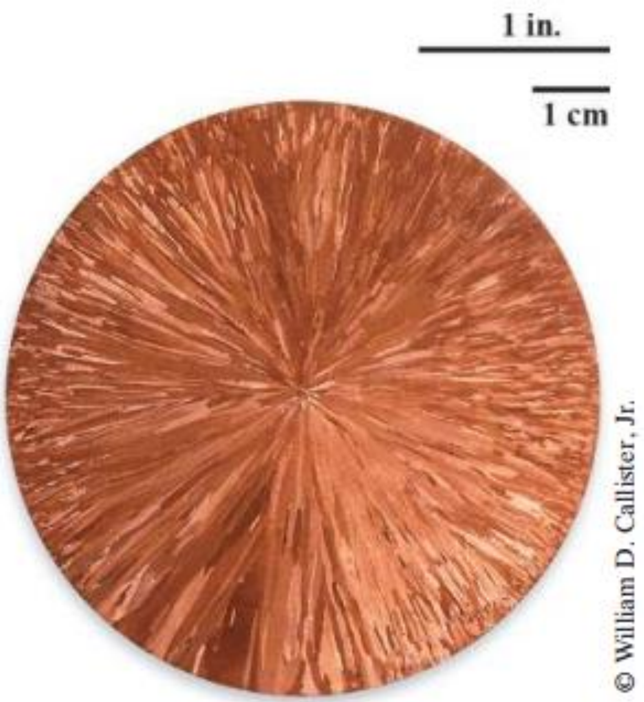
Microscopic Examination

Microstructure

- Many structural elements are large enough to me observed with the unaided eye.
- For others, microscopic investigation is necessary to observe the microstructure.
- Generally microstructure refers to grain size and shape.



- Optical, Electron and Scanning Probe microscopes are commonly used in microscopy.
- Some employ photographic equipment, photograph on which image is recorded is called photomicrograph.
- While others may be computer generated/enhanced.

Why is Microscopic Examination done?

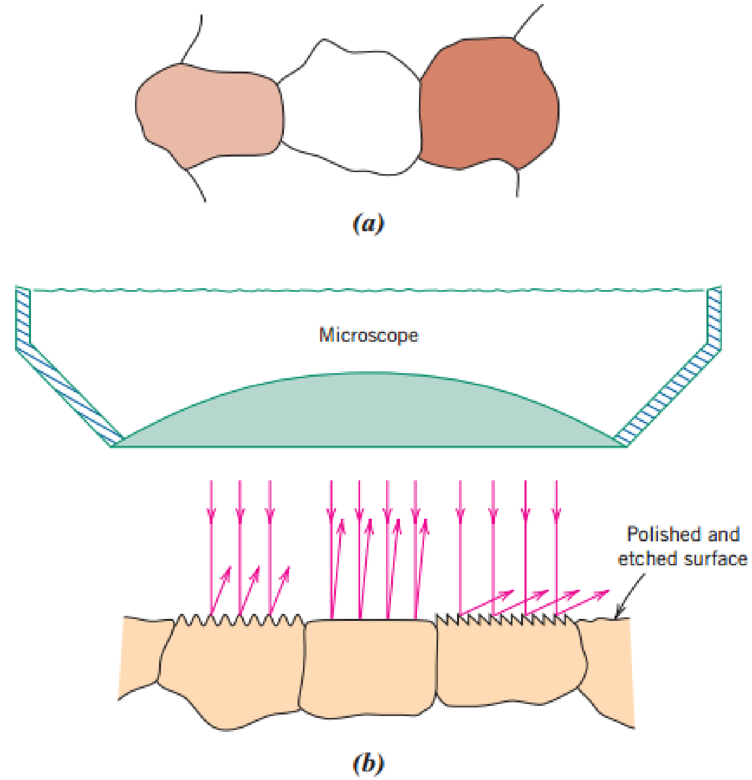
- To ensure the associations between properties and structure (and defects).
- To predict properties of materials.
- To design alloys with new property combinations.
- To ensure that the processing has been done correctly.

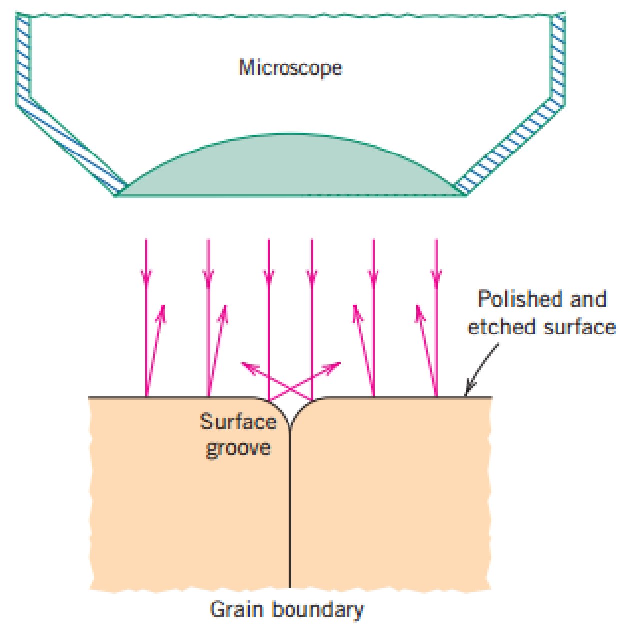
Optical Microscopy

- Optical and illumination systems are basic elements. (approx. 2000x)
- Only surface is observed in opaque specimens.
- Difference in reflectivity produces contrasts in different regions of the image.

Surface preparation

- Surface must be ground and polished.
- Etching is done to reveal the microstructure.
- Grain boundaries are seen as dark lines.
- For alloys, etchant is chosen to produce different texture for the constituents.





Electron Microscopy

- Beam of electrons is used.
- Higher magnification is achieved due to short wavelength (0.003 nm) of electron beams.
- Both transmission and reflection beam modes are possible.

Transmission Electron Microscopy

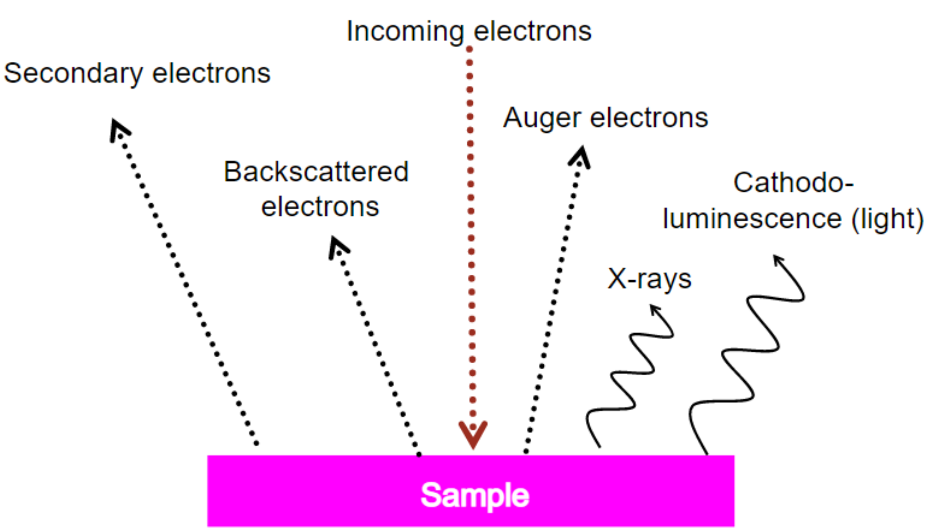
- Electron beam passes through the thin specimen.
- Internal microstructure can be observed.
- Contrast is a result in difference in beam scattering or diffraction.
- Beam is projected on a fluorescent screen to view the image (1,000,000x).

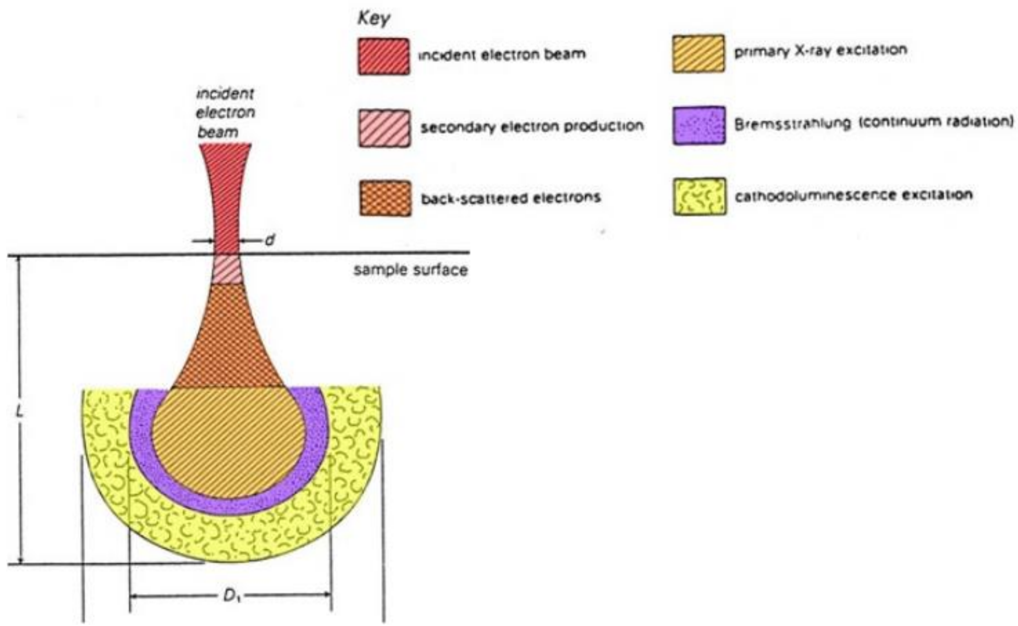
Electron Microscopy

Scanning Electron Microscopy

- Surface of specimen is scanned with an electron beam.
- The reflected beam of electrons is collected and displayed on a cathode ray tube.
- Surface may or may not be polished but should be electrically conductive.
- On non-conducting materials a very thin metallic surface coating is applied.

Signals from the sample



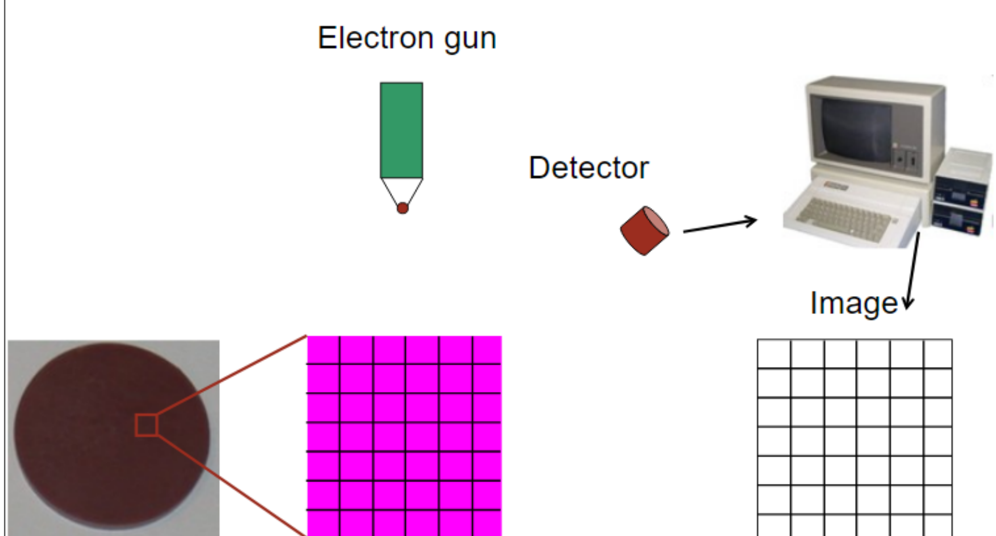


Electron Microscopy

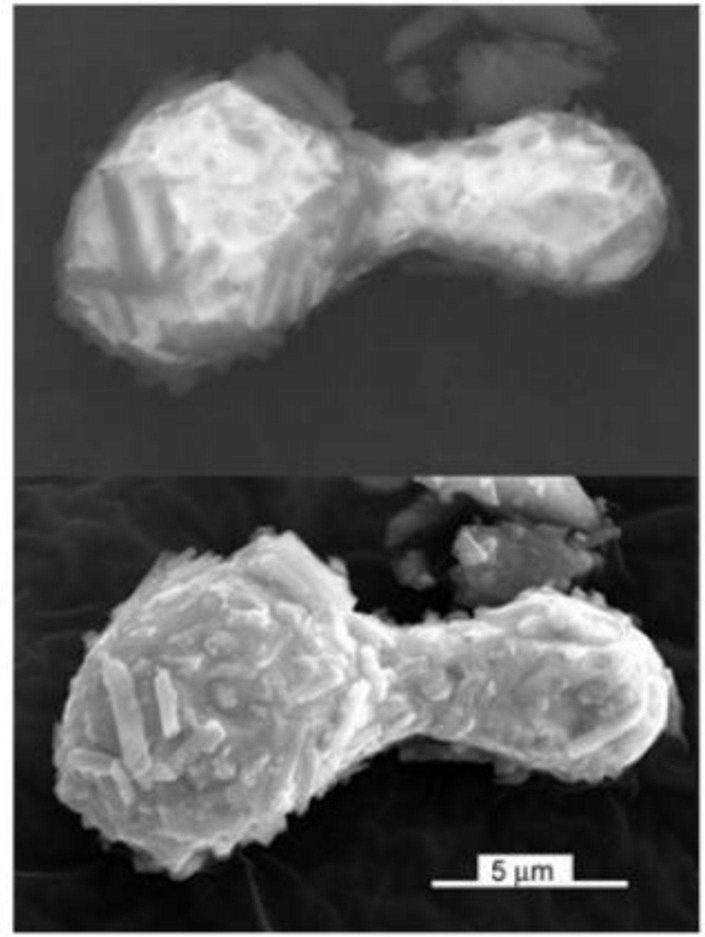
Scanning Electron Microscopy

- Best resolution obtained is the size of electron beam on the specimen.
- SE image has a higher resolution than BSE image.
- X-rays (photons) have poorer resolution.

How do we get an image?

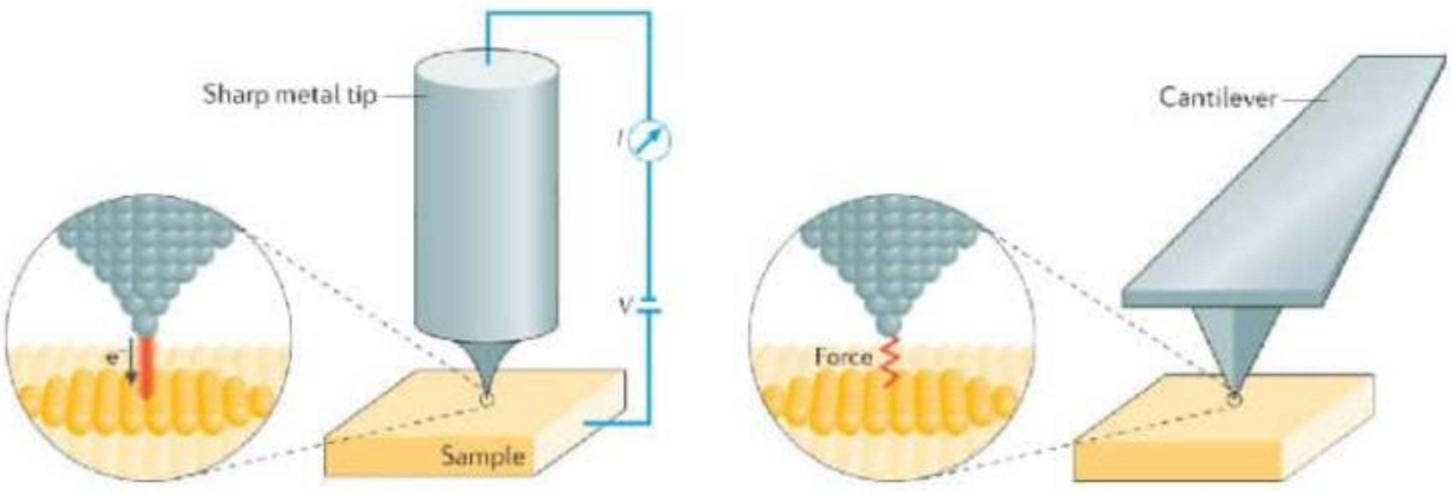


BSE vs SE

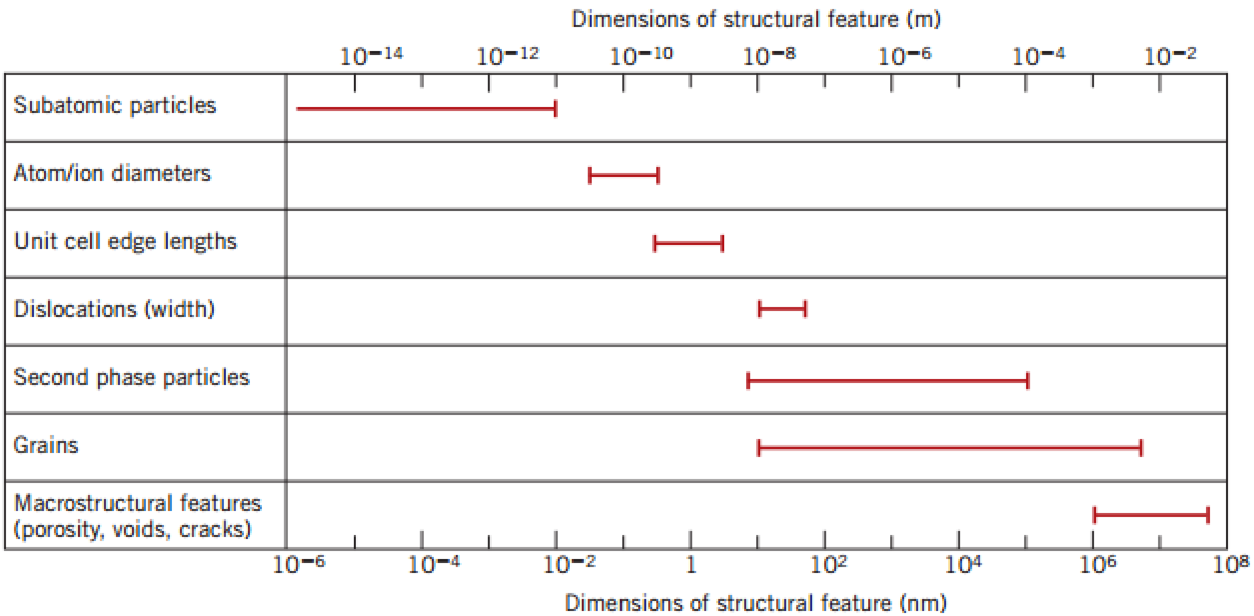


Scanning Probe Microscopy

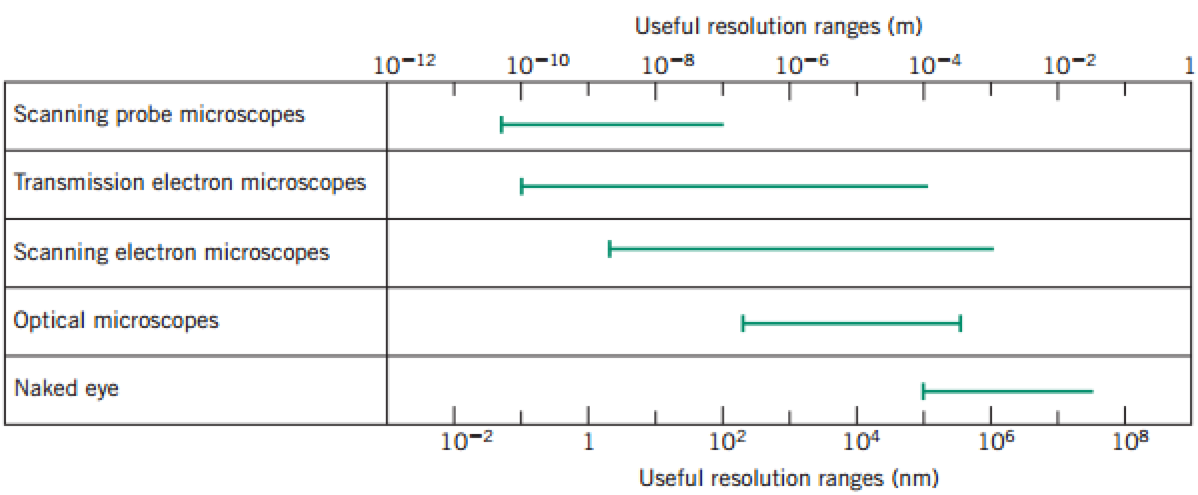
- Neither light nor electrons are used.
- Generates a topological map, on an atomic scale.
- Much better resolution and magnification up to 10^9x is possible.
- 3D images are generated, can be used in vacuum, air, liquid.
- Tiny probe having nanometer resolution is used.
- Probe movements are monitored and used to generate an image.
- Helped a lot in development of nanomaterials.



Microscopy



(a)

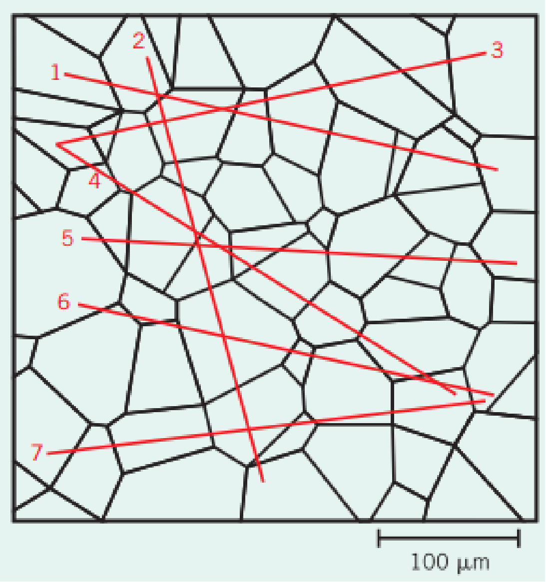


Grain Size Determination

- Grain size are determined to know about the properties of the polycrystalline and single-crystal materials.
- Grains have varying shape and size so mean grain diameter is used.
- Two methods:

1. Linear intercept

Step 1:



Step 2:

Line Number	Number of Grain-Boundary Intersections
1	8
2	8
3	8
4	9
5	9
6	9
7	7
Total	58

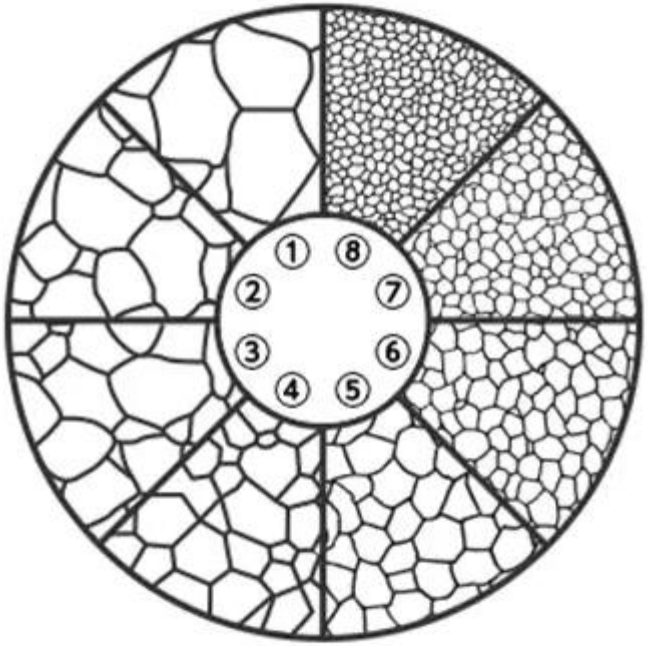
Step 3: $\bar{l} = \frac{L_T}{PM}$

where
$\bar{l}$ = mean intercept length (measure of grain diameter)
L_T = Total length of all lines
P = total no. of intersections
M = magnification

Grain Size Determination

2. Comparison

- Compare photomicrograph at 100x magnification with ASTM comparison charts and find the suitable grain size number.



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

For 100x magnification

$$n_M\left(\frac{M}{100}\right)^2 = 2^{G-1}$$

For other magnification

where
G is grain-size number
n is avg. no. of grains per square inch at 100x magnification
n_M is avg. no. of grains per square inch at magnification M

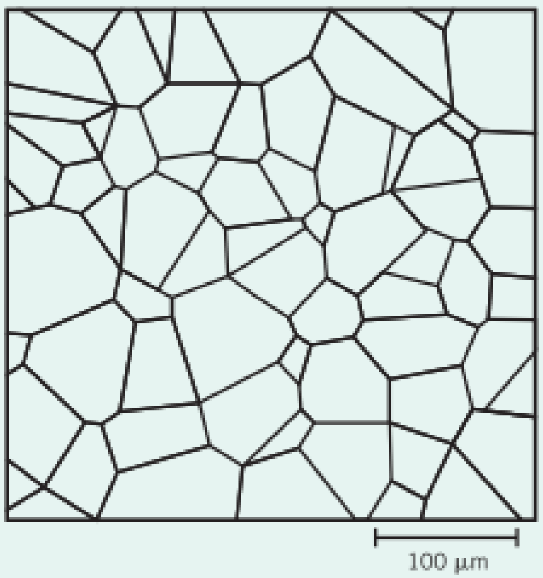
Relationship between grain-size number and mean intercept length

$$G = -6.6457 log \bar{l} - 3.298$$

for $\bar{l}$ in mm

Problem

1. Determine the following if length of scale bar is 16 mm and length of each line is 50 mm
   a) Mean intercept length
   b) ASTM grain-size number

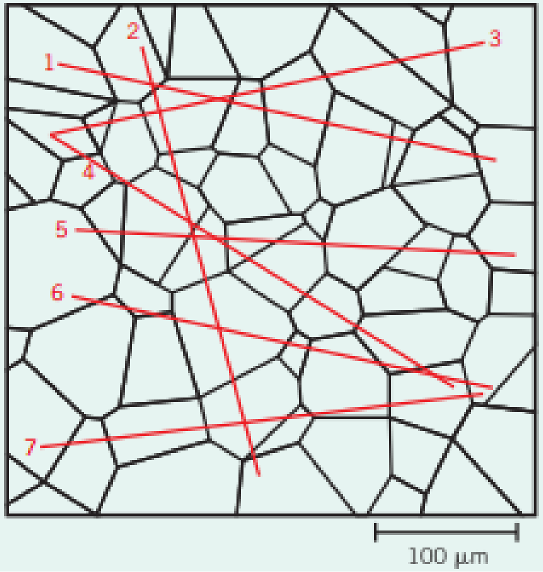


Find Magnification

$$M = \frac{16{,}000\ \mu m}{100\ \mu m} = 160\times$$

Total Line Length

$$(7\ \text{lines})(50\ \text{mm/line}) = 350\ \text{mm}$$



Mean intercept Length

$$\bar{\ell} = \frac{L_T}{PM}$$

$$= \frac{350\ \text{mm}}{(58\ \text{grain boundary intersections})(160\times)} = 0.0377\ \text{mm}$$

CHAPTER 4:
Defects in Solids

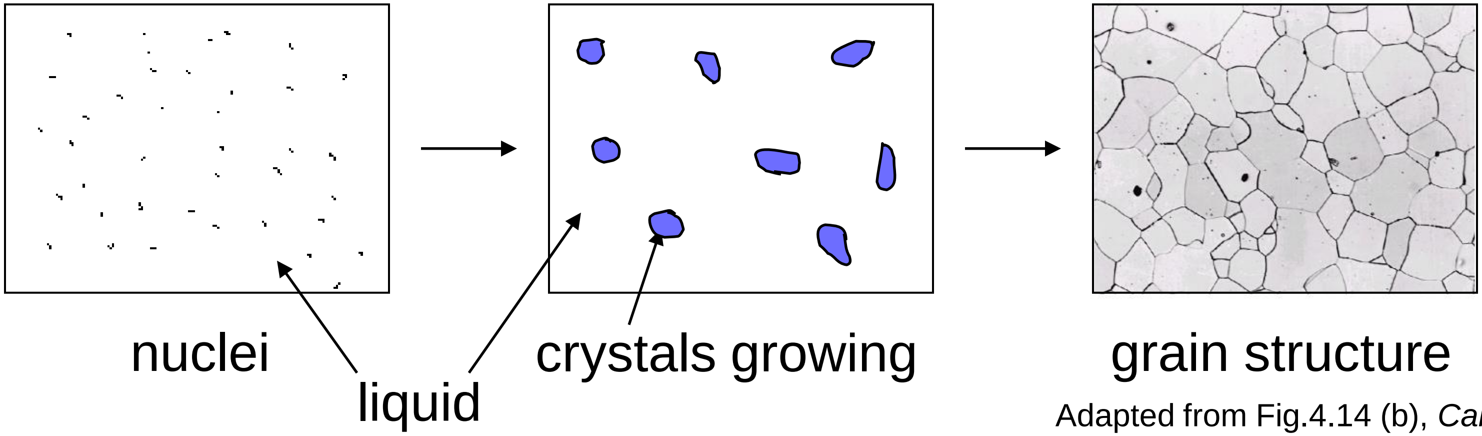
CHAPTER 4: Defects in Solids

ISSUES TO ADDRESS...

- What are the solidification mechanisms?
- What types of defects arise in solids?
- Can the number and type of defects be varied and controlled?
- How do defects affect material properties?
- Are defects undesirable?

Imperfections in Solids

- Solidification- result of casting of molten material
  - 2 steps
    - Nuclei form
    - Nuclei grow to form crystals – grain structure
- Start with a molten material – all liquid



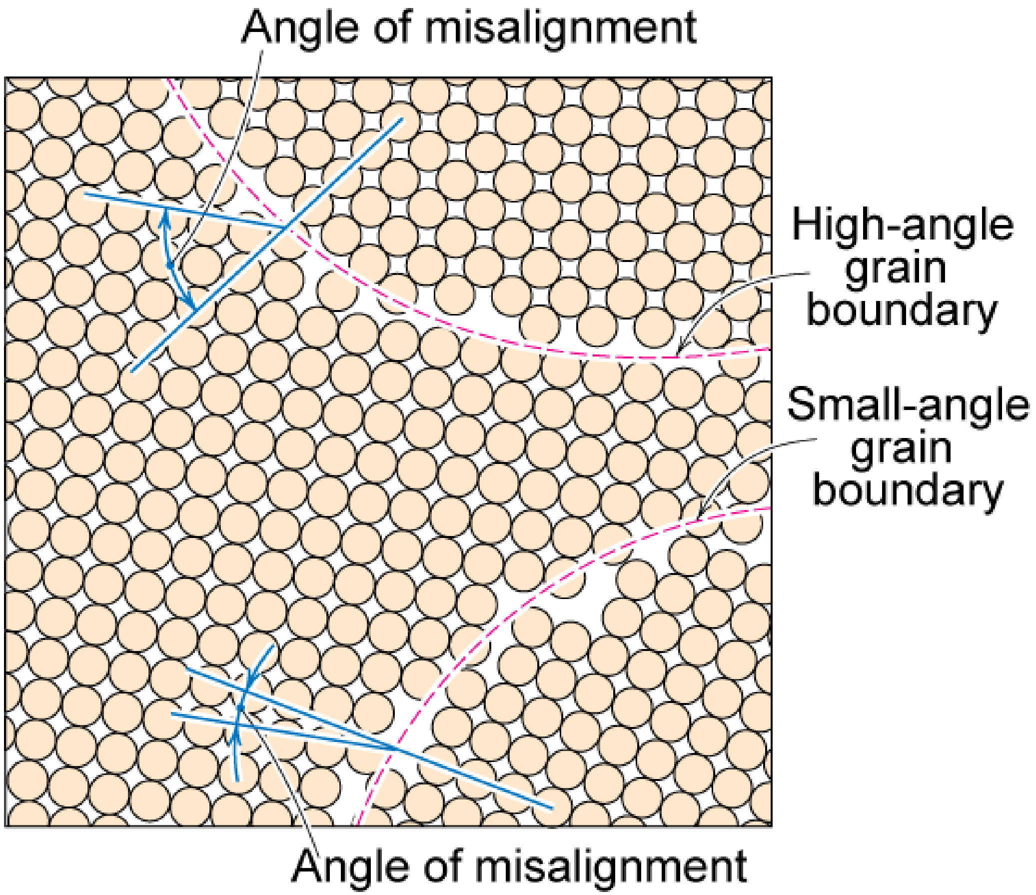
Adapted from Fig.4.14 (b), *Callister 7e.*

- Crystals grow until they meet each other

Polycrystalline Materials

Grain Boundaries

- regions between crystals
- transition from lattice of one region to that of the other
- slightly disordered
- low density in grain boundaries
  - high mobility
  - high diffusivity
  - high chemical reactivity

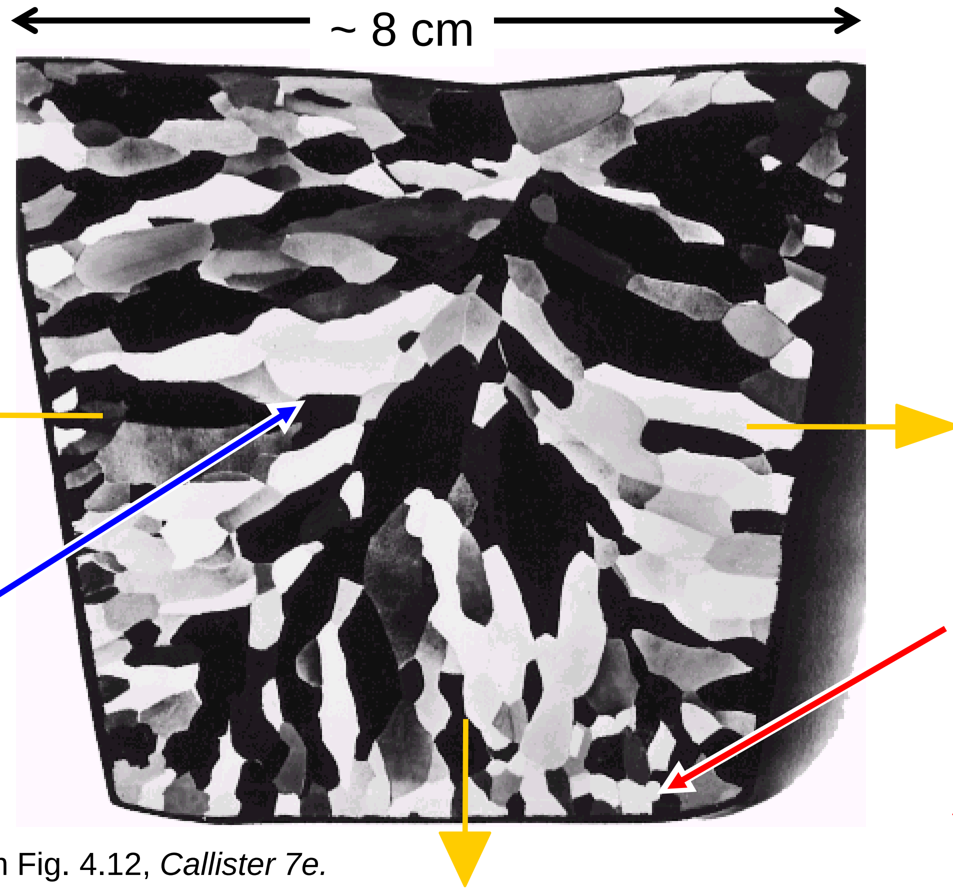


Adapted from Fig. 4.7, *Callister 7e.*

Solidification

Grains can be - equiaxed (roughly same size in all directions)

- columnar (elongated grains)



Adapted from Fig. 4.12, *Callister 7e.*

Grain Refiner - added to make smaller, more uniform, equiaxed grains.

Imperfections in Solids

There is no such thing as a perfect crystal.

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

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

Types of Imperfections

- Vacancy atoms
- Interstitial atoms
- Substitutional atoms

Point defects

- Dislocations

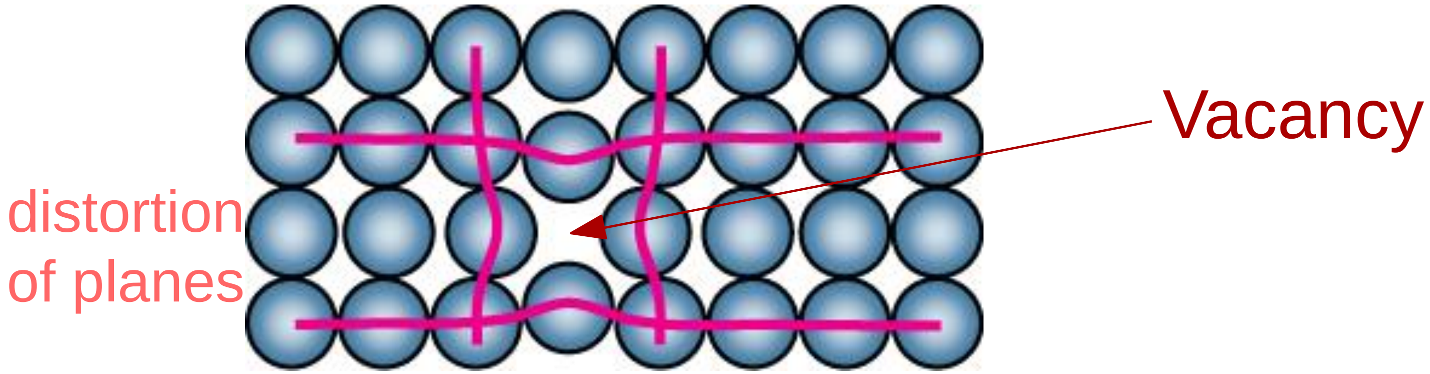
Line defects

- Grain Boundaries

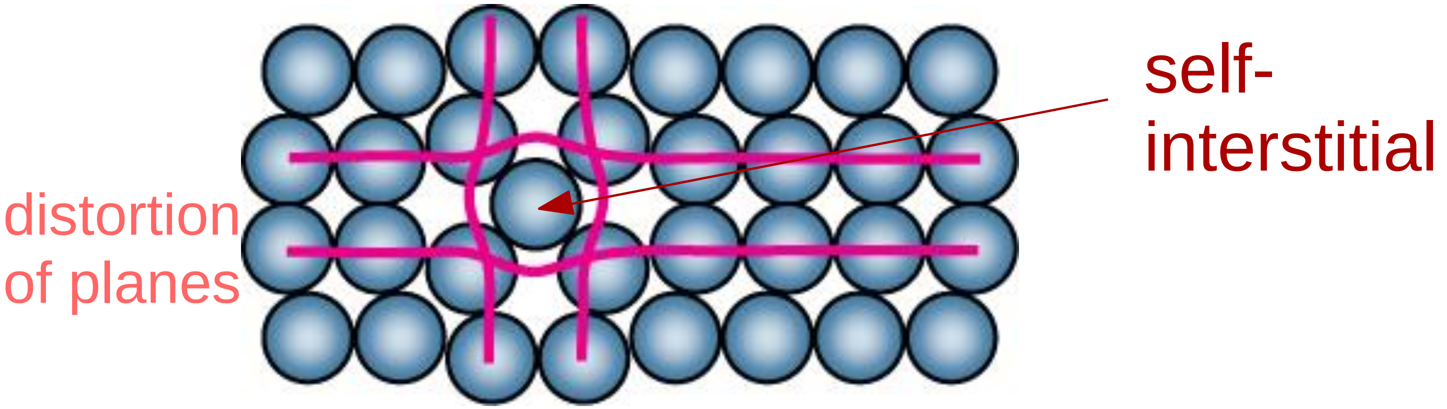
Area defects

Point Defects

- Vacancies:
  -vacant atomic sites in a structure.



- Self-Interstitials:
  -"extra" atoms positioned between atomic sites.



Equilibrium Concentration: Point Defects

- Equilibrium concentration varies with temperature!

No. of defects

Activation energy

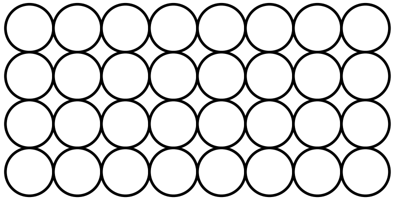
No. of potential defect sites.

$$\frac{N_v}{N} = \exp\left(\frac{-Q_v}{kT}\right)$$

Temperature

Boltzmann's constant

(1.38 x 10 $^{-23}$ J/atom-K)



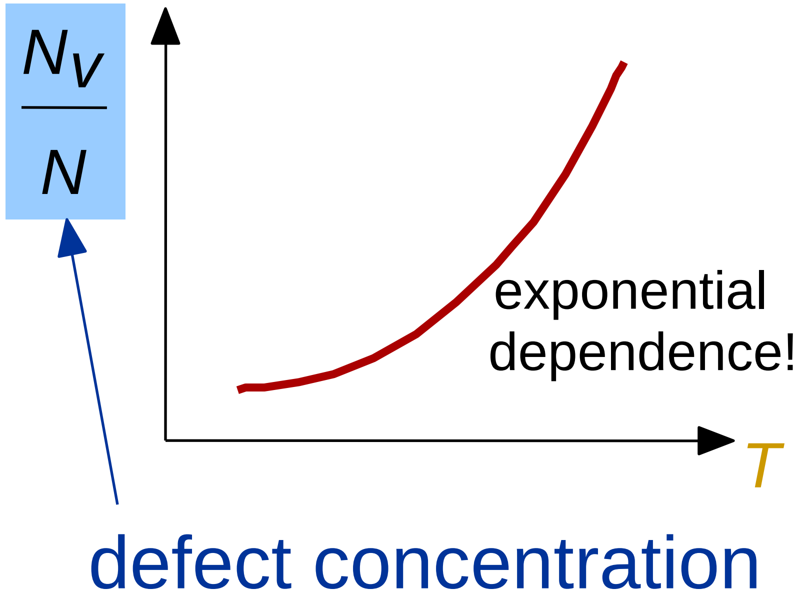
Each lattice site is a potential vacancy site

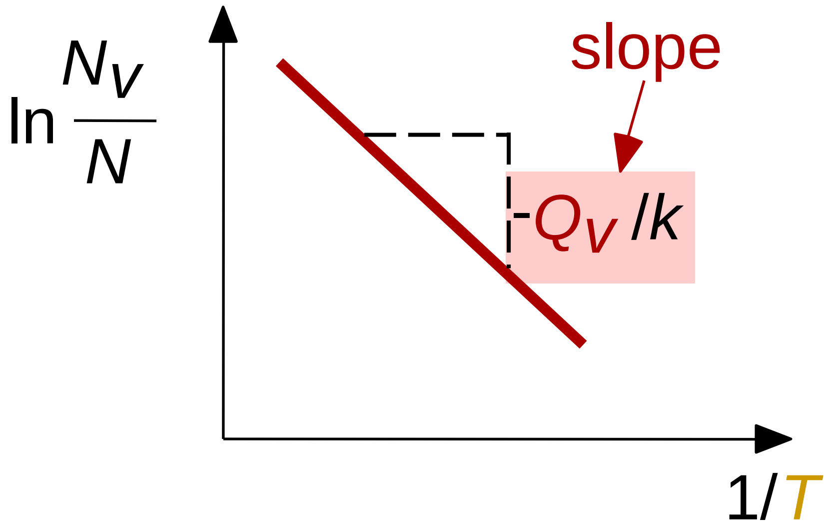
Measuring Activation Energy

- We can get Q_v from an experiment.

$$\frac{N_v}{N} = \exp\left(\frac{-Q_v}{kT}\right)$$

- Measure this...
- Replot it...





Estimating Vacancy Concentration

- Find the equil. # of vacancies in 1 m^3 of Cu at 1000°C.
- Given:

$$\rho = 8.4 \text{ g/cm}^3 \qquad A_{Cu} = 63.5 \text{ g/mol}$$

$$Q_V = 0.9 \text{ eV/atom} \qquad N_A = 6.02 \times 10^{23} \text{ atoms/mol}$$

$$\frac{N_V}{N} = \exp\left(\frac{-\overset{0.9 \text{ eV/atom}}{Q_V}}{\underset{8.62 \times 10^{-5}\ \text{eV/atom-K}}{k}\ \underset{1273\text{K}}{T}}\right) = 2.7 \times 10^{-4}$$

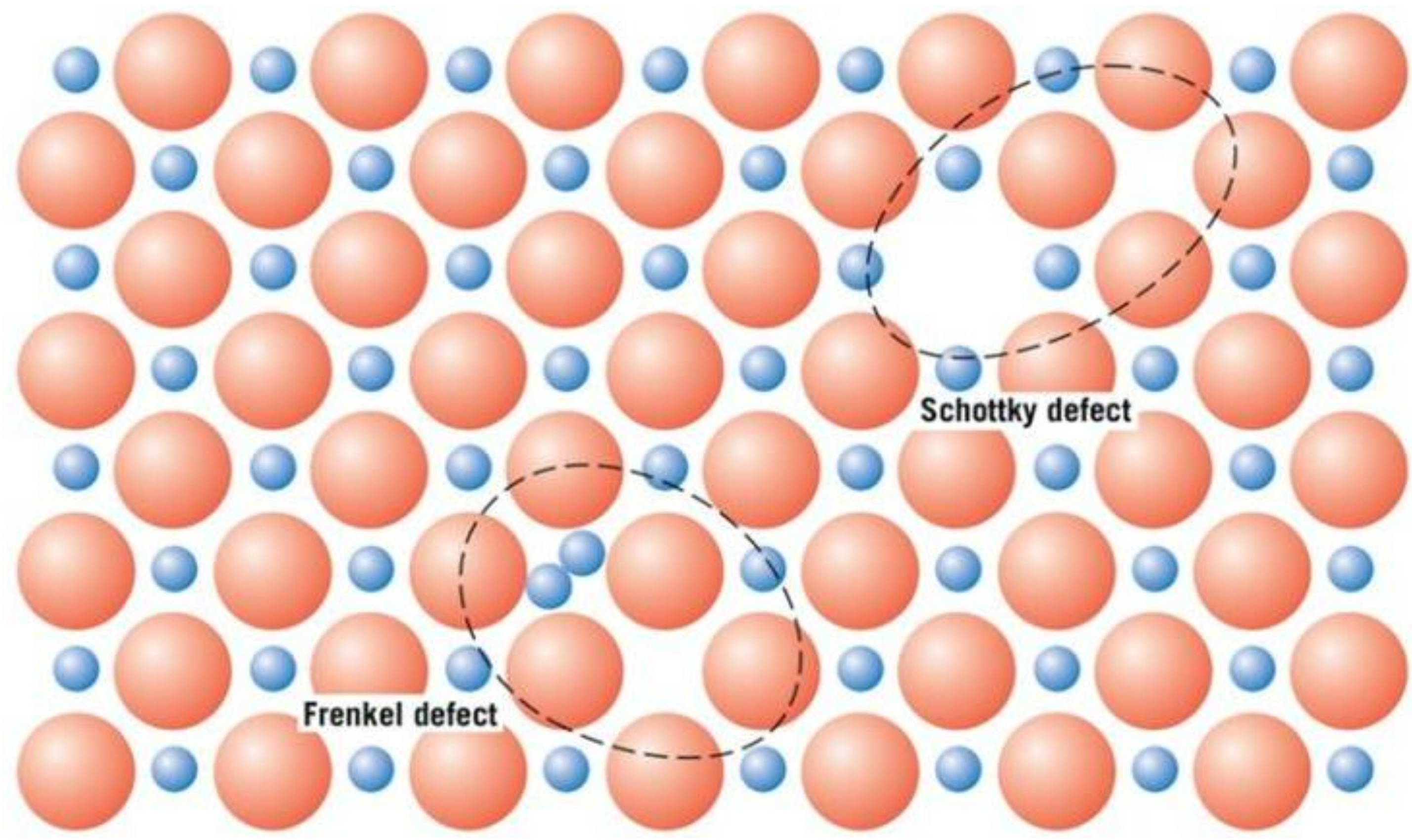
For 1 m^3, $N = \rho \times \dfrac{N_A}{A_{Cu}} \times 1 \text{ m}^3 = 8.0 \times 10^{28}$ sites

- Answer:

$N_V = (2.7 \times 10^{-4})(8.0 \times 10^{28})$ sites $= 2.2 \times 10^{25}$ vacancies

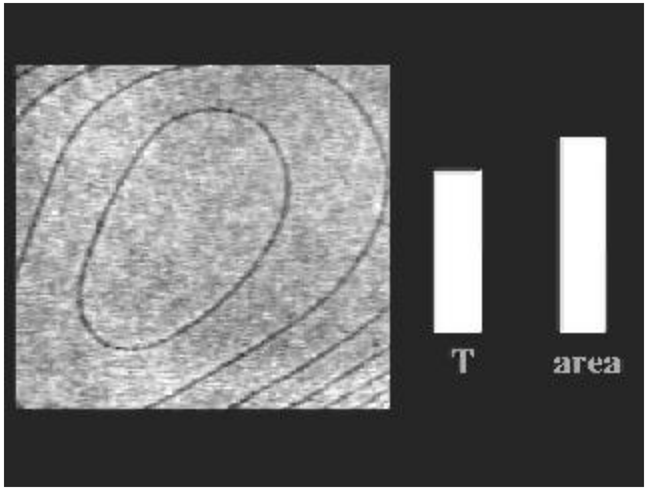
Point Defects

- Frenkel defect:
  -cation vacancy and cation interstitial pair.
- Schottky defect:
  -cation vacancy and anion vacancy pair.



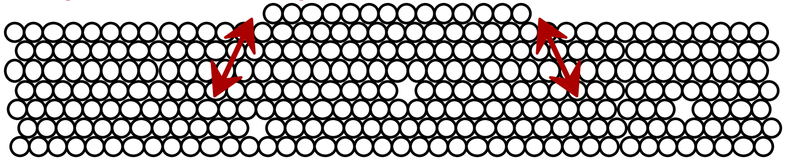
Observing Equilibrium Vacancy Conc.

- Low energy electron microscope view of a (110) surface of NiAl.
- Increasing *T* causes surface island of atoms to grow.
- Why? The equil. vacancy conc. increases via atom motion from the crystal to the surface, where they join the island.



Reprinted with permission from Nature (K.F. McCarty, J.A. Nobel, and N.C. Bartelt, "Vacancies in Solids and the Stability of Surface Morphology", Nature, Vol. 412, pp. 622-625 (2001). Image is 5.75 μm by 5.75 μm.) Copyright (2001) Macmillan Publishers, Ltd.

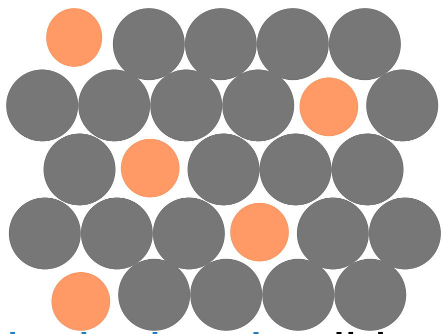
Island grows/shrinks to maintain equil. vancancy conc. in the bulk.



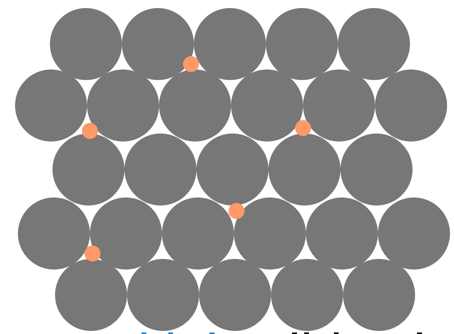
Point Defects in Alloys

Two outcomes if impurity (B) added to host (A):

- Solid solution of B in A (i.e., random dist. of point defects)



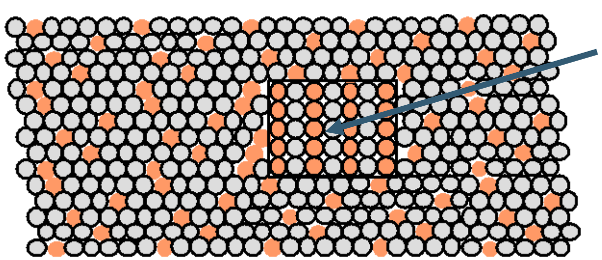
OR



Substitutional solid soln.
(e.g., Cu in Ni)

Interstitial solid soln.
(e.g., C in Fe)

- Solid solution of B in A plus particles of a new phase (usually for a larger amount of B)



Second phase particle
--different composition
--often different structure.

Imperfections in Solids

Conditions for substitutional solid solution (S.S.)

- W. Hume – Rothery rule
  - 1. Δr (atomic radius) < 15%
  - 2. Proximity in periodic table
    - i.e., similar electronegativities
  - 3. Same crystal structure for pure metals
  - 4. Valency
    - All else being equal, a metal will have a greater tendency to dissolve a metal of higher valency than one of lower valency

Imperfections in Solids

Application of Hume–Rothery rules – Solid Solutions

1. Would you predict more Al or Ag to dissolve in Zn?

2. More Zn or Al in Cu?

Element	*Atomic Radius (nm)*	*Crystal Structure*	*Electro-nega-tivity*	*Valence*
Cu	0.1278	FCC	1.9	+2
C	0.071			
H	0.046			
O	0.060			
Ag	0.1445	FCC	1.9	+1
Al	0.1431	FCC	1.5	+3
Co	0.1253	HCP	1.8	+2
Cr	0.1249	BCC	1.6	+3
Fe	0.1241	BCC	1.8	+2
Ni	0.1246	FCC	1.8	+2
Pd	0.1376	FCC	2.2	+2
Zn	0.1332	HCP	1.6	+2

Table on p. 106, *Callister 7e.*

Imperfections in Solids

- Specification of composition

  - weight percent

$$C_1 = \frac{m_1}{m_1 + m_2} \text{ x } 100$$

m_1 = mass of component 1

  – atom percent

$$C_1' = \frac{n_{m1}}{n_{m1} + n_{m2}} \text{ x } 100$$

n_{m1} = number of moles of component 1

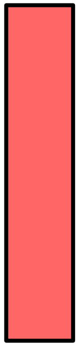
Line Defects

Dislocations:

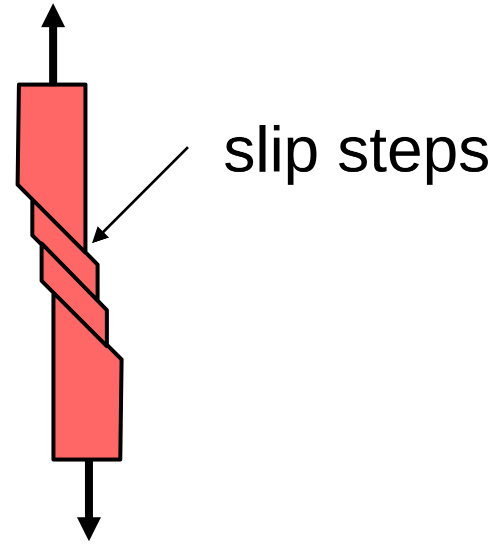
- are line defects,
- slip between crystal planes result when dislocations move,
- produce permanent (plastic) deformation.

Schematic of Zinc (HCP):

- before deformation



- after tensile elongation



Adapted from Fig. 7.8, *Callister 7e.*

Imperfections in Solids

Linear Defects (Dislocations)

- Are one-dimensional defects around which atoms are misaligned

- Edge dislocation:
  - extra half-plane of atoms inserted in a crystal structure
  - **b** $\perp$ to dislocation line
- Screw dislocation:
  - spiral planar ramp resulting from shear deformation
  - **b** $||$ to dislocation line

Burger's vector, **b**: measure of lattice distortion

Imperfections in Solids

Edge Dislocation

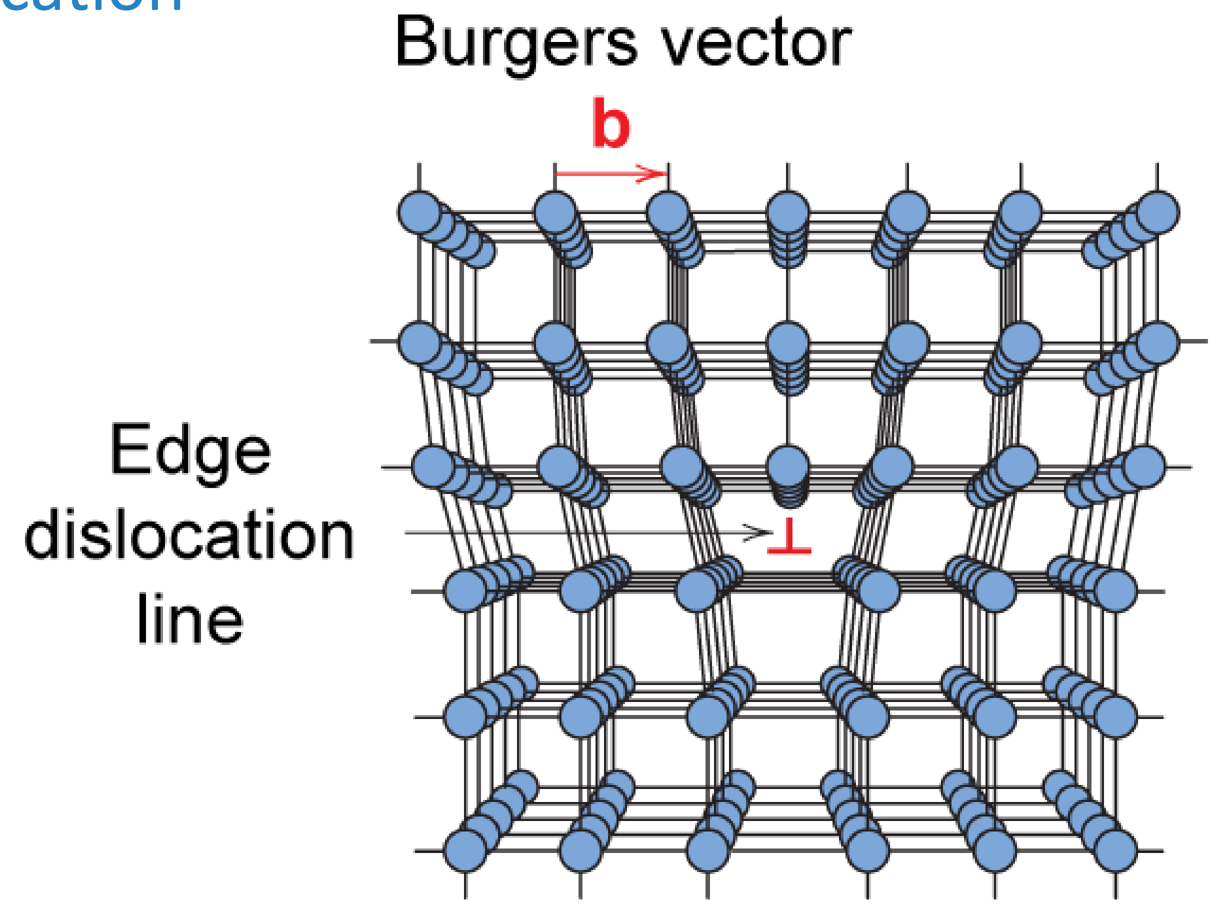
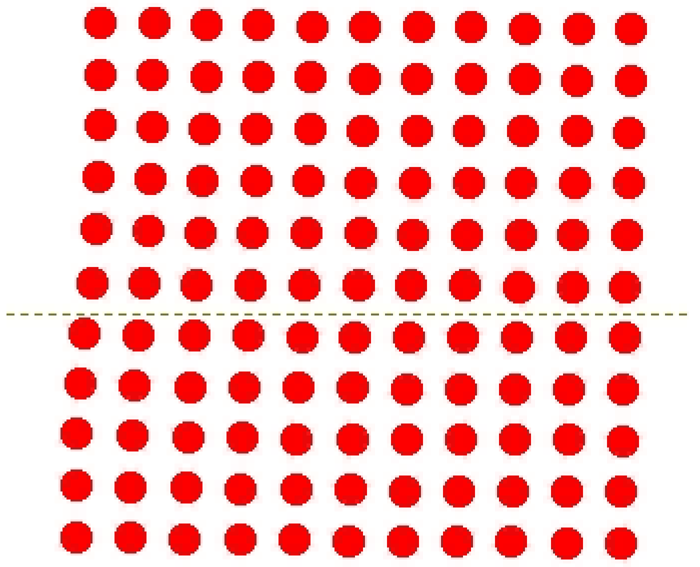


Fig. 4.3, *Callister 7e.*

Motion of Edge Dislocation

- Dislocation motion requires the successive bumping of a half plane of atoms (from left to right here).
- Bonds across the slipping planes are broken and remade in succession.

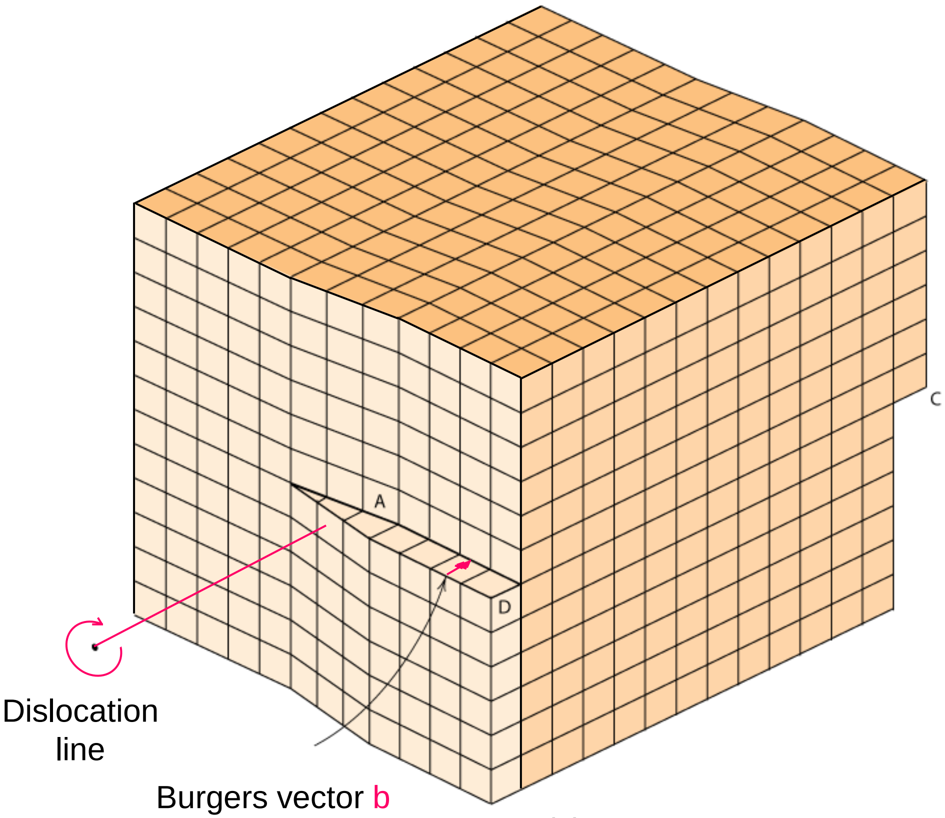


Atomic view of edge dislocation motion from left to right as a crystal is sheared.

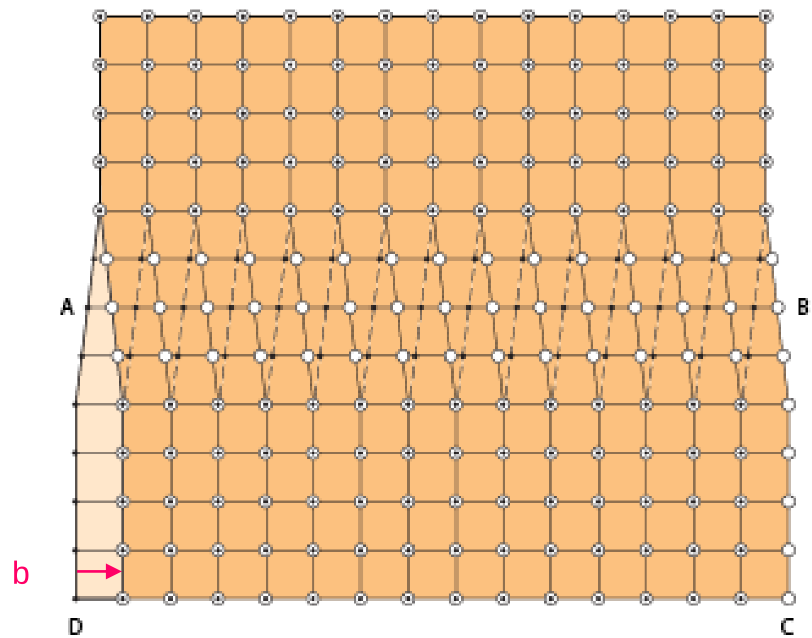
(Courtesy P.M. Anderson)

Imperfections in Solids

Screw Dislocation



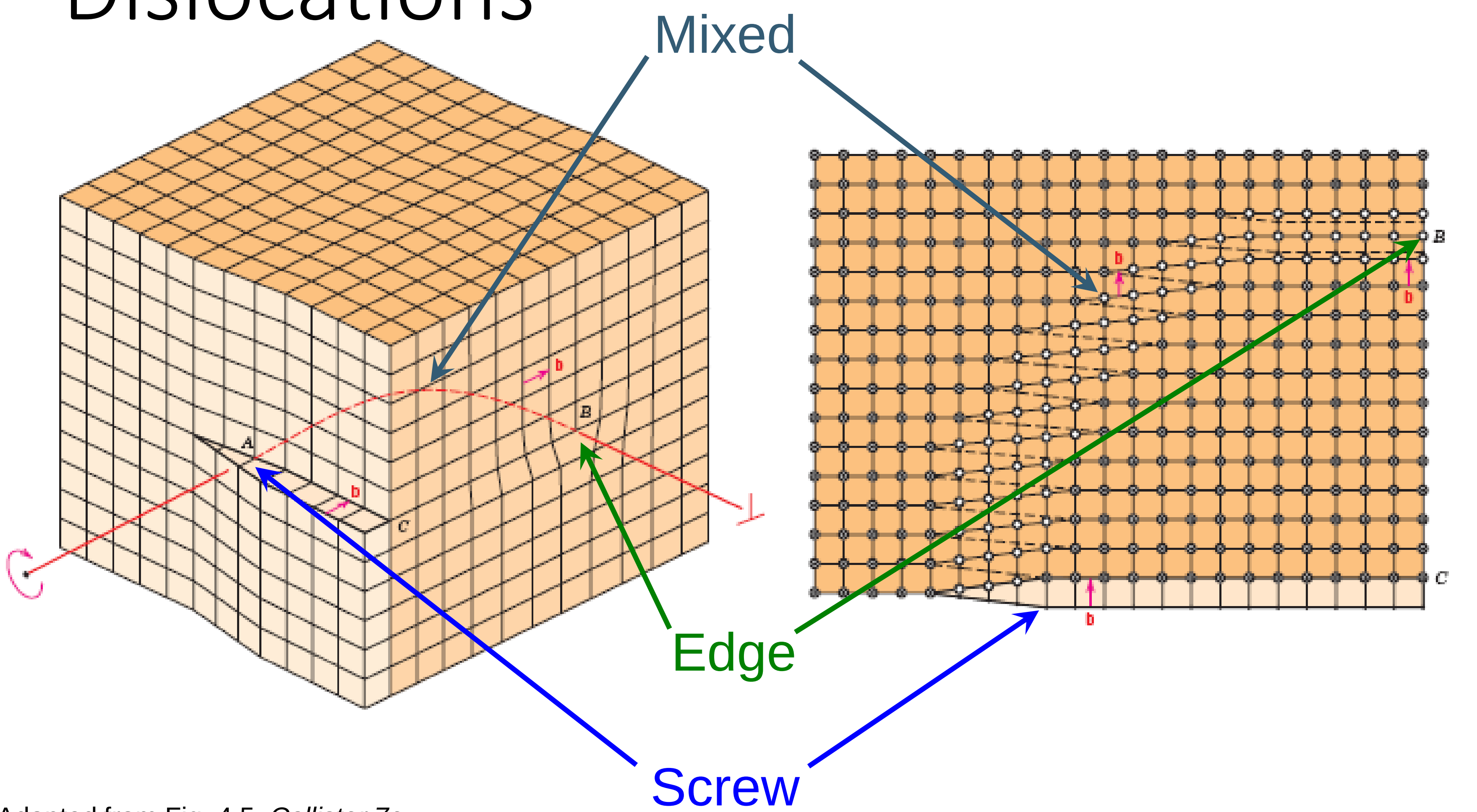
(a)



(b)

Adapted from Fig. 4.4, *Callister 7e.*

Edge, Screw, and Mixed Dislocations



Adapted from Fig. 4.5, *Callister 7e.*

Imperfections in Solids

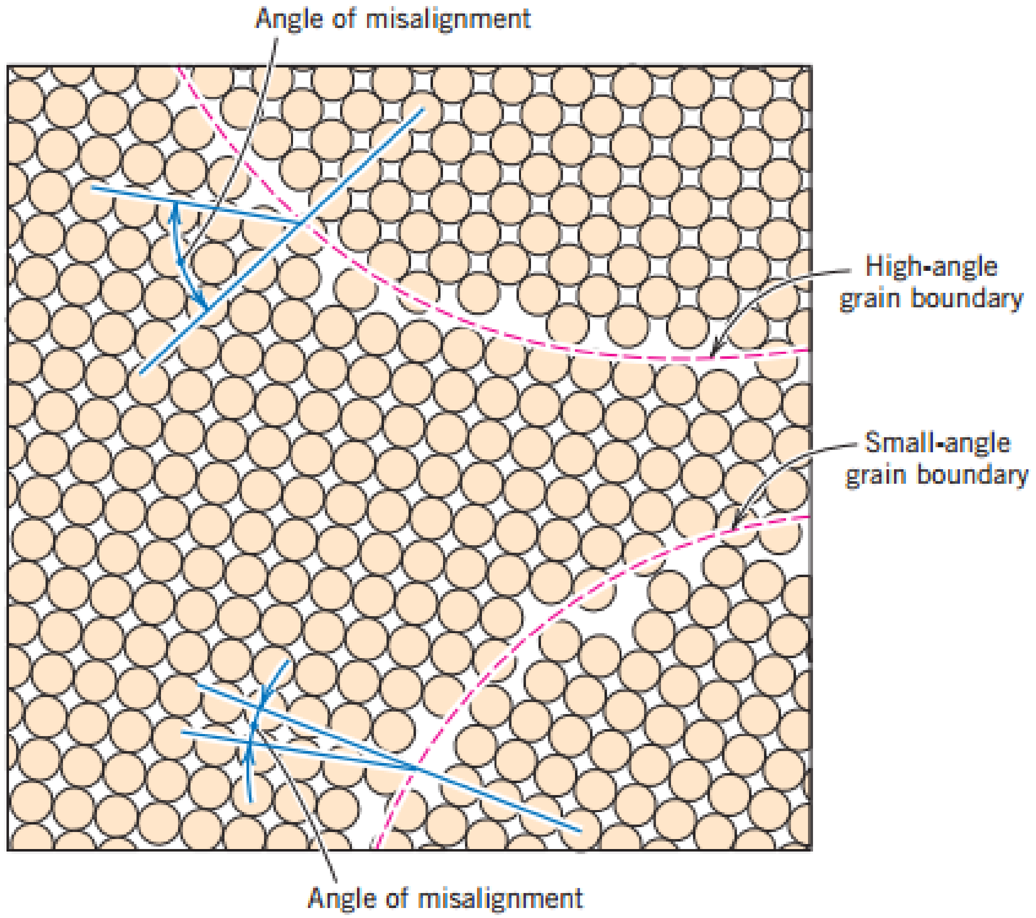
Dislocations are visible in electron micrographs

Adapted from Fig. 4.6, *Callister 7e.*

Interfacial Defects

Have a planar dimension

- External Surfaces:
  - Bonds of surface atoms are not satisfied (J/m^2)
  - To reduce this material tend to minimize, if possible, their surface area.
- Grain boundaries:
  - Due to orientation mismatch across grain boundaries
  - Can be low-angle or high-angle grain boundary.



Interfacial Defects

- Grain boundaries:
  - Tilt boundaries: due to consecutive edge dislocations.
  - Twist boundary: angle of misorientation parallel to boundary.

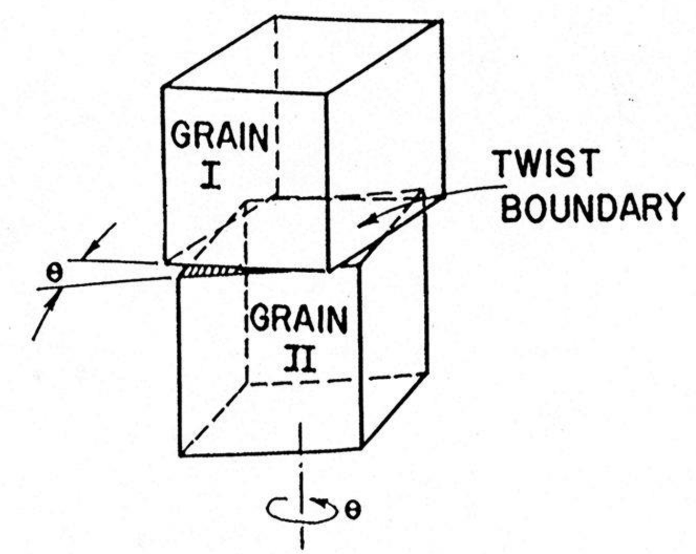
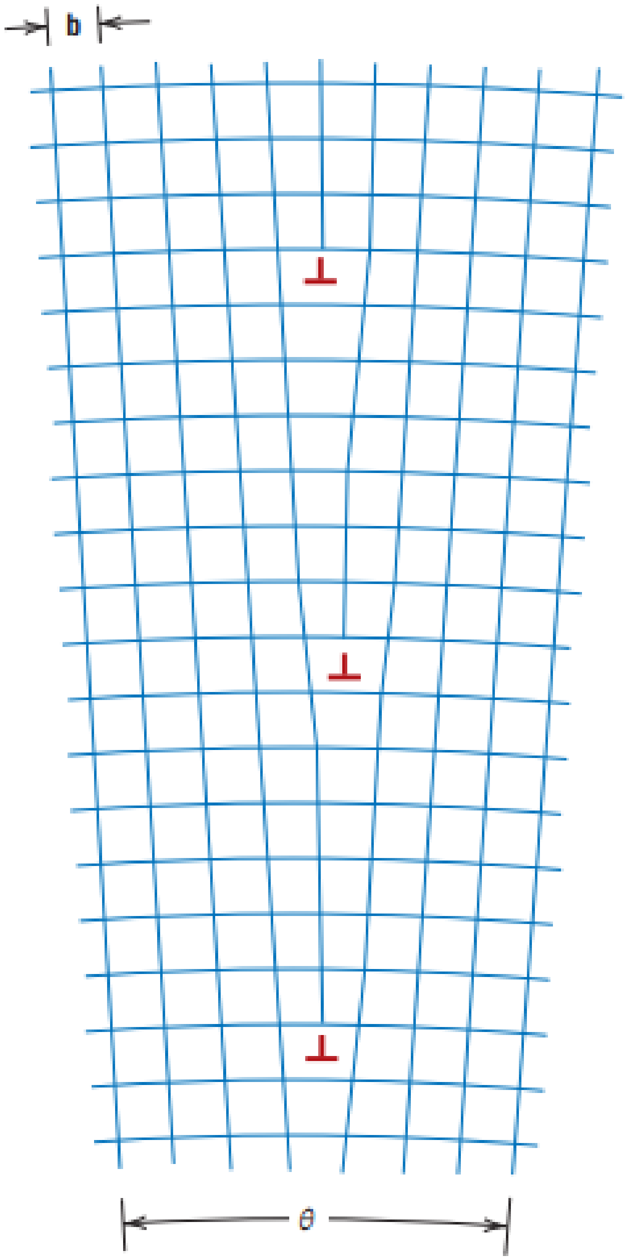
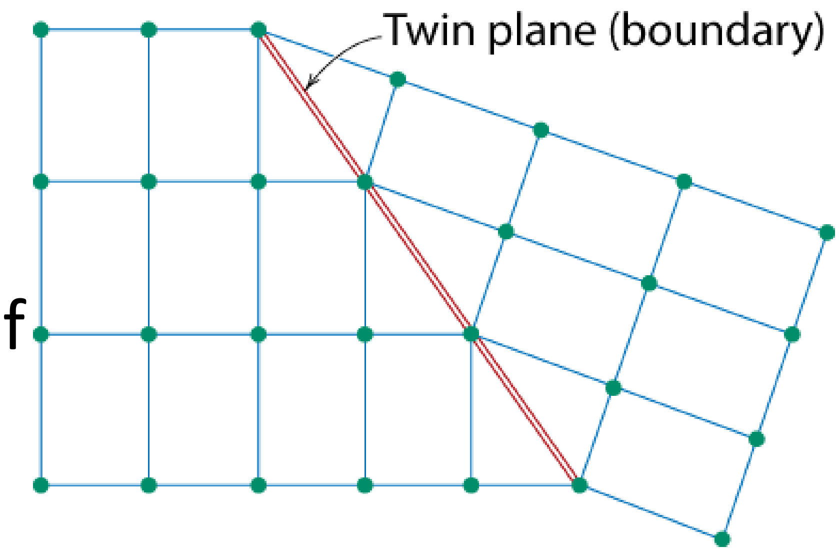


Figure 16.4. Low-angle twist boundary.



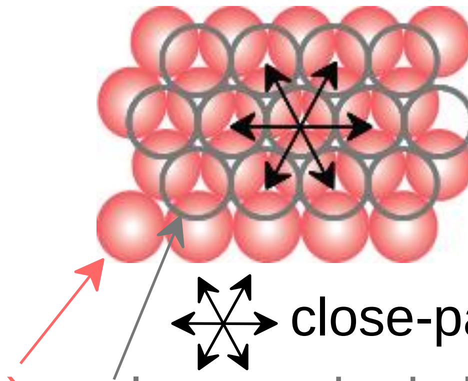
Interfacial Defects

- Twin boundaries:
  - Essentially a reflection of atom positions across the twin plane.
  - Results from application of shear forces.
- Miscellaneous Interfacial defects:
  - For FCC metals an error in ABCABC packing sequence
  - Ex: ABCABABC
- Bulk defects such as pores cracks, foreign inclusions are caused due to processing.



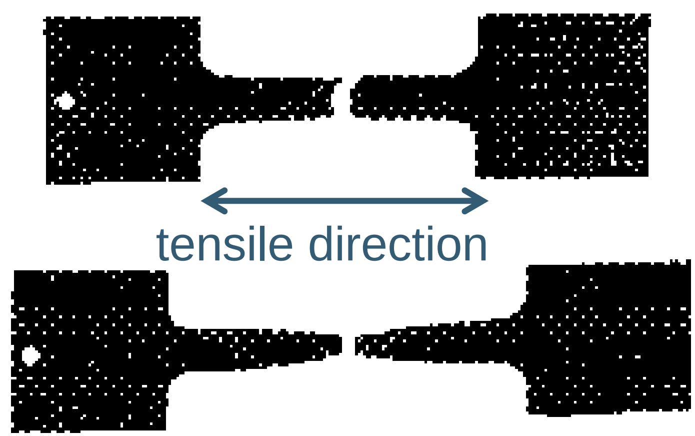
Dislocations & Crystal Structures

- Structure: close-packed planes & directions are preferred.



- Comparison among crystal structures:
  FCC: many close-packed planes/directions;
  HCP: only one plane, 3 directions;
  BCC: none

- Specimens that were tensile tested.



Summary

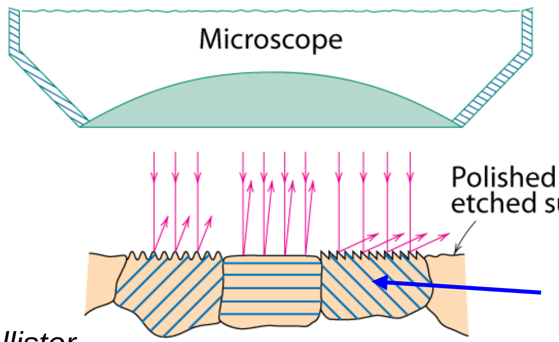
- Point, Line, and Area defects exist in solids.
- The number and type of defects can be varied and controlled (e.g., *T* controls vacancy conc.)
- Defects affect material properties (e.g., grain boundaries control crystal slip).
- Defects may be desirable or undesirable (e.g., dislocations may be good or bad, depending on whether plastic deformation is desirable or not.)

Microscopic Examination

- Crystallites (grains) and grain boundaries. Vary considerably in size. Can be quite large
  - ex: Large single crystal of quartz or diamond or Si
  - ex: Aluminum light post or garbage can - see the individual grains
- Crystallites (grains) can be quite small (mm or less) – necessary to observe with a microscope.

Optical Microscopy

- Useful up to 2000X magnification.
- Polishing removes surface features (e.g., scratches)
- Etching changes reflectance, depending on crystal orientation.



Adapted from Fig. 4.13(b) and (c), *Callister 7e.* (Fig. 4.13(c) is courtesy of J.E. Burke, General Electric Co.

Micrograph of brass (a Cu-Zn alloy)

Optical Microscopy

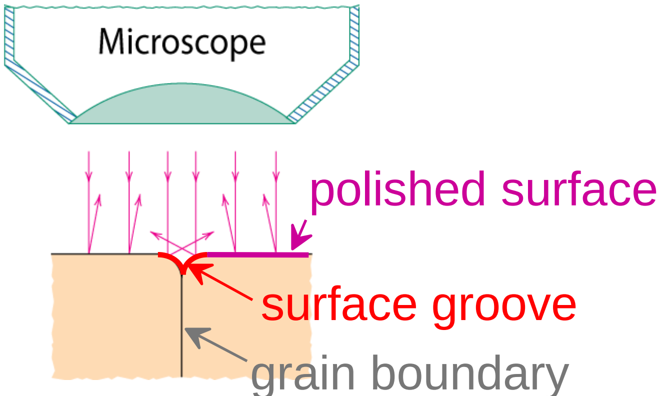
Grain boundaries...

- are imperfections,
- are more susceptible to etching,
- may be revealed as dark lines,
- change in crystal orientation across boundary.

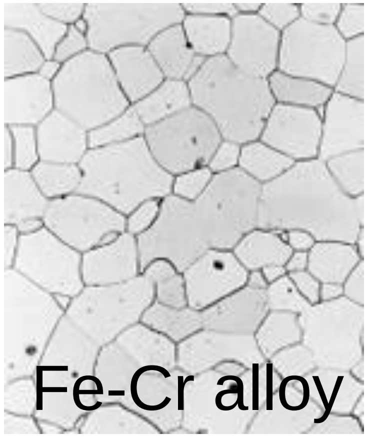
ASTM grain size number

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

number of grains/in^2 at 100x magnification



(a)



(b)

Adapted from Fig. 4.14(a) and (b), *Callister 7e.* (Fig. 4.14(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC [now the National Institute of Standards and Technology, Gaithersburg, MD].)

Optical Microscopy

- Polarized light
  - metallographic scopes often use polarized light to increase contrast
  - Also used for transparent samples such as polymers

Microscopy

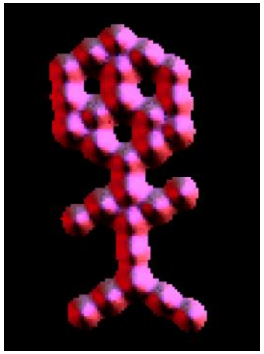
Optical resolution ca. 10^{-7} m = 0.1 μm = 100 nm

For higher resolution need higher frequency

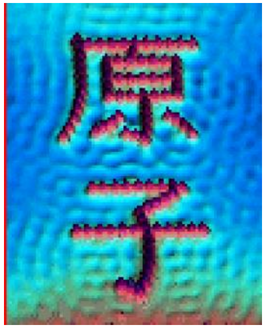
- X-Rays? Difficult to focus.
- Electrons
  - wavelengths ca. 3 pm (0.003 nm)
    - (Magnification - 1,000,000X)
  - Atomic resolution possible
  - Electron beam focused by magnetic lenses.

Scanning Tunneling Microscopy (STM)

- Atoms can be arranged and imaged!



Carbon monoxide molecules arranged on a platinum (111) surface.



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Iron atoms arranged on a copper (111) surface. These Kanji characters represent the word “atom”.

ANNOUNCEMENTS

Reading:

Core Problems:

Self-help Problems: