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CHAPTER

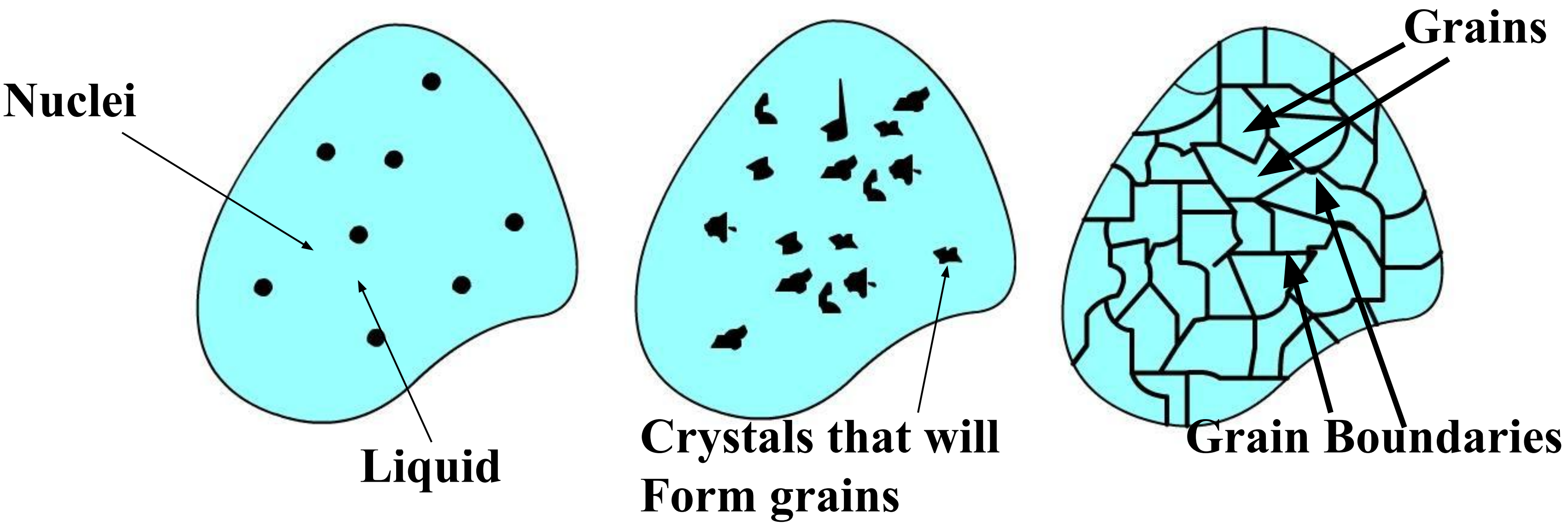
4

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.

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.

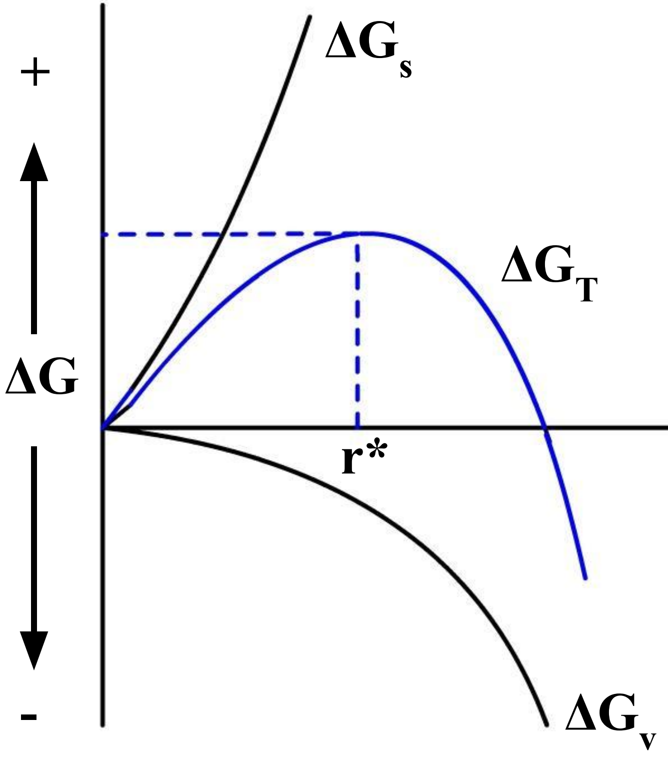
Then $\Delta G_s = 4\pi r^2 \gamma$

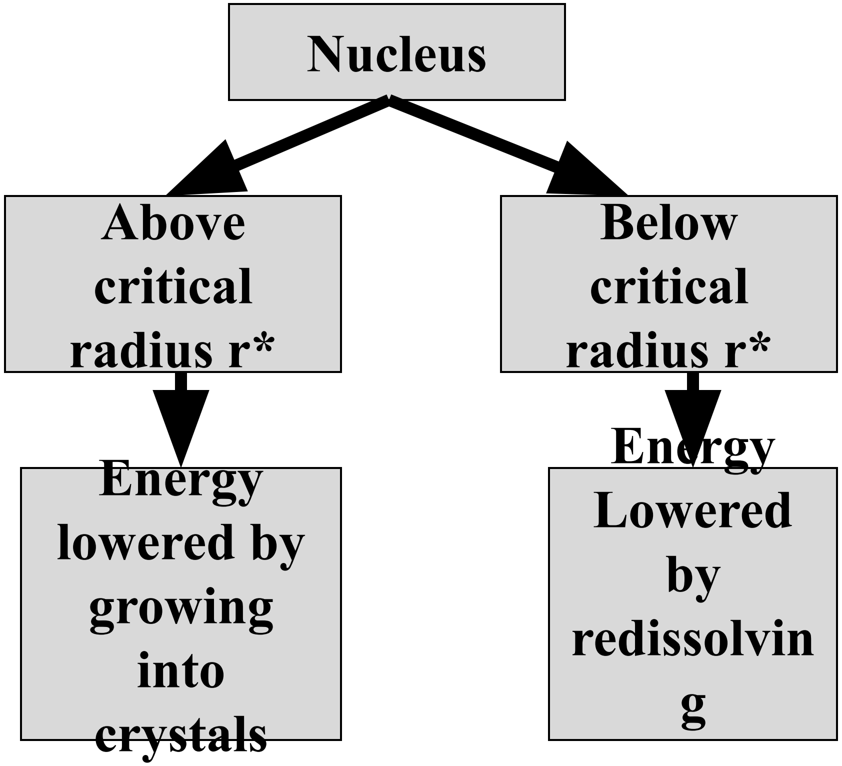
- ΔG_s is retarding energy.

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

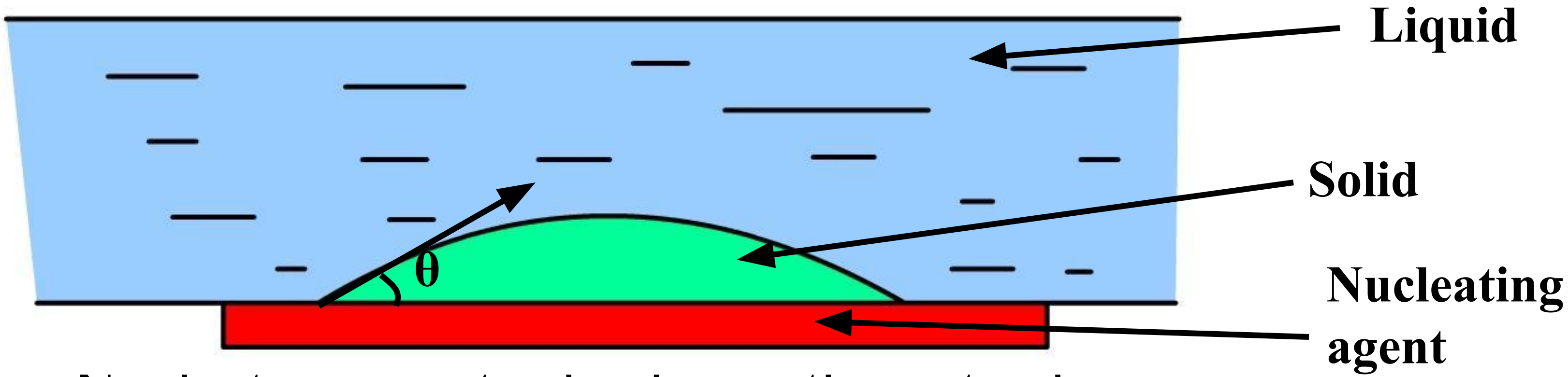
- Greater the degree of undercooling, greater the change in volume free energy ΔG_v
- ΔGs does not change significantly.
- As the amount of *undercooling* ΔT increases, critical nucleus size decreases.
- Critical radius is related to undercooling by relation

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

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

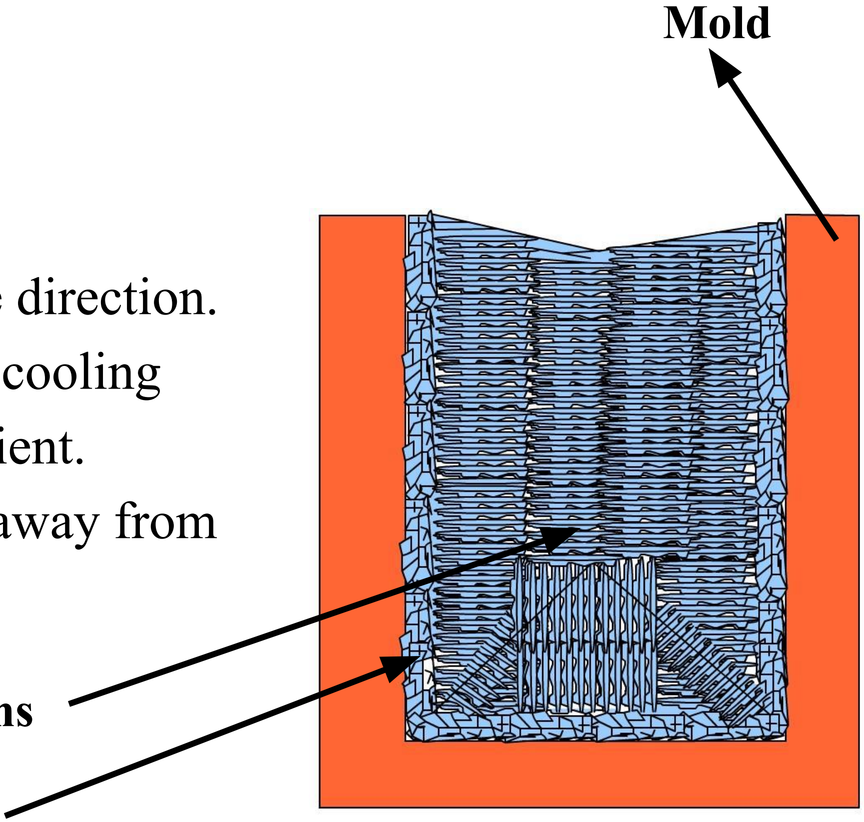
- Nucleus grow into crystals in different orientations.
- ***Crystal boundaries*** are formed when crystals join together at complete solidification.
- Crystals in solidified metals are called grains.
- Grains are separated by ***grain boundaries***.
- More the number of nucleation sites available, more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

Nuclei growing into grains
Forming grain boundaries

Types of Grains

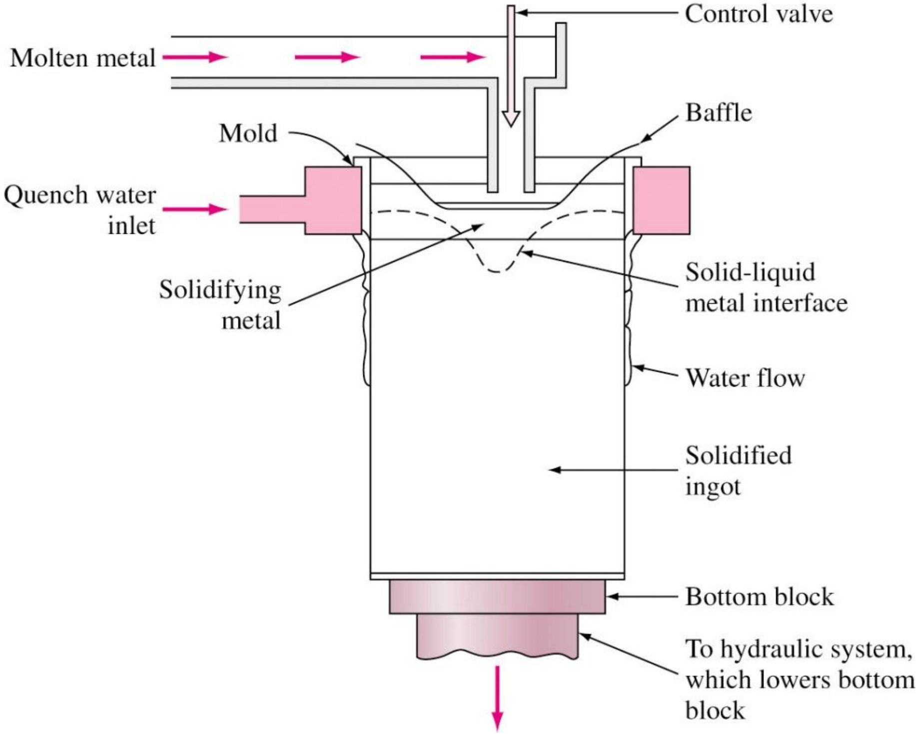
- **Equiaxed Grains:**
  - Crystals, smaller in size, grow equally in all directions.
  - Formed at the sites of high concentration of the nuclie.
  - Example:- Cold mold wall

- **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.

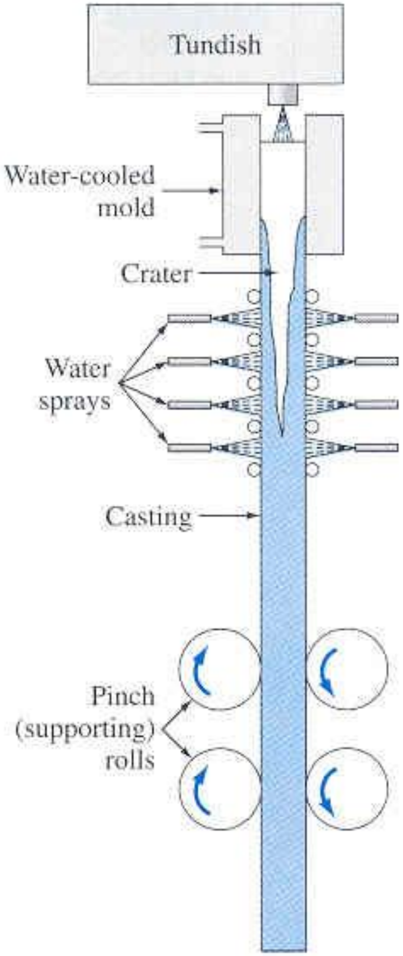


Casting in Industries

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



Direct-Chill semicontinuous Casting unit for aluminum



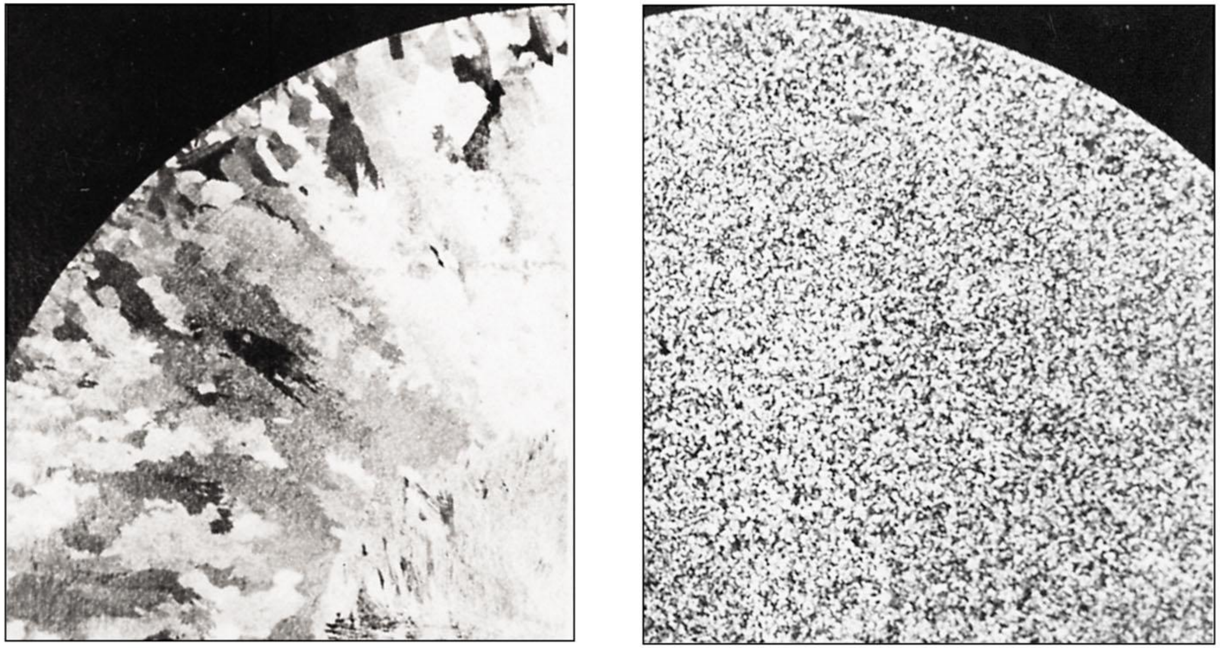
Continuous casting Of steel ingots

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.



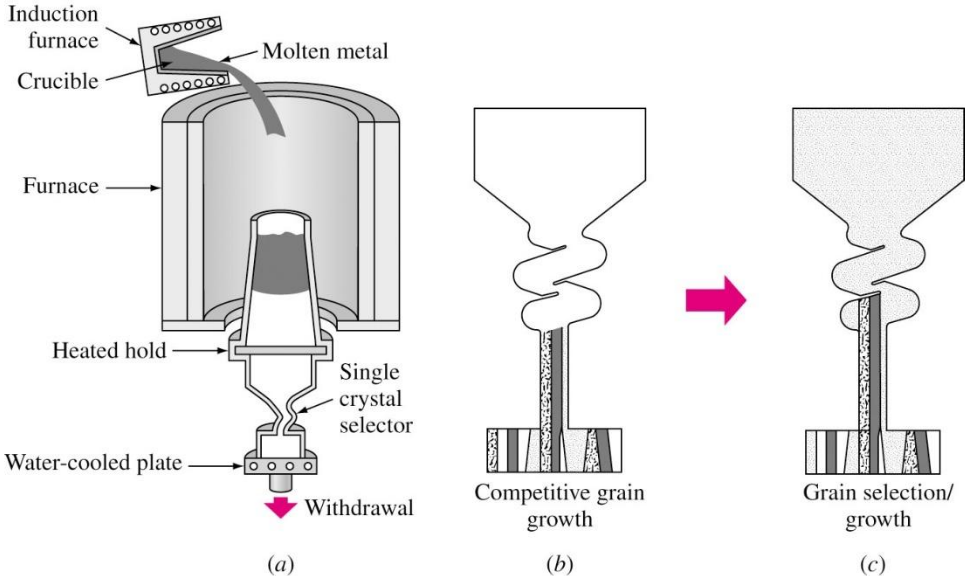
(a)

(b)

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

Solidification of Single Crystal

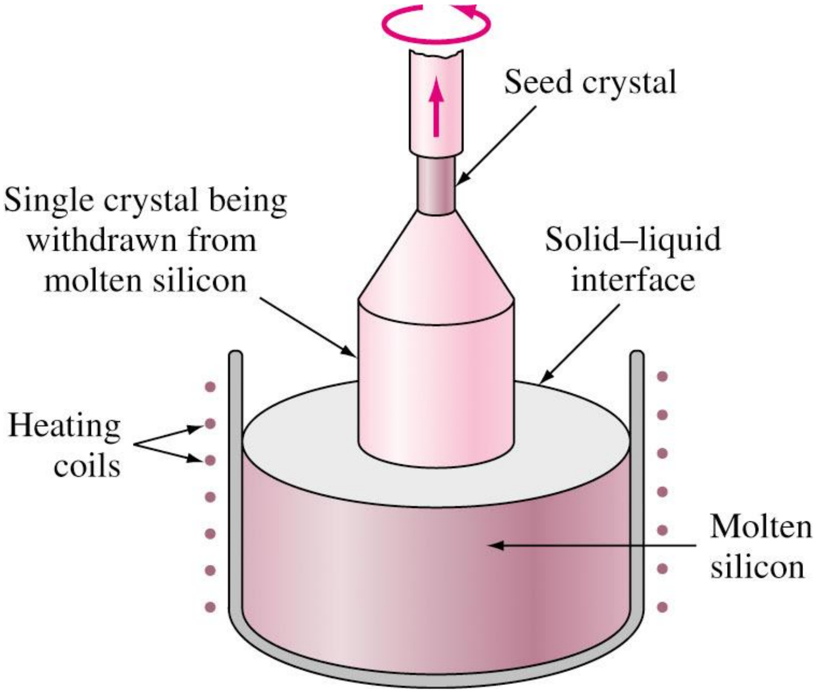
- For some applications (Eg: Gas turbine blades-high temperature environment), single crystals are needed.
- Single crystals have high temperature creep resistance.
- Latent head of solidification is conducted through solidifying crystal to grow single crystal.
- Growth rate is kept slow so that temperature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



Growth of single crystal for turbine airfoil.

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.



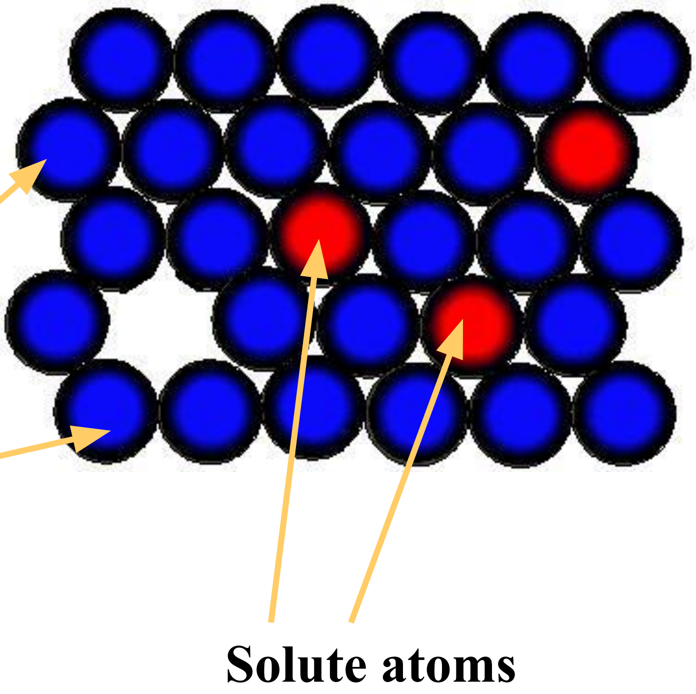
Metallic Solid Solutions

- 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..)

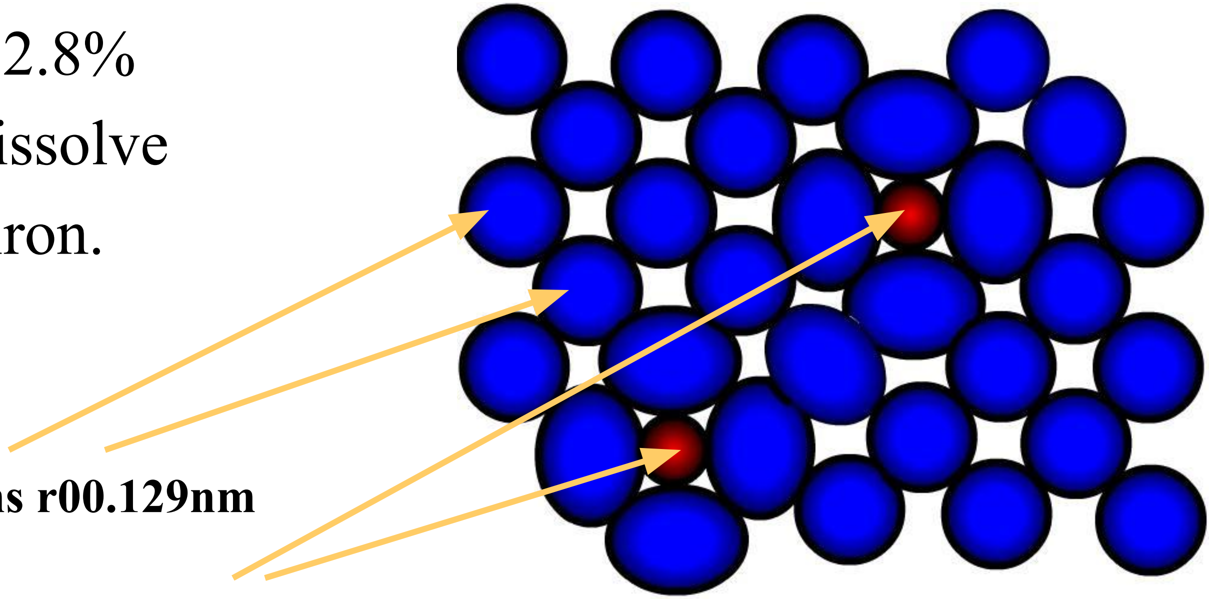
- The solubility of solids is greater if
  - The diameter of atoms not differ by more than 15%
  - Crystal structures are similar.
  - No much difference in electronegativity (else compounds will be formed).
  - Have some valence.

- Examples:-

System	**Atomic radius Difference**	**Electron-egativity 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

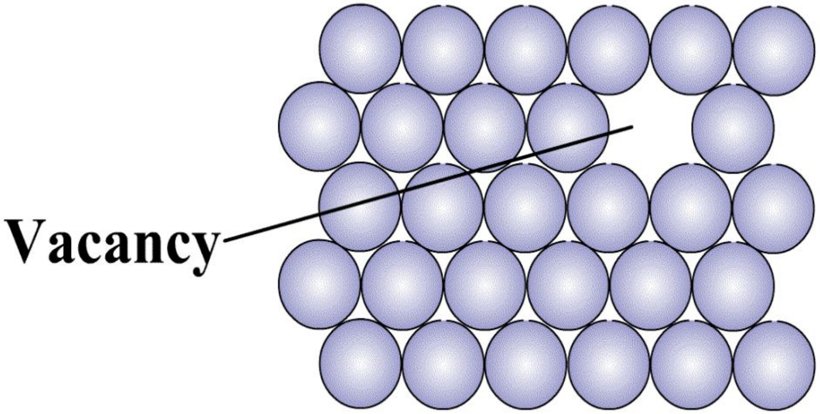
Carbon atoms r=0.075nm

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

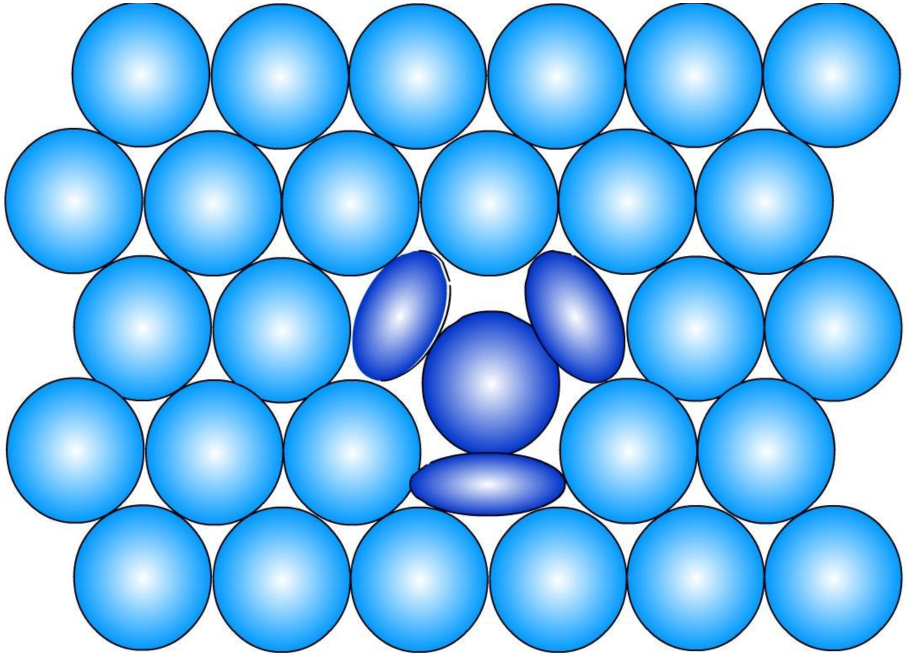
- Vacancy is formed due to a missing atom.
- Vacancy is formed (one in 10000 atoms) during crystallization or mobility of atoms.
- Energy of formation is 1 ev.
- Mobility of vacancy results in cluster of vacancies.
- Also caused due to plastic deformation, rapid cooling or particle bombardment.



Vacancies moving to form vacancy cluster

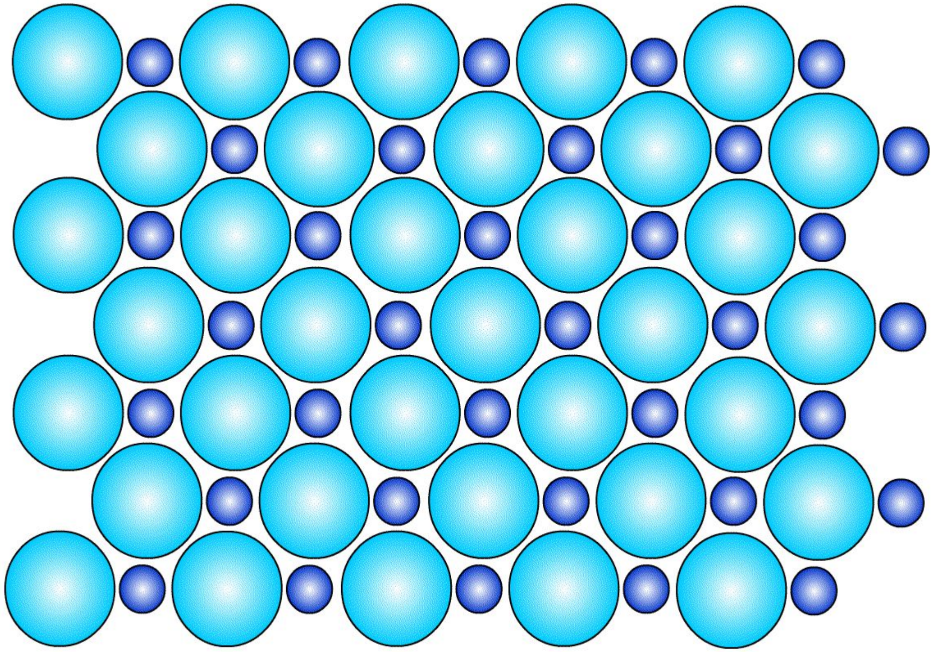
Point Defects - Interstitially

- 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.

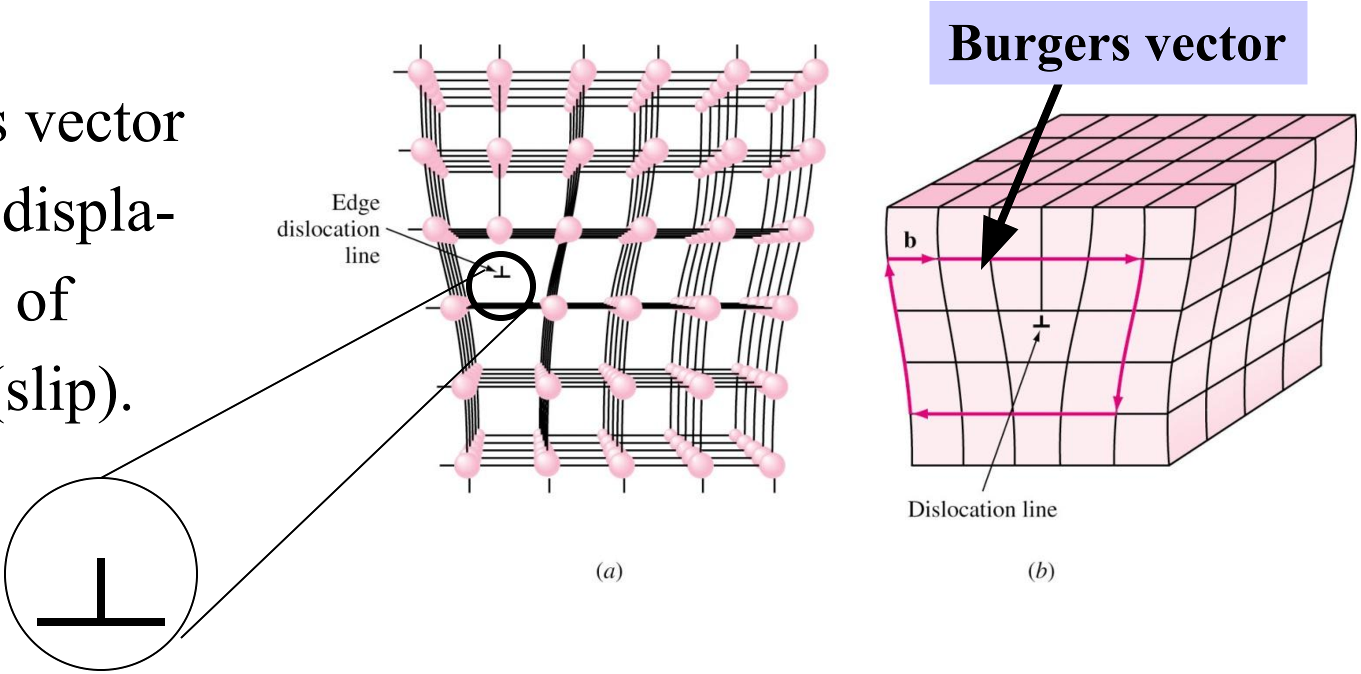


Line Defects – (Dislocations)

- 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

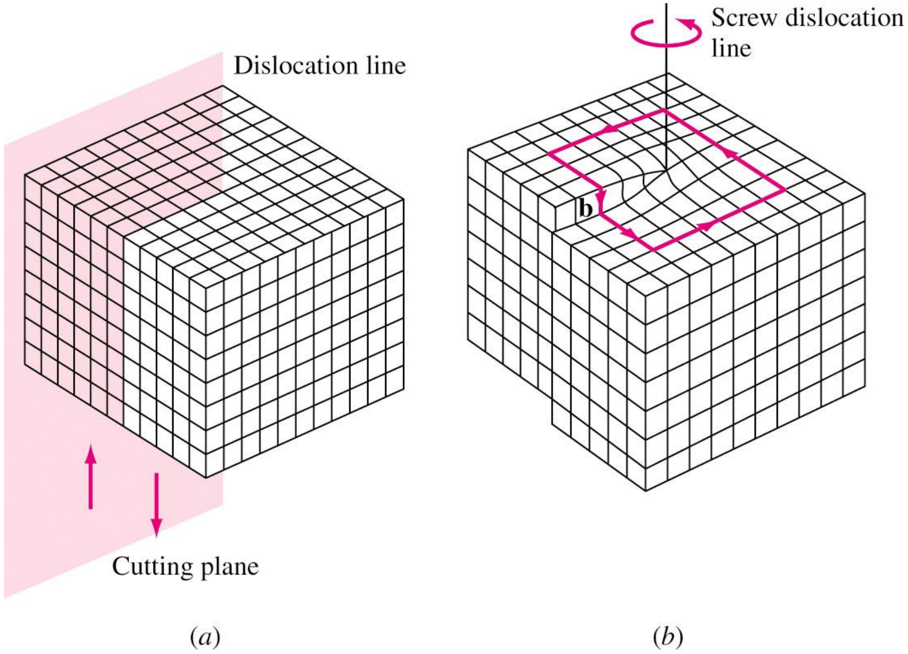
Edge Dislocation

- Created by insertion of extra half planes of atoms.
- ⊥ → Positive edge dislocation
- ⊤ → Negative edge dislocation
- Burgers vector Shows displacement of atoms (slip).


Burgers vector

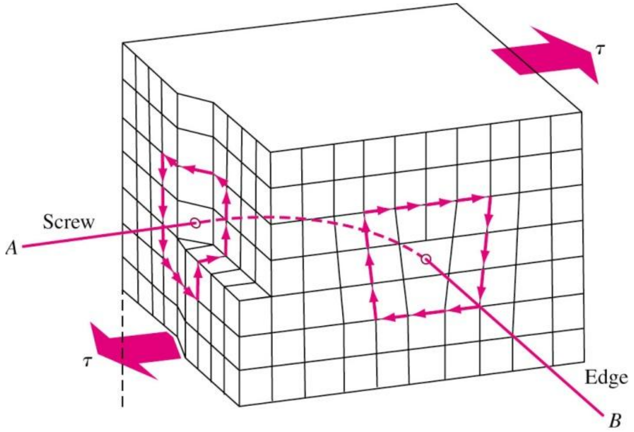
Screw Dislocation

- 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.

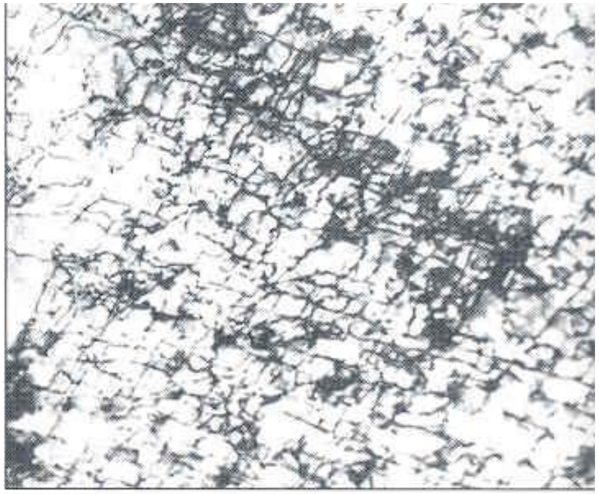


Mixed Dislocation

- 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.



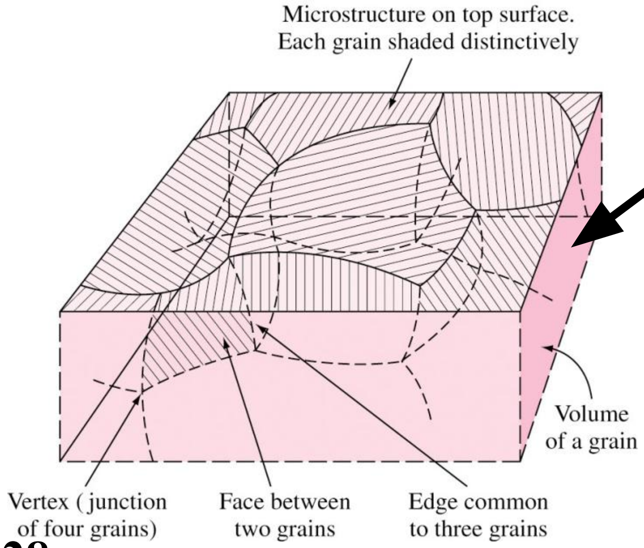
Dislocation structure of iron deformed 14% at -195^0C

Planar Defects

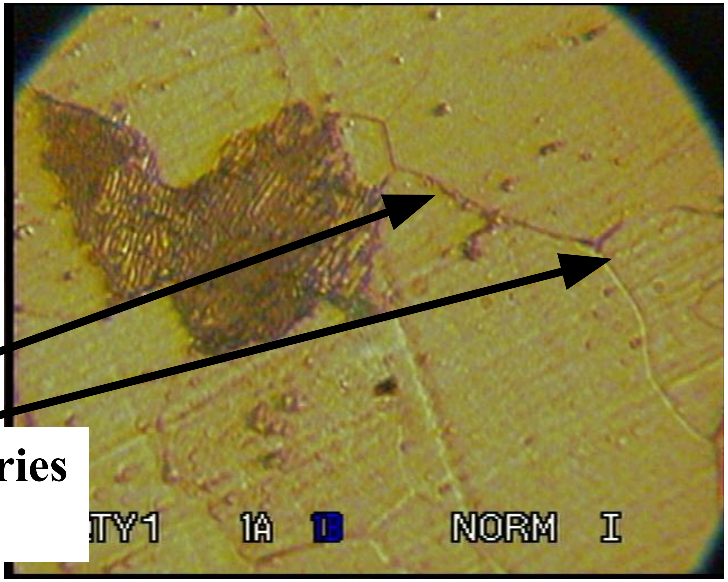
- ***Grain boundaries***, twins, low/high angle boundaries, twists and stacking faults
- Free surface is also a defect : Bonded to atoms on only one side and hence has higher state of energy → Highly reactive
- Nanomaterials have small clusters of atoms and hence are highly reactive.

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.



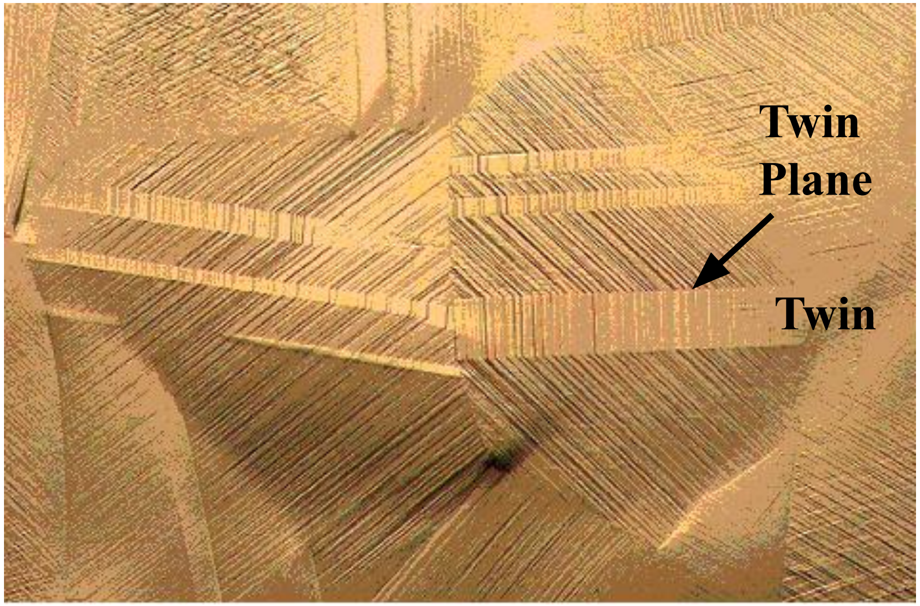
3D view of grains



Grain Boundaries In 1018 steel

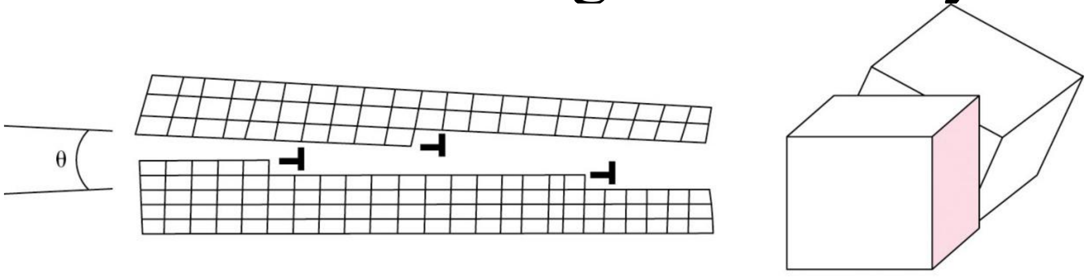
Twin Boundaries

- 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 $< 10^0$



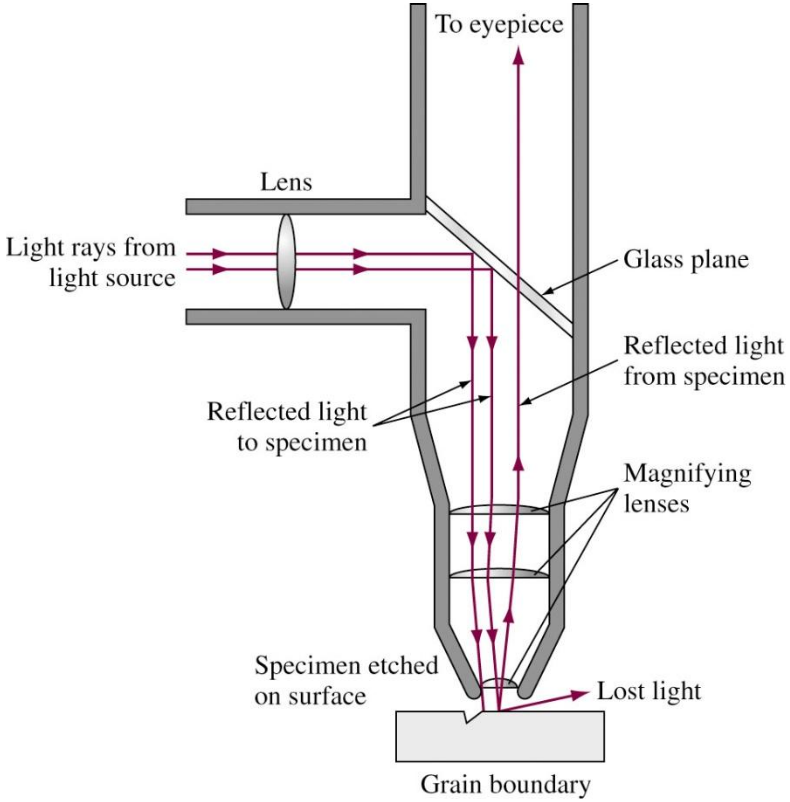
(a) (b)

- **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

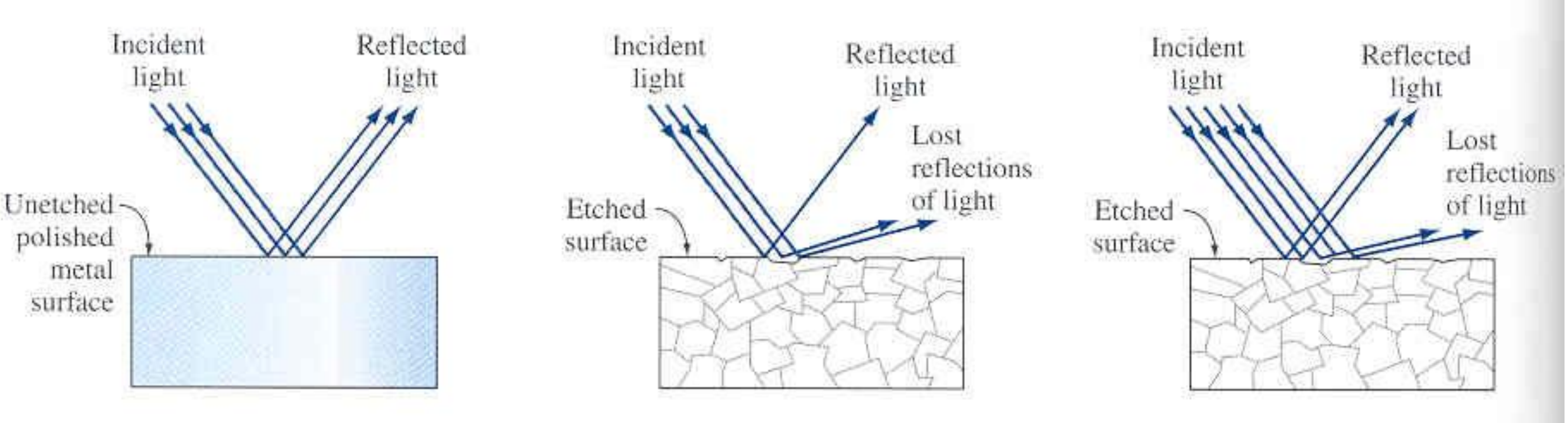
Virtual Lab Modules

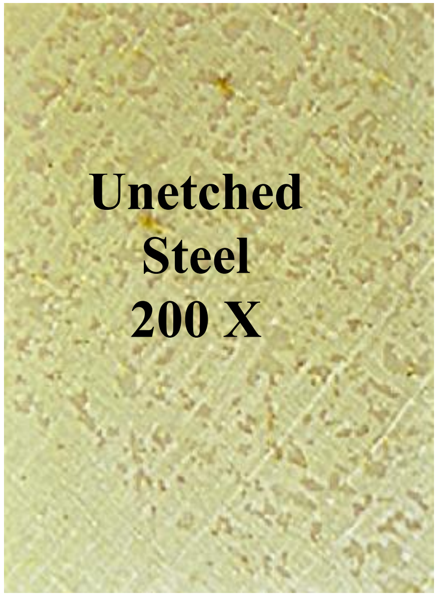
- Click on the following figures to open the virtual lab modules related to polishing the specimen for Metallography.

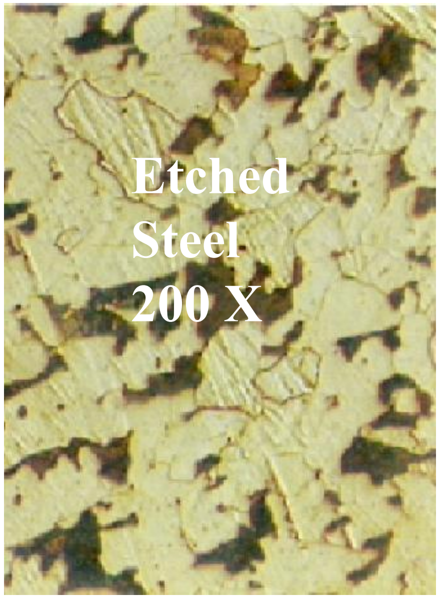
Polishing

1. Turn on the polishing heel
2. Add a small ammount of polishing grit to the wheel
3. Polish sample-90 seconds
4. Turn sample -90 degrees and Polish for 90 seconds

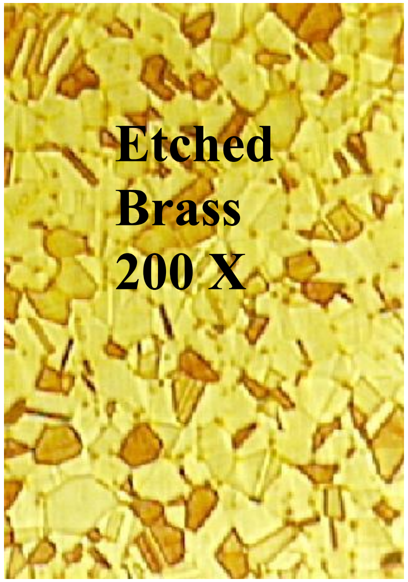
Effect of Etching




Unetched
Steel
200 X

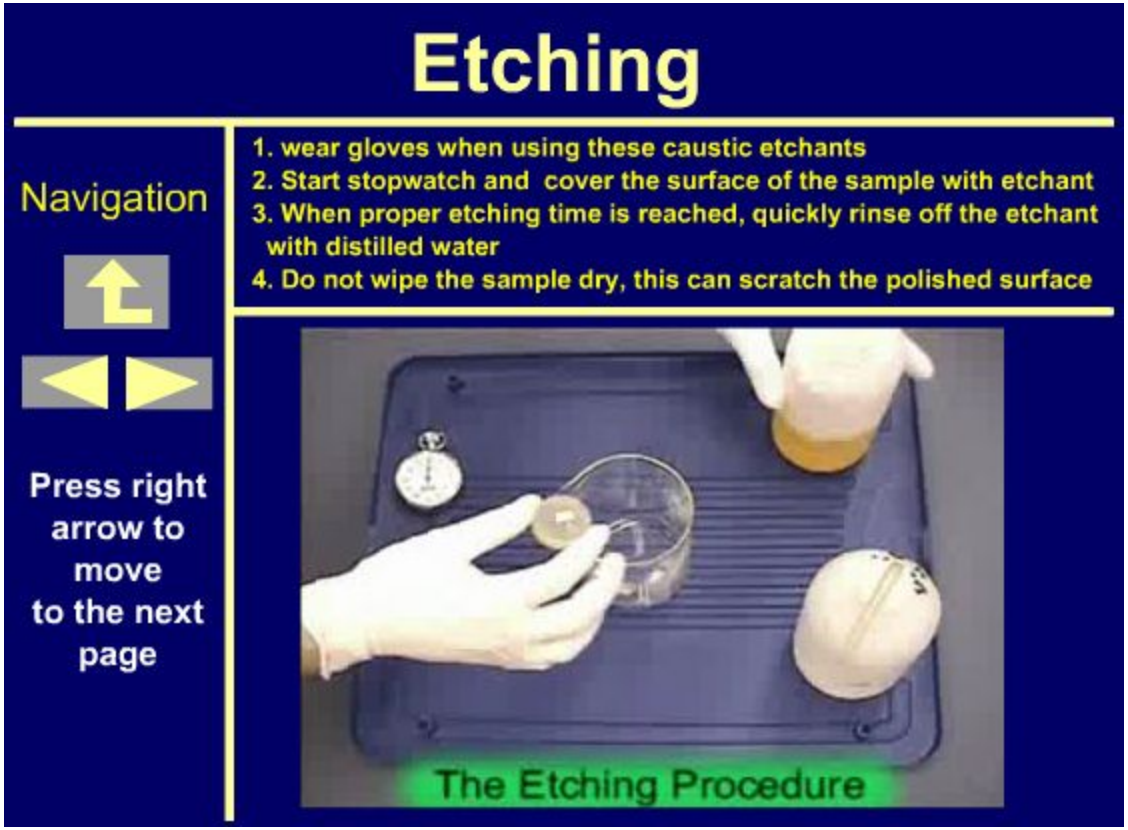

Etched
Steel
200 X


Unetched
Brass
200 X


Etched
Brass
200 X

Virtual Lab Modules

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



Etching

1. wear gloves when using these caustic etchants
2. Start stopwatch and cover the surface of the sample with etchant
3. When proper etching time is reached, quickly rinse off the etchant with distilled water
4. Do not wipe the sample dry, this can scratch the polished surface

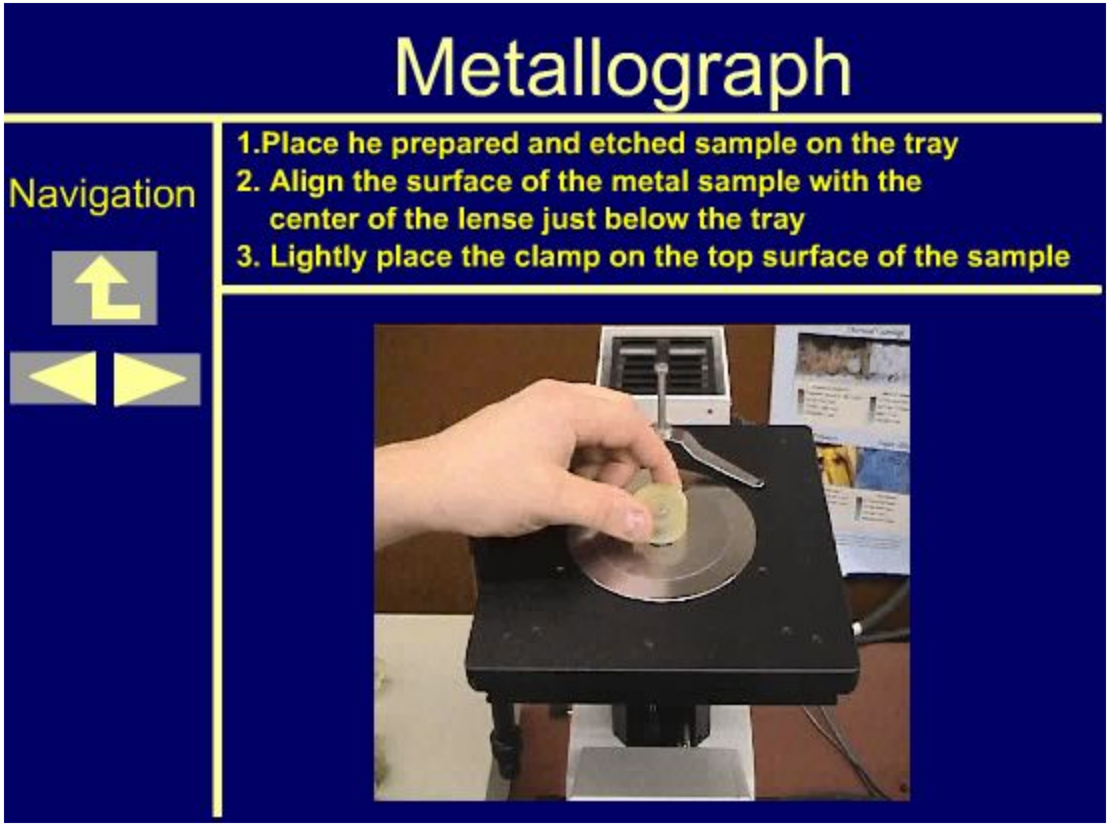
Navigation

Press right arrow to move to the next page

The Etching Procedure

Virtual Lab Modules

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



Metallograph

1.Place he prepared and etched sample on the tray

2. Align the surface of the metal sample with the center of the lense just below the tray

3. Lightly place the clamp on the top surface of the sample

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

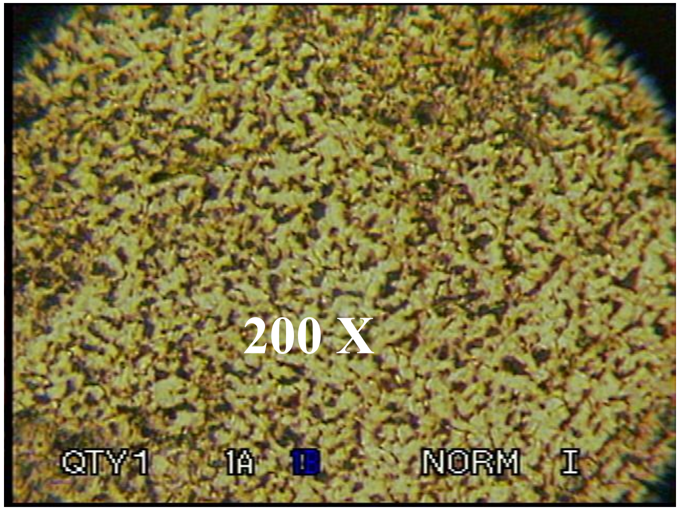
- ASTM grain size number ‘n’ is a measure of grain size.

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

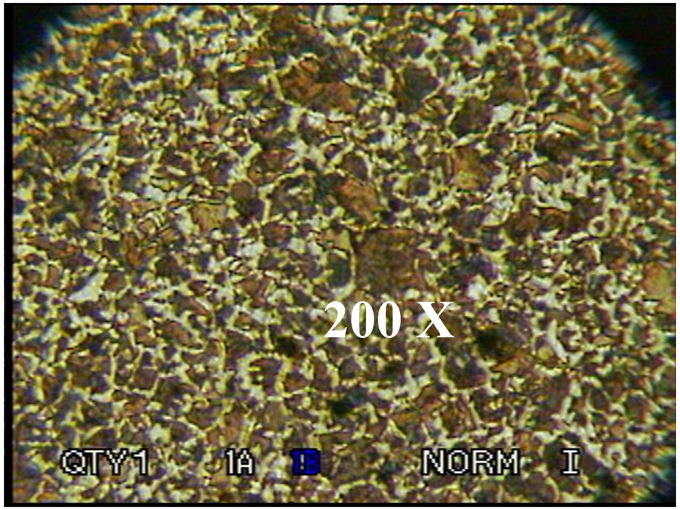
N = Number of grains per square inch of a polished and etched specimen at 100 x.

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.

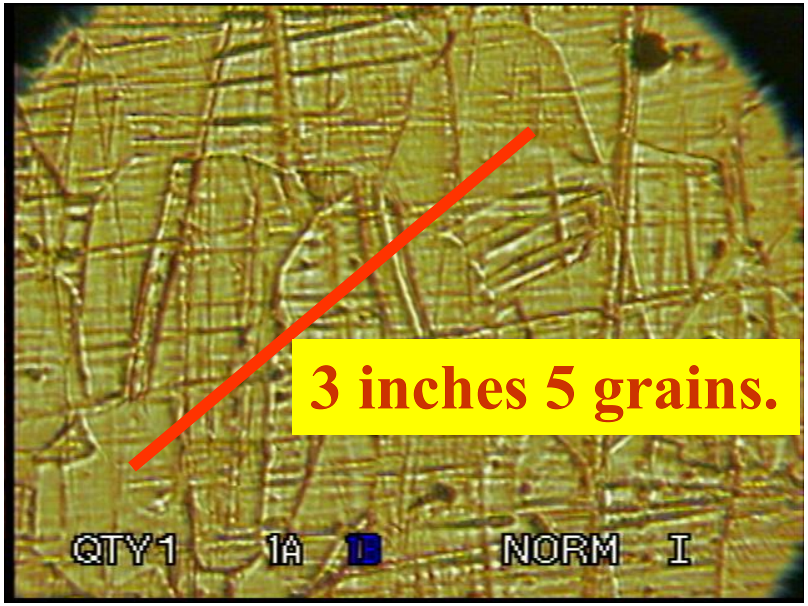

ASTM Grain Size Determination

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.

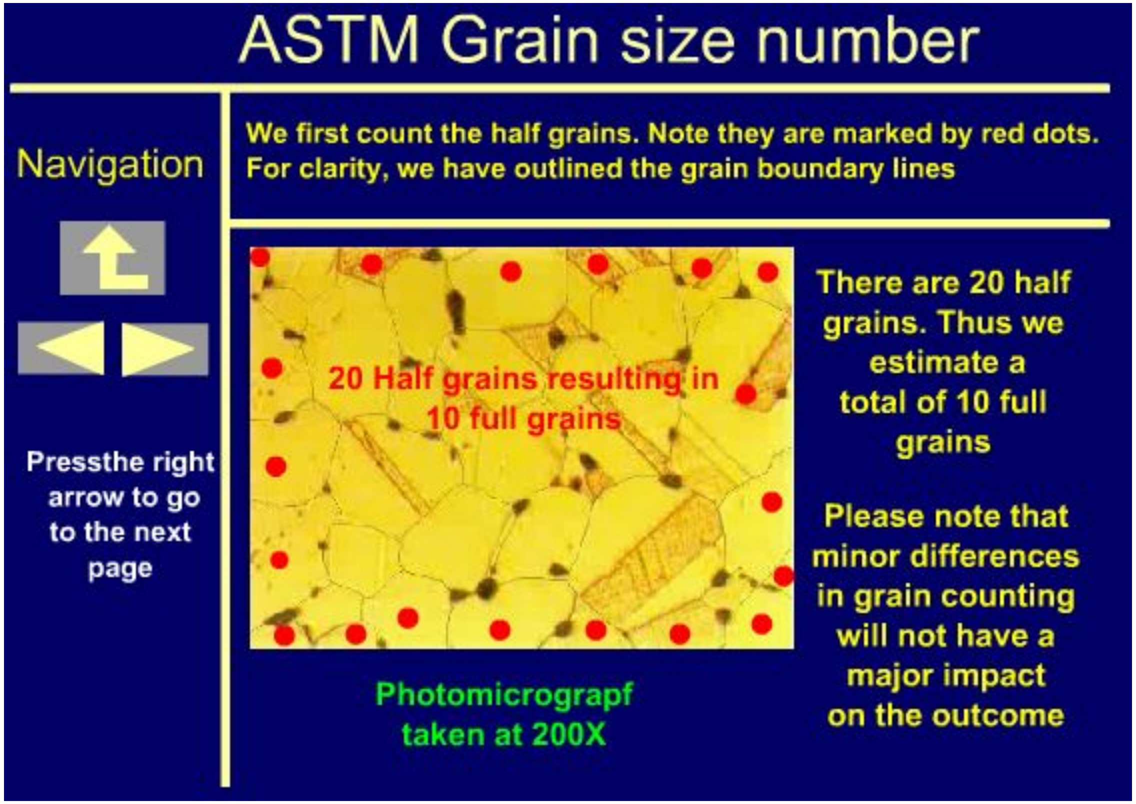
$$d = C/n_L M$$

C=1.5, and M is magnification


3 inches 5 grains.

Virtual Lab Module

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



ASTM Grain size number

We first count the half grains. Note they are marked by red dots. For clarity, we have outlined the grain boundary lines

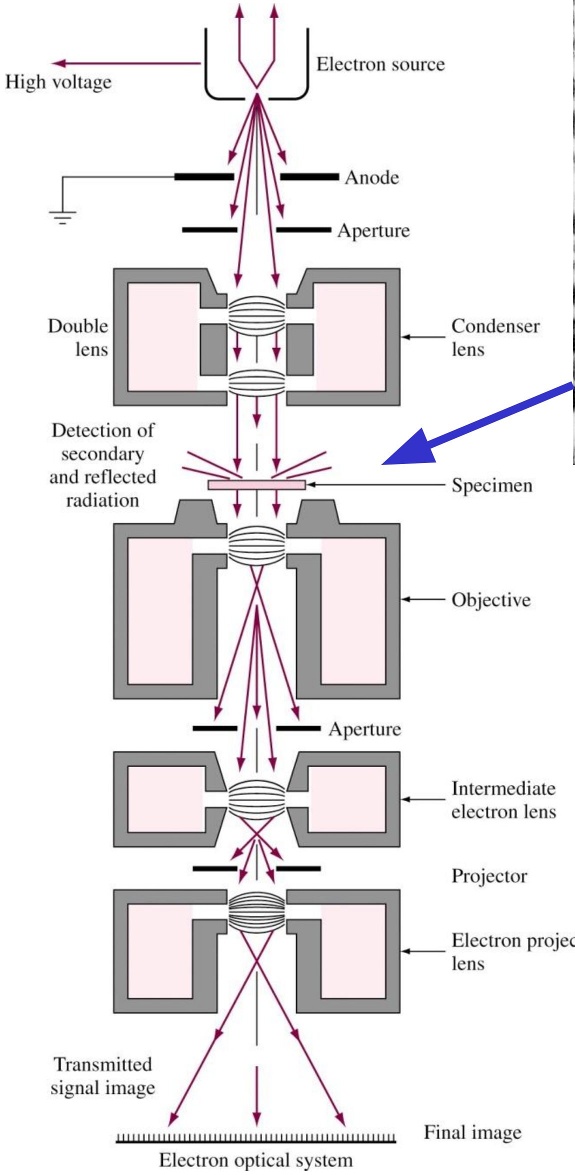
There are 20 half grains. Thus we estimate a total of 10 full grains

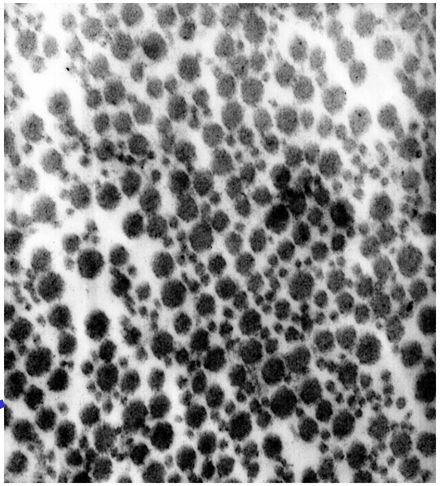
Please note that minor differences in grain counting will not have a major impact on the outcome

Pressthe right arrow to go to the next page

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.

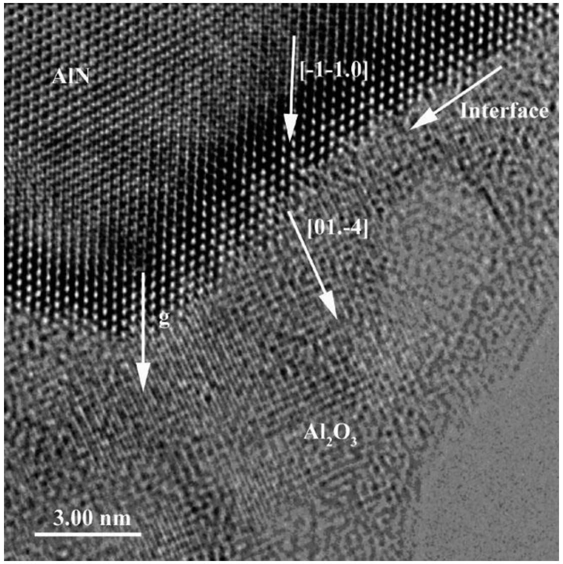




Collagen Fibrils of ligament as seen in TEM

TEM (..Cont)

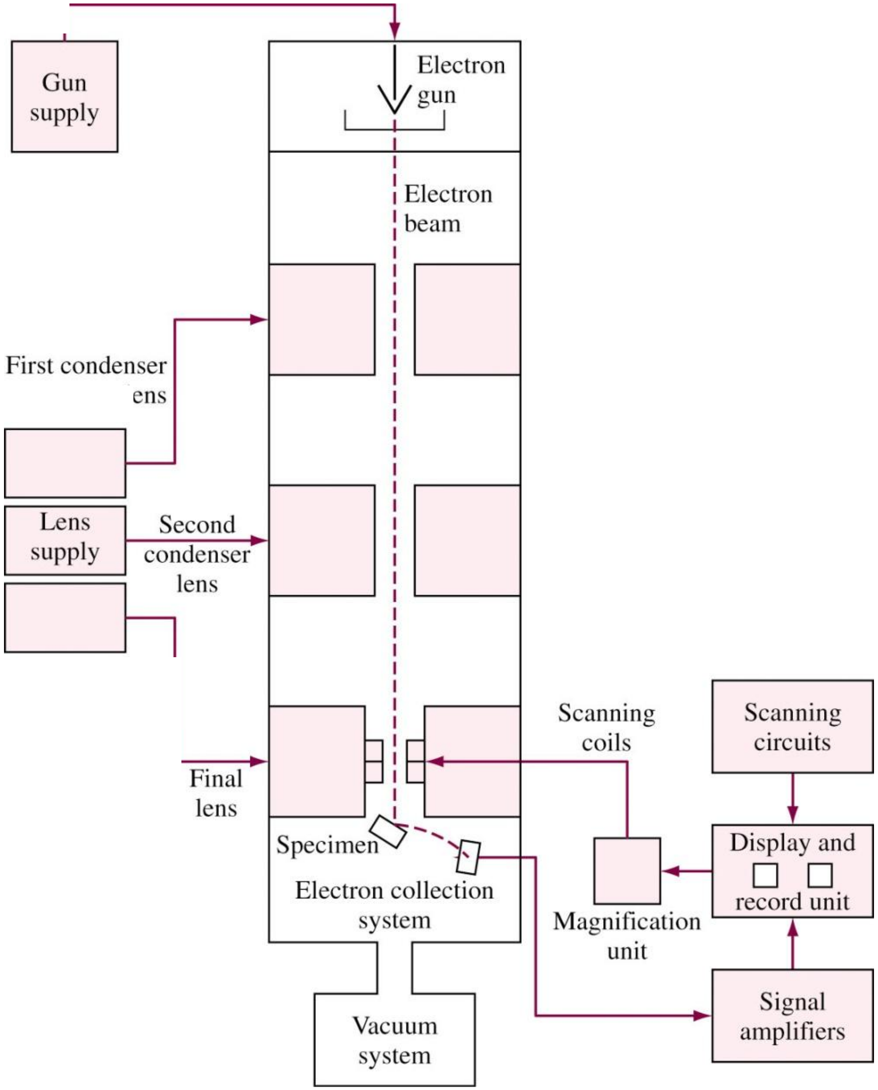
- TEM needs complex sample preparation
- Very thin specimen needed (several hundred nanometers)
- High resolution TEM (HRTEM) allows resolution of 0.1 nm.
- 2-D projections of a crystal with accompanying defects can be observed.

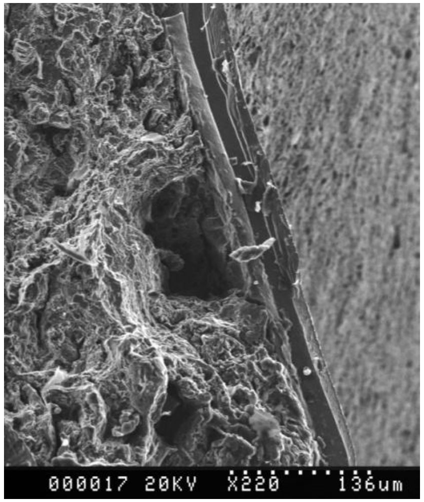


Low angle
boundary
As seen
In HTREM

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.



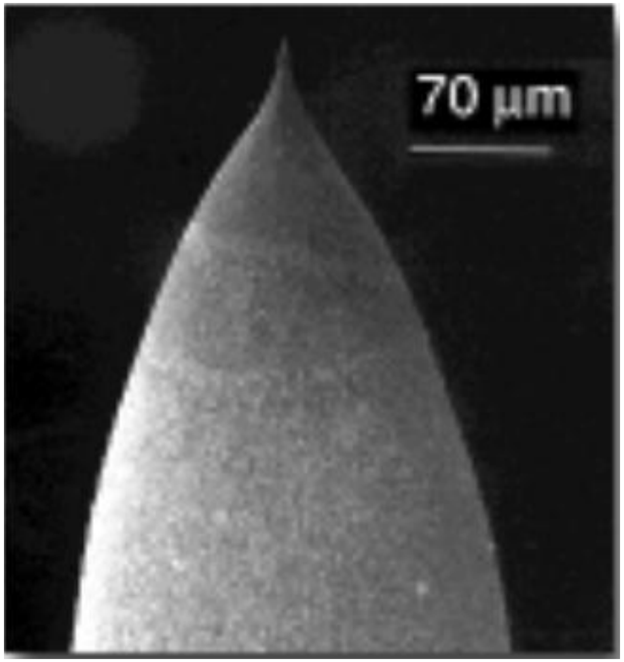


TEM of fractured metal end

Scanning Probe Microscopy

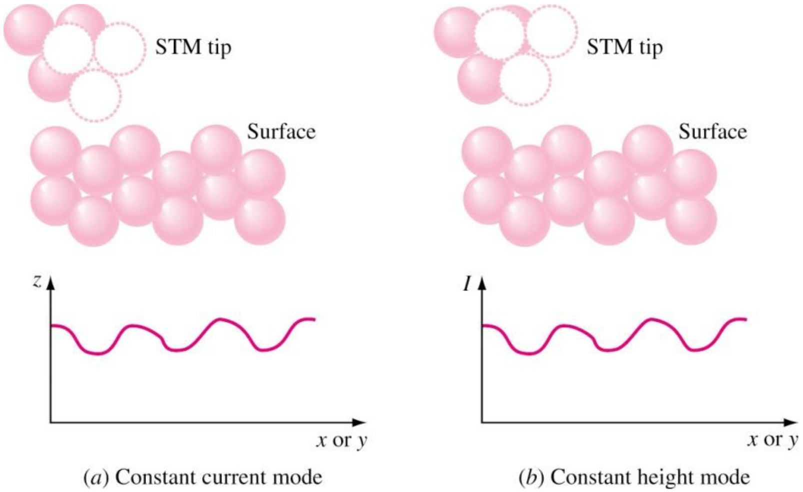
- Scanning Tunneling Microscope (STM) and Atomic Force Microscope (AFM).
- Sub-nanometer magnification.
- Atomic scale topographic map of surface.
- STM uses extremely sharp tip.
- Tungsten, nickel, platinum
  - iridium or carbon nanotubes

  are used for tips.



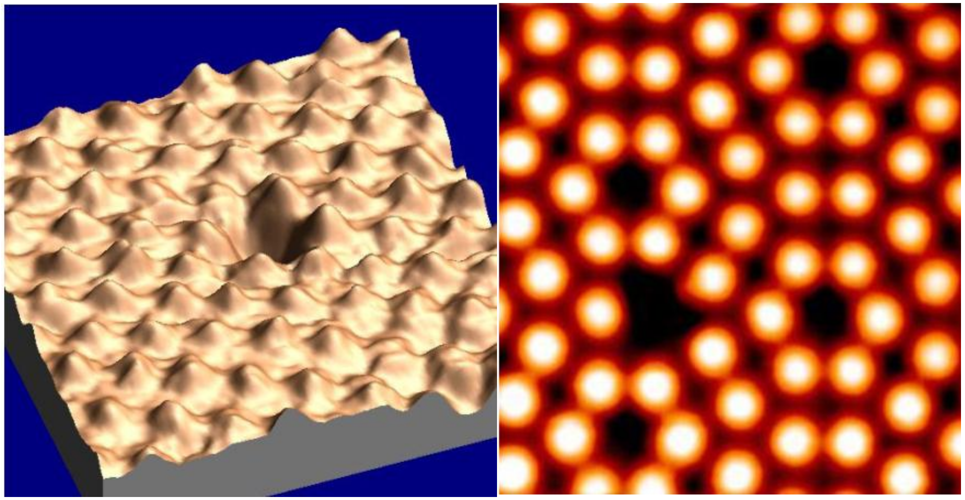
Scanning Tunneling Microscope

- 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.