

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

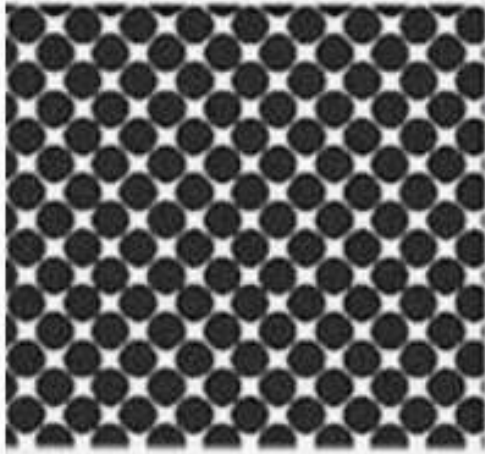
There is no such thing as a perfect crystal.

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

Nothing is perfect. The crystalline structures that we have looked at all have imperfections. We will quantify these imperfections here.

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

Imperfection



**Perfectly ordered
crystalline structure**



Such an idealized solid generally does not exist



All solids contain large number of various **defects** or **imperfections**

Deviation from the perfect or ideal atomic arrangement in a given crystal structure

Defects may exist:

- 1) In impure metals or alloys (Substitutional or interstitial foreign atoms)**
- 2) During solidification (e.g. Grain boundaries, dislocations, vacancies)**
- 3) During deformation (e.g. Dislocations)**

Why study Imperfections in Solids?

- ❑ The **properties (mechanical, optical, electrical, etc.)** of the materials are profoundly influenced by the presence of imperfections (defects)
- ❑ The influence is not always adverse, often specific characteristics are enhanced.

EXAMPLE 1: Mechanical property

- *Materials are stronger when they have defects*

Pure iron & Fe-C alloy

Pure iron : soft and ductile

Fe-C alloy (steel) : strong and tough

EXAMPLE 2: Electrical conductivity

- *Electrical conductivity decreases when materials have defects*

Electrical conductivity of pure copper is higher than that of impure copper

Impure Copper: Copper containing impurity (unwanted) elements

Types of Imperfections

- (1) Point defects**
- Vacancy atoms
 - Interstitial atoms
 - Substitutional atoms

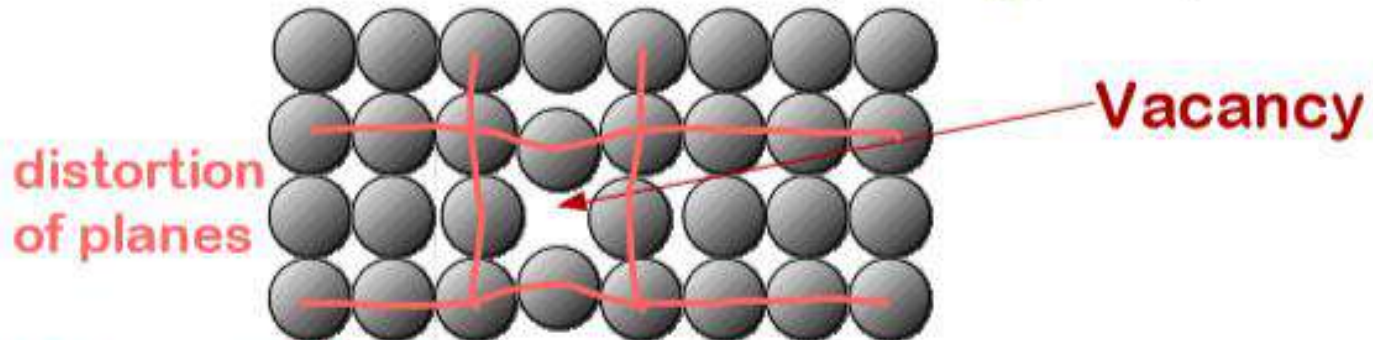
- (2) Line defects**
- Dislocations

- (3) Area defects**
- Grain Boundaries

(1) POINT DEFECTS

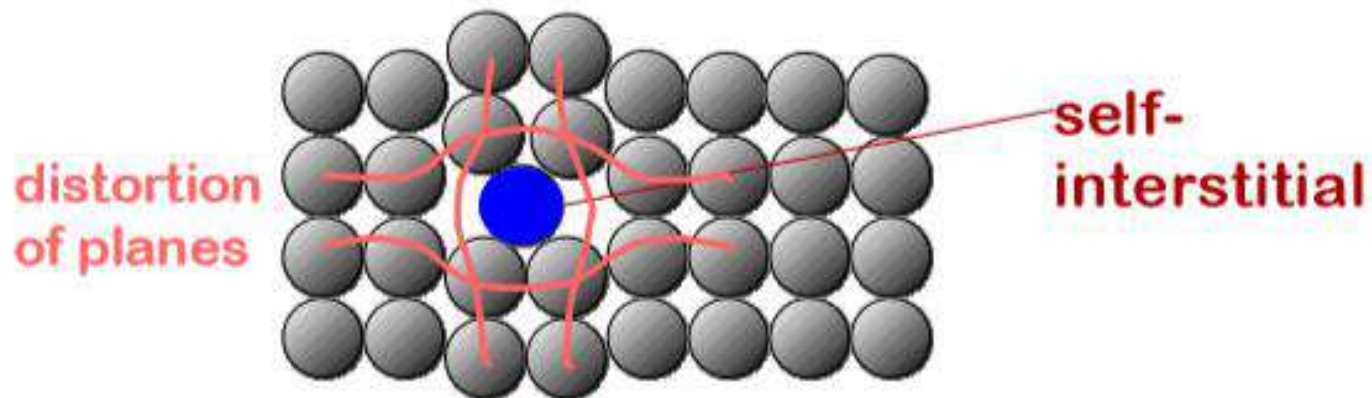
- **Vacancies:**

-vacant atomic sites in a structure (*missing atoms*)



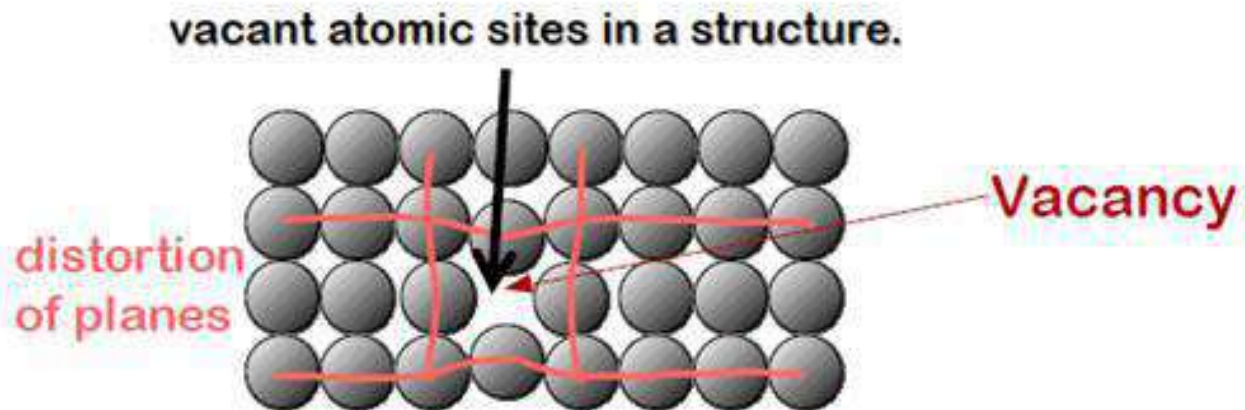
- **Self-Interstitials:**

-"extra" atoms positioned between atomic sites.



1) Vacancy

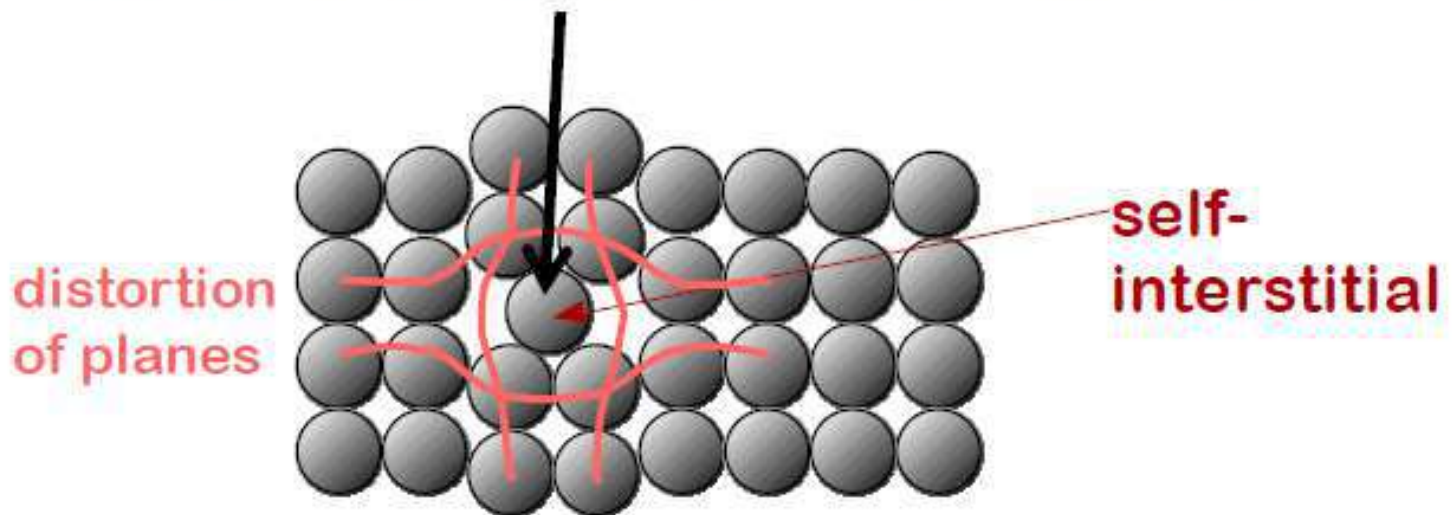
- ❑ A lattice vacancy is equivalent to missing atom or ions (in case of ionic crystal).
- ❑ Formed during solidification or as a result of atomic vibration (atomic vibration increases by temperature)



2) Self-Interstitials:

- ❑ Atoms of same type accommodate into interstitial sites, which are not occupied under ordinary circumstances.
- ❑ Self interstitial defects produce large lattice distortion. Because self-interstitial atoms are usually larger than the void space (interstitial sites).

"extra" atoms positioned between atomic sites.



Equilibrium Concentration: Point Defects

- Equilibrium concentration varies with temperature!

No. of defects $\rightarrow N_v$

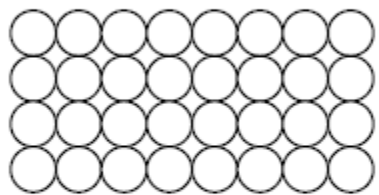
No. of potential defect sites. $\rightarrow N$

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

Activation energy $\rightarrow Q_v$

Boltzmann's constant $\rightarrow k$

Temperature $\rightarrow T$



Each lattice site
is a potential
vacancy site

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

ESTIMATING VACANCY CONC.

- Find the equil. # of vacancies in 1m^3 of Cu at 1000°C .
- Given: $\rho = 8.4 \text{ g/cm}^3$ $A_{\text{Cu}} = 63.5\text{g/mol}$
 $Q_V = 0.9\text{eV/atom}$ $N_A = 6.02 \times 10^{23}$ atoms/mole

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

Annotations:
- $Q_D = 0.9\text{eV/atom}$ (red arrow)
- $kT = 8.62 \times 10^{-5} \text{ eV/atom-K}$ (green arrow)
- $T = 1273\text{K}$ (yellow arrow)

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

- Answer:

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

Impurities

- ❑ A pure metal consisting of only one type of atom just isn't possible; impurity or foreign atoms will always be present, and some will exist as crystalline point defects.
- ❑ The addition of impurity atoms to a metal will result in the formation of **SOLID SOLUTION** or a **new second phase** (α , β , ϵ)
- ❑ **Solvent**: Represents the element or compound that is present in the greatest amount (**host atoms**)
- ❑ **Solute**: An element or compound present in a minor concentration (e.g. Impurity atoms)

Point Defects in Alloys

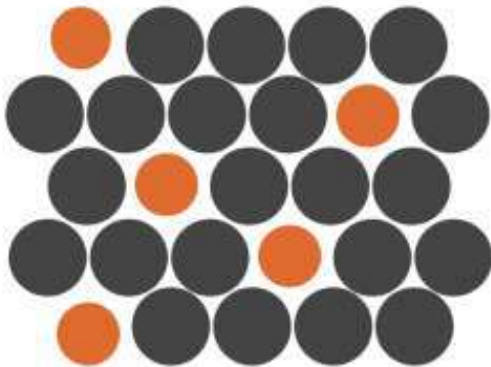
□ A foreign atom (the solute), whether it be an impurity atom or deliberate alloying addition, can occupy one of two distinct positions in a crystal,

Solid Solutions

(1) Substitutional alloy

(e.g., Cu in Ni)

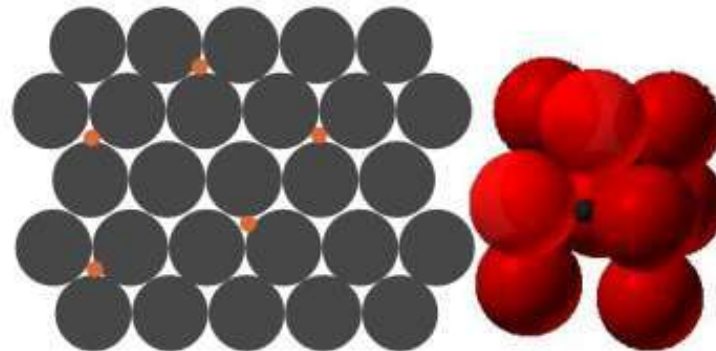
Solute atoms substitute for solvent atoms in a crystalline lattice



(2) Interstitial alloy

(e.g., C in Fe)

Solute atoms (C, H, O, N) fit into spaces between solvent atoms in a crystalline lattice.



Some important features for substitutional solid solution

W. Hume – Rothery rule

- 1) **Atomic size difference** should be less than 15%. Otherwise the solute atoms will create substantial lattice distortions and a new phase will form.
- 2) **Crystal structure** should be the same.
- 3) **Electronegativities** should be similar to prevent the ionic bonding.
- 4) **Valances:** Other factors being equal, a metal has a higher tendency to dissolve another metal of higher valency.

EXAMPLE: Cu-Ni solid solution. The type is substitutional. WHY?

Because:

- a) Radii for Cu and Ni are 0.128 and 0.125 nm respectively.
- b) They both have FCC structure.
- c) Their electronegativities are 1.9 and 1.8 for Cu and Ni respectively.
- d) The most common valence is +1 for Cu and +2 for Ni.

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?

<i>Element</i>	<i>Atomic Radius (nm)</i>	<i>Crystal Structure</i>	<i>Electro-negativity</i>	<i>Valence</i>
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. 177, *Callister & Rethwisch 9e.*

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

Example Question

Composition Conversion—From Weight Percent to Atom Percent

Determine the composition, in atom percent, of an alloy that consists of 97 wt% aluminum and 3 wt% copper.

Solution

If we denote the respective weight percent compositions as $C_{\text{Al}} = 97$ and $C_{\text{Cu}} = 3$, substitution into Equations 4.6a and 4.6b yields

$$\begin{aligned}C'_{\text{Al}} &= \frac{C_{\text{Al}}A_{\text{Cu}}}{C_{\text{Al}}A_{\text{Cu}} + C_{\text{Cu}}A_{\text{Al}}} \times 100 \\ &= \frac{(97)(63.55 \text{ g/mol})}{(97)(63.55 \text{ g/mol}) + (3)(26.98 \text{ g/mol})} \times 100 \\ &= 98.7 \text{ at\%}\end{aligned}$$

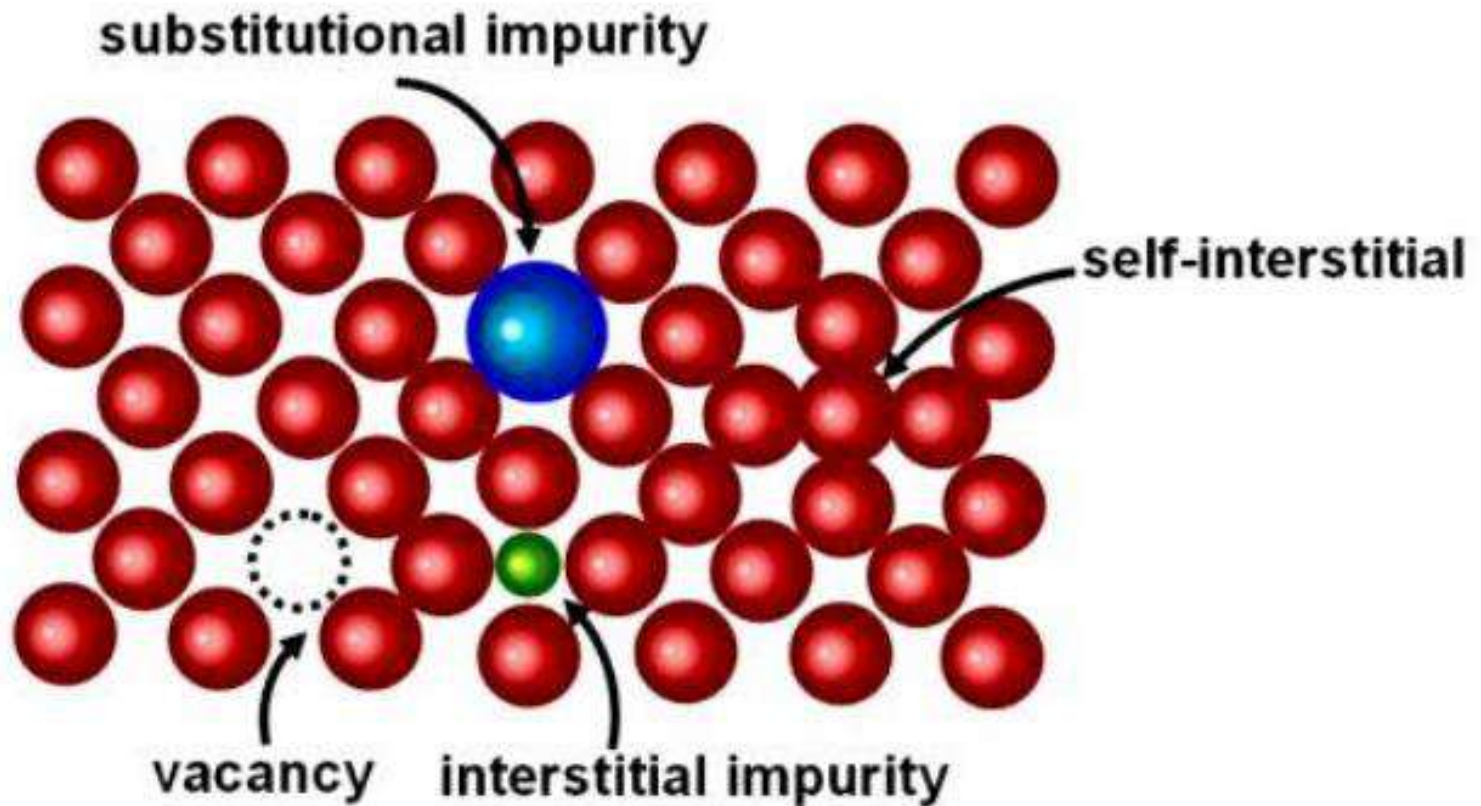
and

$$\begin{aligned}C'_{\text{Cu}} &= \frac{C_{\text{Cu}}A_{\text{Al}}}{C_{\text{Cu}}A_{\text{Al}} + C_{\text{Al}}A_{\text{Cu}}} \times 100 \\ &= \frac{(3)(26.98 \text{ g/mol})}{(3)(26.98 \text{ g/mol}) + (97)(63.55 \text{ g/mol})} \times 100 \\ &= 1.30 \text{ at\%}\end{aligned}$$

Some important features for interstitial solid solutions

- ❑ Impurity atoms fill the voids or interstices among the host atoms.
- ❑ Interstitial atoms introduce lattice strains since most of the interstitial atoms have atomic radii higher than interstitial site's radius
- ❑ For metals with a high APF, the interstitial positions are small in size and therefore the diameter of the impurity atoms should be smaller than that of the host atoms.
- ❑ The concentration of impurity atoms is low (<10 %).
(**For example**, in Fe-C alloys in which carbon is an interstitial atom, max. Carbon solubility is 2%)

Summary of point defects



(2) LINE DEFECTS

Dislocations:

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

Schematic of a Zinc (HCP):

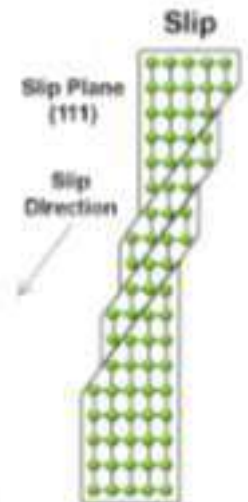
• before deformation



• after tensile elongation



slip steps



(2) Line Defects (Dislocations)

- ❖ Are one-dimensional defects around which atoms are misaligned
 - ❖ Type of (Dislocations)
 - ✓ Edge dislocation
 - extra half-plane of atoms inserted in a crystal structure
 - \mathbf{b} perpendicular (\perp) to dislocation line
 - ✓ Screw dislocation
 - spiral planar ramp resulting from shear deformation
 - \mathbf{b} parallel (\parallel) to dislocation line
-

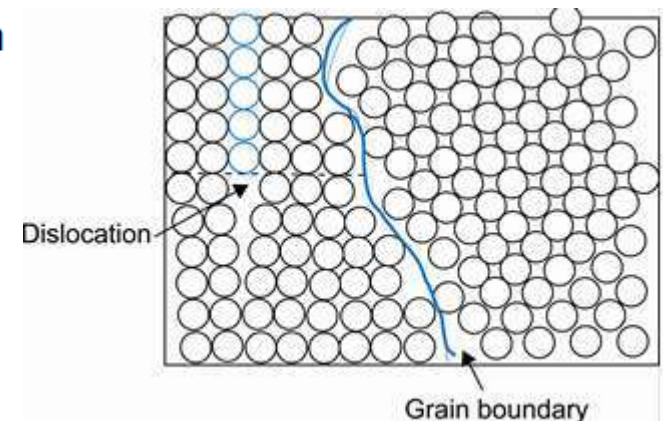
Imperfections in Solids



Linear Defects (Dislocations)

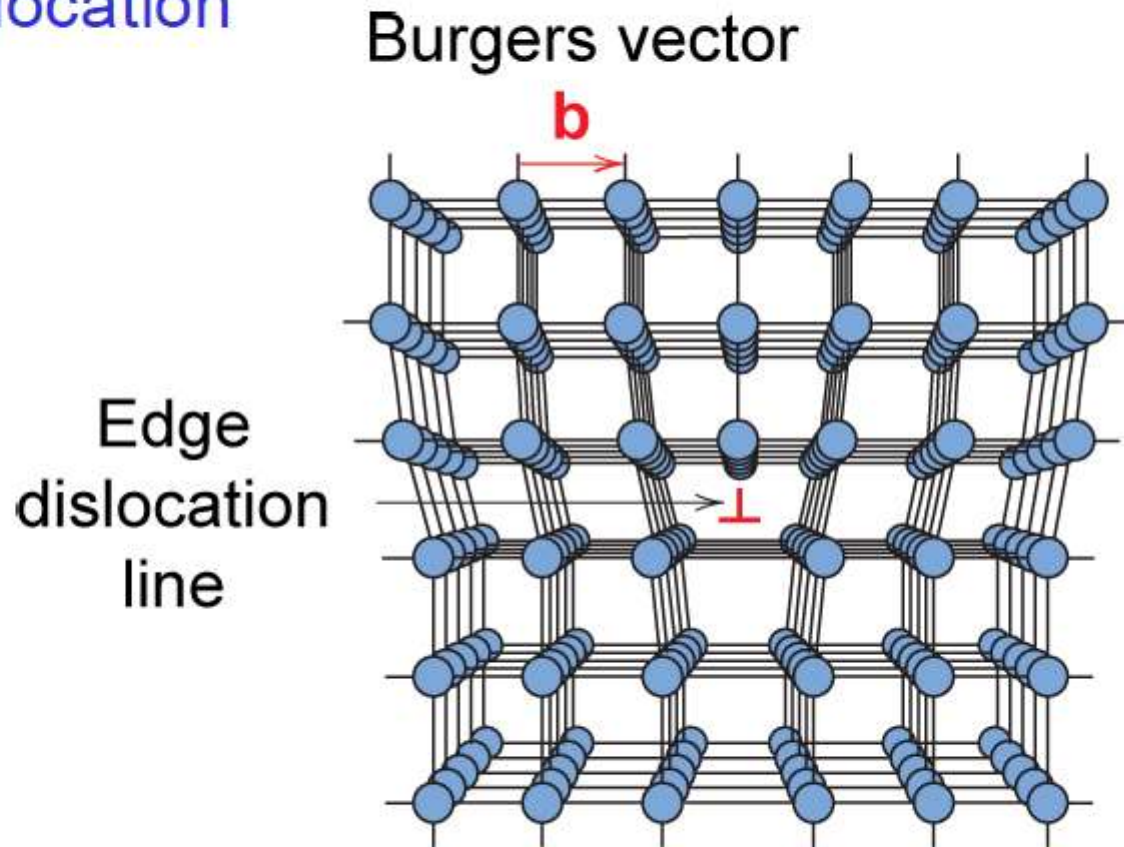
- Are one-dimensional defects around which atoms are misaligned
- **Edge dislocation:**
 - extra half-plane of atoms inserted in a crystal structure
 - $\mathbf{b} \perp$ to dislocation line
- **Screw dislocation:**
 - spiral planar ramp resulting from shear deformation
 - $\mathbf{b} \parallel$ to dislocation line
 - there will be shear strain fields in the crystal lattice in their vicinity

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

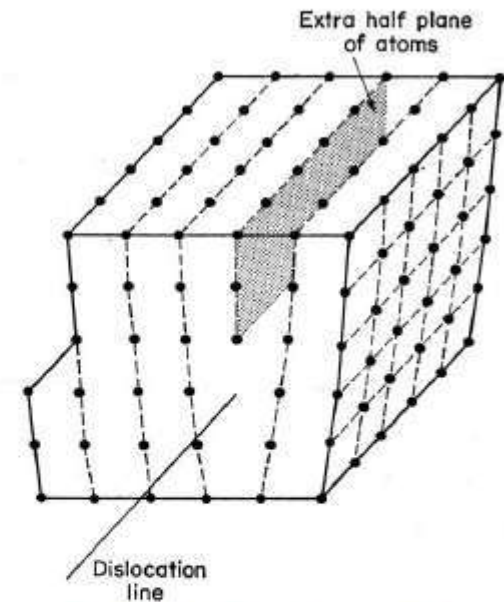
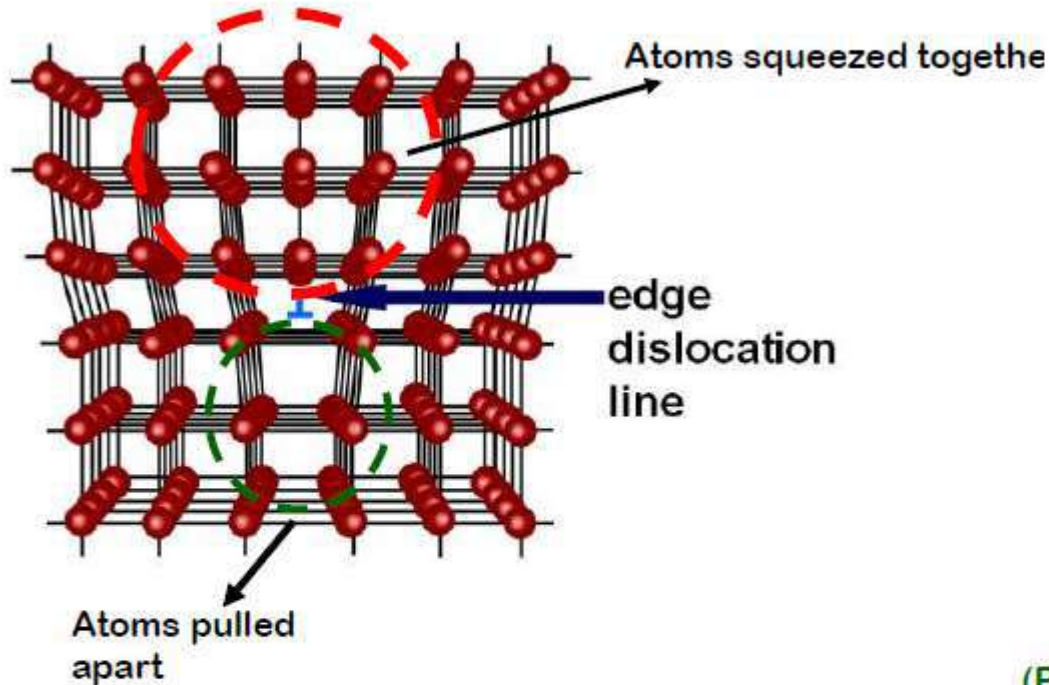


Imperfections in Solids

Edge Dislocation



1) Edge dislocation: is created in a crystal by insertion of an extra half plane of atoms

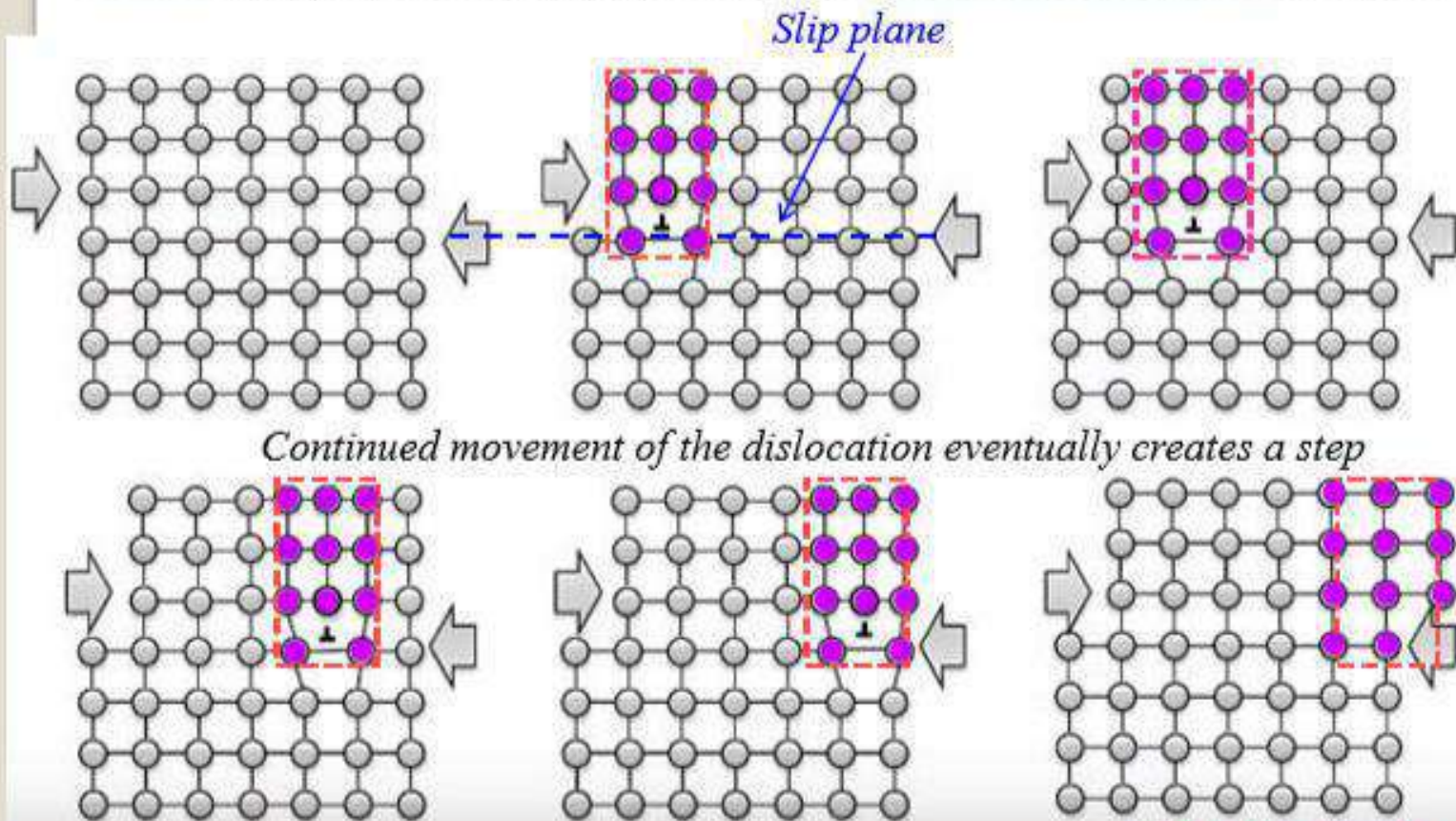


(Perpendicular to the plane of page)

- Edge dislocation is shown by symbol " \perp "
- Extra plane of atoms causes localized lattice distortion.
- The magnitude and direction of lattice distortion is expressed in terms of a **Burgers vector, b** , which is perpendicular to edge dislocation line.

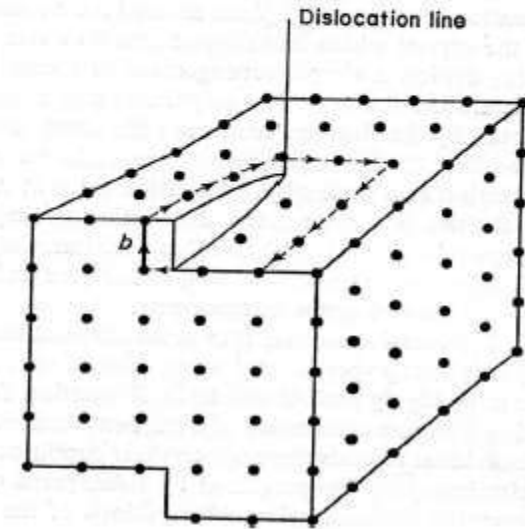
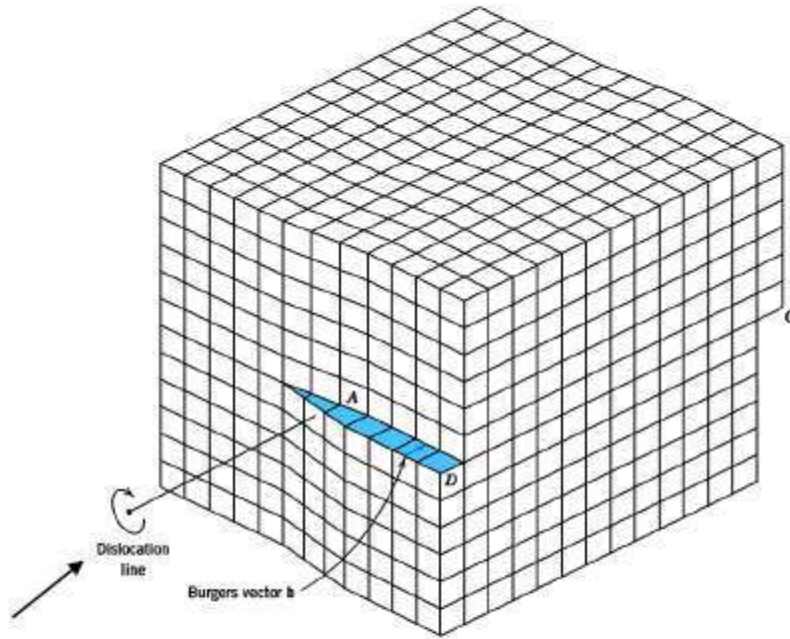
Motion of Edge Dislocation

- **Slip** - The process by which plastic deformation is produced by dislocation motion
- 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.



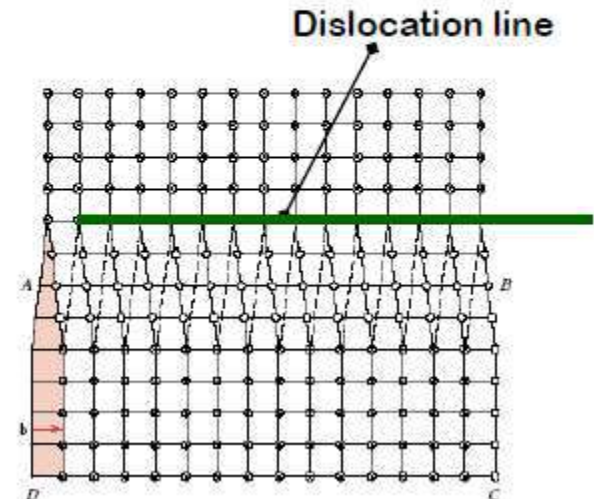
 The crystal is deformed

2) Screw Dislocation: can be formed in a perfect crystal by applying upward and downward shear stresses to regions of a perfect crystal

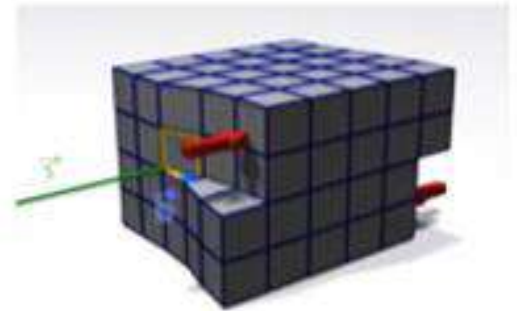
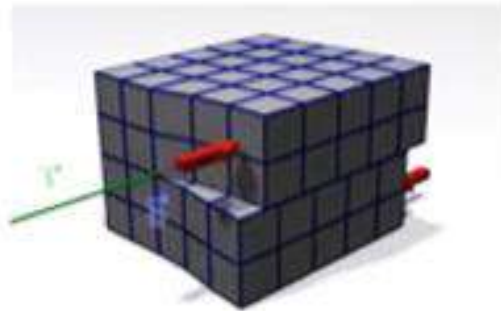
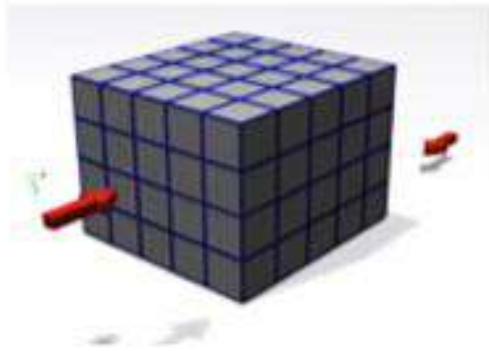


Dislocation line is linear.

Burgers vector is parallel to dislocation line

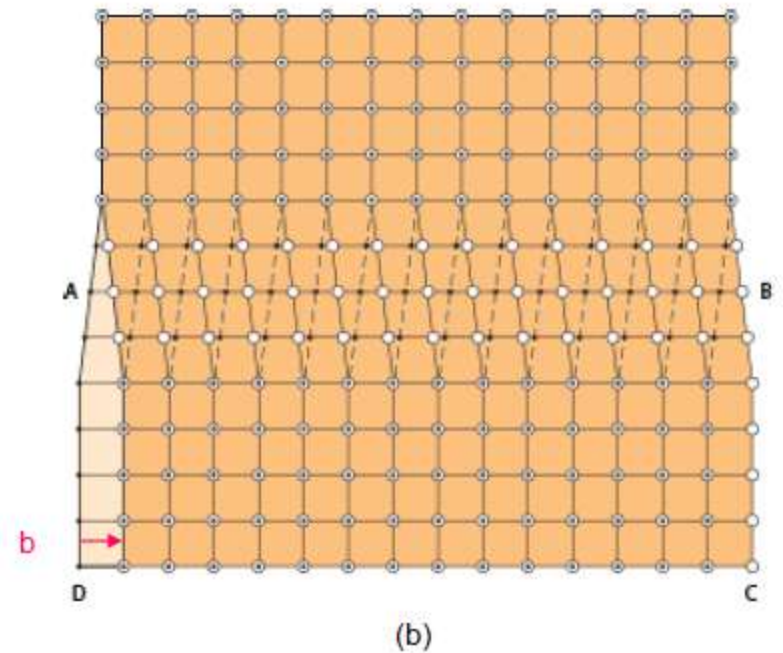
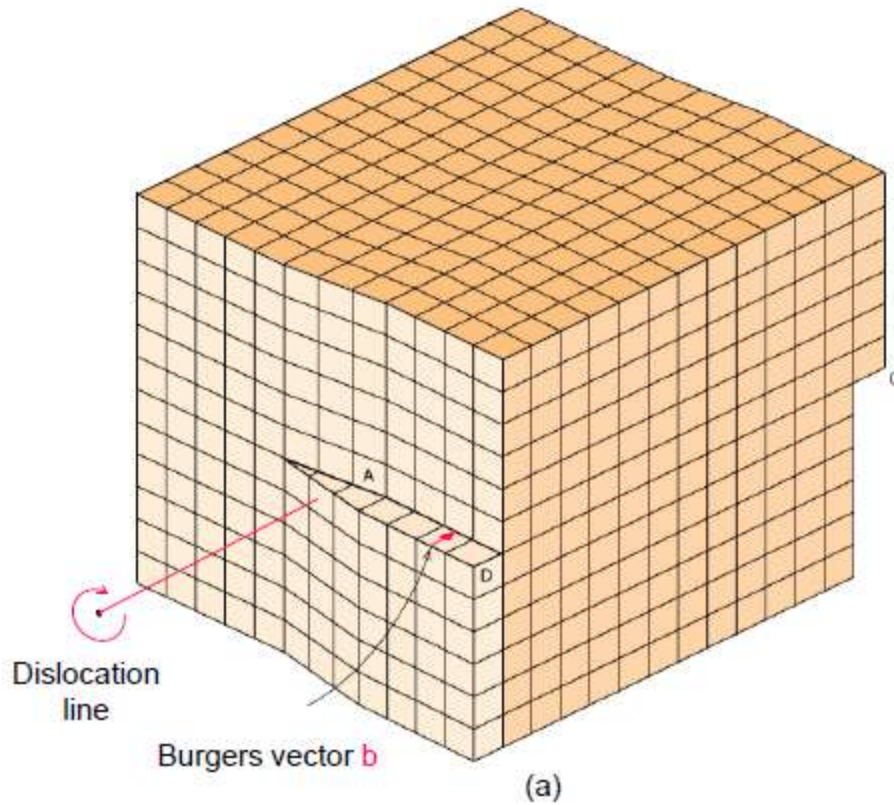


Motion of Screw Dislocation



Imperfections in Solids

Screw Dislocation



Dislocation line and Burger's vector (\vec{b}) Relation

□ Nature of dislocation is defined by relative orientations of dislocation line and Burgers vector

	Edge	Screw	Mixed
Relative orientation	Perpendicular	Parallel	Neither parallel nor perpendicular

□ Direction and magnitude of Burger's vector;

Direction : In the close packed crystallographic direction

Magnitude: One interatomic distance

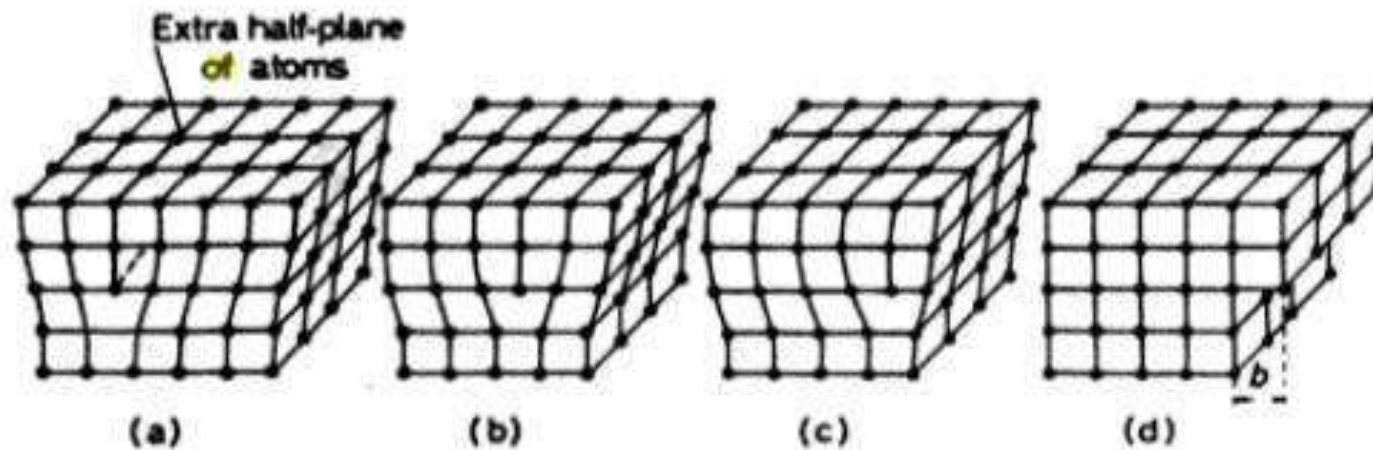


Figure 4.13 Slip caused by the movement of an edge dislocation.

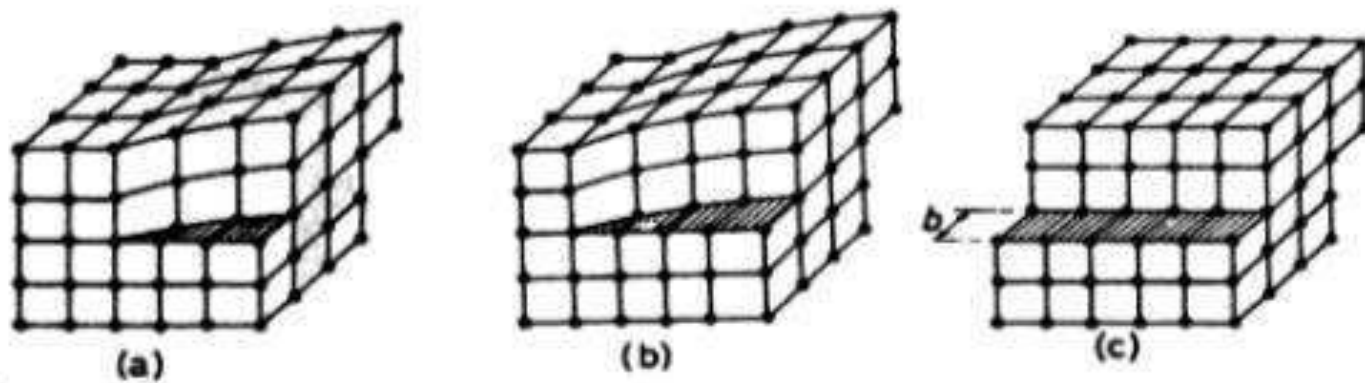
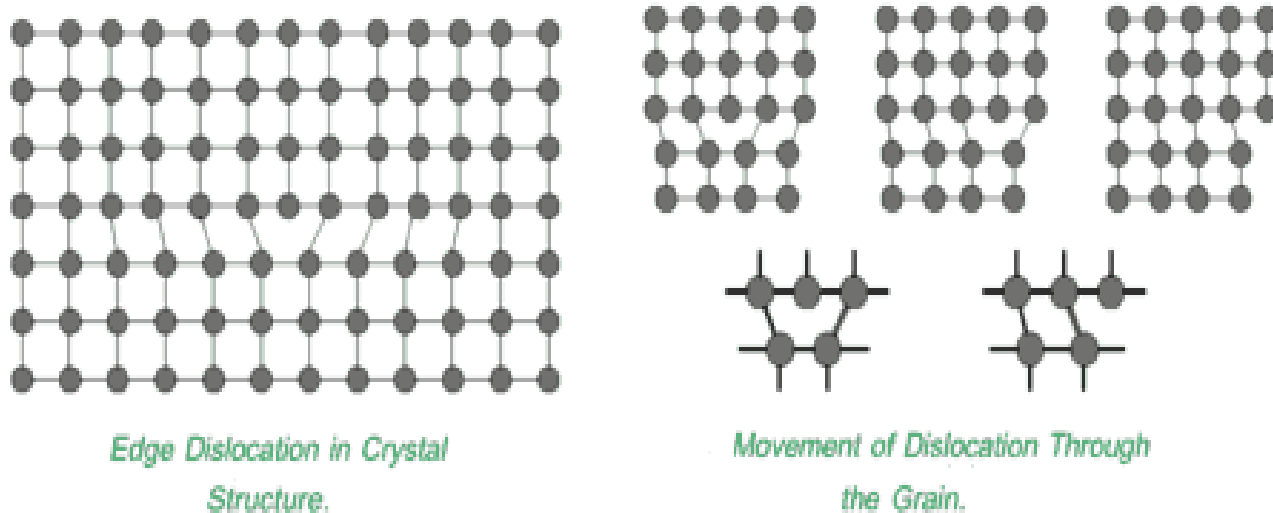


Figure 4.14 Slip caused by the movement of a screw dislocation.

- When the metal is cold worked by forging, stamping or rolling its shape is permanently changed (DEFORMED) this is only possible because of **defects (DISLOCATIONS) in the grain structure which move through the crystal structure. These dislocations or slips in the grain structure allow the overall change in shape of the metal.** Each grain can have a very large number of dislocations (only visible under a powerful microscope).



- Of course if the metal is hot worked there is more energy to available for the dislocations to move. This is why the strength of most materials falls as the temperature goes up.
- Strong materials are those that can slow down or stop the movement of the dislocations.
- This can be achieved by increasing the number of dislocations by **cold work** or **work hardening (together known as stress hardening)**. **Alloying** where the other metal interacts with the crystal lattice blocking the movement of the dislocation. (Brass is a good example of this where the small percentage of zinc makes the brass stronger than either copper or zinc.)

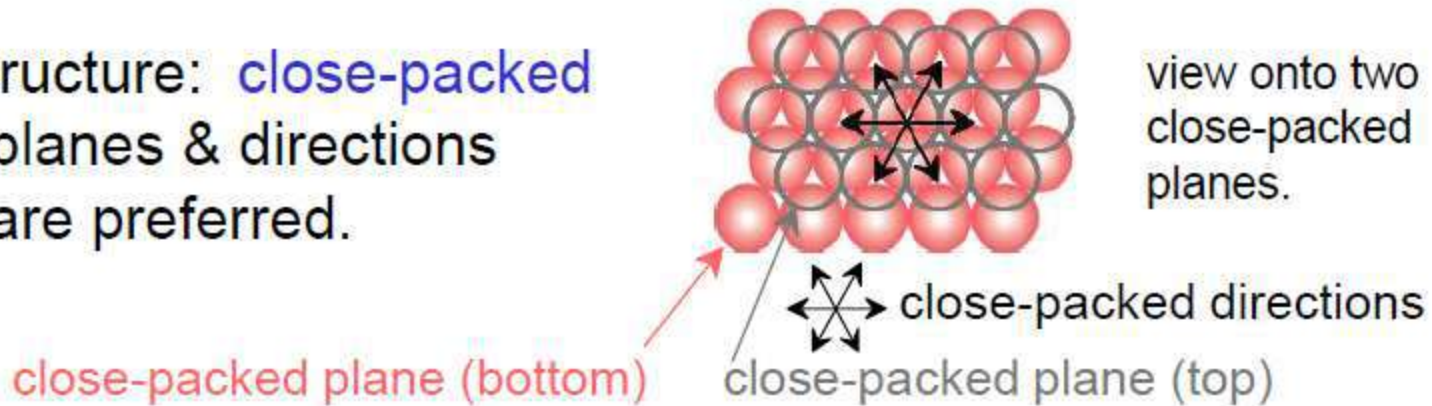
Imperfections in Solids

Dislocations are visible in electron micrographs



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.

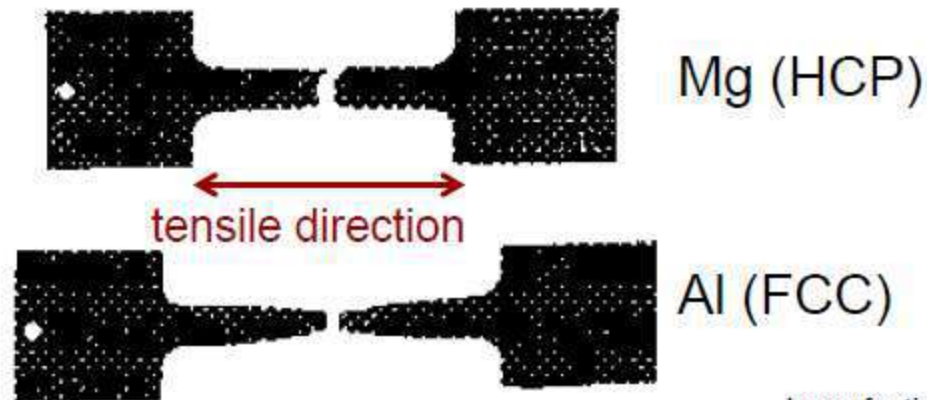


TABLE 4-2 ■ Summary of factors affecting slip in metallic structures

Factor	FCC	BCC	HCP ($\frac{c}{a} \approx 1.633$)
Critical resolved shear stress (psi)	50-100	5,000-10,000	50-100 ^a
Number of slip systems	12	48	3 ^b
Cross-slip	Can occur	Can occur	Cannot occur ^b
Summary of properties	Ductile	Strong	Relatively brittle

^aFor slip on basal planes.
^bBy alloying or heating to elevated temperatures, additional slip systems are active in HCP metals, permitting cross-slip to occur and thereby improving ductility.

- ❑ Plastic deformation take place by slid or sliding on the close pack planes, the greater the number of slip system available, the greater the capacity for plastic deformation.
- ❑ FCC has 12 slip system and therefor capable of moderate to *extensive plastic deformation*.
- ❑ Slip system of HCP is less than FCC and BCC, their plastic deformation is *much more restricted @poor ductility*.

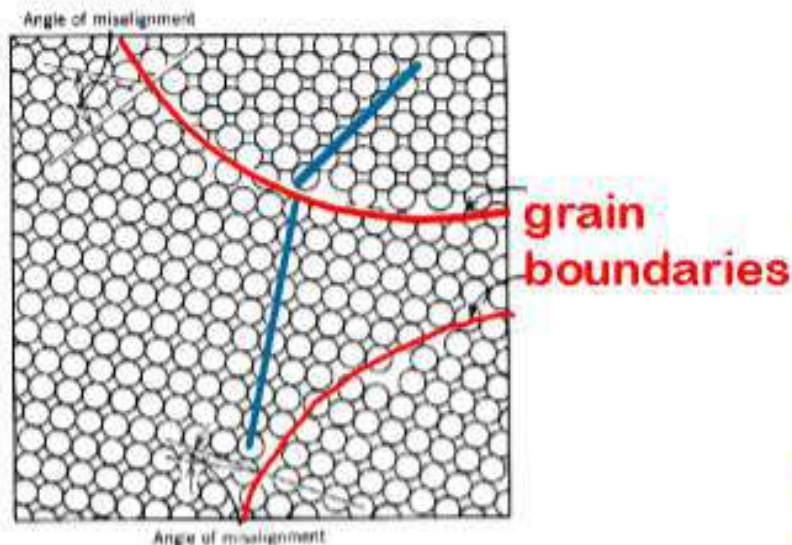
*#The ductile metal is stretched beyond the elastic capability of the bonds
 Brittle deformation; when the elastic stretching of the bonds is exceeded it immediately fails with little or no evidence of plastic deformation*

(3) AREA DEFECTS: GRAIN BOUNDARIES

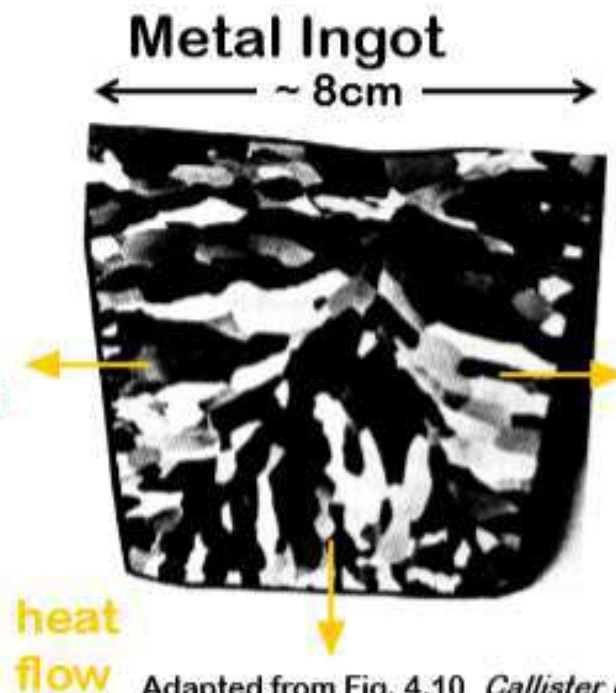
Grain boundaries:

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

Schematic



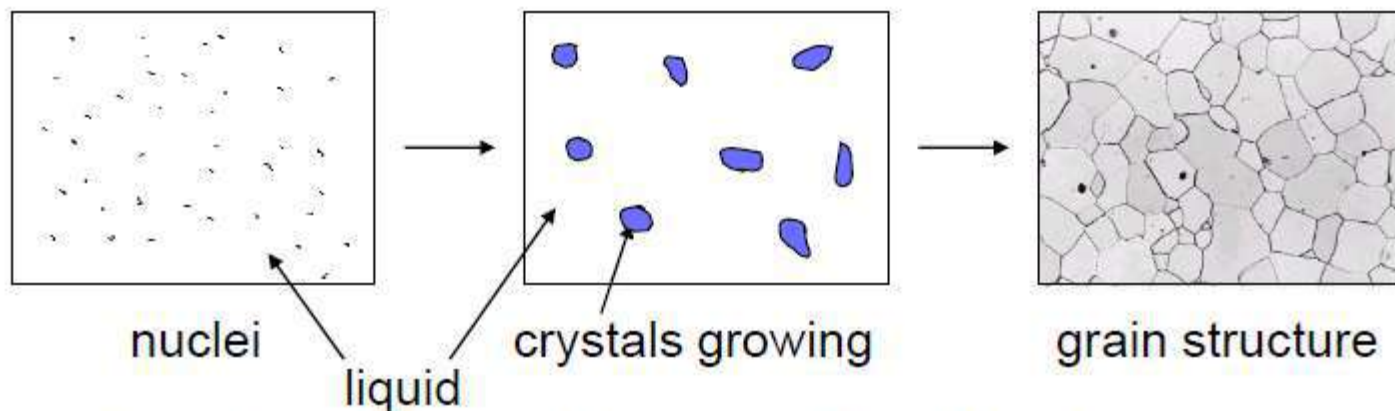
Adapted from Fig. 4.7, *Callister 6e*.



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.)

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

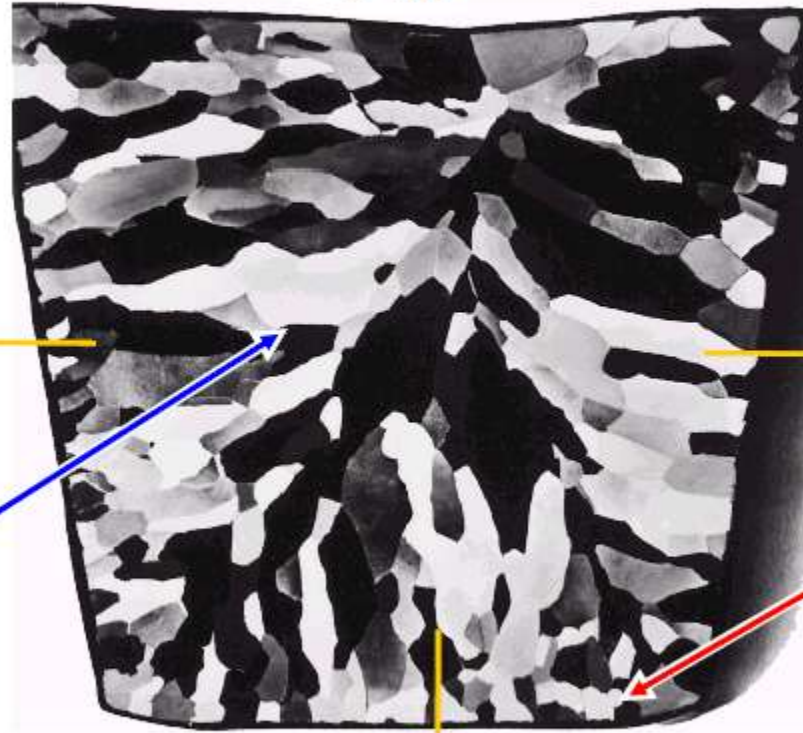


- Crystals grow until they meet each other

Solidification

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

~ 8 cm



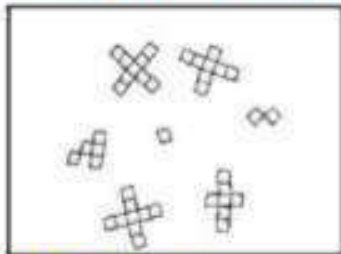
heat
flow

Columnar in
area with less
undercooling

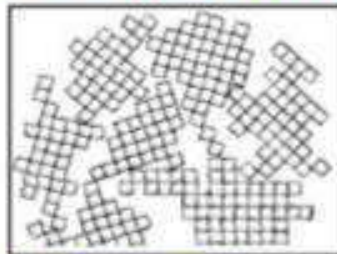
Shell of
equiaxed grains
due to rapid
cooling (greater
 ΔT) near wall

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

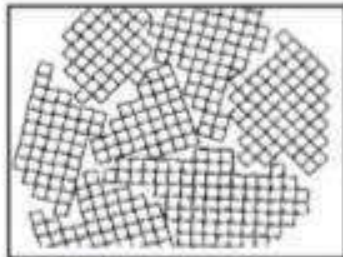
Stages during the Solidification in metals.



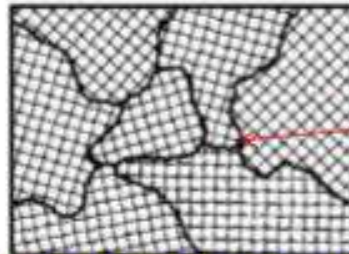
1. **Nucleation:** It begins at foreign particles in melt.



2. **Crystal growth:** Crystals begin to grow from each.

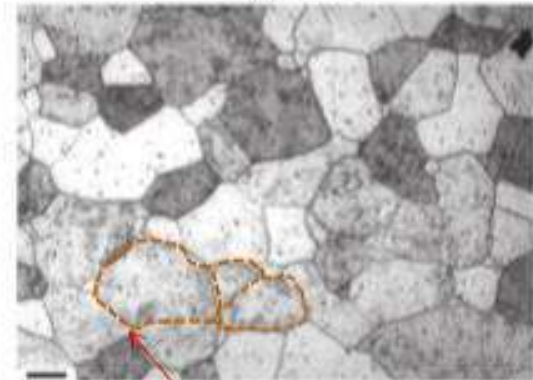


3. **Grain Formation:** Interface develops.



4. **Polycrystalline structure:** Grain growth is limited by another grain, creating a boundary between them.

SS

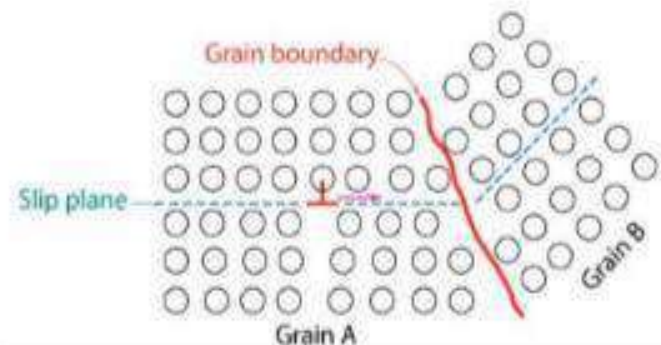


Grain boundary

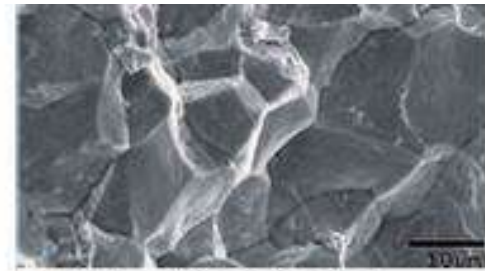
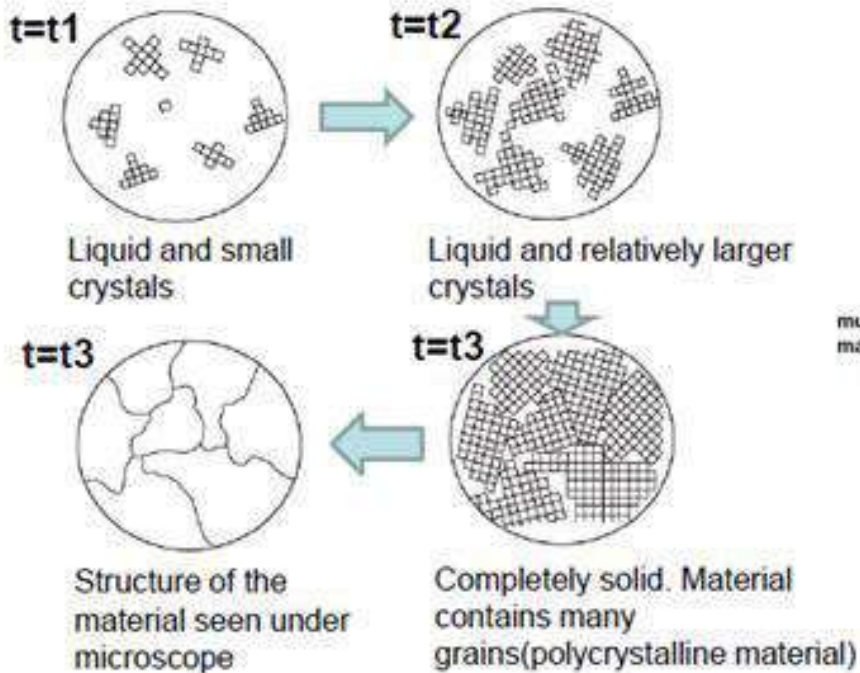
Grain boundaries are barrier to slip

1. change direction

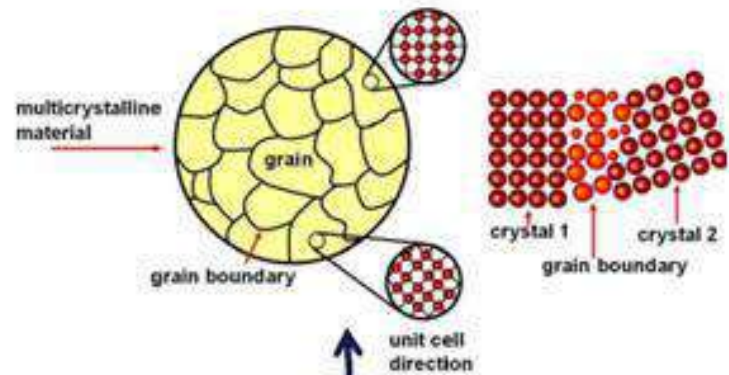
2. discontinuity of slip planes



□ Formed during solidification



Fracture surface of a steel



Observation of Crystal Defects

- ❑ Macroscopic Examination
- ❑ Microscopic Examination (optical and electron microscopes (SEM, TEM))

Sample Preparation Steps for Microscopic Examination

Surfaces of metals are prepared before examination

- 1) Cutting
- 2) Grinding (with emery papers)
- 3) Polishing (water+Al₂O₃ solution or diamond paste)
- 4) Etching (acid solutions)



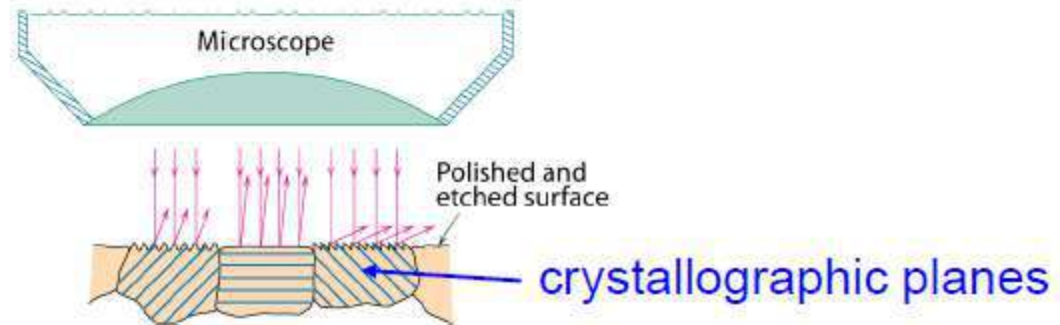
More reaction is observed in defects having higher energies

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.



← 0.75mm →

Micrograph of
brass (a Cu-Zn alloy)

Optical Microscopy

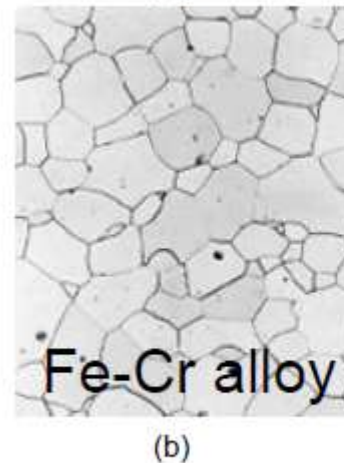
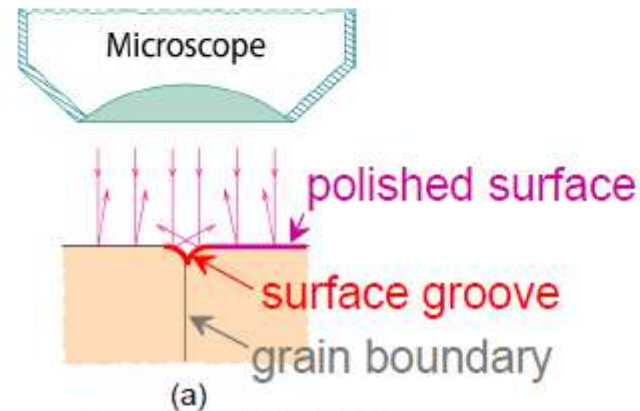
Grain boundaries...

- 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/in²
at 100x
magnification



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.)