# CHAPTER 4:
IMPERFECTIONS IN SOLIDS

ISSUES TO ADDRESS...

- What types of defects arise in solids?

- Can the number and type of defects be varied and controlled?

- How do defects affect material properties?
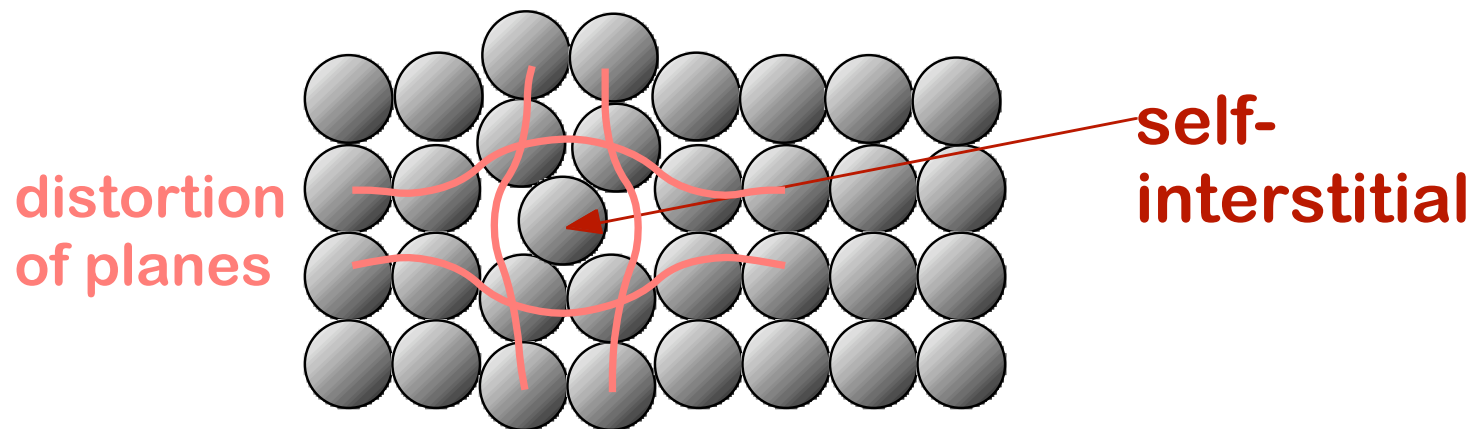
- Are defects undesirable?

TYPES OF IMPERFECTIONS

- **Vacancy atoms**
- **Interstitial atoms**   Point defects
- **Substitutional atoms**

- **Dislocations**   Line defects

- **Grain Boundaries**   Area defects

POINT DEFECTS

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

distortion of planes
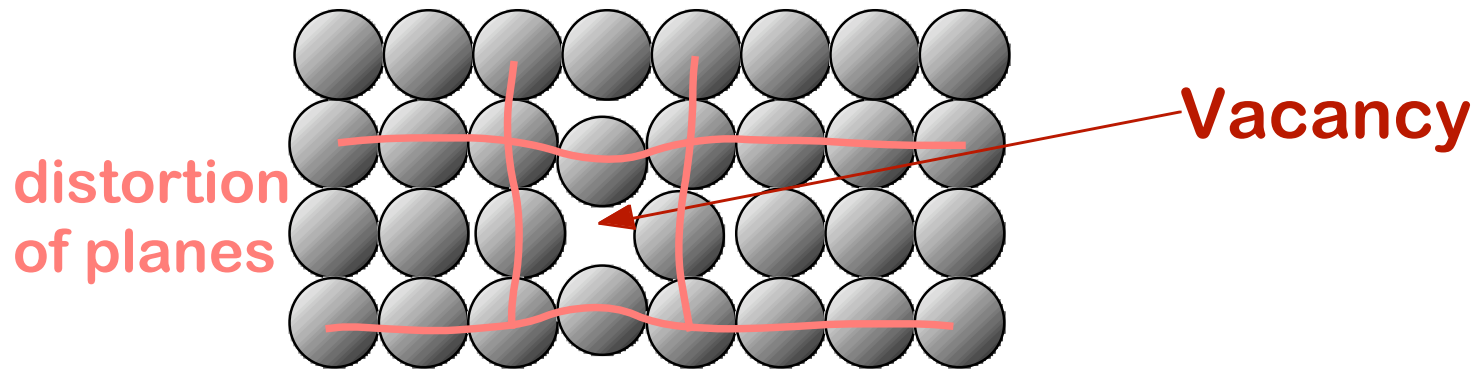
Vacancy

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

distortion of planes
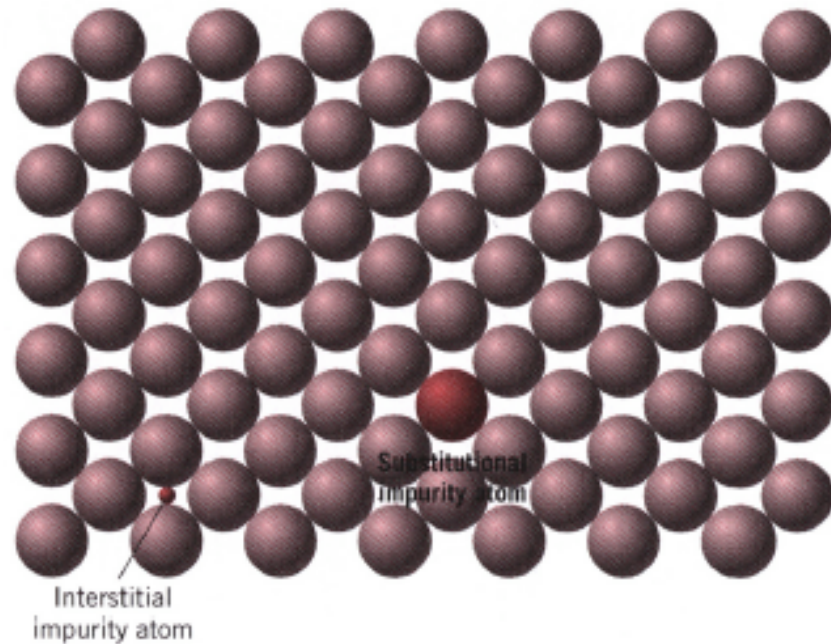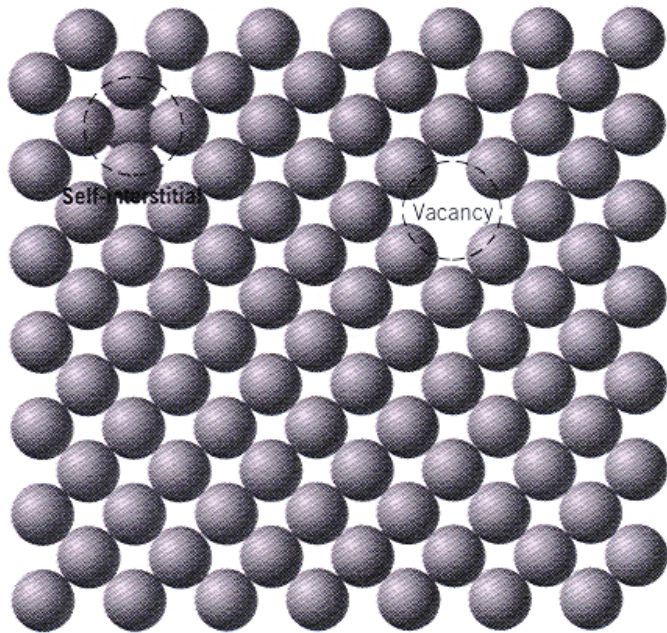
self-interstitial

Point defects

- Vacancy:
- Self-interstitial:
- Substitutional

- Fundamental concepts
  - alloy
  - solute
  - solvent
  - solid solution
- Solute solutions
  - substitution
    - **atomic size factor**
    - **crystal structure**
    - **electronegativity**
    - **valences**
  - interstitial

EQUIL. CONCENTRATION: POINT DEFECTS

- **Equilibrium concentration varies with temperature!**

No. of defects

Activation energy

$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right)$$

No. of potential defect sites.

Temperature

Boltzmann's constant

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

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

Each lattice site is a potential vacancy site

MEASURING ACTIVATION ENERGY

- **We can get Q from an experiment.**

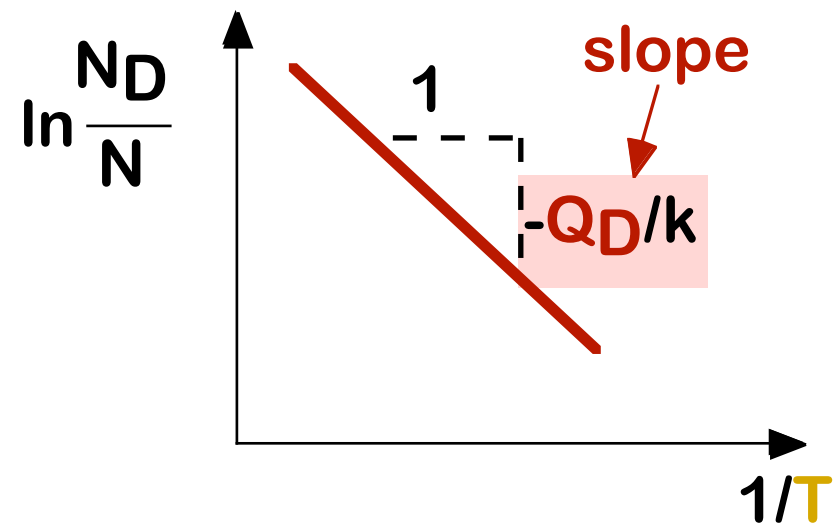$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right)$$

- **Measure this…**

- **Replot it…**

$\frac{N_D}{N}$

exponential dependence!

T

defect concentration

$\ln \frac{N_D}{N}$

slope

1

-Q_D/k
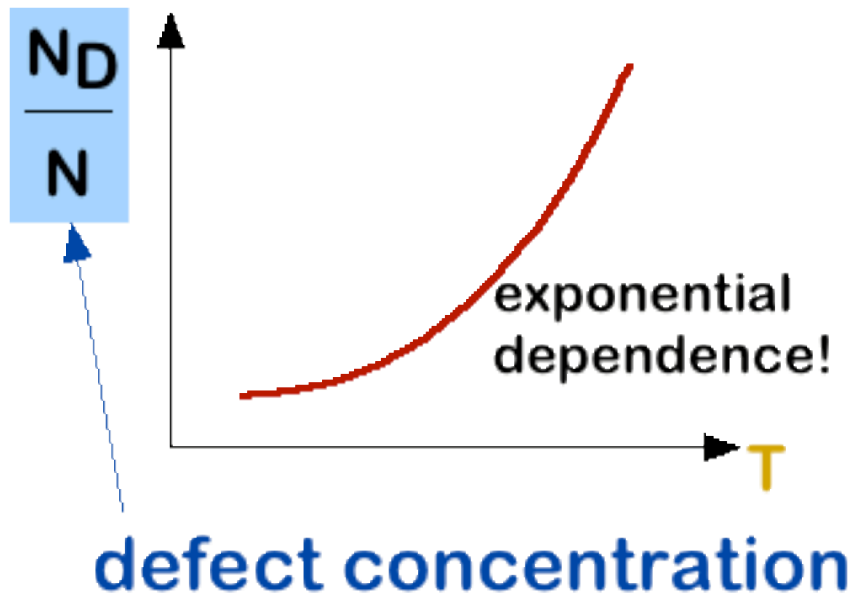
1/T

ESTIMATING VACANCY CONC.

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

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

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

$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right) = 2.7 \cdot 10^{-4}$$

0.9eV/atom

1273K

8.62×10^{-5} eV/atom-K

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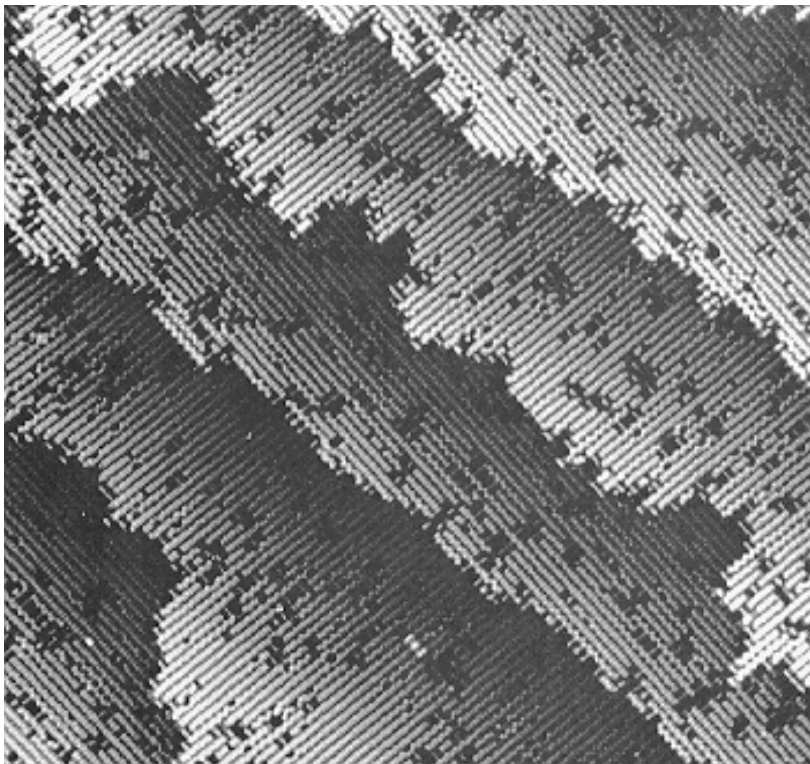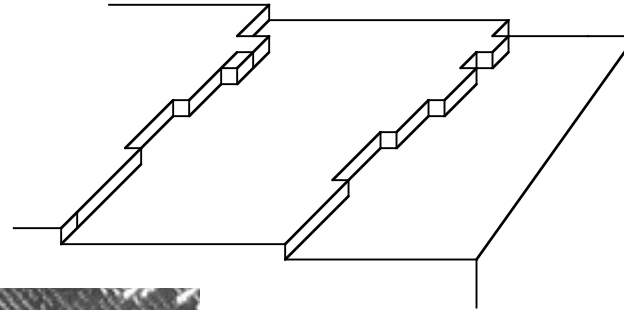
- **Answer:**

$N_D = 2.7 \cdot 10^{-4} \cdot 8.0 \times 10^{28}$ sites $= 2.2 \times 10^{25}$ vacancies

T = terrace

L = ledge
K = kink

OBSERVING EQUIL. 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.

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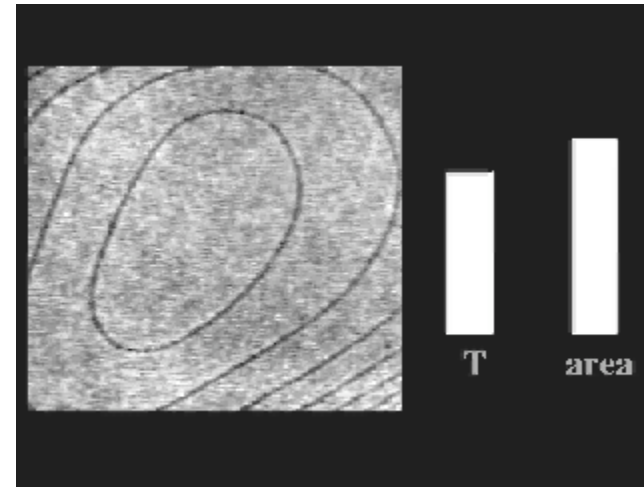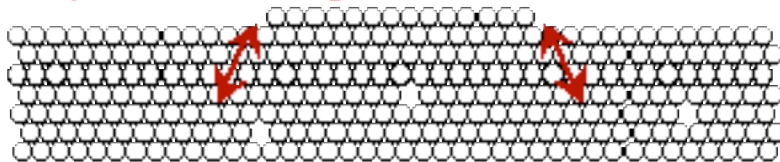
Reprinted with permission from Nature (K.F. McCarty, J.A. Nobel, and N.C. Bartelt, "Vacancies in Solids and the Stability of Surface Morphology", Nature, Vol. 412, pp. 622-625 (2001). Image is 5.75 μm by 5.75 μm.) Copyright (2001) Macmillan Publishers, Ltd.

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 alloy
(e.g., **Cu** in **Ni**)

Interstitial alloy
(e.g., **C** in **Fe**)
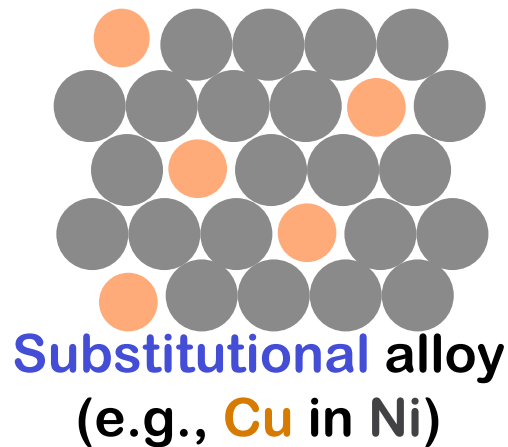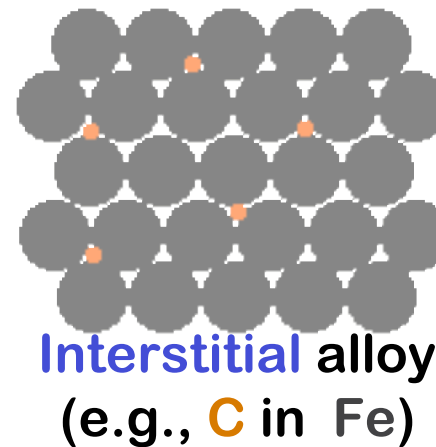
- **Solid solution of B in A plus particles of a new phase (usually for a larger amount of B)**
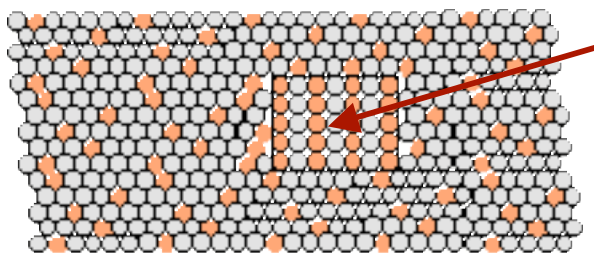
Second phase particle
--different composition
--often different structure.

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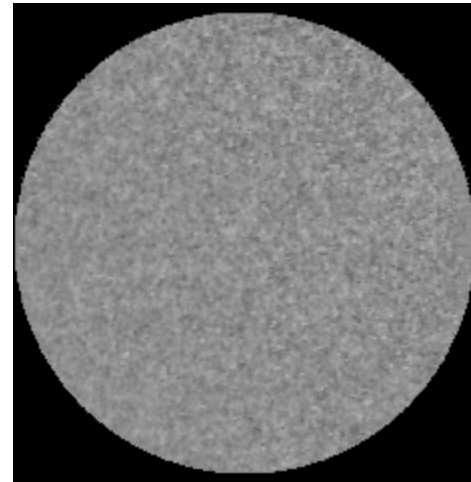
Reprinted with permission from: A.K. Schmid, N.C. Bartelt, and R.Q. Hwang, "Alloying at Surfaces by the Migration of Reactive Two-Dimensional Islands", Science, Vol. 290, No. 5496, pp. 1561-64 (2000). Field of view is 1.5 μm and the temperature is 290K.

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:**

mass of B = moles of B x A_B ⟵ atomic weight of B

mass of A = moles of A x A_A ⟵ atomic weight of A

LINE DEFECTS

Dislocations:
- are line defects,
- cause slip between crystal plane when they move,
- produce permanent (plastic) deformation.

Schematic of a Zinc (HCP):
- before deformation
- after tensile elongation

slip steps
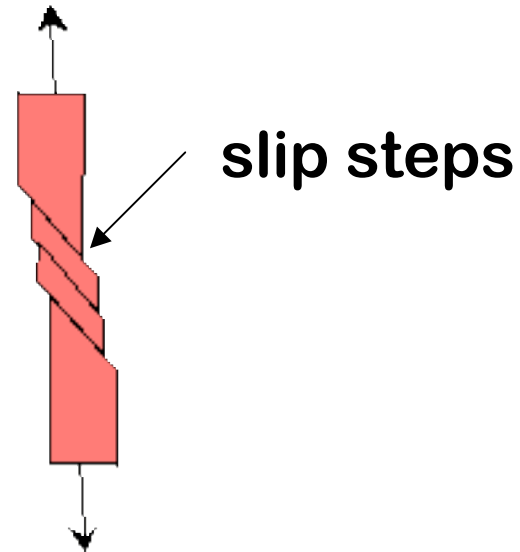
INCREMENTAL SLIP

- **Dislocations slip planes *incrementally*...**
- **The dislocation line (the moving red dot)...**
  ...separates slipped material on the left
  from unslipped material on the right.
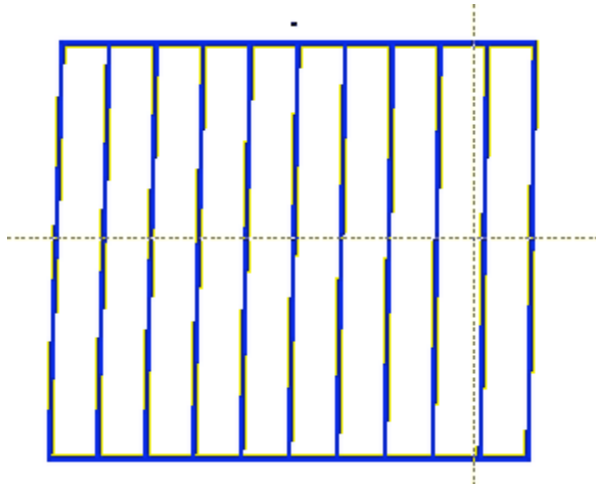
Simulation of dislocation
motion from left to right
as a crystal is sheared.

(Courtesy P.M. Anderson)

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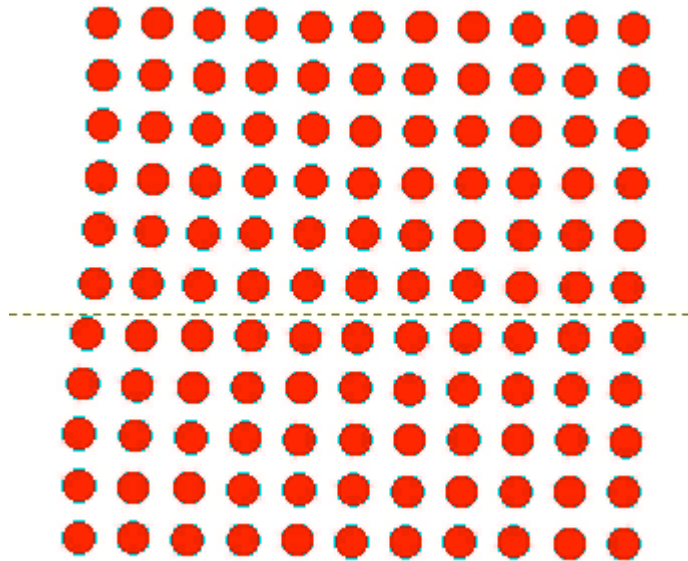
Atomic view of edge dislocation motion from left to right as a crystal is sheared.

(Courtesy P.M. Anderson)

Dislocations-linear   defects

- Edge dislocation:
- Dislocation line:

Edge dislocation

Burgers vector
b

Edge
dislocation
line
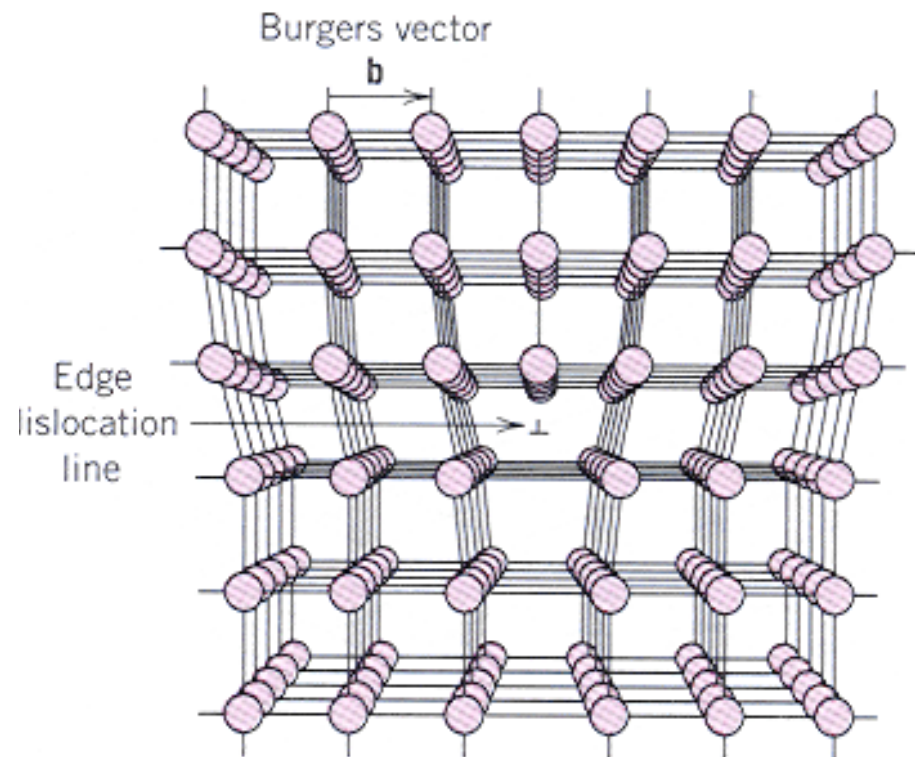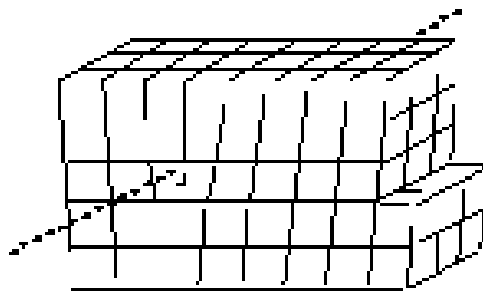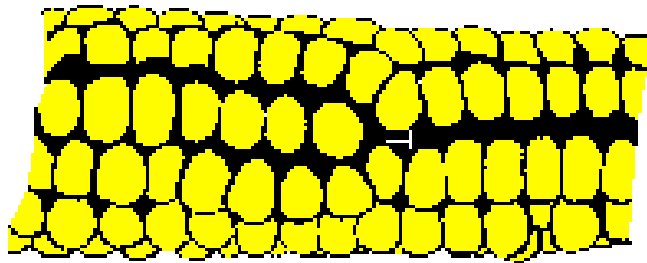
Dislocations-linear defects

- Screw dislocation:
- ❒ Slip plane:
- ❒ Slip plane contains both Burgers Vectors and dislocation line

Dislocation line

Burgers vector **b**

(a)
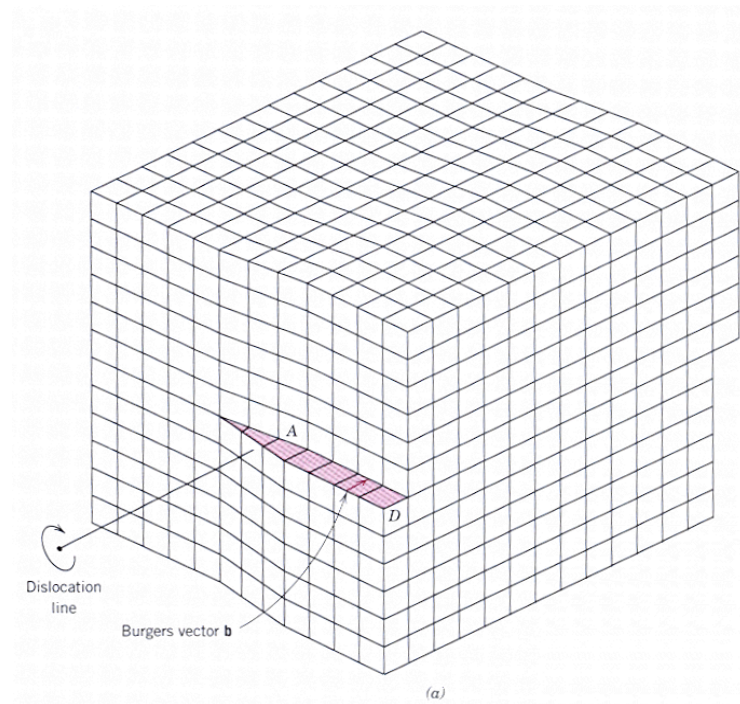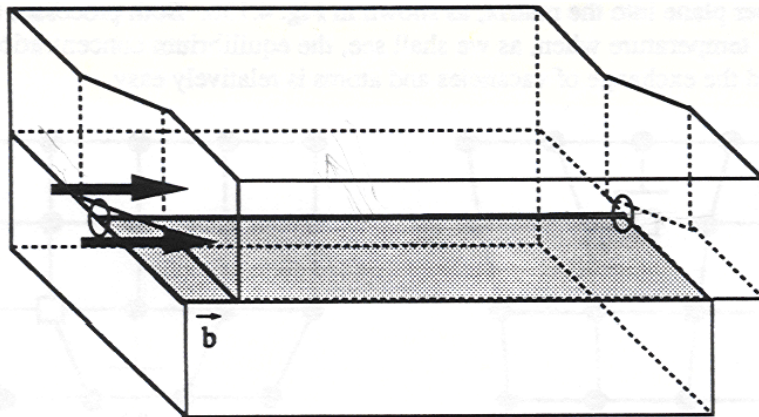
Dislocations-linear defects

- Mixed dislocation
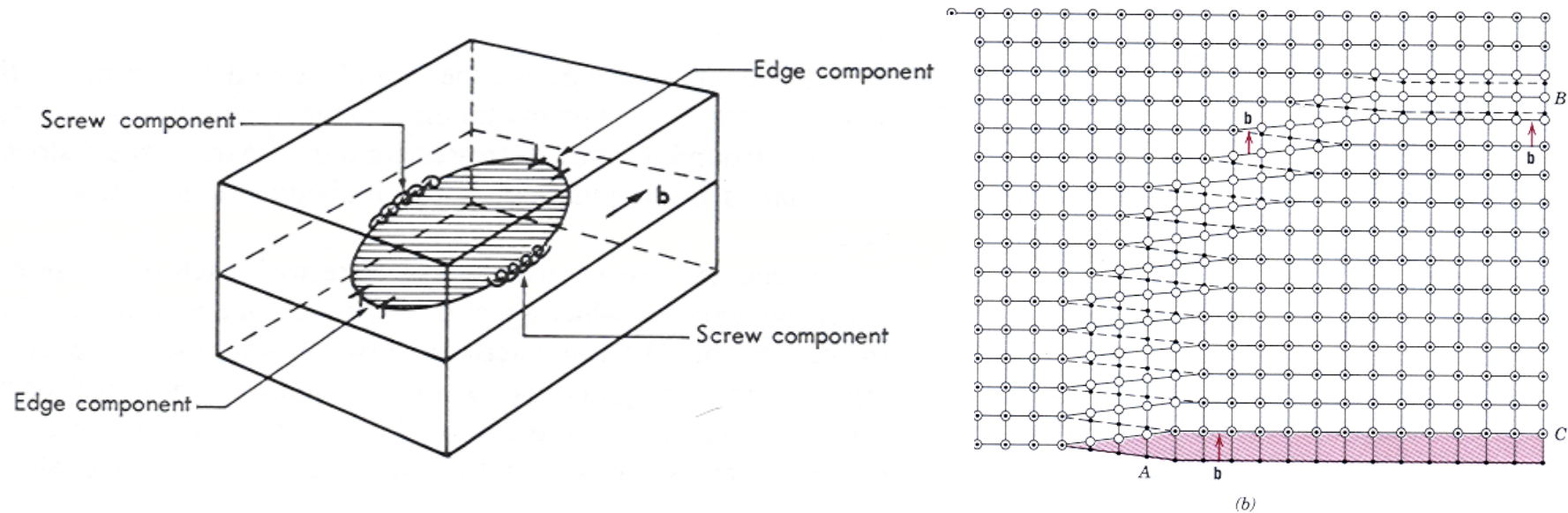
Burgers Circuit & Burgers Vector

□ Burgers circuit: any close loop contain dislocations by an atom to atom path

□ Burgers vectors: the vector required to complete the circuit in a perfect crystal; the direction of atom displacement
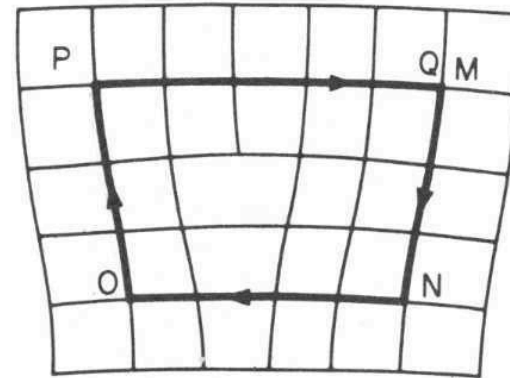
(a)
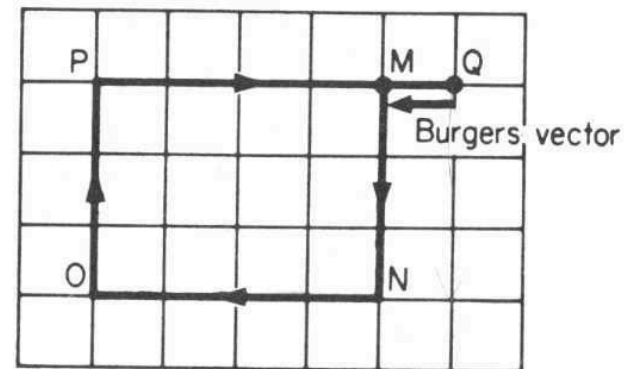
(b)

(a) Burgers circuit round an edge dislocation
(b) the same circuit in a perfect crystal

DISLOCATIONS & CRYSTAL STRUCTURE

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

view onto two
close-packed
planes.

close-packed directions

close-packed plane (bottom) close-packed plane (top)
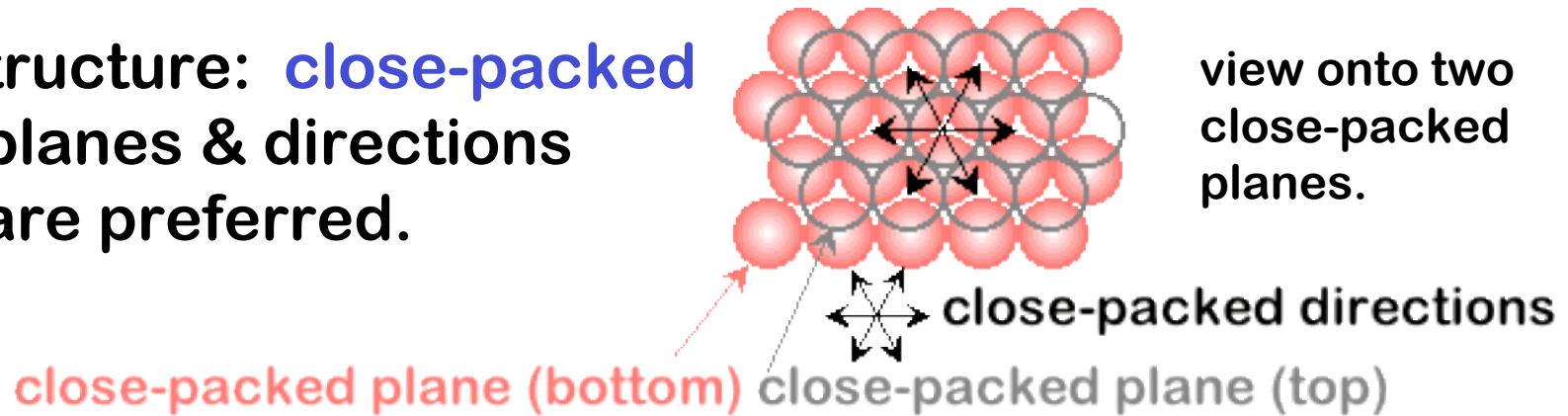
• **Comparison among crystal structures:**
  FCC: many close-packed planes/directions;
  HCP: only one plane, 3 directions;
  BCC: none

• **Results of tensile**
  testing.

Mg (HCP)

tensile direction

Al (FCC)
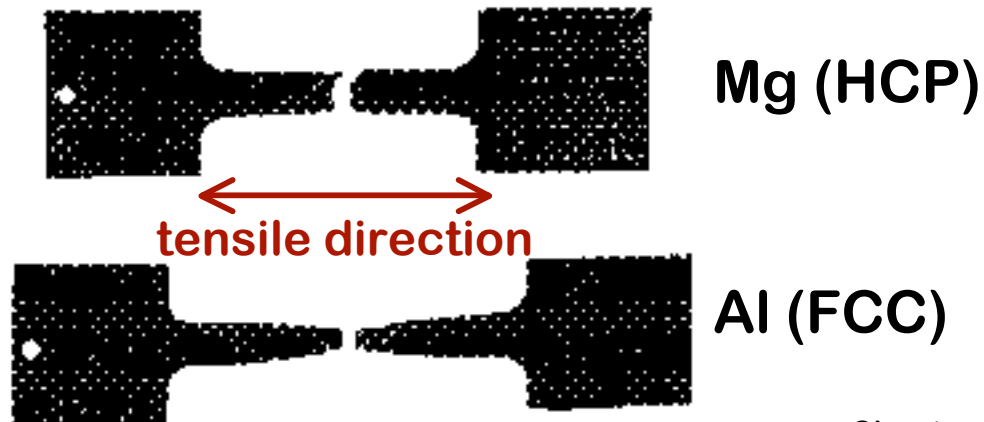
Dislocations- linear defects

- What cause dislocations?
  - processing
  - plastic deformation
  - thermal stresses
- Observation of dislocations
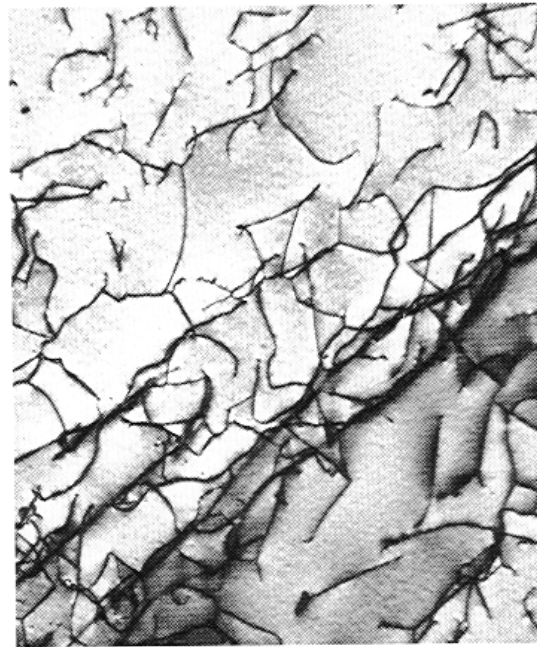
A TEM micrograph of a titanium alloy

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

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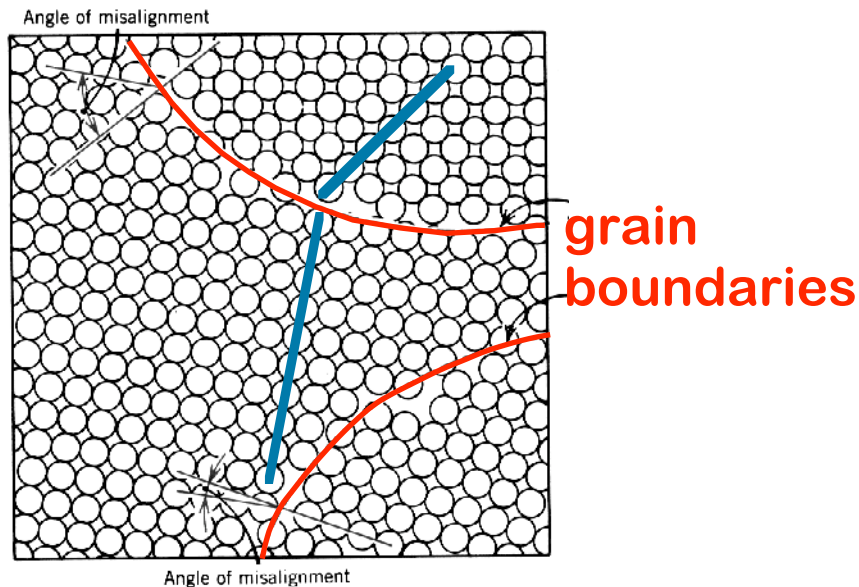
Adapted from Fig. 4.7, *Callister 6e.*

Metal Ingot

← ~ 8cm →

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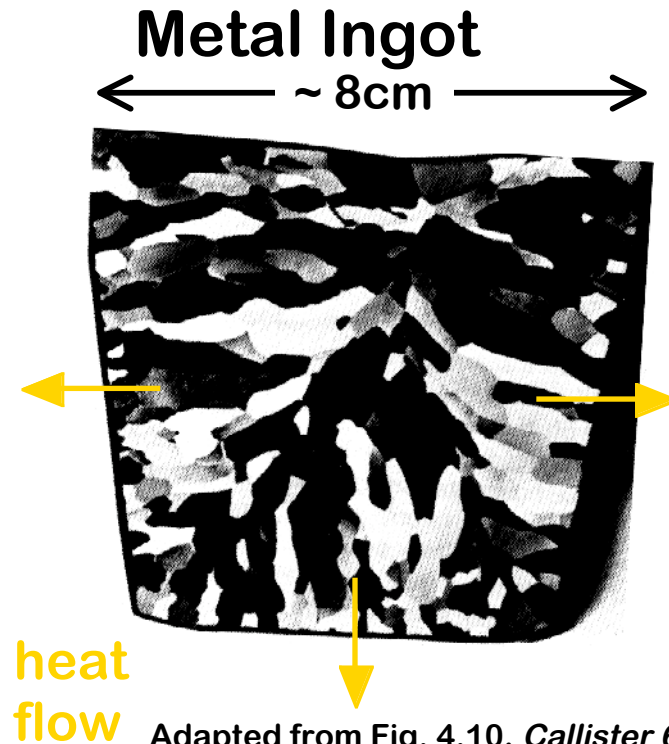
Adapted from Fig. 4.10, *Callister 6e.*
(Fig. 4.10 is from *Metals Handbook*, Vol. 9, 9th edition, *Metallography and Microstructures*, Am. Society for Metals, Metals Park, OH, 1985.)

OPTICAL MICROSCOPY (1)

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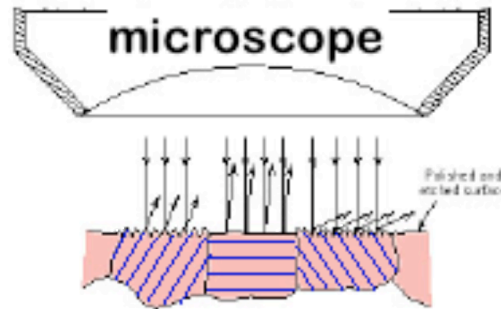
close-packed planes

Adapted from Fig. 4.11(b) and (c),
Callister 6e. (Fig. 4.11(c) is courtesy
of J.E. Burke, General Electric Co.

micrograph of Brass (Cu and Zn)

← 0.75mm →

OPTICAL MICROSCOPY (2)

Grain boundaries...

- are imperfections,
- are more susceptible to etching,
- may be revealed as dark lines,
- change direction in a polycrystal.

ASTM grain size number

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

no. grains/in^2 at 100x magnification

polished surface

surface groove

grain boundary

Surface groove

Grain boundary

(a)

(b)
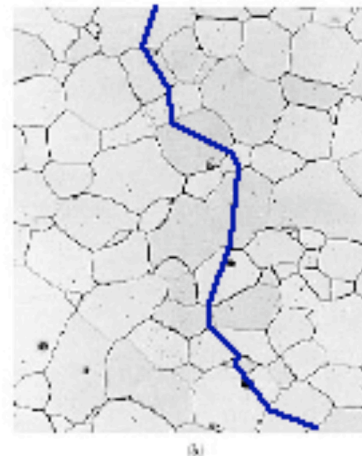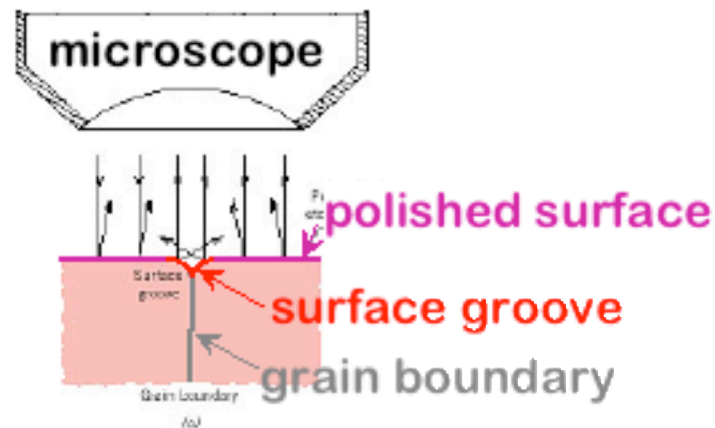
Adapted from Fig. 4.12(a) and (b), *Callister 6e.* (Fig. 4.12(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC [now the National Institute of Standards and Technology, Gaithersburg, MD].)

Interfacial defects (two dimension)

- External surfaces
- Grain boundaries

Angle of misalignment

High-angle grain boundary

Low-angle grain boundary

Angle of misalignment
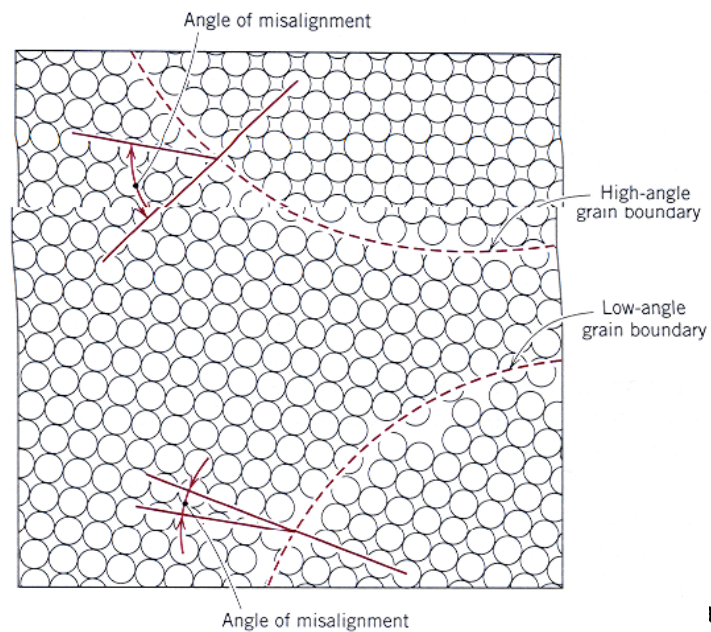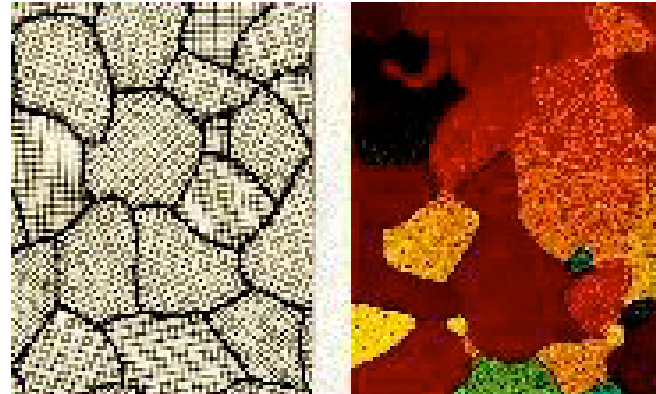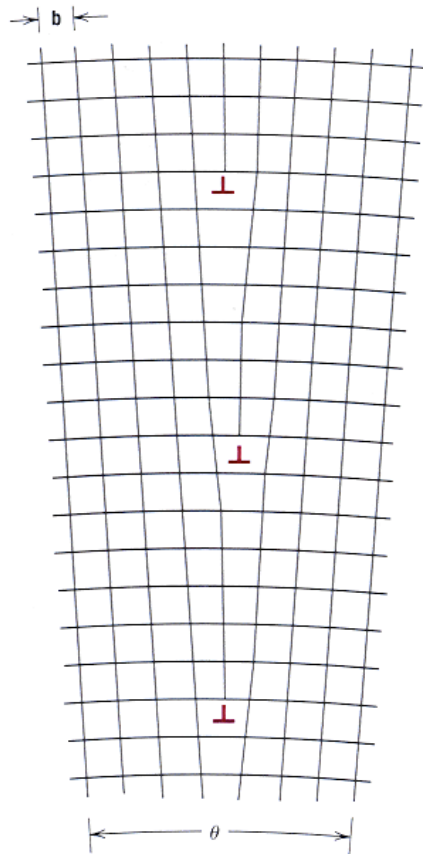
Bulk Defects (three dimension)

- ❐ Void
- ❐ Cracks
- ❐ Inclusions

TEM image of voids

(plus the naked eye) are presented in the bar chart of Figure 4.16b. For three of these techniques (SPM, TEM, and SEM), an upper resolution value is not imposed by the characteristics of the microscope and, therefore, is somewhat arbitrary and not well defined. Furthermore, by comparing Figures 4.16a and 4.16b, it is possible to decide which microscopic technique(s) is (are) best suited for examination of each of the structure types.

4.11 GRAIN-SIZE DETERMINATION

grain size

The grain size is often determined when the properties of polycrystalline and single-phase materials are under consideration. In this regard, it is important to realize that for each material, the constituent grains have a variety of shapes and a distribution of sizes. Grain size may be specified in terms of average or mean grain diameter, and a number of techniques have been developed to measure this parameter.

Before the advent of the digital age, grain-size determinations were performed manually using photomicrographs. However, today, most techniques are automated and use digital images and image analyzers with the capacity to record, detect, and measure accurately features of the grain structure (i.e., grain intercept counts, grain boundary lengths, and grain areas).

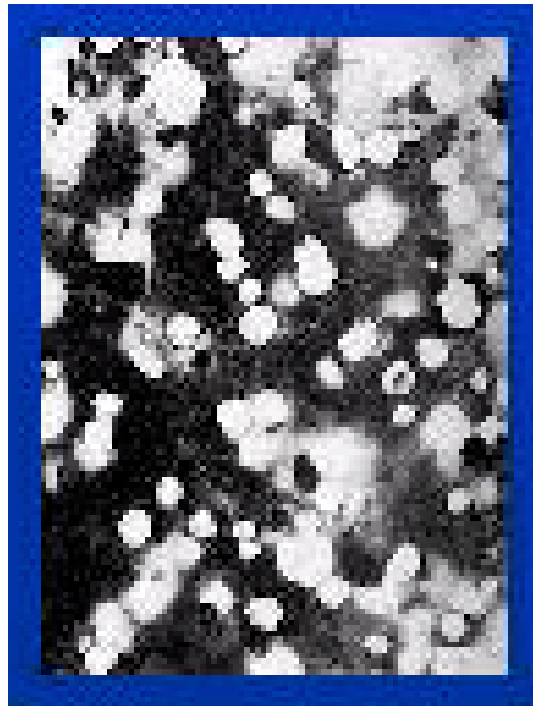We now briefly describe two common grain-size determination techniques: (1) *linear intercept*—counting numbers of grain boundary intersections by straight test lines; and (2) *comparison*—comparing grain structures with standardized charts, which are based upon grain areas (i.e., number of grains per unit area). Discussions of these techniques is from the manual perspective (using photomicrographs).

For the linear intercept method, lines are drawn randomly through several photomicrographs that show the grain structure (all taken at the same magnification). Grain boundaries intersected by all the line segments are counted. Let us represent the sum of the total number of intersections as P and the total length of all the lines by L_T. The mean intercept length $\bar{\ell}$ [in real space (at 1×—i.e., not magnified)], a measure of grain diameter, may be determined by the following expression:

$$\bar{\ell} = \frac{L_T}{PM} \tag{4.16}$$

where M is the magnification.

The comparison method of grain-size determination was devised by the American Society for Testing and Materials (ASTM).[11] The ASTM has prepared several standard comparison charts, all having different average grain sizes and referenced to photomicrographs taken at a magnification of 100×. To each chart is assigned a number ranging from 1 to 10, which is termed the *grain-size number*. A specimen must be prepared properly to reveal the grain structure, which is then photographed. Grain size is expressed as the grain-size number of the chart that most nearly matches the grains in the micrograph. Thus, a relatively simple and convenient visual determination of grain-size number is possible. Grain-size number is used extensively in the specification of steels.

Relationship between ASTM grain size number and number of grains per square inch (at 100×)

The rationale behind the assignment of the grain-size number to these various charts is as follows: Let G represent the grain-size number, and let n be the average number of grains per square inch at a magnification of 100×. These two parameters are related to each other through the expression[12]

$$n = 2^{G-1} \tag{4.17}$$

[11]ASTM Standard E112, "Standard Test Methods for Determining Average Grain Size."

[12]Please note that in this edition, the symbol n replaces N from previous editions; also, G in Equation 4.17 is used in place of the previous n. Equation 4.17 is the standard notation currently used in the literature.

For photomicrographs taken at magnifications other than 100×, use of the following modified form of Equation 4.17 is necessary:

$$n_M\left(\frac{100}{M}\right)^2 = 2^{G-1} \tag{4.18}$$

In this expression, n_M is the number of grains per square inch at magnification M. In addition, the inclusion of the $\left(\frac{M}{100}\right)^2$ term makes use of the fact that, whereas magnification is a length parameter, area is expressed in terms of units of length squared. As a consequence, the number of grains per unit area increases with the square of the increase in magnification.

Relationships have been developed that relate mean intercept length to ASTM grain-size number; these are as follows:

$$G = -6.6457 \log \bar{\ell} - 3.298 \quad \text{(for } \bar{\ell} \text{ in mm)} \tag{4.19a}$$
$$G = -6.6353 \log \bar{\ell} - 12.6 \quad \text{(for } \bar{\ell} \text{ in in.)} \tag{4.19b}$$

At this point, it is worthwhile to discuss the representation of magnification (i.e., linear magnification) for a micrograph. Sometimes magnification is specified in the micrograph legend (e.g., "60×" for Figure 4.14b); this means the micrograph represents a 60 times enlargement of the specimen in real space. *Scale bars* are also used to express degree of magnification. A scale bar is a straight line (typically horizontal), either superimposed on or located near the micrograph image. Associated with the bar is a length, typically expressed in microns; this value represents the distance in magnified space corresponding to the scale line length. For example, in Figure 4.15b, a scale bar is located below the bottom right-hand corner of the micrograph; its "100 μm" notation indicates that 100 μm correlates with the scale bar length.

To compute magnification from a scale bar, the following procedure may be used:

1. Measure the length of the scale bar in millimeters using a ruler.

2. Convert this length into microns [i.e., multiply the value in step (1) by 1000 because there are 1000 microns in a millimeter].

3. Magnification M is equal to

$$M = \frac{\text{measured scale length (converted to microns)}}{\text{the number appearing by the scale bar (in microns)}} \tag{4.20}$$

For example, for Figure 4.15b, the measured scale length is approximately 10 mm, which is equivalent to (10 mm)(1000 μm/mm) = 10,000 μm. Inasmuch as the scale bar length is 100 μm, the magnification is equal to

$$M = \frac{10,000 \text{ μm}}{100 \text{ μm}} = 100\times$$

This is the value given in the figure legend.

Concept Check 4.4 Does the grain-size number (G of Equation 4.17) increase or decrease with decreasing grain size? Why?

[*The answer may be found at* www.wiley.com/college/callister (*Student Companion Site*).]