

CHAPTER 4: IMPERFECTIONS IN SOLIDS

ISSUES TO ADDRESS...

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



Nothing is perfect.

The crystalline structures that we have looked at all have imperfections.

We will quantify these imperfections here.



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.



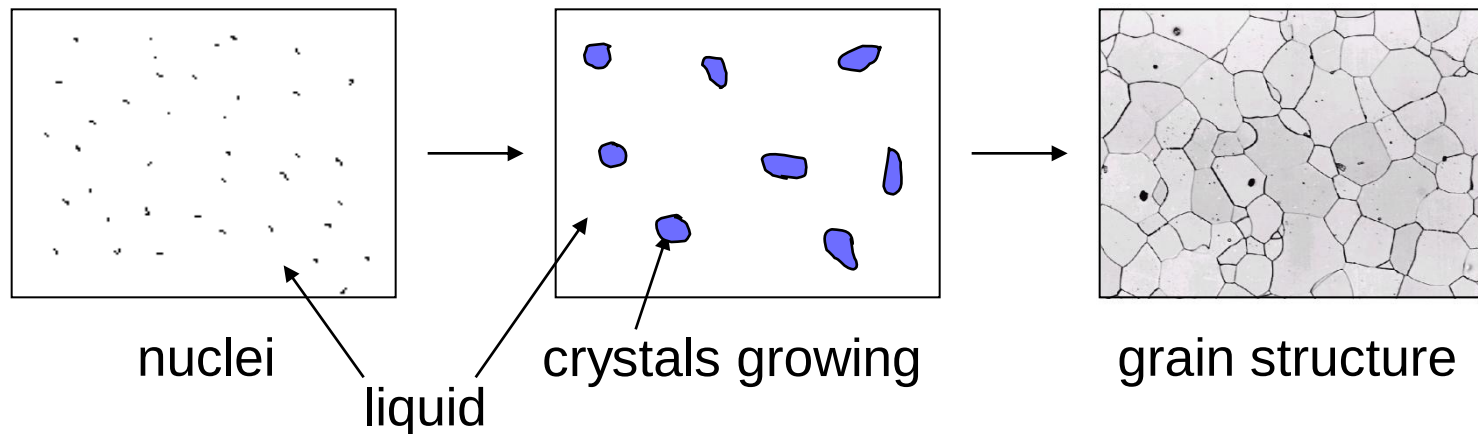
Crystalline Defects

A crystalline defect is a lattice irregularity having one or more of its dimensions on the order of an atomic dimension.



Imperfections in Solids

- **Solidification-**
 - result of casting of molten material(metals and alloys)
 - the size and shape of the structure depends on the cooling rate
 - 2 steps
 - Nuclei form
 - Nuclei grow to form crystals – grain structure
- Start with a molten material – all liquid



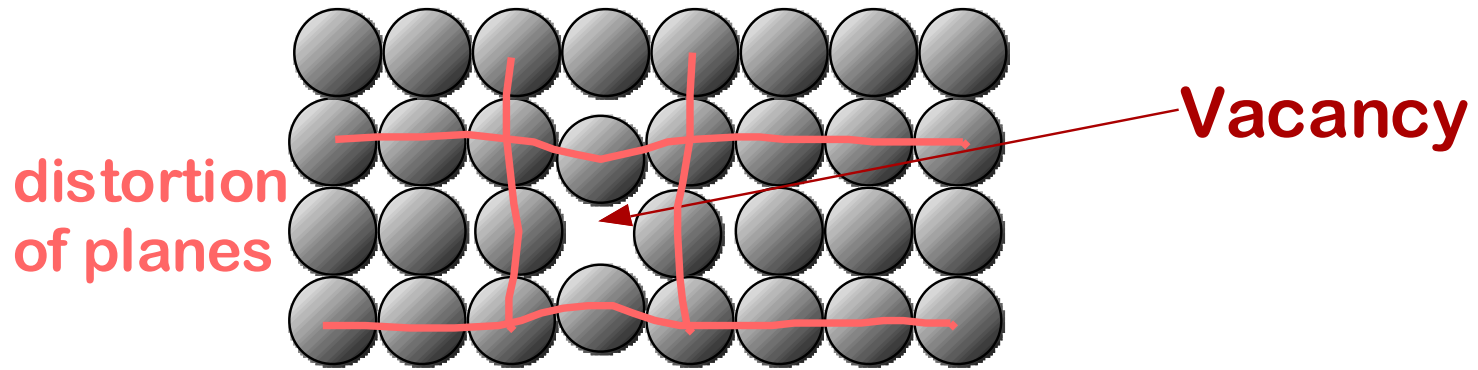
- Crystals grow until they meet each other

- Defect are created during the processing of materials

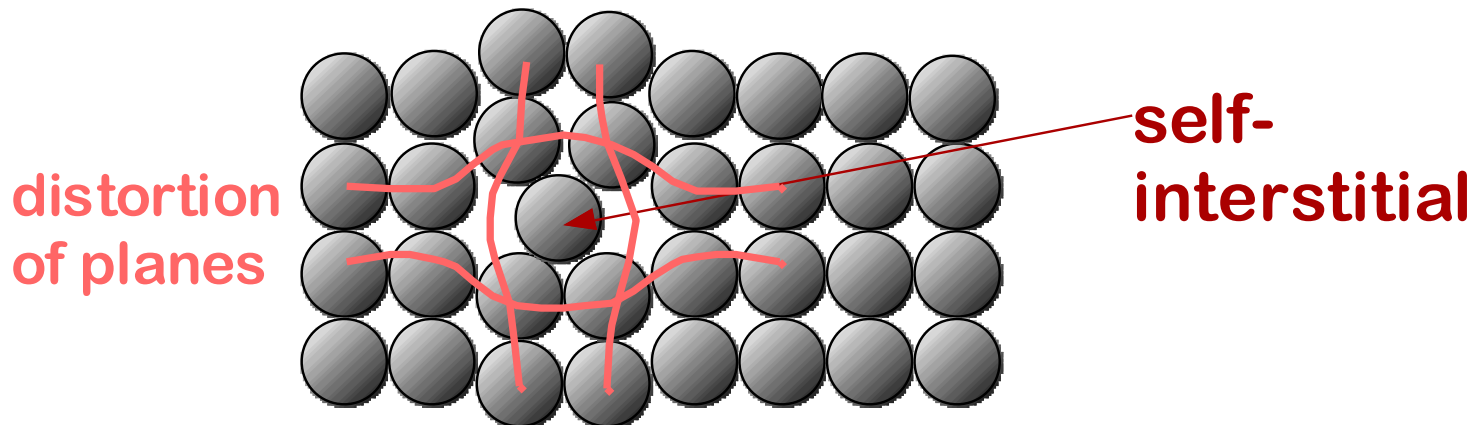


(1) POINT DEFECTS

- **Vacancies:**
-vacant atomic sites in a structure.



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



- Impurities:
- May be interstitial or substitutional
- Ex, carbon added in small amount to iron make steel, which is stronger than pure iron
- Ex, Boron added to silicon to change its electrical properties



Impurities in Solids

- “**Alloys**”: impurity atoms are added *intentionally* to modify specific properties of the material.
- “**Solvent**” is the material with the higher concentration. “**Solute**” is the element present in the minor concentration, also called “impurity”.
- “**Solid Solution**” forms when, as the solute atoms are added to the host material, the crystal structure is maintained. It is compositionally homogeneous



- The addition of impurities atoms to a impurities metals will result in the formation of a solid solution and /or a new second phase ,depending on the kind of impurities ,its concentration, and the temperature on alloy.



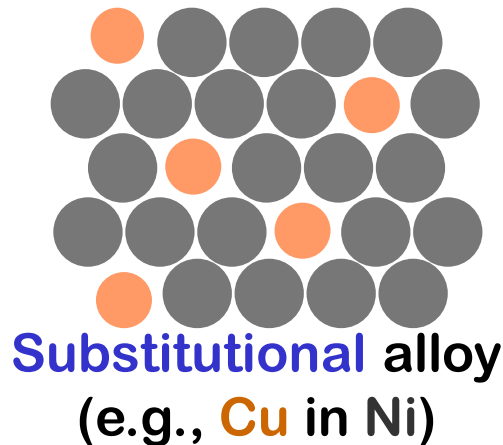
- Solid solution maybe **substitutional** or **interstitial** depending in atomic radii in solute and host atoms



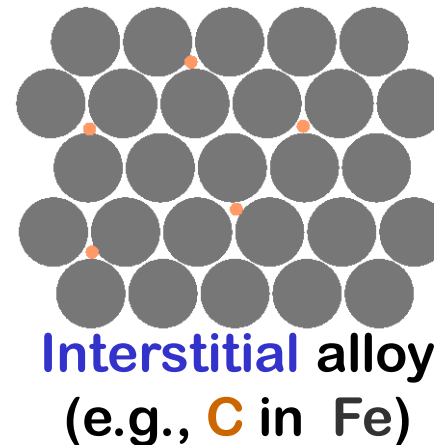
POINT DEFECTS IN ALLOYS

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

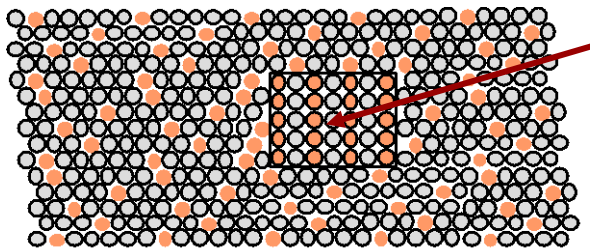
- **Solid solution** of **B** in A (i.e., random dist. of point defects)



OR



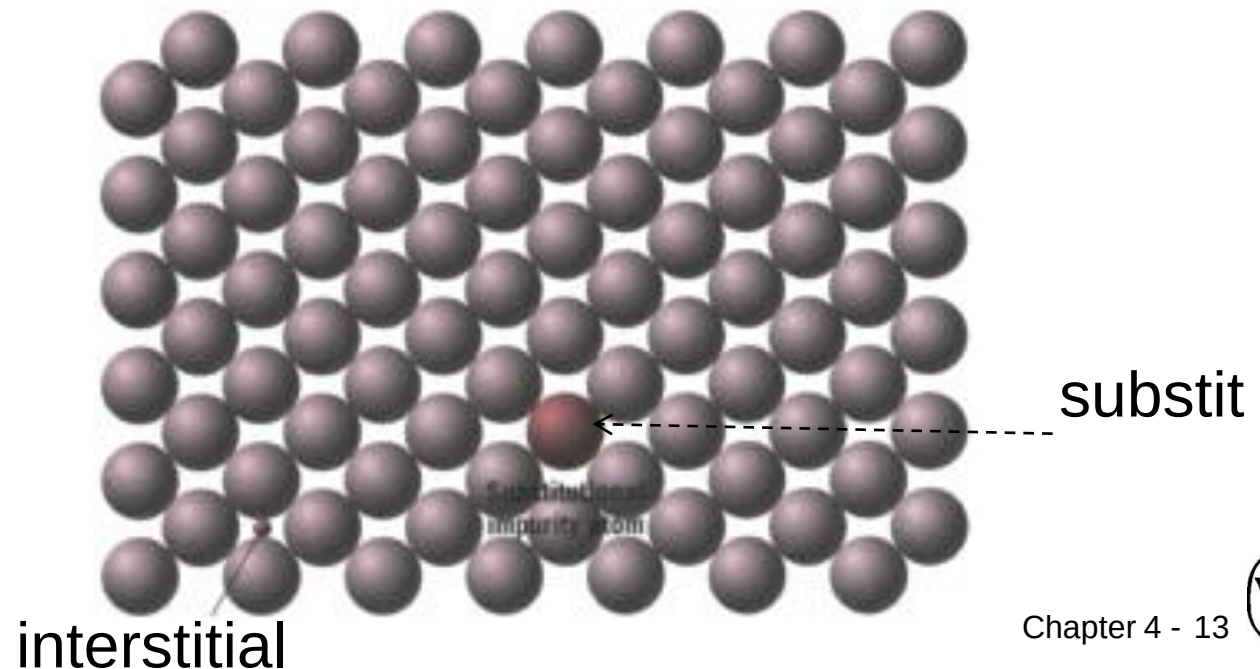
- Solid solution of **B** in A plus particles of a new phase (usually for a larger amount of B)



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

Impurities defects: Substitutional or interstitial

- **Substitutional** : impurity atoms type A substitutional atoms type B in structure
- **Interstitial** : atoms type A fill the voids or interstices among the atoms type B



The Degree of Solubility(substitutional)depend on:

- The solvency of solutes in solvents depends on:
 - Atomic Size Factor ($\pm 15\%$)
 - Crystal Structure (same)
 - Electronegativity (low)
 - Valences (solvents have lower valency)



- Copper and nickel have the same complete solubility in one another at all proportion:

- Atomic Size Factor ($\pm 15\%$)

Atomic radii Cu = 0.128 nm, Ni = 0.125 nm

- Crystal Structure (same)

Both Cu and Ni have fcc crystal structure

- Electronegativity (low)

Cu = 1.9, Ni = 1.8

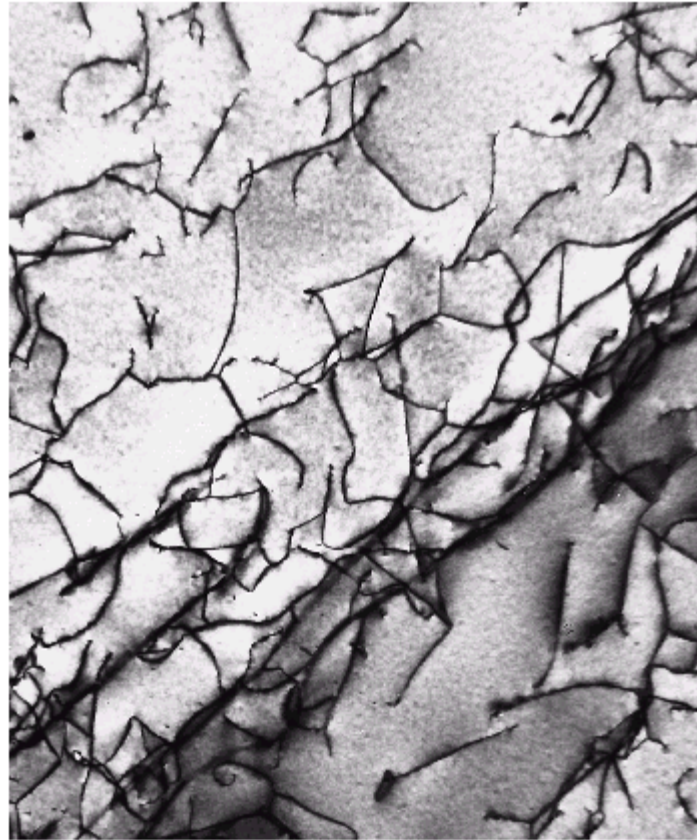
- Valences

1 and 2 for Cu, and 2 for Ni



Imperfections in Solids

Dislocations are visible in electron micrographs



Types of Imperfections

Point defects

- Vacancy atoms
- Interstitial atoms
- Impurities defects (for solid solution)

Line defects (dislocation)

- Edge dislocation
- Screw dislocation
- mixed dislocation



TYPES OF IMPERFECTIONS

1. Point defects

- Vacancy atoms
- Interstitial atoms
- Substitutional atoms

2. Line defects

- Dislocations
 - Edge Dislocations
 - Screw Dislocation
 - mixed dislocation

3. Area defects

- Grain Boundaries

4. Volume defects

- Cracks, Pores, Inclusions



Line Defects

Dislocations:

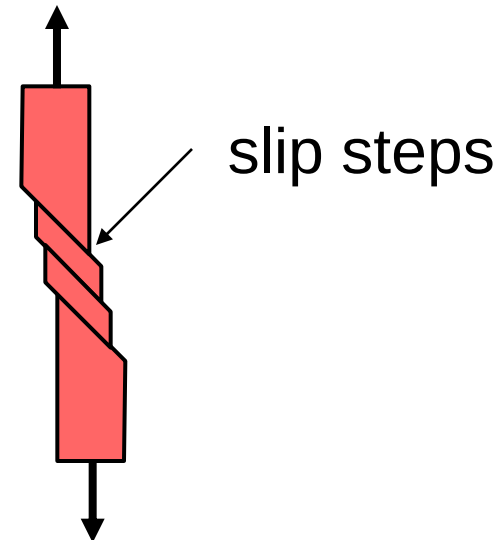
- are line defects,
- slip between crystal planes result when dislocations move,
- produce permanent (plastic) deformation.

Schematic of Zinc (HCP):

- before deformation



- after tensile elongation



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
 - $\mathbf{b} \perp$ to dislocation line
- Screw dislocation:
 - spiral planar ramp resulting from shear deformation
 - $\mathbf{b} \parallel$ to dislocation line

Burger's vector, $\mathbf{b}$: measure of lattice distortion



Imperfections in Solids

Edge Dislocation

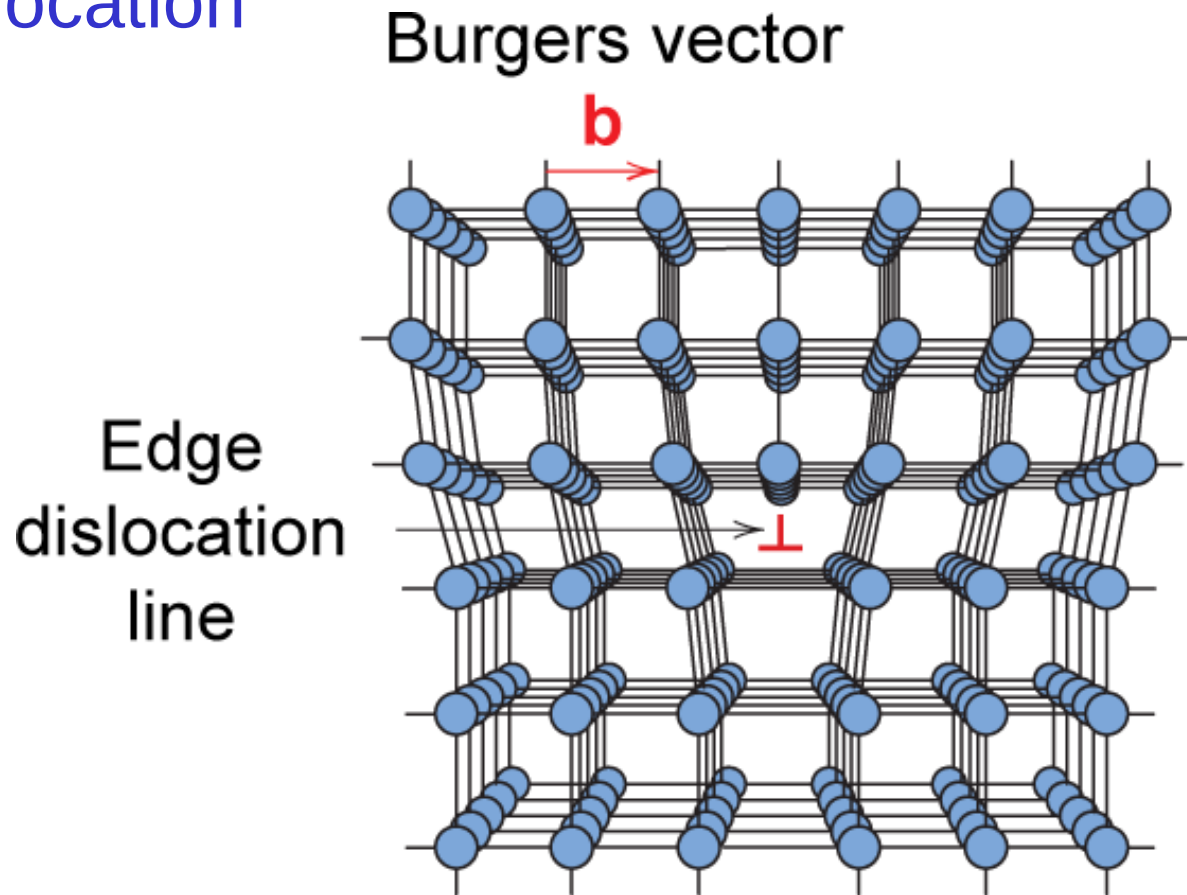
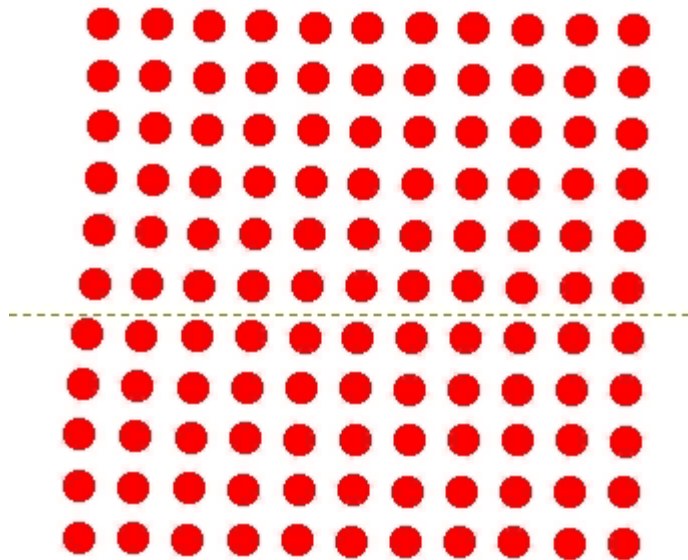


Fig. 4.3, *Callister 7e*.

Motion of Edge Dislocation

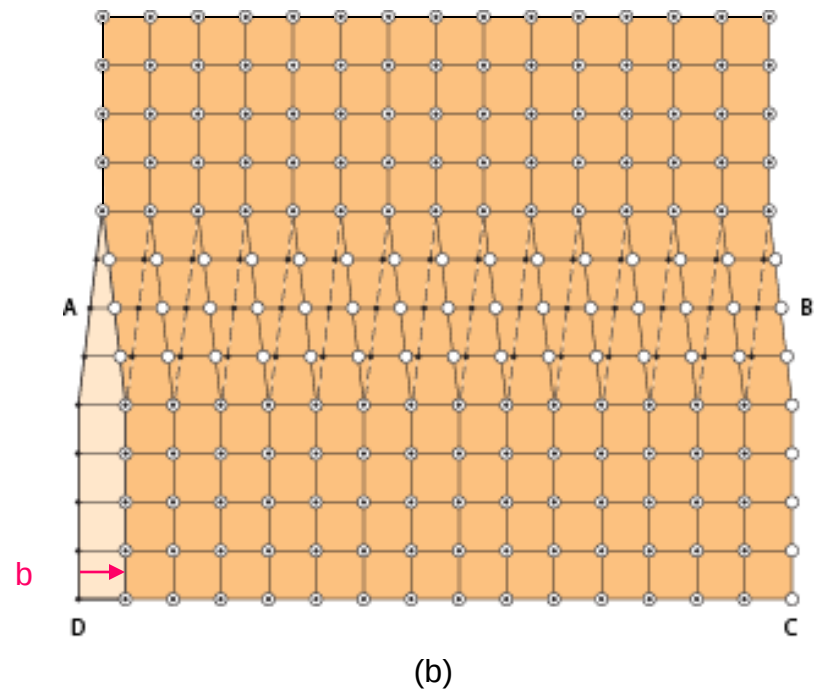
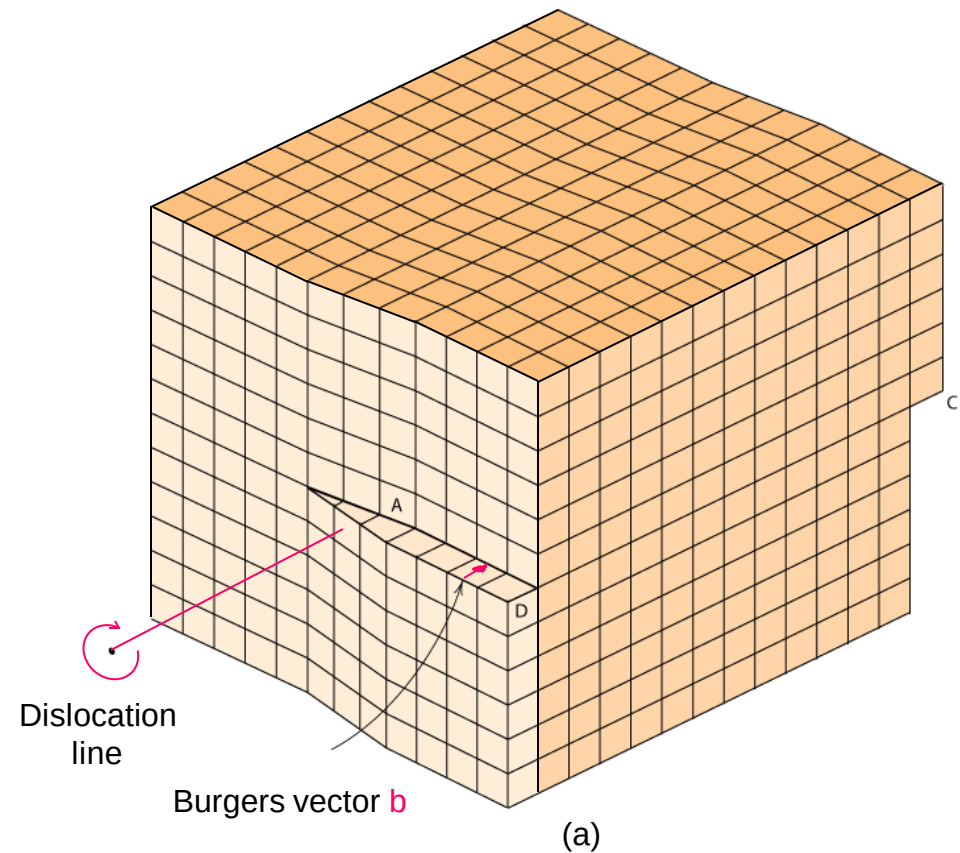
- Dislocation motion requires the successive bumping of a half plane of atoms (from left to right here).
- Bonds across the slipping planes are broken and remade in succession.



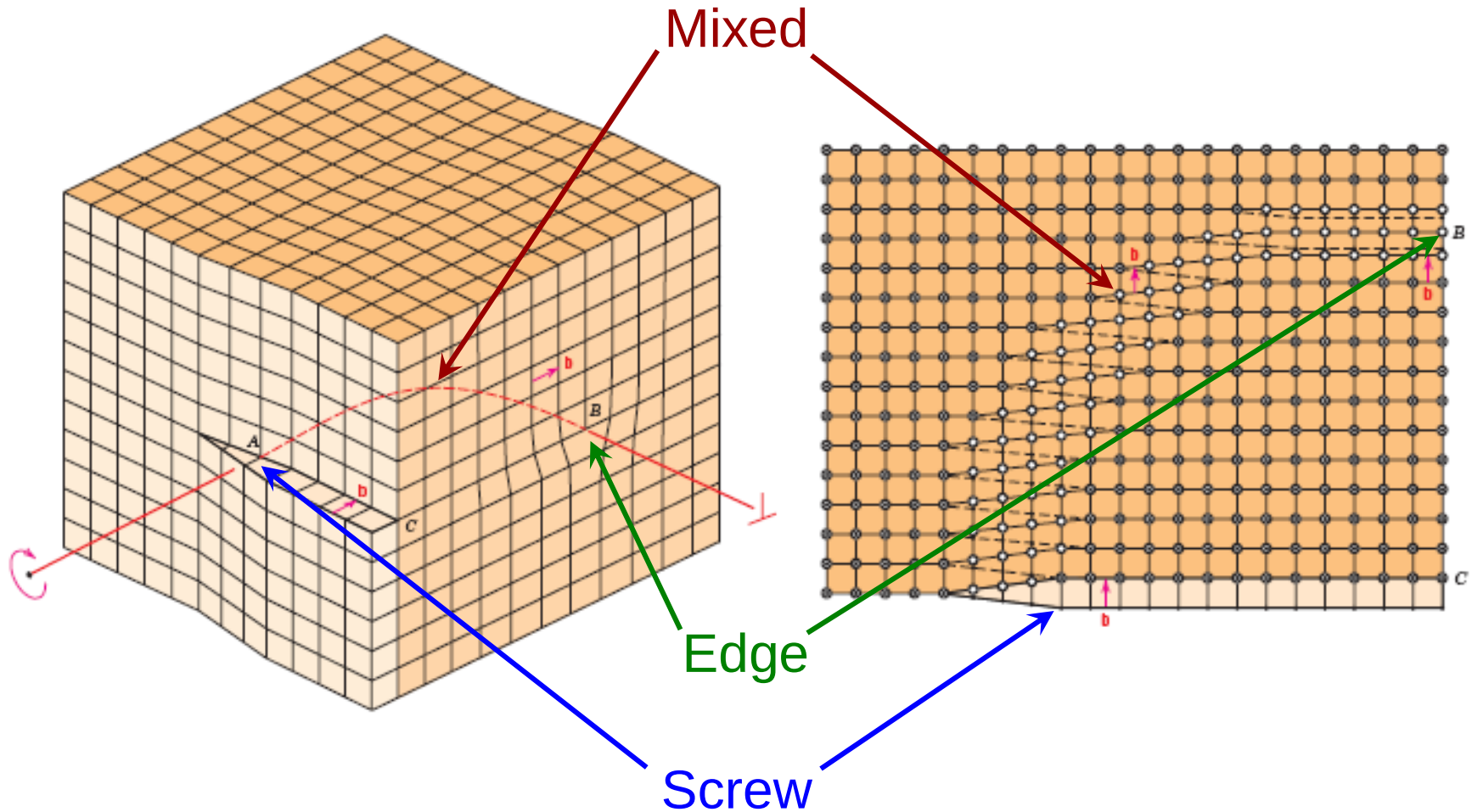
Atomic view of edge dislocation motion from left to right as a crystal is sheared.

Imperfections in Solids

Screw Dislocation



Edge, Screw, and Mixed Dislocations



(2) LINEAR DEFECTS

2.a. Edge Dislocations: an extra portion of a plane of atoms, or half-plane, the edge of which terminates within the crystal.

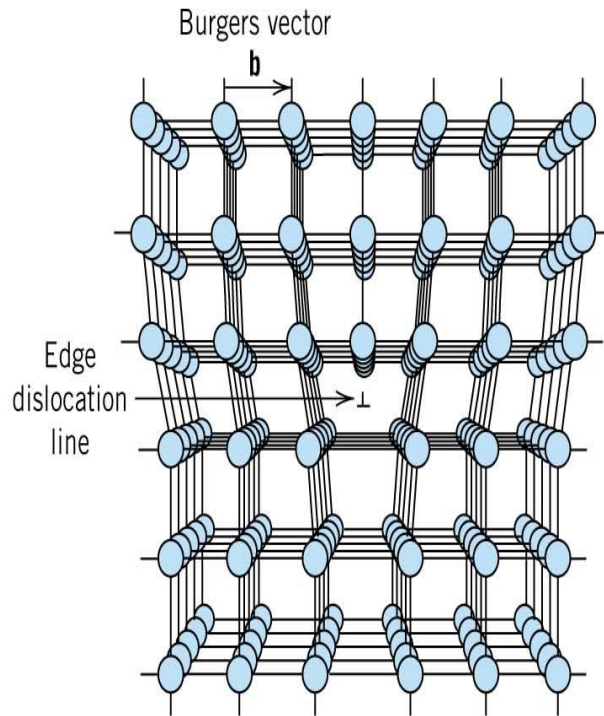
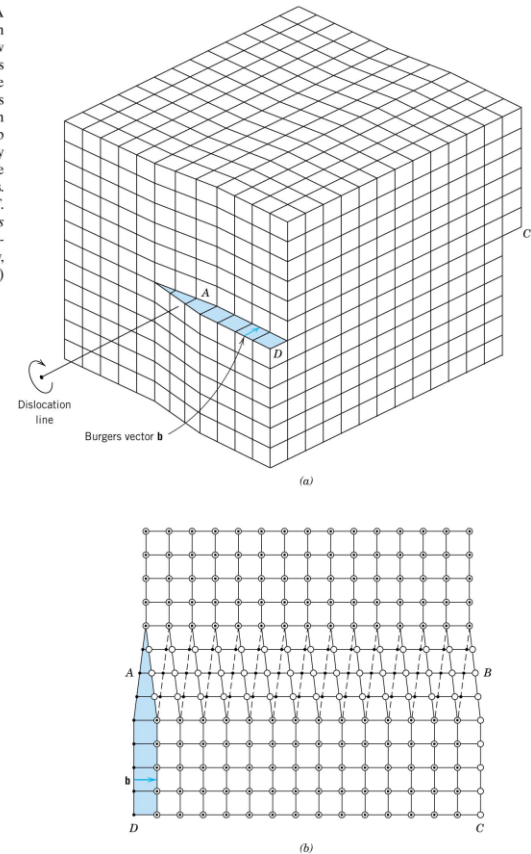


FIGURE 4.3 The atom positions around an edge dislocation; extra half-plane of atoms shown in perspective. (Adapted from A. G. Guy, *Essentials of Materials Science*, McGraw-Hill Book Company, New York, 1976, p. 153.)

2.b. Screw Dislocation:

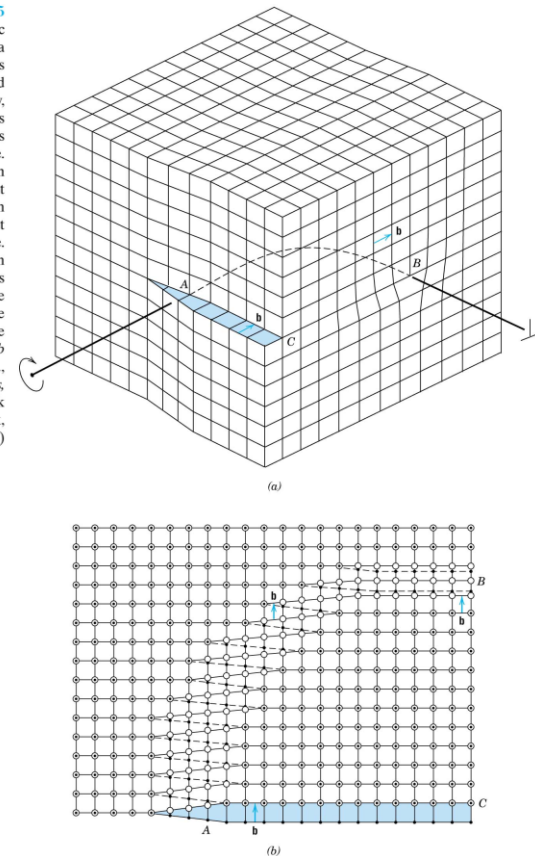
Shear stresses cause shifts between two parts of the crystal.

FIGURE 4.4 (a) A screw dislocation within a crystal. (b) The screw dislocation in (a) as viewed from above. The dislocation line extends along line AB . Atom positions above the slip plane are designated by open circles, those below by solid circles. (Figure b from W. T. Read, Jr., *Dislocations in Crystals*, McGraw-Hill Book Company, New York, 1953.)



2.c. Mixed Dislocations: Edge and Screw dislocations combined.

FIGURE 4.5
(a) Schematic representation of a dislocation that has edge, screw, and mixed character. (b) Top view, where open circles denote atom positions above the slip plane. Solid circles, atom positions below. At point A, the dislocation is pure screw, while at point B, it is pure edge. For regions in between where there is curvature in the dislocation line, the character is mixed edge and screw. (Figure b from W. T. Read, Jr., *Dislocations in Crystals*, McGraw-Hill Book Company, New York, 1953.)



Area (interfacial) Defects in Solids

- **External surfaces** one of most obvious boundaries, along which the crystal structure terminates. Surface atoms are not bonded to the maximum number of nearest neighbors, and are therefore in a higher energy state than the atoms at interior positions
- **Grain boundaries** occur where the crystallographic direction of the lattice abruptly changes. This usually occurs when two crystals begin growing separately and then meet.

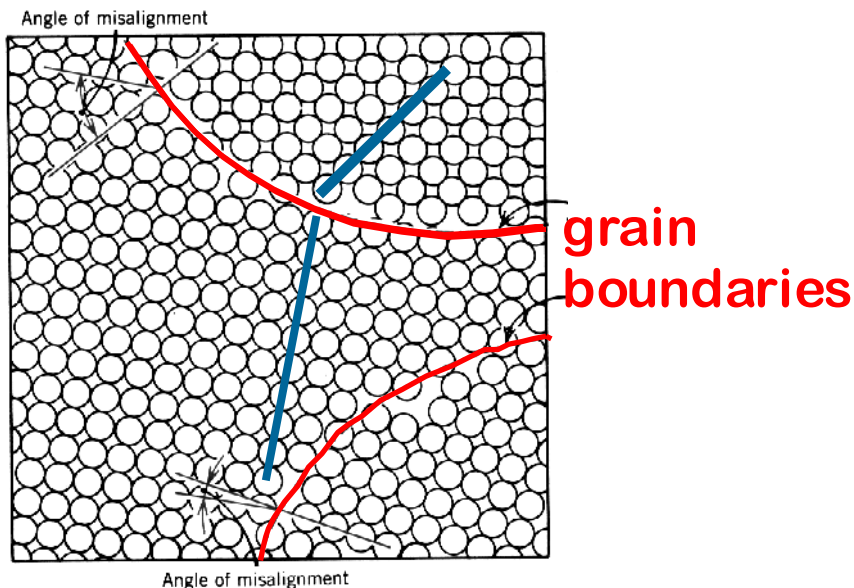


(3) INTERFACIAL/AREA DEFECTS: GRAIN BOUNDARIES

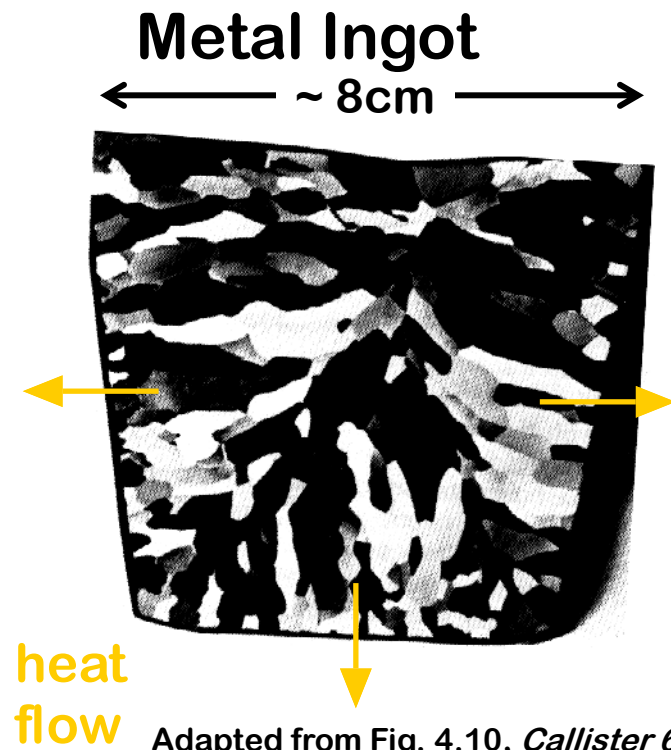
Grain boundaries:

- are boundaries between crystals.
- are produced by the solidification process, for example.
- have a change in crystal orientation across them.
- impede dislocation motion.

Schematic



Adapted from Fig. 4.7, *Callister 6e*.



Adapted from Fig. 4.10, *Callister 6e*. (Fig. 4.10 is from *Metals Handbook*, Vol. 9, 9th edition, *Metallography and Microstructures*, Am. Society for Metals, Metals Park, OH, 1985.)



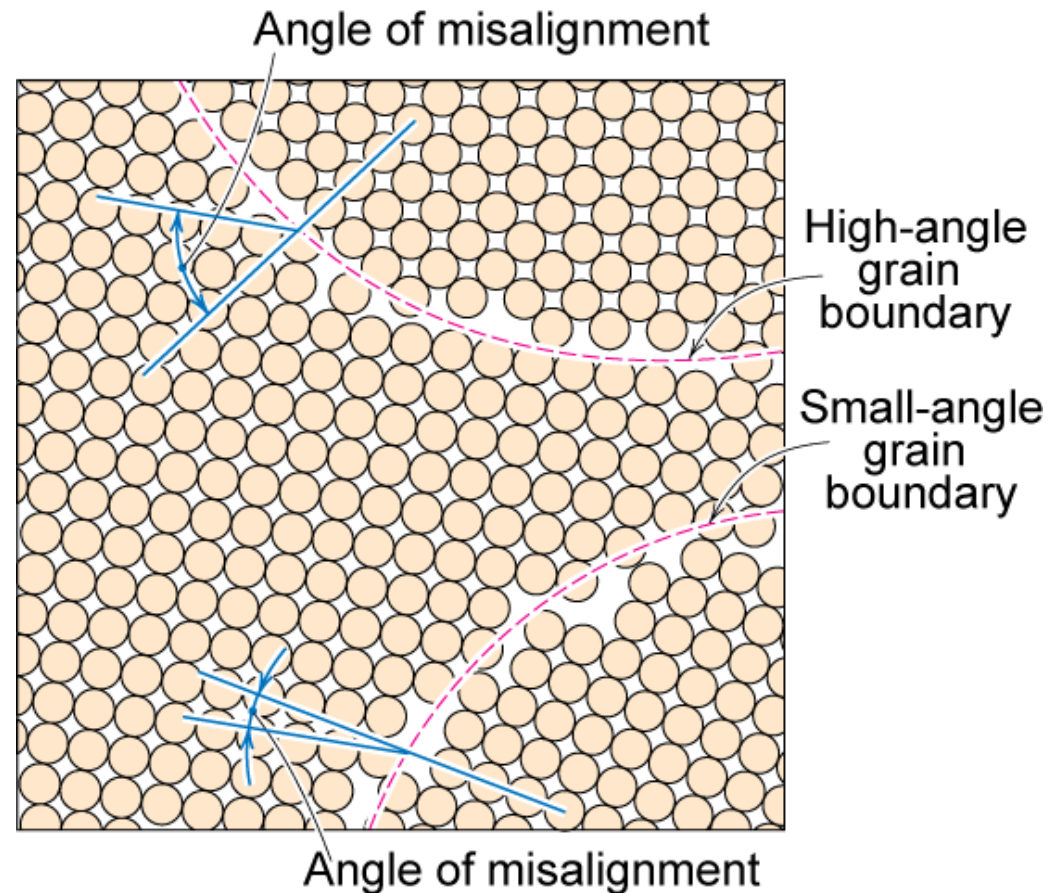
- The grain boundary are classified according to the angel of misorientation between the grains to (low and high) angle grain boundary



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



- Grain boundaries have higher energy than the grains themselves.
- The magnitude of the grain boundary energy is proportional to the angle of misorientation, being larger for high angle boundary



- Thus the grain boundaries are more chemically reactive than the grains themselves.
- Impurity atoms often preferentially segregate along these boundaries because of their high energy
- The total energy is lower in coarse grained materials , Than the fine grained one, since there is less boundary area in the former.



COMPOSITION

Definition: Amount of impurity (B) and host (A) in the **system**.

Two descriptions:

- Weight %

$$C_B = \frac{\text{mass of B}}{\text{total mass}} \times 100$$

- Atom %

$$C'_B = \frac{\# \text{ atoms of B}}{\text{total \# atoms}} \times 100$$

- Conversion between wt % and at% in an A-B alloy:

$$C_B = \frac{C'_B A_B}{C'_A A_A + C'_B A_B} \times 100$$

$$C'_B = \frac{C_B / A_B}{C_A / A_A + C_B / A_B}$$

- Basis for conversion:

$$\text{mass of B} = \text{moles of B} \times A_B$$

$$\text{mass of A} = \text{moles of A} \times A_A$$

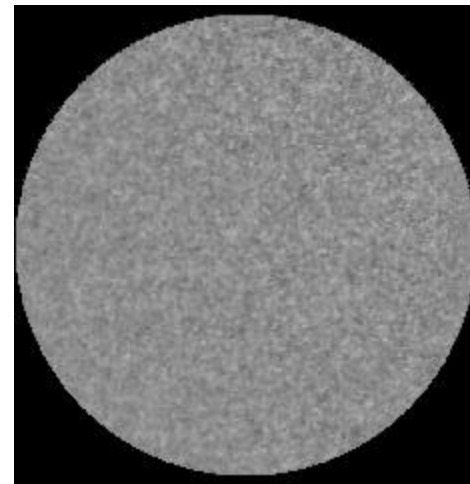
atomic weight of B

atomic weight of A



ALLOYING A SURFACE

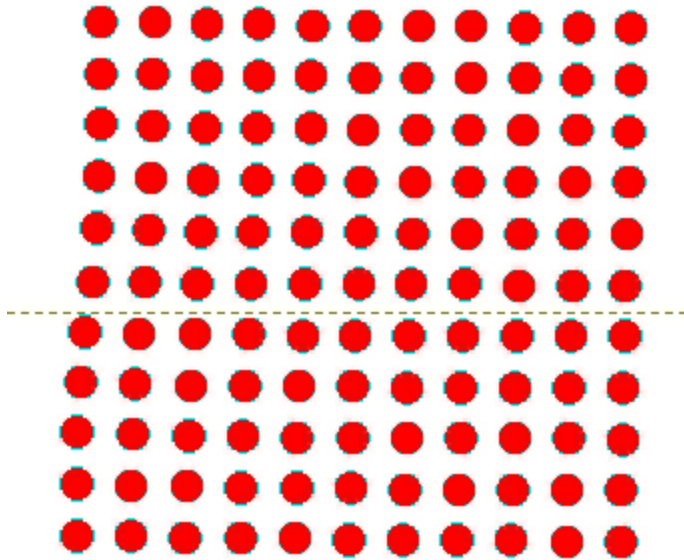
- Low energy electron microscope view of a (111) surface of Cu.
- Sn islands move along the surface and "alloy" the Cu with Sn atoms, to make "bronze".
- The islands continually move into "unalloyed" regions and leave tiny bronze particles in their wake.
- Eventually, the islands disappear.



Reprinted with permission from: A.K. Schmid, N.C. Bartelt, and R.Q. Hwang, "Alloying at Surfaces by the Migration of Reactive Two-Dimensional Islands", Science, Vol. 290, No. 5496, pp. 1561-64 (2000). Field of view is 1.5 μm and the temperature is 290K.

BOND BREAKING AND REMAKING

- 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.



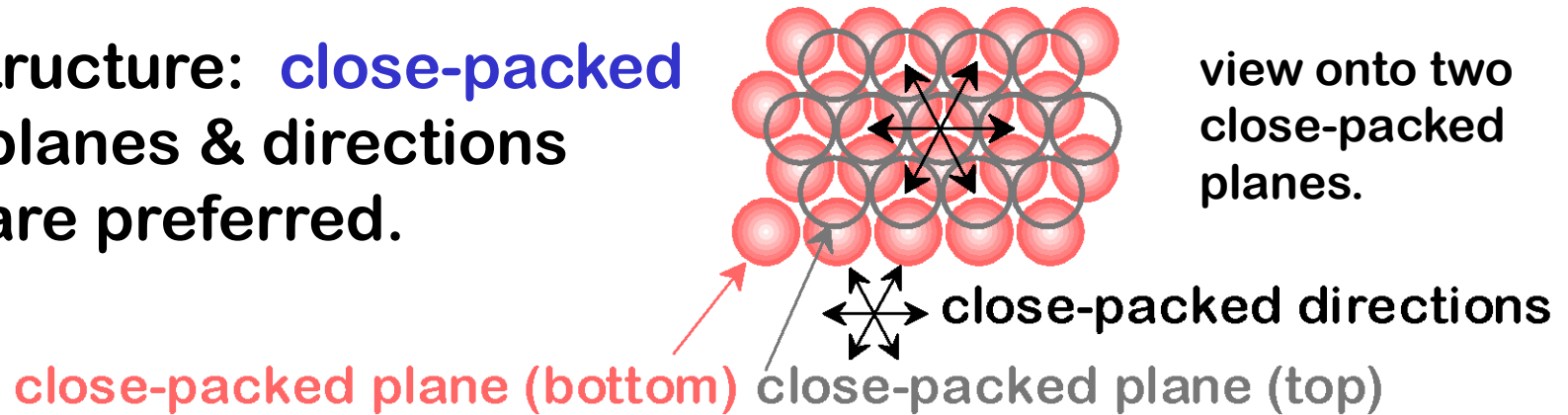
Atomic view of edge dislocation motion from left to right as a crystal is sheared.

(Courtesy P.M. Anderson)



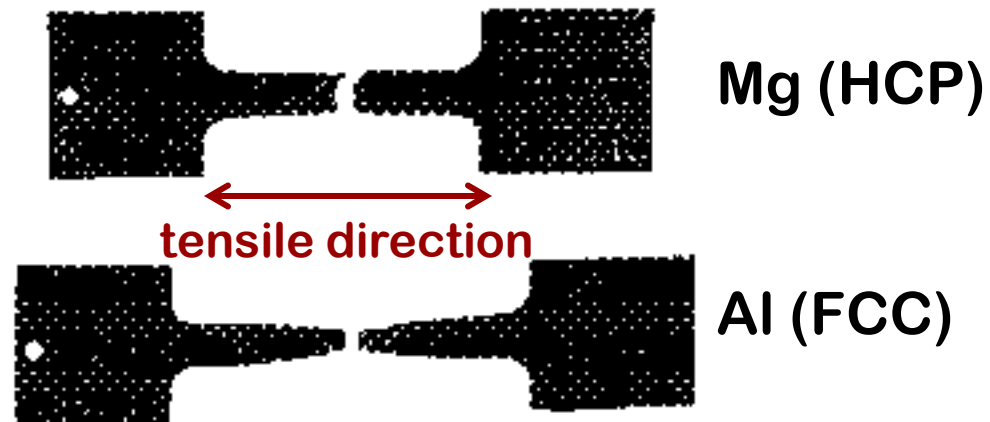
DISLOCATIONS & CRYSTAL STRUCTURE

- 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

- Results of tensile testing.

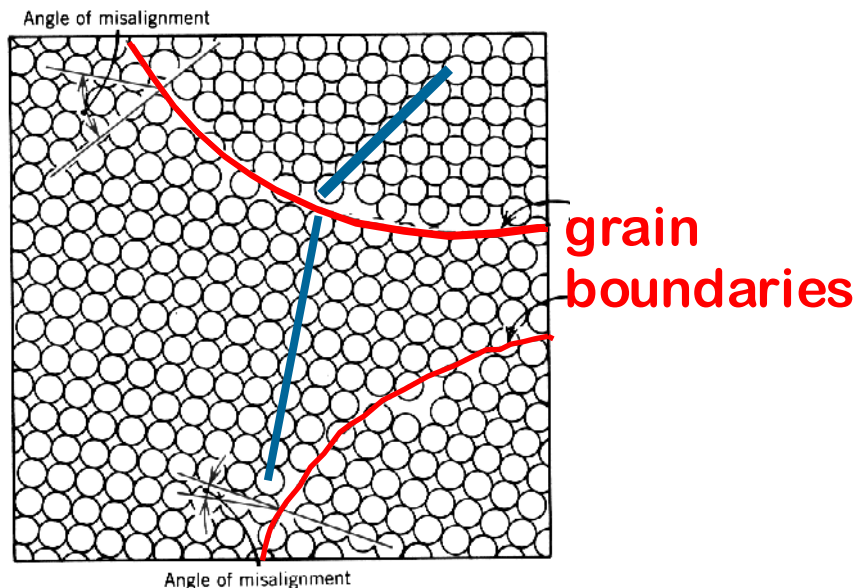


(3) INTERFACIAL/AREA DEFECTS: GRAIN BOUNDARIES

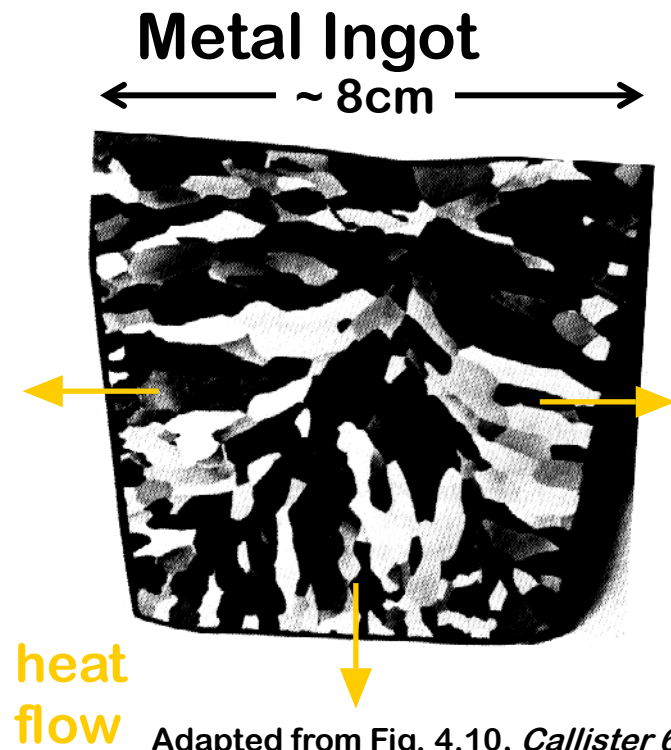
Grain boundaries:

- are boundaries between crystals.
- are produced by the solidification process, for example.
- have a change in crystal orientation across them.
- impede dislocation motion.

Schematic



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Twin Boundaries

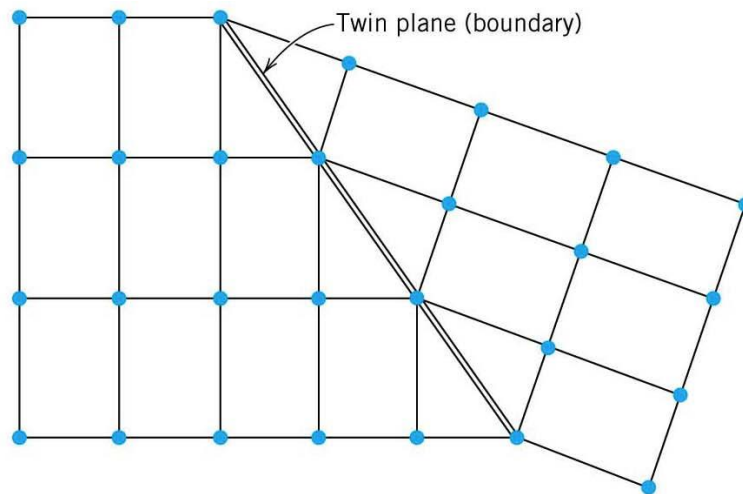
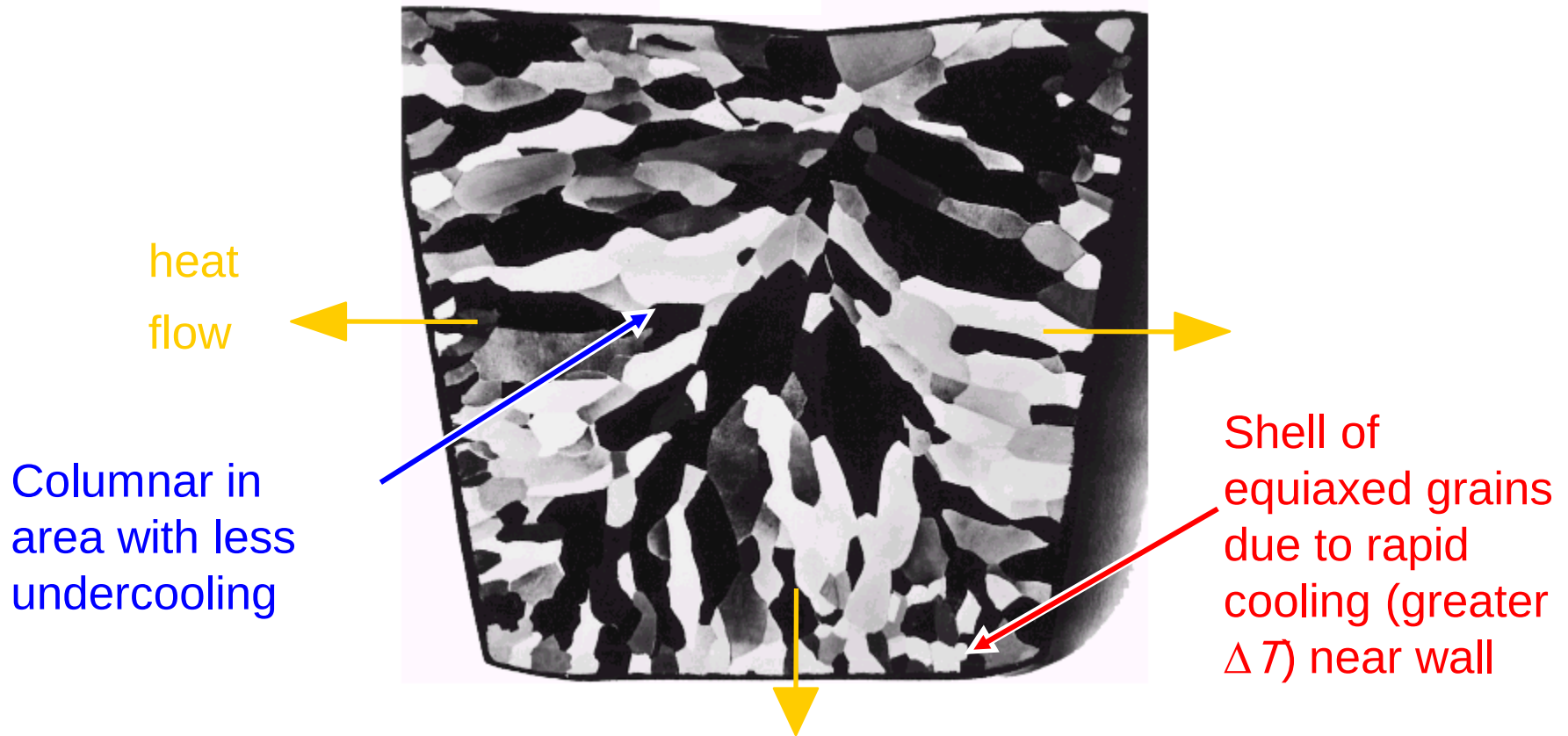


FIGURE 4.9 Schematic diagram showing a twin plane or boundary and the adjacent atom positions (dark circles).

Solidification

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

← ~ 8 cm →



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

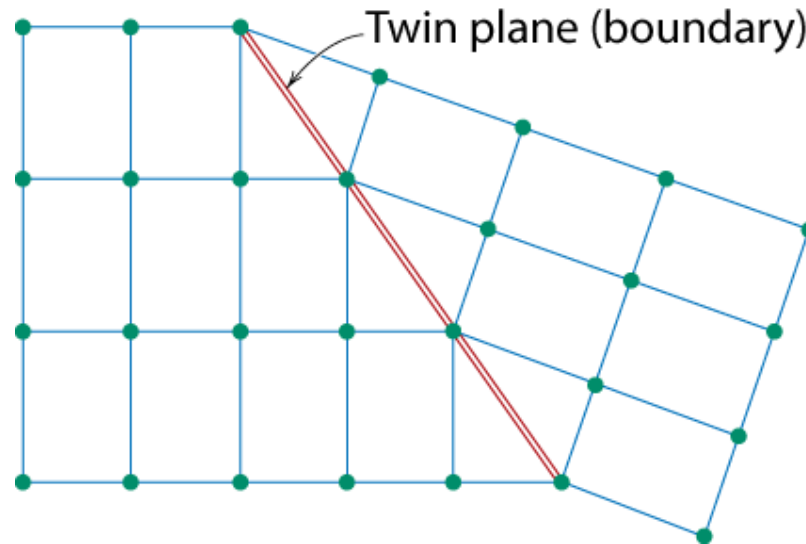
Planar (interfacial) Defects in Solids

- **External surfaces** one of most obvious boundaries, along which the crystal structure terminates. Surface atoms are not bonded to the maximum number of nearest neighbors, and are therefore in a higher energy state than the atoms at interior positions
- **Grain boundaries** occur where the crystallographic direction of the lattice abruptly changes. This usually occurs when two crystals begin growing separately and then meet.



Planar Defects in Solids

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



there is a specific mirror lattice symmetry; that is, atoms on one side of the boundary are located in mirror-image positions of the atoms on the other side. The region of material between these boundaries is appropriately termed a twin

Stacking faults: occur in a number of crystal structures, but the common example is in close-packed structures. Face centered cubic (FCC) structures differ from hexagonal close packed (HCP) structures only in stacking order

For FCC metals an error in **ABCABC** packing sequence

Ex: **ABCABABC**

Anti phase boundaries: occur in ordered alloys: in this case, the crystallographic direction remains the same, each side of the boundary has an opposite phase: For example if the ordering is usually **ABABABAB**, an anti phase boundary takes the form of **ABABBABA**



problem

- For each of the following stacking sequences found in FCC metals, cite the type of planar defect that exists:

a) *.....A B C A B C B A C B A*

b) *.....A B C A B C B C A B C*



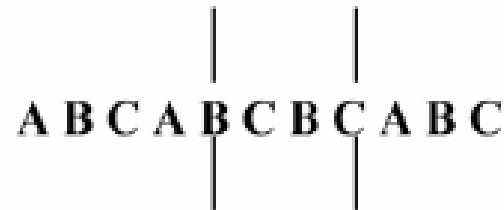
Solution:

- a) The interfacial defect that exists for this stacking sequence is a twin boundary, which occurs at the indicated position



The stacking sequence on one side of this position is mirrored on the other side

- b) The interfacial defect that exists within this FCC stacking sequence is a stacking fault, which occurs between the two lines.



Within this region, the stacking sequence is HCP.



Bulk(volume) defects

- These include pores, cracks, foreign inclusions, and other phases. They are normally introduced during processing and fabrication steps
- Voids are small regions where there are no atoms, and can be thought of as clusters of vacancies.
- Impurities can cluster together to form small regions of a different phase. These are often called precipitates.



Microscopic Examination

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



Microscopic Examination

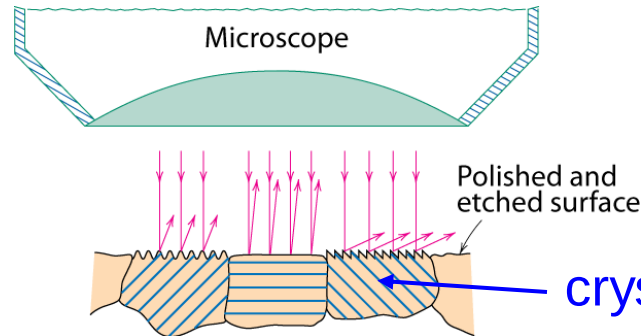
Several important applications of micro-structural examinations are as follows:

- To ensure that the association between the properties and structure (and defects) are properly understood
- To predict the properties of materials once these relationship have been established
- To design the alloys with new property combinations
- To determine whether or not a material has been correctly heat treated
- To ascertain the mode of mechanical fracture



Optical Microscopy

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



• the chemical reactivity of the grains of some single-phase materials depends on crystallographic orientation



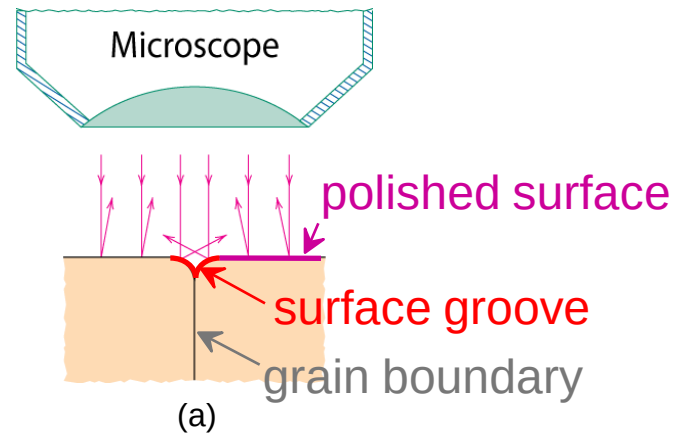
Micrograph of brass (a Cu-Zn alloy)

← 0.75mm →

Optical Microscopy

Grain boundaries...

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



(b)

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 μ m = 100 nm

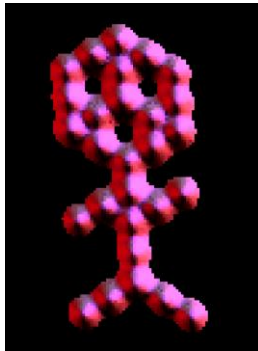
For higher resolution need higher frequency

- 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.

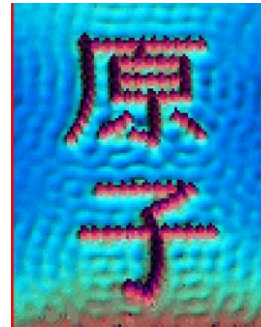


Scanning Tunneling Microscopy (STM)

- 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”.

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.)

