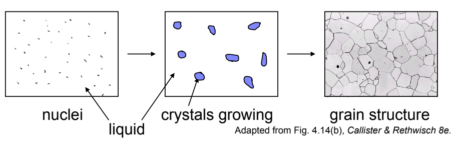
Chapter 4:
Imperfections in Solids

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

- ____________- result of casting of molten material
  - 2 steps
    - _____ form
    - _____ grow to form crystals – ___________
- Start with a _________ material – all liquid



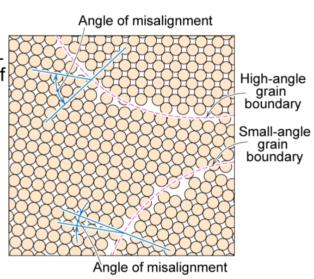
Adapted from Fig. 4.14(b), *Callister & Rethwisch 8e.*

- __________ grow until they meet each other

Polycrystalline Materials

Grain Boundaries

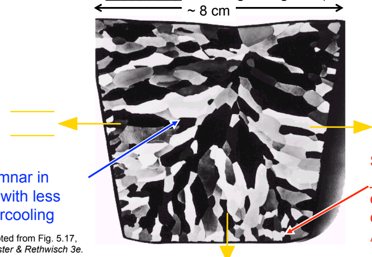
- regions between ______
- transition from ______ of one region to that of the other
- slightly __________
- low density in grain boundaries
  - high ________
  - high ________
  - high chemical reactivity



Adapted from Fig. 4.7, *Callister & Rethwisch 8e.*

Solidification

Grains can be - _________ (roughly same size in all directions)
- _________ (elongated grains)



Adapted from Fig. 5.17, *Callister & Rethwisch 3e.*

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

Chapter 4 - 4

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.

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Types of Imperfections

- Vacancy atoms
- Interstitial atoms
- Substitutional atoms

_______ defects

- Dislocations

_______ defects

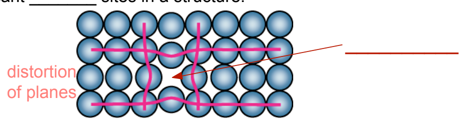
- Grain Boundaries

Area defects

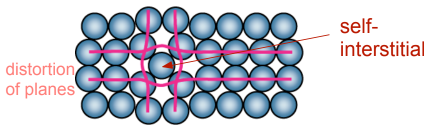
Chapter 4 - 6

Point Defects in Metals

- Vacancies:
  -vacant _______ sites in a structure.



- Self-_____________:
  -"extra" atoms positioned between _______ sites.



Equilibrium Concentration: Point Defects

- Equilibrium ______________ varies with temperature!

No. of defects

____________ energy

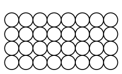
$$\frac{N_v}{N} = \exp\left(\frac{-Q_v}{kT}\right)$$

No. of potential defect sites

Boltzmann's constant

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

$(8.62 \times 10^{-5}$ eV/atom-K)



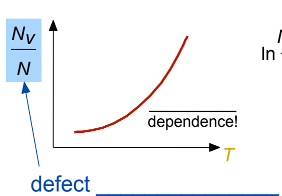
Each _______ site is a potential vacancy site

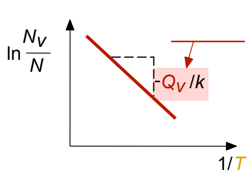
Measuring Activation Energy

- 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:

ρ = ___________ A_{Cu} = _____________

Q_V = 0.9 eV/atom N_A = 6.02 x 10^{23} atoms/mol

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

0.9 eV/atom

1273 K

8.62 x 10^{-5} eV/atom-K

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

- Answer:

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

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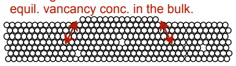
Observing Equilibrium Vacancy Conc.

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

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



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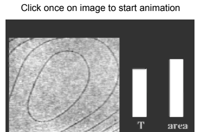

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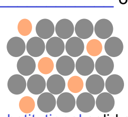
Imperfections in Metals (i)

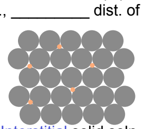
Two outcomes if impurity (B) added to host (A):

- _______________ of B in A (i.e., ________ dist. of point defects)



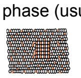
Substitutional solid soln. (e.g., Cu in Ni)

OR



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

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



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

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Imperfections in Metals (ii)

Conditions for ___________ solid solution (S.S.)

- W. Hume – Rothery rule
  - 1. Δr (atomic radius) < 15%
  - 2. Proximity in ___________ table
    - i.e., similar electronegativities
  - 3. Same crystal ___________ 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 Metals (iii)

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. 118, *Callister & Rethwisch 8e.*

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Impurities in Solids

- Specification of composition
  - weight percent $$C_1 = \frac{m_1}{m_1 + m_2} \times 100$$

    m_1 = mass of component 1
  - atom percent $$C_1' = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100$$

    n_{m1} = number of moles of component 1

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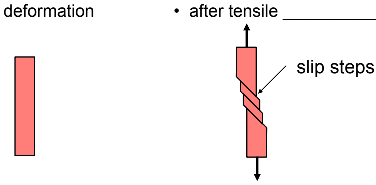
Line Defects

Dislocations:

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

Schematic of Zinc (HCP):

- before deformation
- after tensile ______________



Imperfections in Solids

Linear Defects (____________________)

- Are one-dimensional defects around which atoms are misaligned

- Edge _____________:
  - extra half-plane of atoms inserted in a crystal __________
  - **b** perpendicular (⊥) to dislocation line
- Screw dislocation:
  - _____________ ramp resulting from shear deformation
  - **b** parallel (‖) to dislocation line

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

Imperfections in Solids

Edge Dislocation

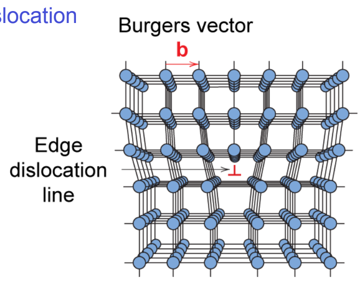
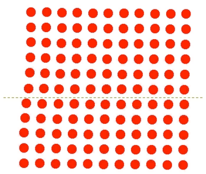


Fig. 4.3, *Callister & Rethwisch 8e.*

Motion of Edge Dislocation

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



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(Courtesy P.M. Anderson)

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

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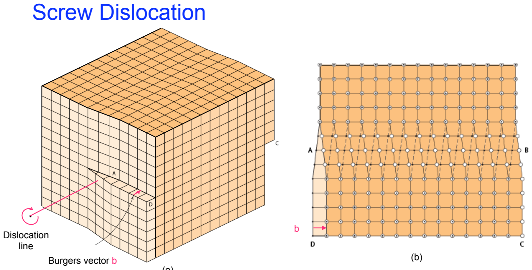
Imperfections in Solids

Screw Dislocation



Adapted from Fig. 4.4, *Callister & Rethwisch 8e.*

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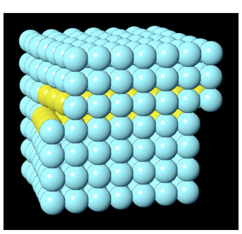
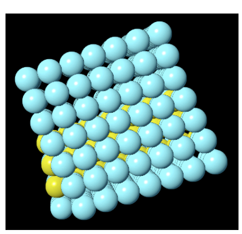
VMSE: Screw Dislocation

- In VMSE:
  - a region of crystal containing a dislocation can be rotated in 3D
  - dislocation motion may be animated



Front View



Top View

VMSE Screen Shots

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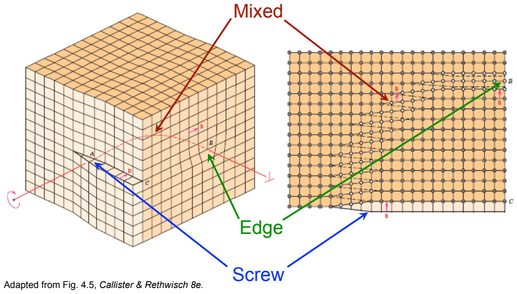
Edge, Screw, and Mixed Dislocations



Adapted from Fig. 4.5, *Callister & Rethwisch 8e.*

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Imperfections in Solids

Dislocations are visible in electron micrographs

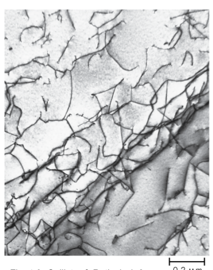

Fig. 4.6, *Callister & Rethwisch 8e.*

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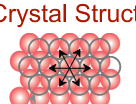
Dislocations & Crystal Structures

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

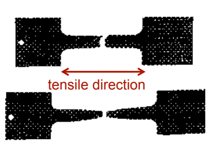


view onto two close-packed _________.

close-packed directions

close-packed plane (bottom) close-packed plane (top)

- Comparison among crystal structures:
  FCC: many close-packed ___________________;
  HCP: only one plane, 3 directions;
  BCC: none
- Specimens that were __________ tested.



Mg (HCP)

Al (FCC)

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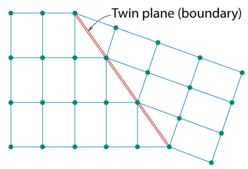
Planar Defects in Solids

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



Adapted from Fig. 4.9, *Callister & Rethwisch 8e.*

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

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Catalysts and Surface Defects

- A catalyst increases the rate of a ___________ __________without being consumed
- __________ on catalysts are normally surface defects

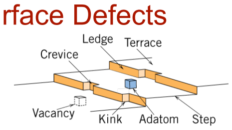

Fig. 4.10, *Callister & Rethwisch 8e.*

Single crystals of $(Ce_{0.5}Zr_{0.5})O_2$ used in an automotive catalytic converter

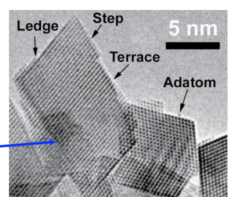

Fig. 4.11, *Callister & Rethwisch 8e.*

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Microscopic Examination

- ____________(grains) and grain boundaries. Vary considerably in size. Can be quite large.
  - ex: Large single crystal of quartz or _______ 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 ____________.

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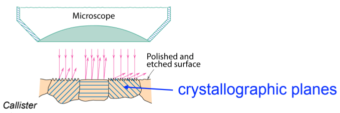
Optical Microscopy

- Useful up to _______ magnification.
- _________ removes surface features (e.g., scratches)
- Etching changes ____________, depending on crystal orientation.



Adapted from Fig. 4.13(b) and (c), *Callister & Rethwisch 8e.* (Fig. 4.13(c) is courtesy of J.E. Burke, General Electric Co.)

Micrograph of brass (a Cu-Zn alloy)

Optical Microscopy

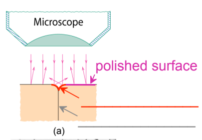
Grain boundaries...

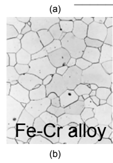
- are _____________,
- are more susceptible to etching,
- may be revealed as dark lines,
- change in _________ orientation across boundary.

ASTM grain size number

$N = 2^{n-1}$

________ of grains/in^2 at 100x magnification





Adapted from Fig. 4.14(a) and (b), *Callister & Rethwisch 8e.* (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

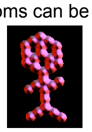
Optical ___________ ca. 10^{-7} m = 0.1 μm = 100 nm

For higher resolution need higher _________

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

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.)