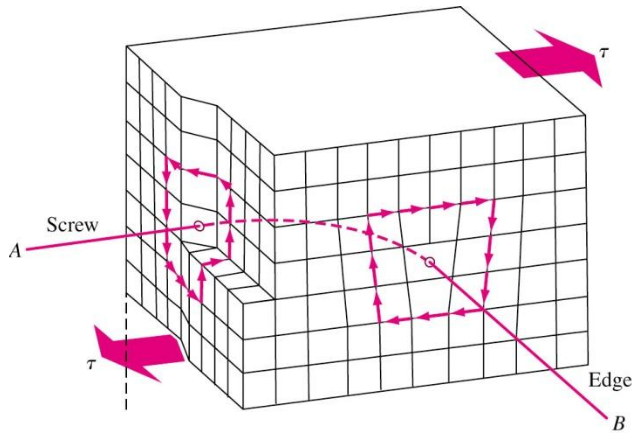
- Created due to *shear stresses* applied to regions of a perfect crystal separated by cutting plane.
- Distortion of lattice in form of a spiral ramp.
- Burgers vector is parallel to dislocation line.



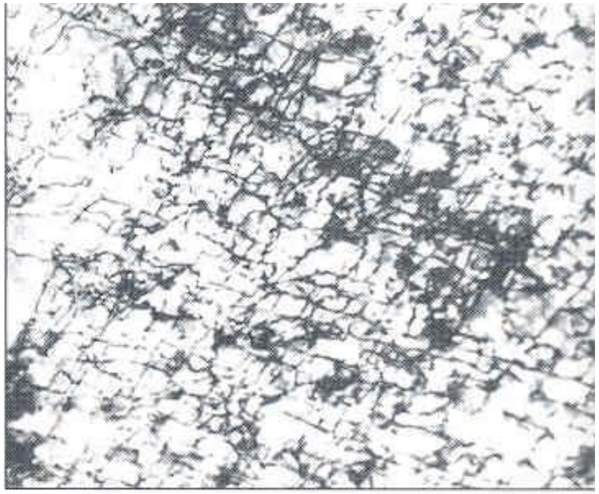
(*a*) (*b*)

Mixed Dislocation

- Most crystal have components of both edge and screw dislocation.



- Dislocation, since have irregular atomic arrangement will appear as dark lines when observed in electron microscope.



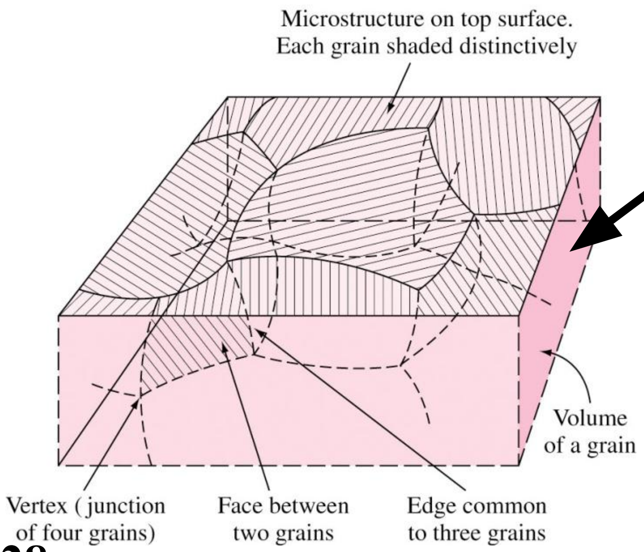
Dislocation structure of iron deformed 14% at –195^{0}C

Planar Defects

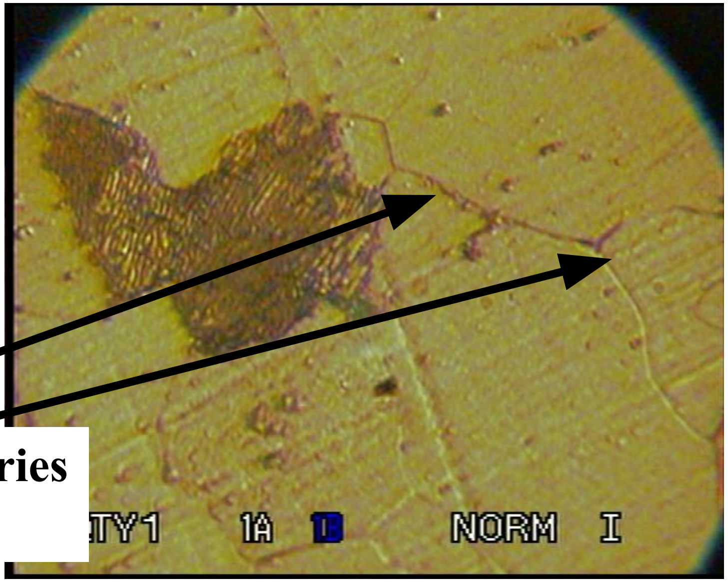
- ***Grain boundaries***, twins, low/high angle boundaries, twists and stacking faults
- Free surface is also a defect : Bonded to atoms on only one side and hence has higher state of energy $\rightarrow$ Highly reactive
- Nanomaterials have small clusters of atoms and hence are highly reactive.

Grain Boundaries

- Grain boundaries separate grains.
- Formed due to simultaneously growing crystals meeting each other.
- Width = 2-5 atomic diameters.
- Some atoms in grain boundaries have higher energy.
- Restrict plastic flow and prevent dislocation movement.



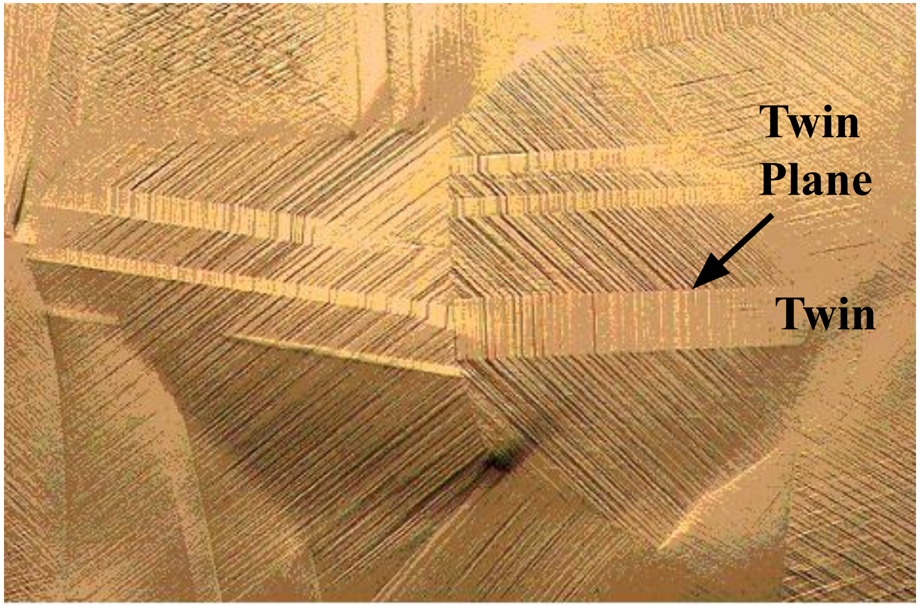
3D view of grains



Grain Boundaries In 1018 steel

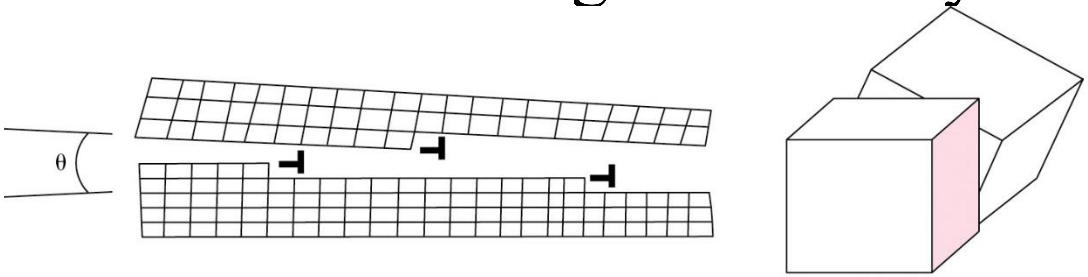
Twin Boundaries

- Twin: A region in which mirror image pf structure exists across a boundary.
- Formed during plastic deformation and *recrystallization*.
- Strengthens the metal.



Other Planar Defects

- **Small angle tilt boundary:** Array of edge dislocations tilts two regions of a crystal by < 10^0



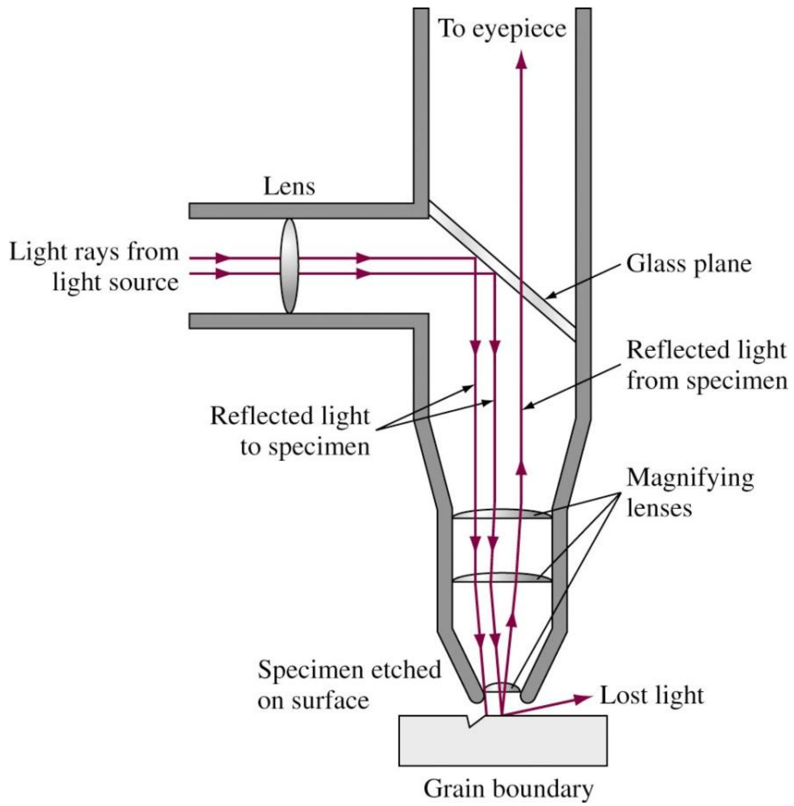
(a) (b)

- **Stacking faults:** Piling up faults during recrystallization due to collapsing.
  - Example: ABCABAACBABC → FCC fault

- **Volume defects:** Cluster of point defects join to form 3-D void.

Observing Grain Boundaries - Metallography

- To observe grain boundaries, the metal sample must be first mounted for easy handling
- Then the sample should be ground and polished with different grades of abrasive paper and abrasive solution.
- The surface is then etched chemically.
- Tiny groves are produced at grain boundaries.
- Groves do not intensely reflect light. Hence observed by optical microscope.

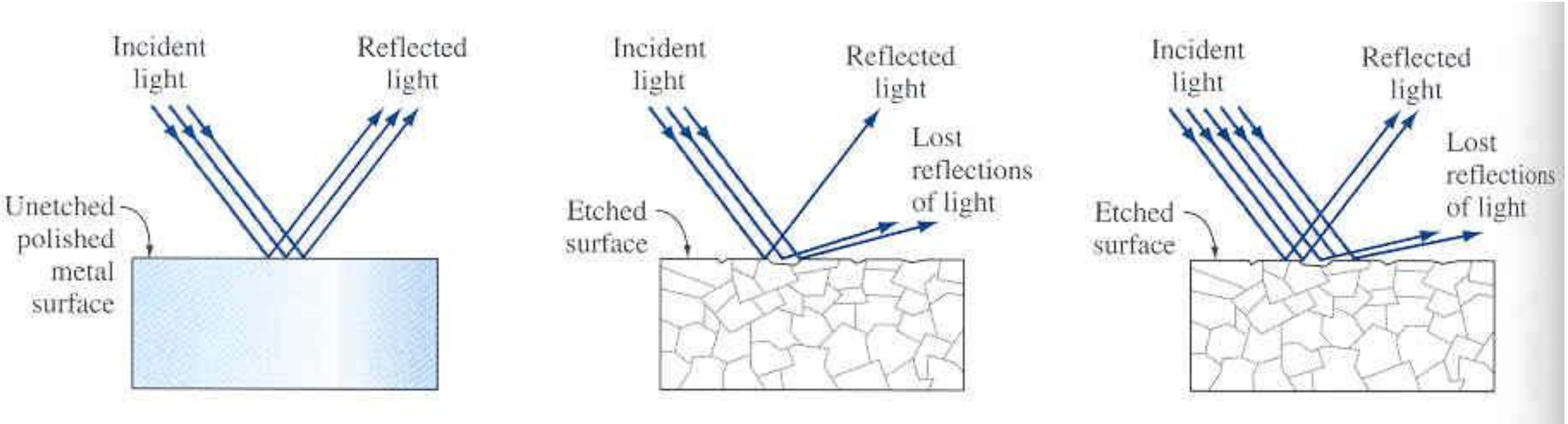


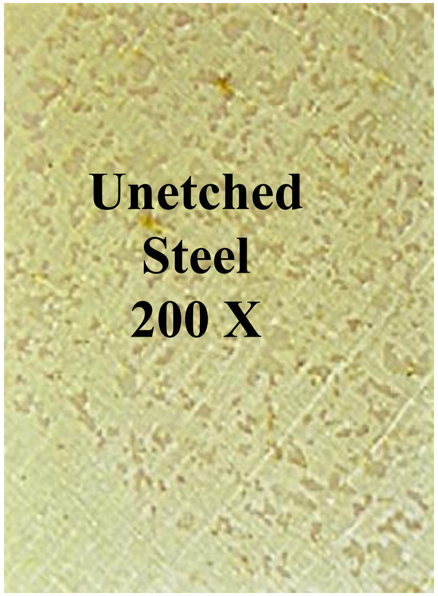
After M. Eisenstadt, "Introduction to Mechanical Properties of Materials," Macmillan, 1971, p.126

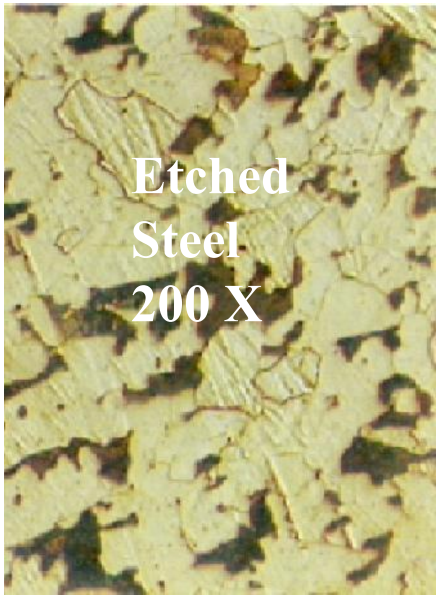
Virtual Lab Modules

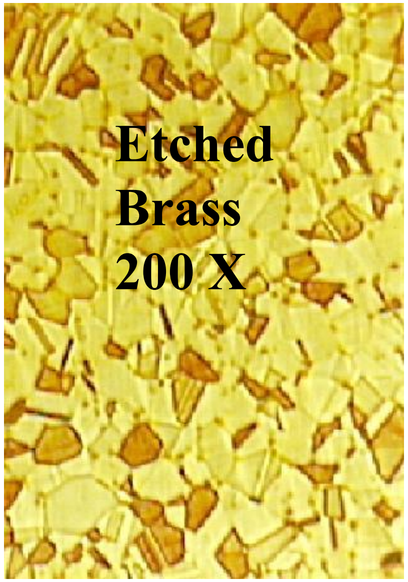
- Click on the following figures to open the virtual lab modules related to polishing the specimen for Metallography.

Effect of Etching



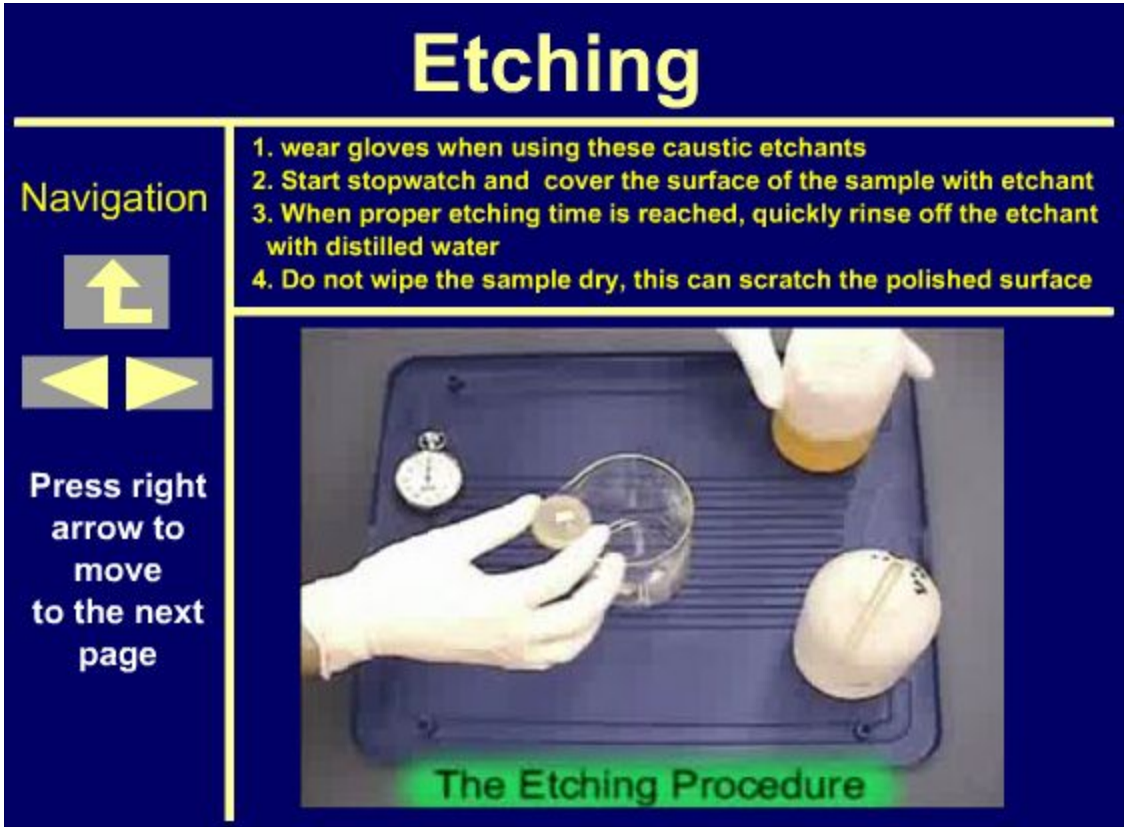






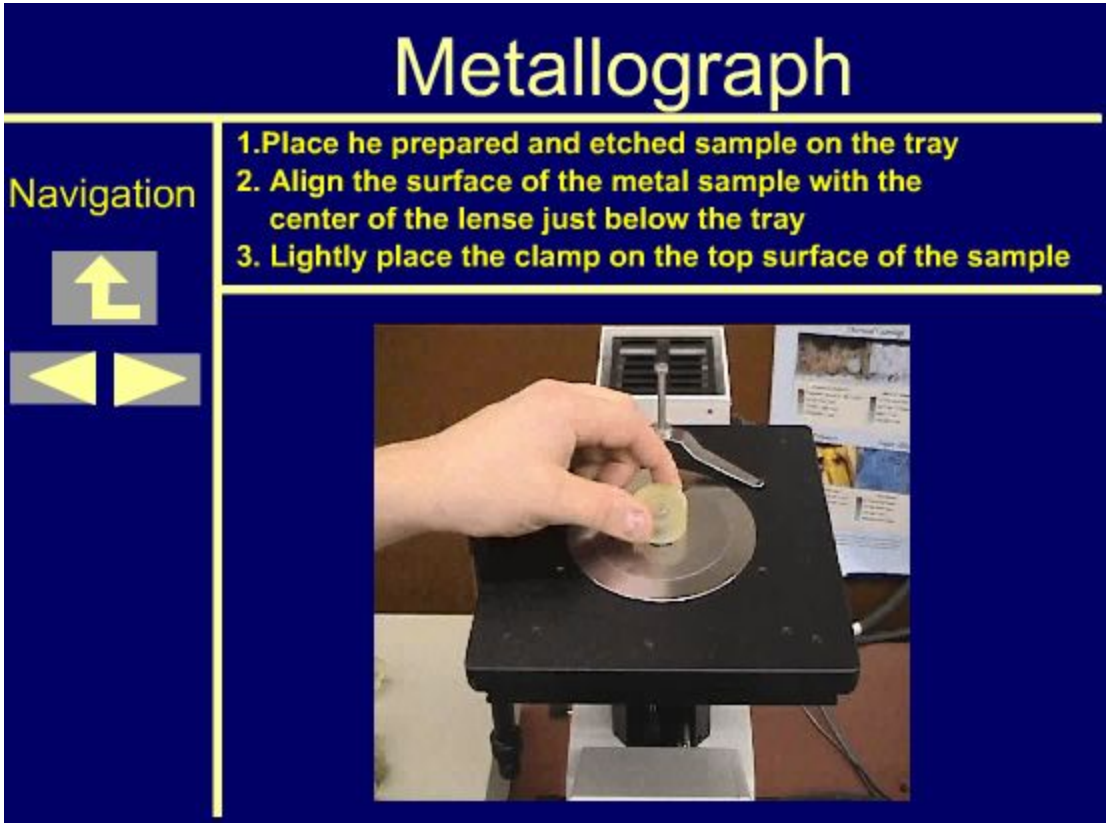
Virtual Lab Modules

- Click on the following figures to open the virtual lab modules related to etching the specimen.



Virtual Lab Modules

- Click on the following figures to open the virtual lab modules related to metallographic observation.



Grain Size

- Affects the mechanical properties of the material
- The smaller the grain size, more are the grain boundaries.
- More grain boundaries means higher resistance to slip (plastic deformation occurs due to slip).
- More grains means more uniform the mechanical properties are.

Measuring Grain Size

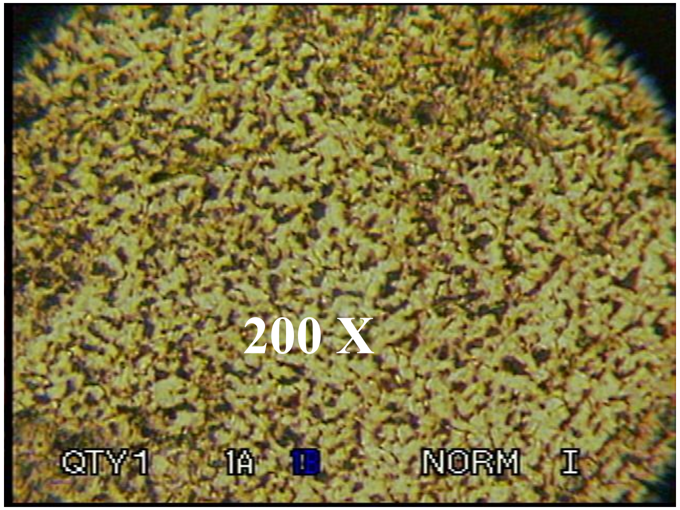
- ASTM grain size number 'n' is a measure of grain size.

$$N = 2^{n-1}$$

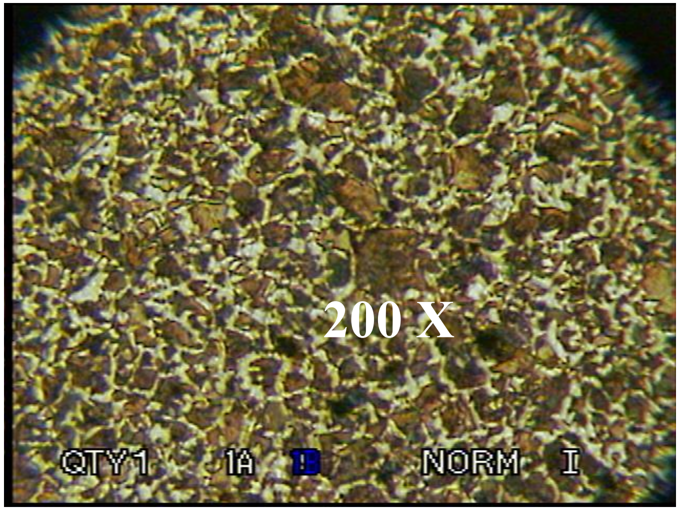
N = Number of grains per square inch of a polished and etched specimen at 100 x.

n = ASTM grain size number.

N < 3 – Coarse grained
4 < n < 6 – Medium grained
7 < n < 9 – Fine grained
N > 10 – ultrafine grained



1018 cold rolled steel, n=10



1045 cold rolled steel, n=8

Measuring ASTM Grain Size Number

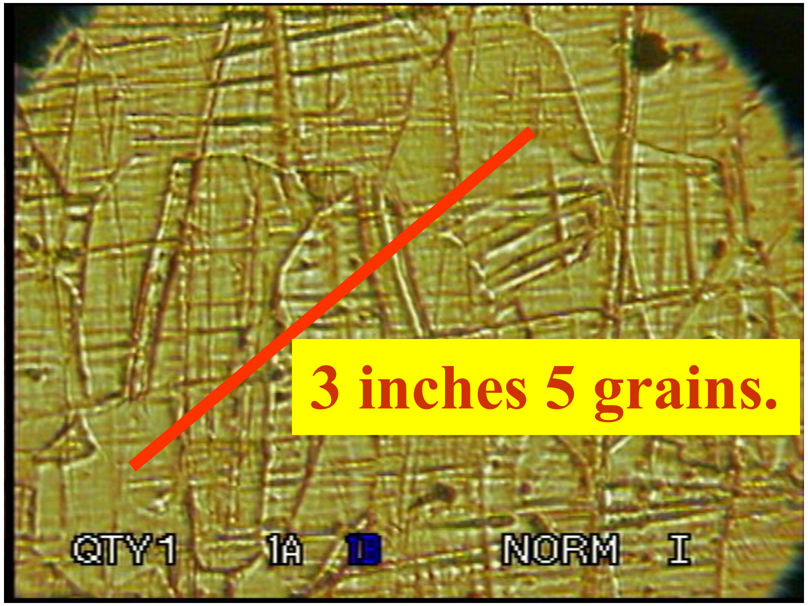
- Click the Image below to play the tutorial.

Average Grain Diameter

- Average grain diameter more directly represents grain size.
- Random line of known length is drawn on photomicrograph.
- Number of grains intersected is counted.
- Ratio of number of grains intersected to length of line, n_L is determined.

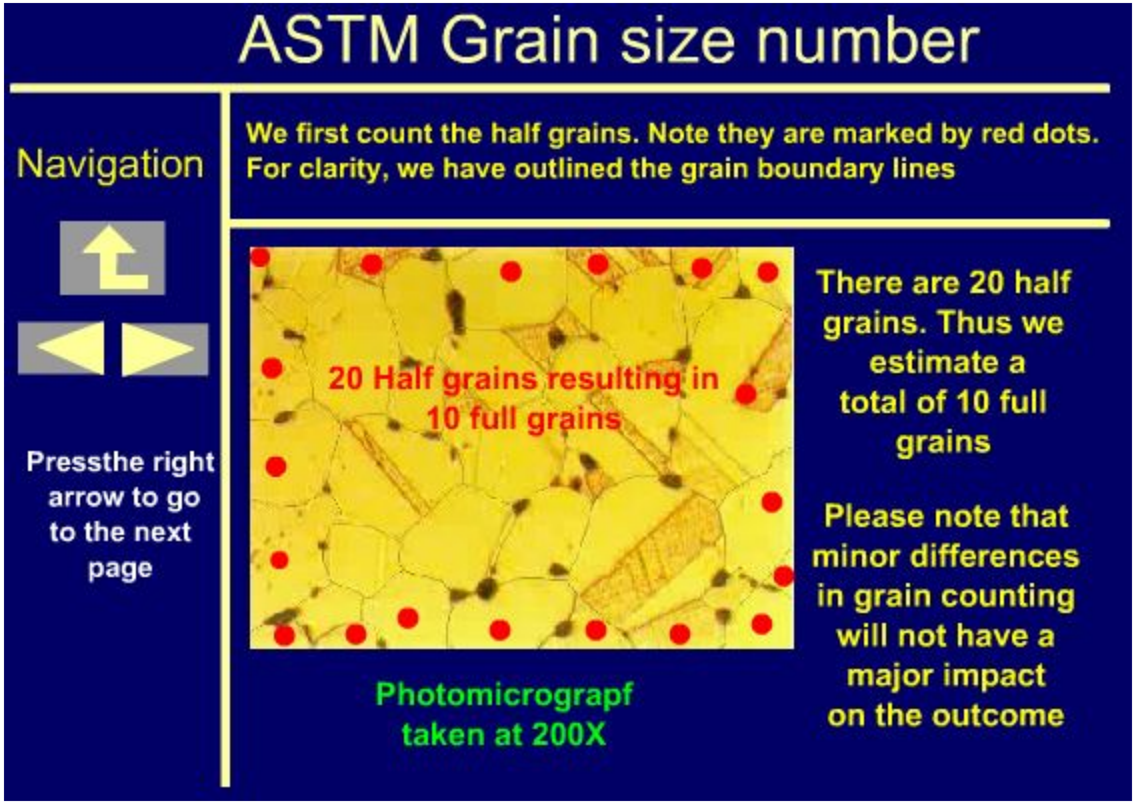
$d = C/n_L M$

C=1.5, and M is magnification



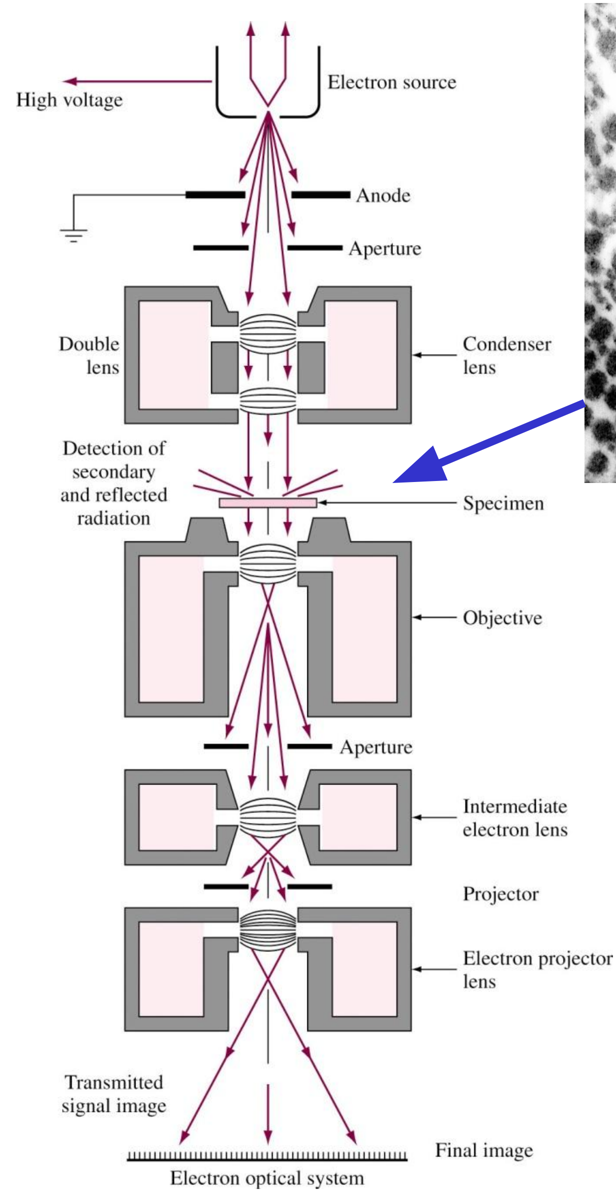
Virtual Lab Module

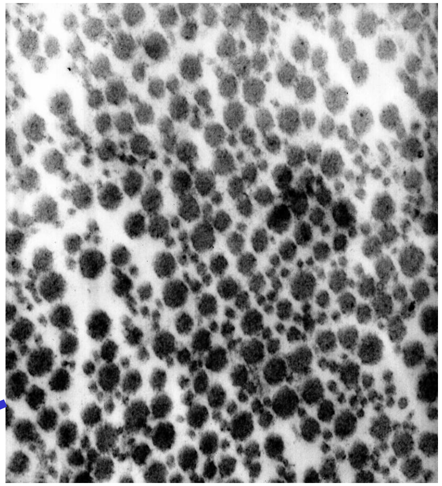
- Click on the following figures to open the virtual lab modules related to grain size measurement.



Transmission Electron Microscope

- Electron produced by heated tungsten filament.
- Accelerated by high voltage (75 - 120 KV)
- Electron beam passes through very thin specimen.
- Difference in atomic arrangement change directions of electrons.
- Beam is enlarged and focused on fluorescent screen.

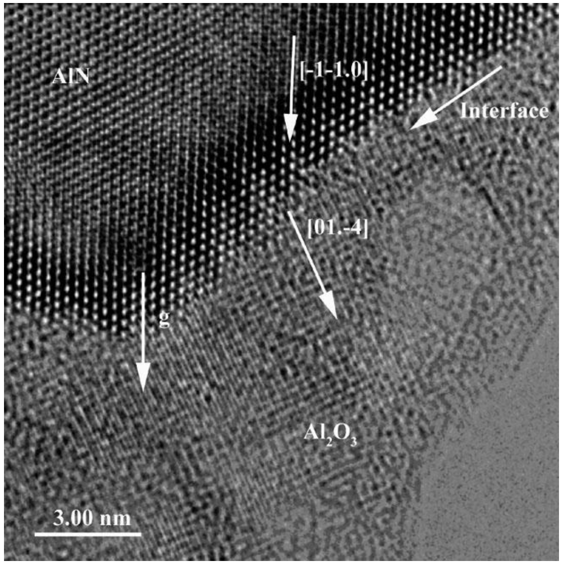




Collagen Fibrils of ligament as seen in TEM

TEM (..Cont)

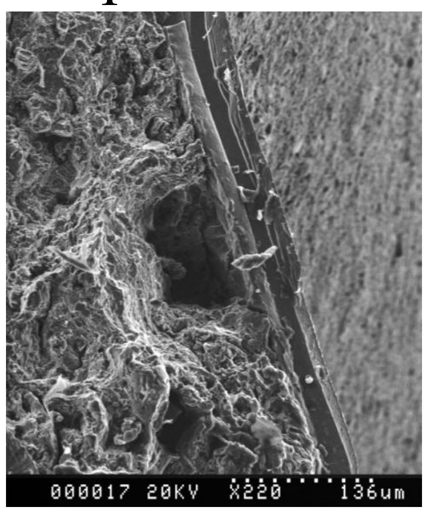
- TEM needs complex sample preparation
- Very thin specimen needed (several hundred nanometers)
- High resolution TEM (HRTEM) allows resolution of 0.1 nm.
- 2-D projections of a crystal with accompanying defects can be observed.



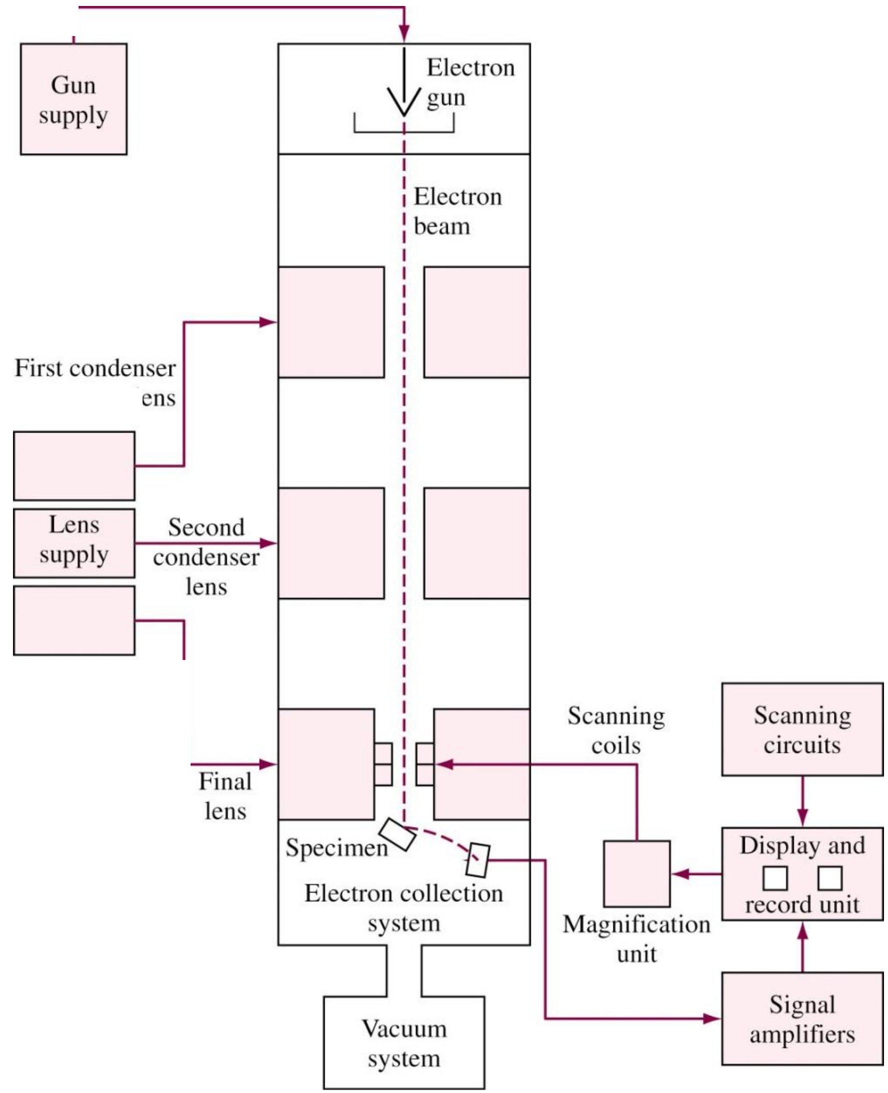
Low angle boundary As seen In HTREM

The Scanning Electron Microscope

- Electron source generates electrons.
- Electrons hit the surface and secondary electrons are produced.
- The secondary electrons are collected to produce the signal.
- The signal is used to produce the image.



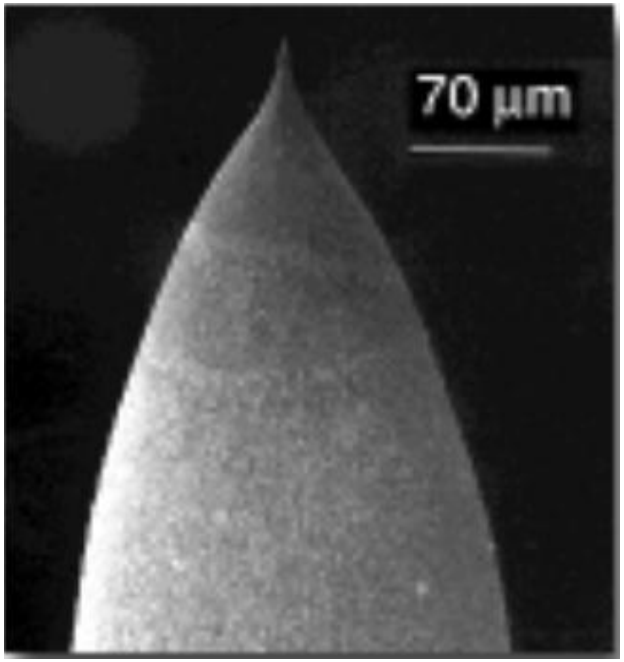
TEM of fractured metal end



Scanning Probe Microscopy

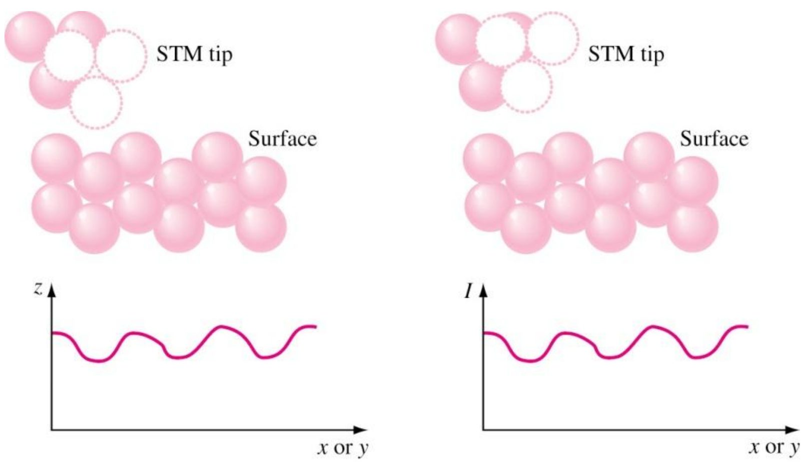
- Scanning Tunneling Microscope (STM) and Atomic Force Microscope (AFM).
- Sub-nanometer magnification.
- Atomic scale topographic map of surface.
- STM uses extremely sharp tip.
- Tungsten, nickel, platinum
  - iridium or carbon nanotubes

  are used for tips.



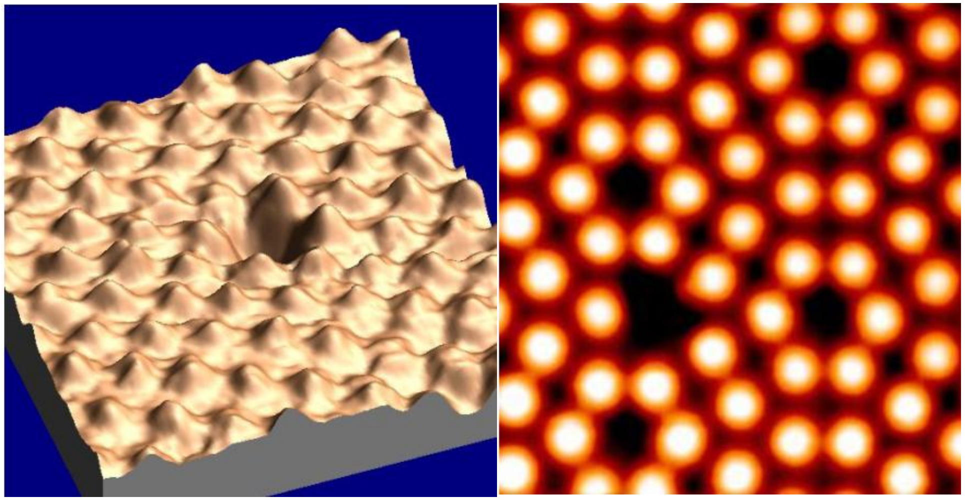
Scanning Tunneling Microscope

- Tip placed one atom diameter from surface.
- Voltage applied across tip and surface.
- Electrons tunnel the gap and produce current.
- Current produced is proportional to change in gap.
- Can be used only for conductive materials.



(a) Constant current mode (b) Constant height mode

Constant height and current modes



Surface of platinum with defects

Atomic Force Microscope

- Similar to STM but tip attached to cantilever beam.
- When tip interacts with surface, van der waals forces deflect the beam.
- Deflection detected by laser and photodetector.
- Non-conductive materials can be scanned.
- Used in DNA research and polymer coating technique.