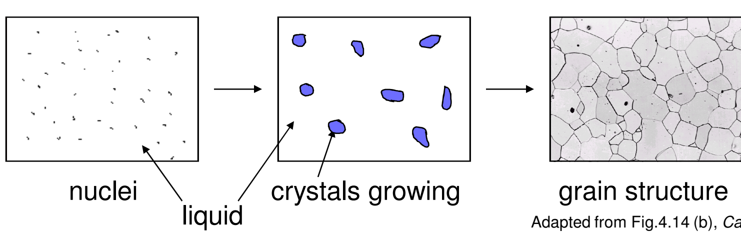
CHAPTER 4:
IMPERFECTIONS IN SOLIDS

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



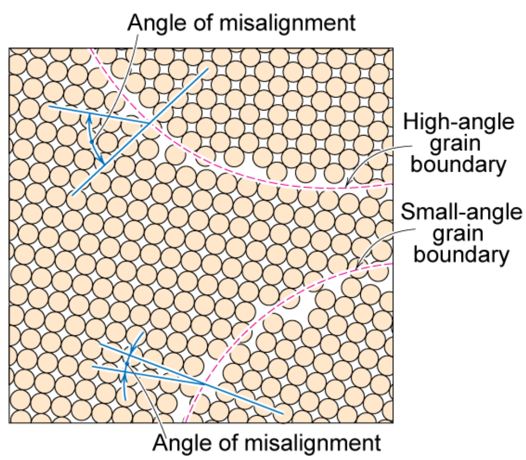
Adapted from Fig.4.14 (b), *Callister 7e.*

- Crystals grow until they meet each other

Polycrystalline Materials

Grain Boundaries

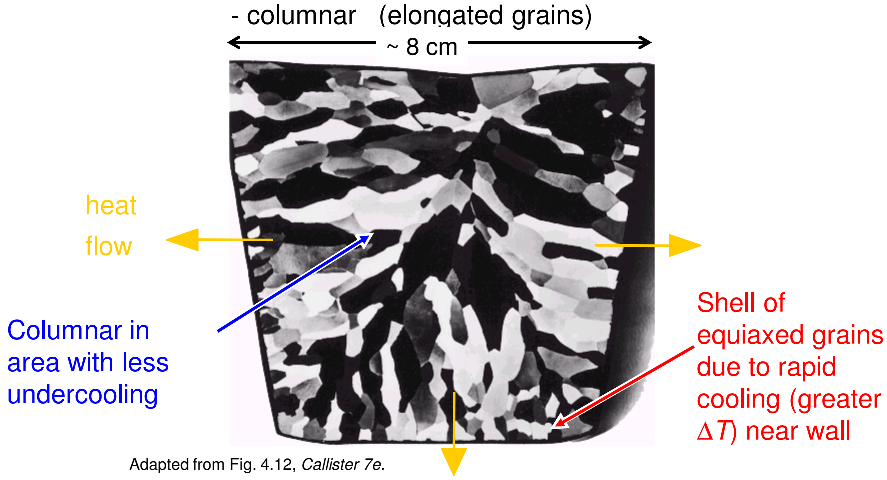
- regions between crystals
- transition from lattice of one region to that of the other
- slightly disordered
- low density in grain boundaries
  - high mobility
  - high diffusivity
  - high chemical reactivity



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

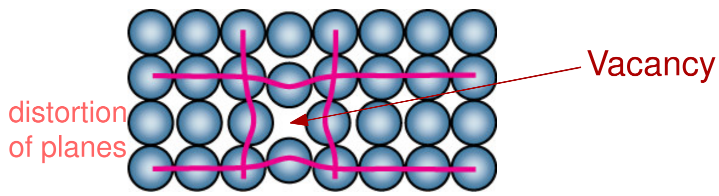
Line defects

- Grain Boundaries

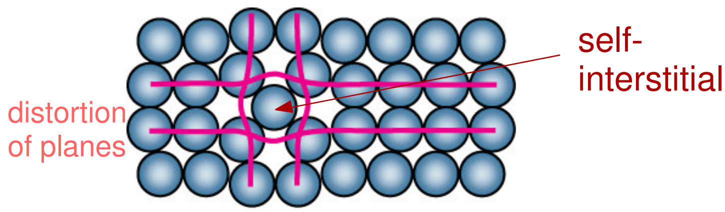
Area defects

Point Defects

- Vacancies:
  -vacant atomic sites in a structure.



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



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Equilibrium Concentration: Point Defects

- Equilibrium concentration varies with temperature!

No. of defects

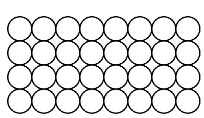
Activation energy

No. of potential defect sites.

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

Temperature

Boltzmann's constant
(1.38×10^{-23} J/atom-K)
(8.62×10^{-5} eV/atom-K)



Each lattice site is a potential vacancy site

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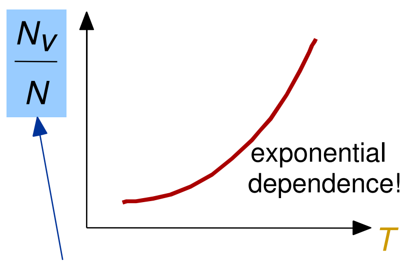
Measuring Activation Energy

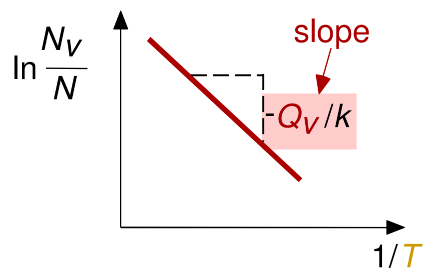
- We can get Q_v from an experiment.

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

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



defect concentration



Estimating Vacancy Concentration

- Find the equil. # of vacancies in 1 m³ of Cu at 1000°C.
- Given:

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

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

$$\frac{N_v}{N} = \exp\left(\frac{-Q_v}{kT}\right) = 2.7 \times 10^{-4}$$

0.9 eV/atom

1273K

8.62×10^{-5} eV/atom-K

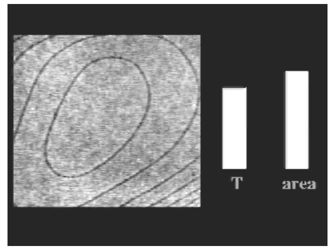
For 1 m³, $N = \rho \times \frac{N_A}{A_{Cu}} \times 1 \text{ m}^3 = 8.0 \times 10^{28}$ sites

- Answer:

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

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.



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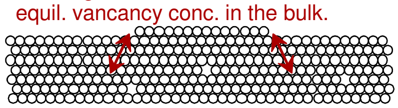
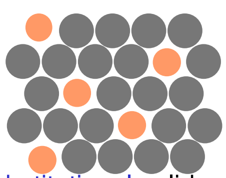
Island grows/shrinks to maintain equil. vancancy conc. in the bulk.



Point Defects in Alloys

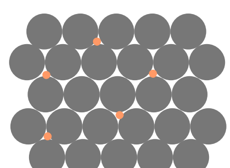
Two outcomes if impurity (B) added to host (A):

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



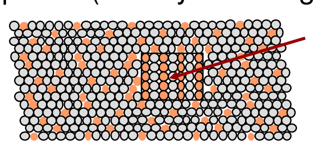
Substitutional solid soln.
(e.g., Cu in Ni)

OR



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

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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.*

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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

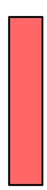
Line Defects

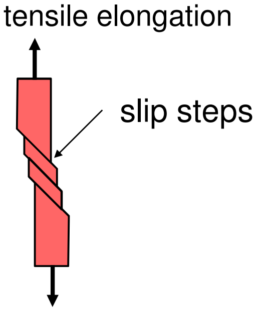
Dislocations:

- 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** ⊥ to dislocation line
- Screw dislocation:
  - spiral planar ramp resulting from shear deformation
  - **b** || to dislocation line

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

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Imperfections in Solids

Edge Dislocation

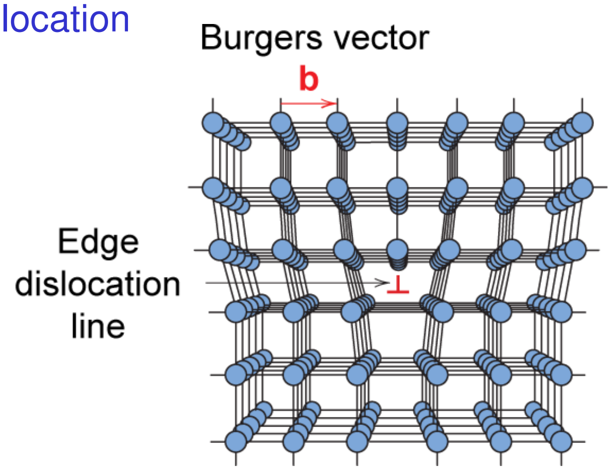

Fig. 4.3, *Callister 7e.*

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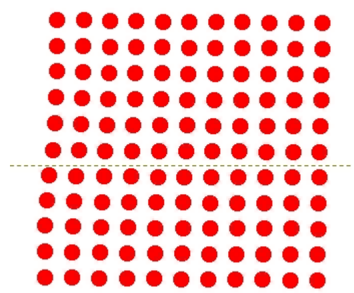
Motion of Edge Dislocation

- 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.

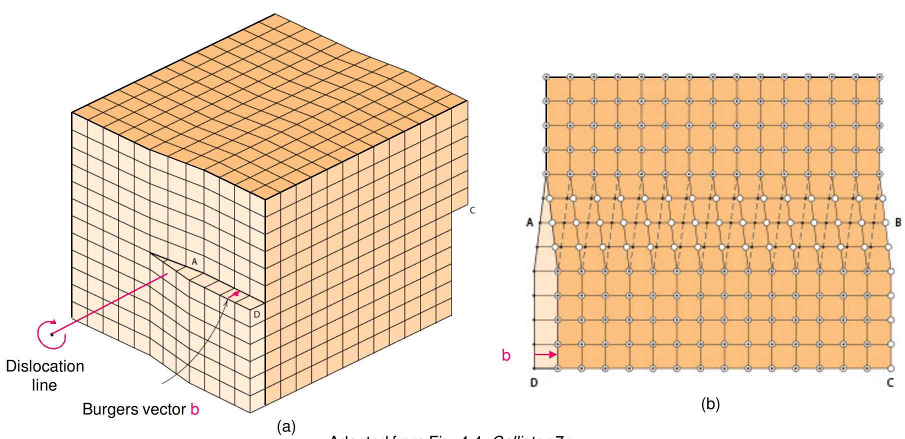


Atomic view of edge dislocation motion from left to right as a crystal is sheared.

(Courtesy P.M. Anderson)

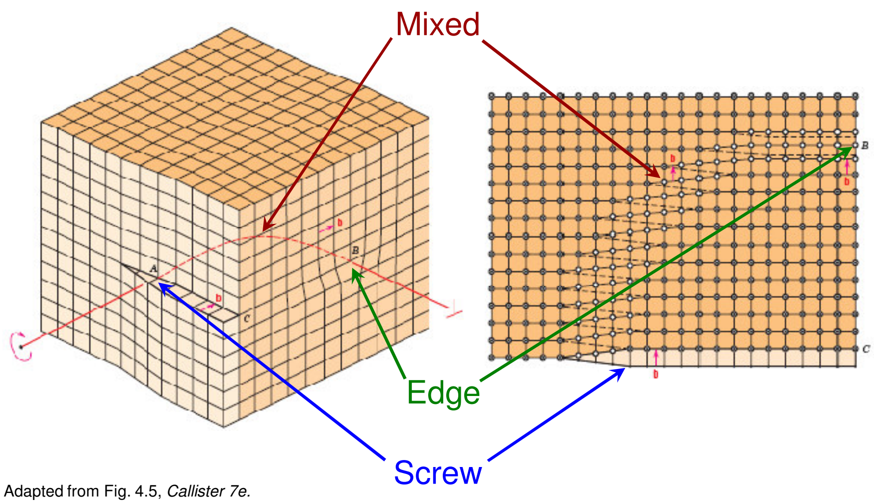
Imperfections in Solids

Screw Dislocation



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

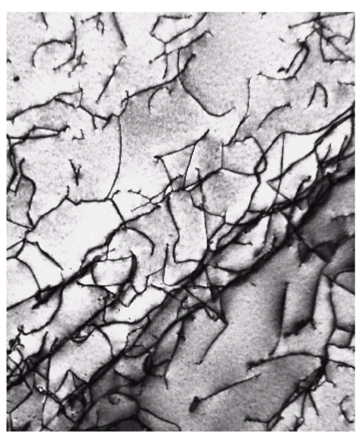
Edge, Screw, and Mixed Dislocations



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

Imperfections in Solids

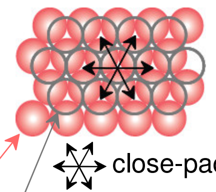
Dislocations are visible in electron micrographs



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

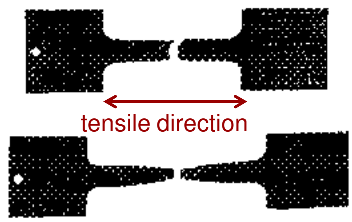
Dislocations & Crystal Structures

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



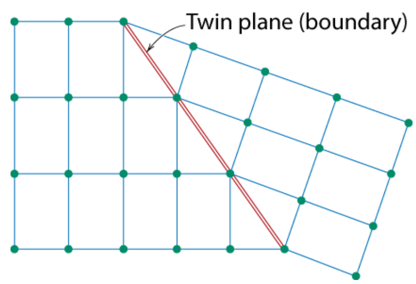
- Comparison among crystal structures:
  FCC: many close-packed planes/directions;
  HCP: only one plane, 3 directions;
  BCC: none

- Specimens that were tensile tested.



Planar Defects in Solids

- One case is a twin boundary (plane)
  - Essentially a reflection of atom positions across the twin plane.



Adapted from Fig. 4.9, *Callister 7e.*

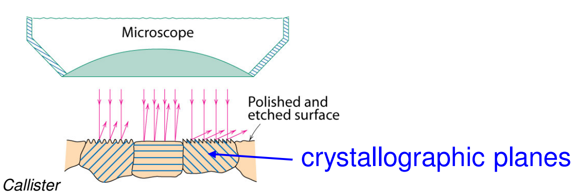
- Stacking faults
  - For FCC metals an error in ABCABC packing sequence
  - Ex: ABCABABC

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

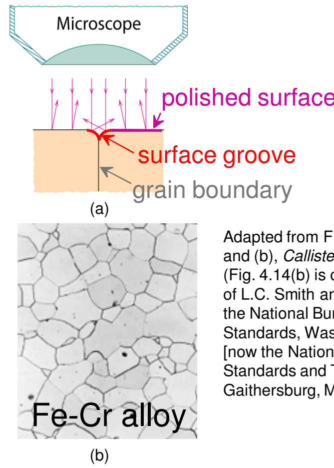
Grain boundaries...

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

ASTM grain size number

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

number of grains/in^2 at 100x magnification



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

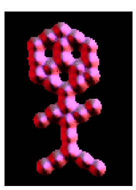
Optical resolution ca. 10^{-7} m = 0.1 μm = 100 nm

For higher resolution need higher frequency

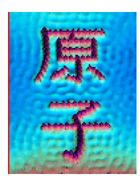
- X-Rays? Difficult to focus.
- Electrons
  - wavelengths ca. 3 pm (0.003 nm)
    - (Magnification - 1,000,000X)
  - Atomic resolution possible
  - Electron beam focused by magnetic lenses.

Scanning Tunneling Microscopy (STM)

- Atoms can be arranged and imaged!



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



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

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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.)