

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?

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Imperfections in Solids

- The properties of some materials are significantly influenced by the presence of imperfections.
- It is important to have a knowledge about the types of imperfections that exist and the roles they play in affecting the behavior of materials.
- The mechanical properties of pure metals experience significant changes when alloyed (i.e., when impurity atoms are added)
 - for example, brass (70% copper–30% zinc) is much harder and stronger than pure copper.

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Imperfections in Solids

- We have been assumed that perfect order exists throughout crystalline materials on an atomic scale, however, there is no such material as a perfect crystal.
- All materials contain large numbers of various **defects** or **imperfections**.
- As a matter of fact, many of the properties of materials are profoundly sensitive to deviations from crystalline perfection.
- The influence is not always adverse, and often specific characteristics are intentionally created by the introduction of controlled amounts or numbers of particular defects.

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Imperfections in Solids

Crystalline defect (imperfection): A lattice irregularity having one or more of its dimensions on the order of an atomic diameter.

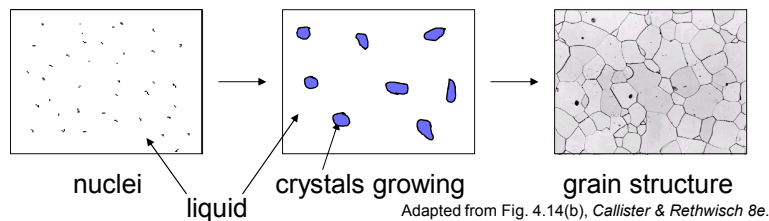
Classification of crystalline imperfections can be made according to geometry and dimensionality of the defect.

- Point defects
- Linear (one dimensional) defects
- Interfacial defects
- Grain boundaries
- Impurities

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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



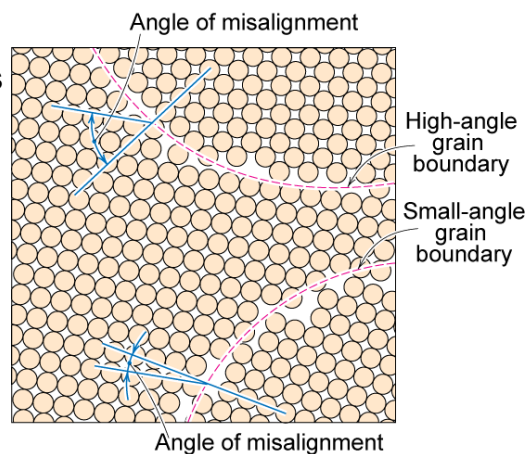
- Crystals grow until they meet each other

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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 & Rethwisch 8e.

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Types of Imperfections

- Vacancy atoms
- Interstitial atoms
- Substitutional atoms

Point defects

(Related to one or two atomic positions)

- Dislocations

Line defects

- Grain Boundaries

Area defects

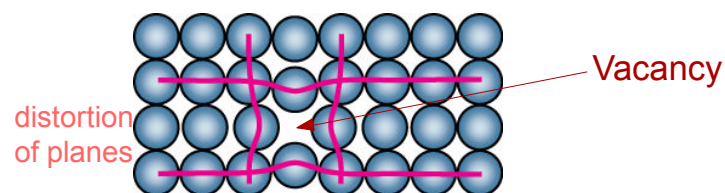
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Point Defects in Metals

- **Vacancies:**

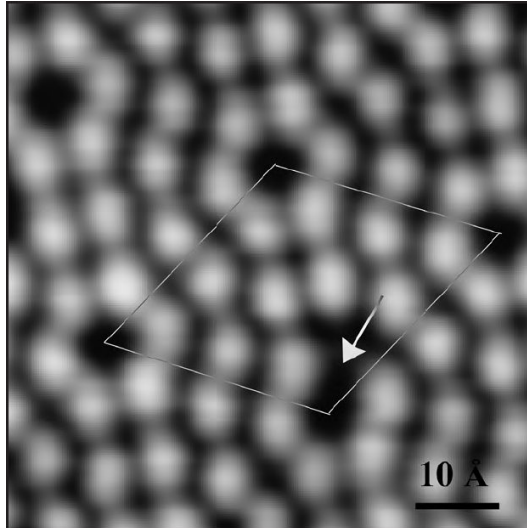
-vacant atomic sites in a structure.

- The simplest of the point defects is a **vacancy, or vacant lattice site**,
- An atom is missing.
- All crystalline solids contain vacancies and, in fact, it is not possible to create such a material that is free of these defects.
- The presence of vacancies increases the randomness of the crystal.



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A scanning probe micrograph that shows a (111) surface plane for silicon:



The arrow points to the location of a silicon atom that was removed using a tungsten nanotip probe. This site from which an atom is missing is the surface analogue of a **vacancy defect**— that is, a vacant lattice site within the bulk material.

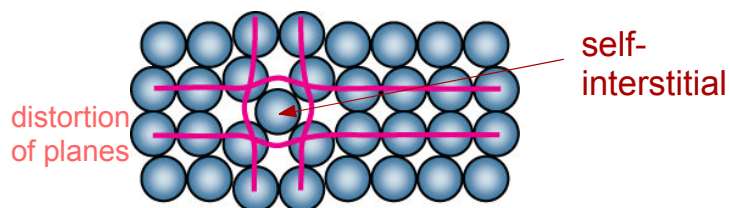
(Micrograph courtesy of D. Huang, Stanford University.)

Approximately x20,000,000.

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- **Self-Interstitials:**

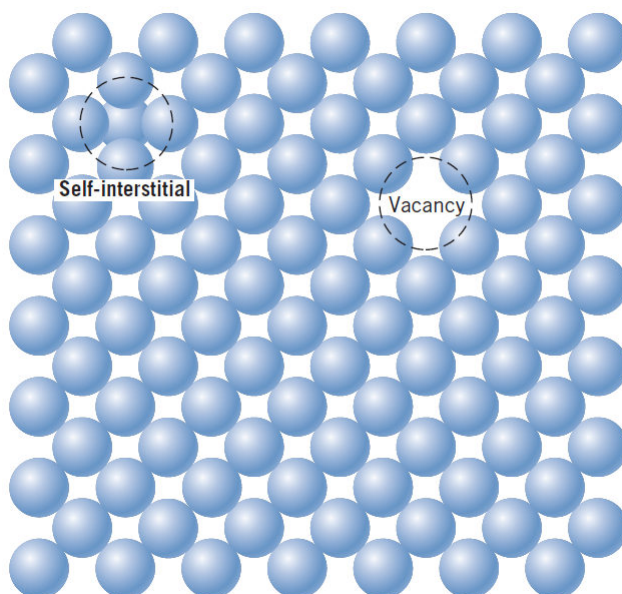
- “Extra” atoms positioned between atomic sites: a small void space that under ordinary circumstances is not occupied.



- In metals, a self-interstitial introduces relatively large distortions in the surrounding lattice because the atom is substantially larger than the interstitial position in which it is situated.
- Consequently, the formation of this defect is not highly probable, and it exists in very small concentrations, which are significantly lower than for vacancies.

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Interstitial Atom: An imperfection in a crystal caused by the presence of an extra atom in an otherwise complete lattice.



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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

The diagram shows a 4x4 grid of white circles with black outlines, representing potential vacancy sites in a lattice.

(1.38 x 10⁻²³ J/atom-K)
 (8.62 x 10⁻⁵ eV/atom-K)

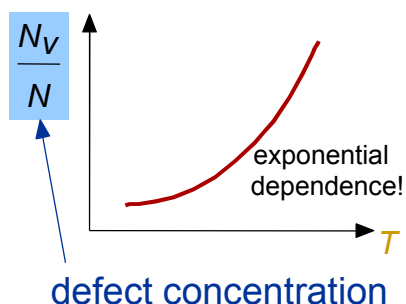
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Measuring Activation Energy

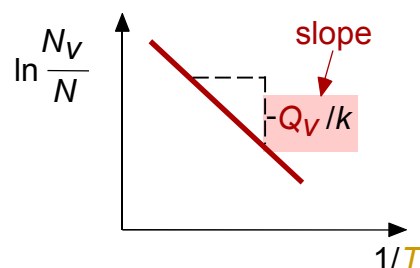
- We can get Q_v from an experiment.

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

- Measure this...



- Replot it...



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Estimating Vacancy Concentration

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

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

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

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

Annotations for the equation above:
 - Red arrow points to $-Q_v$ with label "0.9 eV/atom"
 - Green arrow points to kT with label "1273 K"
 - Green arrow points to the result with label "8.62 x 10⁻⁵ eV/atom-K"

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

- Answer:

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

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Impurities in Solids

- A pure metal consisting of only one type of atom is not possible; impurity or foreign atoms will always be present.
- Even with relatively sophisticated techniques, it is difficult to refine metals to a purity in excess of 99.9999%. At this level, on the order of 10^{22} to 10^{23} impurity atoms will be present in one cubic meter of material.
- Most familiar metals are not highly pure; rather, they are **alloys**, in which impurity atoms have been added intentionally to improve specific characteristics to the material: **Alloying** is used in metals to improve mechanical strength and corrosion resistance.

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Solid Solution:

- The addition of impurity atoms to a metal will result in the formation of a **solid solution**.
- Depending on the kinds of impurity, their concentrations, and the temperature of the alloy, a new second phase can be formed.

Solvent (Host) and Solute Atoms:

“**Solvent**” represents the element or compound that is present in the greatest amount; on occasion, solvent atoms are also called “**host atoms**”.

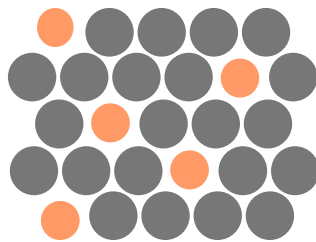
“**Solute**” is used to denote an element or compound present in a minor concentration.

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Imperfections in Metals

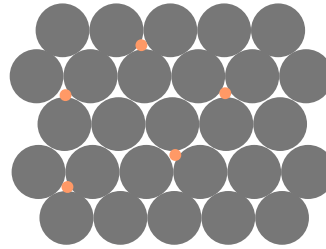
Two outcomes if impurity (B) added to host (A):

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



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

OR



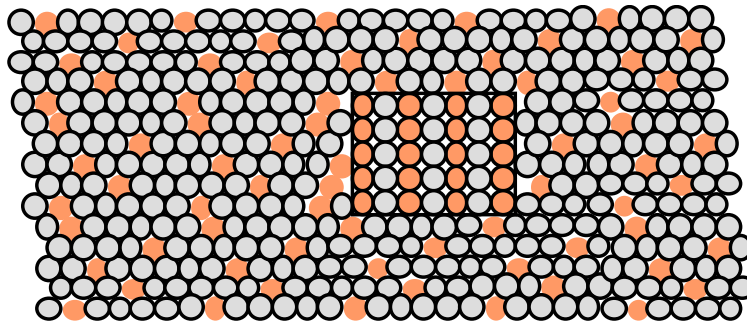
Interstitial solid soln.
(e.g., C in Fe)

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- 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.



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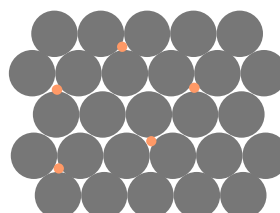
Imperfections in Metals

Conditions for **substitutional** solid solution (S.S.)

- 1. **Δr (atomic radius) < 15%**
Otherwise the solute atoms will create substantial lattice distortions and a new phase will form.
- 2. **Proximity in periodic table**
 - i.e., similar electronegativities
- 3. **Same crystal structure for pure metals:**
For appreciable solid solubility the crystal structures for metals of both atom types must be the same
- 4. **Valency**
 - All else being equal, a metal (*host*) will have a greater tendency to dissolve a metal (*solute*) of higher valency than one of lower valency.

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Interstitial solid solution:



- Impurity atoms fill the voids or interstices among the host atoms.
- For metallic materials that have relatively high atomic packing factors, these interstitial positions are relatively small. Consequently, the atomic diameter of an interstitial impurity must be substantially smaller than that of the host atoms.
- Normally, the maximum allowable concentration of interstitial impurity atoms is low (less than 10%).
- Even very small impurity atoms are ordinarily larger than the interstitial sites, they introduce some lattice strains on the adjacent host atoms.

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Impurities in Solids

Specification of composition:

- It is often necessary to express the composition (or concentration) of an alloy in terms of its constituent elements.
- The two most common ways to specify composition are **weight (or mass) percent** and **atom percent**.
- The basis for **weight percent** (wt%) is the weight of a particular element relative to the total alloy weight.

– **weight percent:**
$$C_1 = \frac{m_1}{m_1 + m_2} \times 100$$

m_1 and m_2 = mass of component 1 and 2, respectively.

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- The basis for **atom percent** (at%) calculations is the number of moles of an element in relation to the total moles of the elements in the alloy.

Number of moles in a specified mass of an element:
$$n_{m1} = \frac{m'_1}{A_1}$$

– **atom percent:**
$$C'_1 = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100$$

n_{m1} and n_{m2} = number of moles of component 1 and 2, respectively

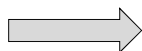
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• Sometimes it is necessary to convert from one composition scheme to another:

— for example, from weight percent to atom percent.

For a two-element alloy:

Conversion of “weight percent” to “atom percent”



$$C'_1 = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100$$

$$C'_2 = \frac{C_2 A_1}{C_1 A_2 + C_2 A_1} \times 100$$

$$C_1 + C_2 = 100$$

$$C'_1 + C'_2 = 100$$

Conversion of “atom percent” to “weight percent”



$$C_1 = \frac{C'_1 A_1}{C'_1 A_1 + C'_2 A_2} \times 100$$

$$C_2 = \frac{C'_2 A_2}{C'_1 A_1 + C'_2 A_2} \times 100$$

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Conversion of “weight percent” to “mass per unit volume”



$$C''_1 = \left(\frac{C_1}{\frac{C_1}{\rho_1} + \frac{C_2}{\rho_2}} \right)$$

$$C''_2 = \left(\frac{C_2}{\frac{C_1}{\rho_1} + \frac{C_2}{\rho_2}} \right)$$

$$C_1 + C_2 = 100$$

$$C''_1 + C''_2 = 100$$

Computation of “average density of an alloy”



$$\rho_{\text{ave}} = \frac{100}{\frac{C_1}{\rho_1} + \frac{C_2}{\rho_2}}$$

$$\rho_{\text{ave}} = \frac{\frac{C'_1 A_1}{\rho_1} + \frac{C'_2 A_2}{\rho_2}}{\frac{C'_1 A_1}{\rho_1} + \frac{C'_2 A_2}{\rho_2}}$$

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Computation of "average atomic weight of an alloy"



$$A_{\text{ave}} = \frac{100}{\frac{C_1}{A_1} + \frac{C_2}{A_2}}$$

$$A_{\text{ave}} = \frac{C'_1 A_1 + C'_2 A_2}{100}$$

Example: Derive the following equation: $C'_1 = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100$

– atom percent: $C'_1 = \frac{n_{C_1}}{n_{C_1} + n_{C_2}} \times 100$

$$C'_1 = \frac{\frac{C_1}{\frac{A_1}{(AN)} + \frac{C_2}{\frac{A_2}{(AN)}}}}{\frac{C_1}{\frac{A_1}{(AN)} + \frac{C_2}{\frac{A_2}{(AN)}}} + \frac{C_2}{\frac{A_2}{(AN)} + \frac{C_1}{\frac{A_1}{(AN)}}}} = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1}$$

$$C_1 + C_2 = 100$$

(AN: Avagadros's number)

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Example:

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 $C_{Al} = 97$ and $C_{Cu} = 3$, substitution into Equations 4.6a and 4.6b yields

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

and

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

$$\begin{aligned} C'_{Al} &= \frac{\frac{M_{Al}}{A_{Al}/(AN)}}{\frac{M_{Al}}{A_{Al}/(AN)} + \frac{M_{Cu}}{A_{Cu}/(AN)}} \\ &= \frac{97}{\frac{26,98/(6,02 \times 10^{23})}{97} + \frac{3}{63,55/(6,02 \times 10^{23})}} \times 100 \\ &= 98.7 \text{ at\%} \end{aligned}$$

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Line Defects

Dislocations:

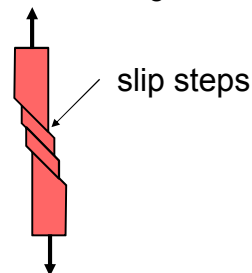
- are line defects,
- slip between crystal planes result when dislocations move,
- the permanent (plastic) deformation of most crystalline materials is by the motion of dislocations.

Schematic of Zinc (HCP):

- before deformation



- after tensile elongation



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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** perpendicular (\perp) to dislocation line
- **Screw dislocation:**
 - spiral planar ramp resulting from shear deformation
 - **b** parallel (\parallel) to dislocation line

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

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Imperfections in Solids

Edge Dislocation:

Extra half-plane of atoms inserted in a crystal structure

- It is a linear defect that centers around the line that is defined along the end of the extra half plane of atoms.

Edge dislocation line

Burgers vector

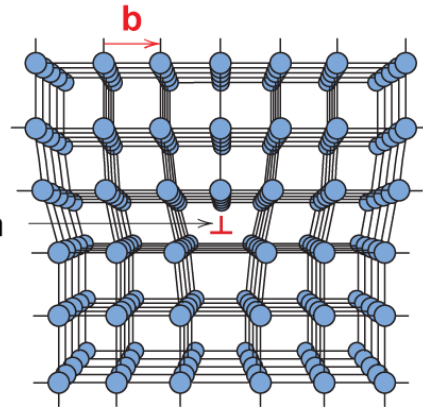
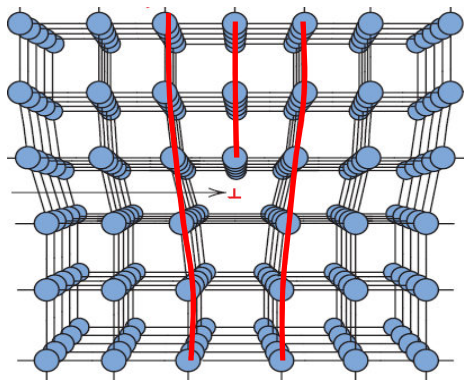


Fig. 4.3, Callister & Rethwisch 8e.

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Edge Dislocation:

- Within the region around the dislocation line there is some localized lattice distortion:

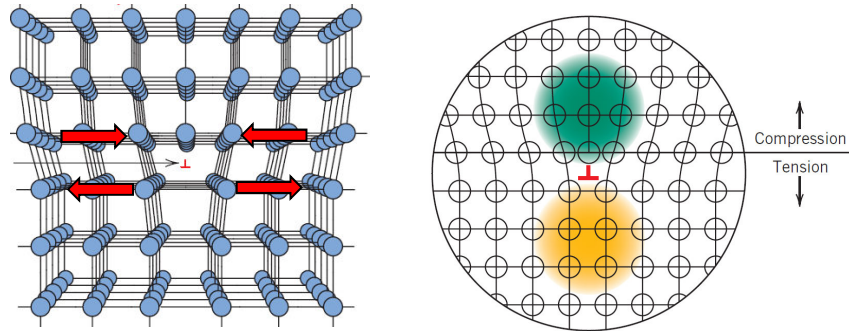


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Edge Dislocation:

- The atoms above the dislocation line are squeezed together, and those below are pulled apart. This is reflected in the slight curvature for the vertical planes of atoms as they bend around this extra half-plane.

- The magnitude of this distortion decreases with distance away from the dislocation line; at positions far removed, the crystal lattice is virtually perfect.

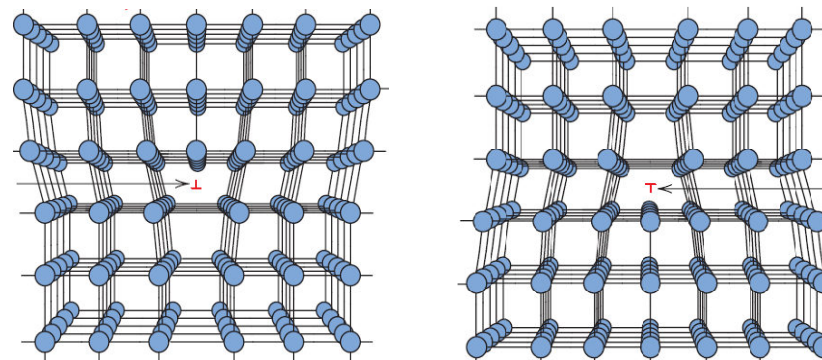


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Edge Dislocation:

- Sometimes the edge dislocation is represented by the symbol \perp which also indicates the position of the dislocation line.

- An edge dislocation may also be formed by an extra half-plane of atoms that is included in the bottom portion of the crystal; its designation is a \top

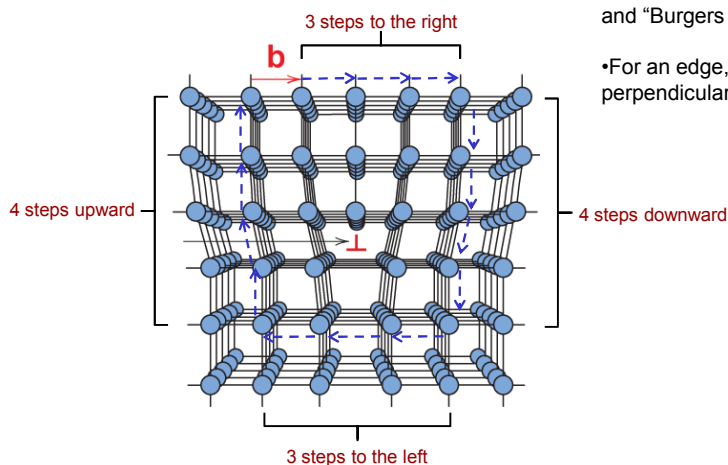


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- The magnitude and direction of the lattice distortion associated with a dislocation is expressed in terms of a **Burgers vector**, denoted by a **b** .

•The nature of dislocation is defined by the relative orientations of "dislocation line" and "Burgers vector".

•For an edge, they are perpendicular.

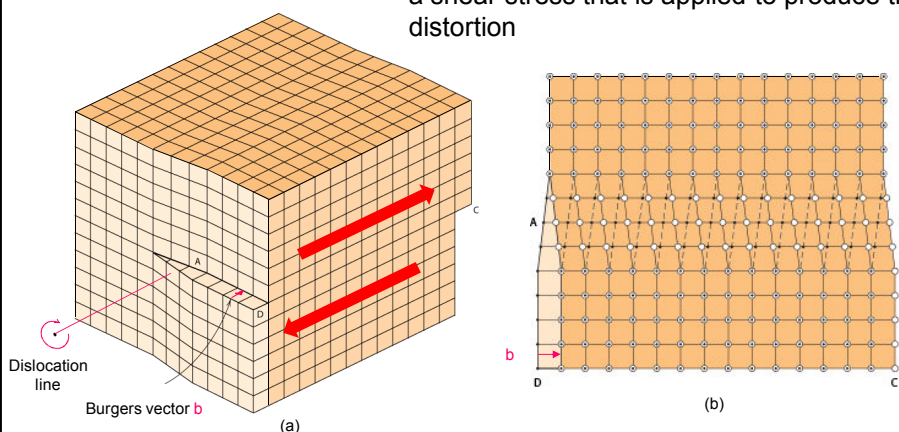


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Imperfections in Solids

Screw Dislocation:

Which may be thought of as being formed by a shear stress that is applied to produce the distortion

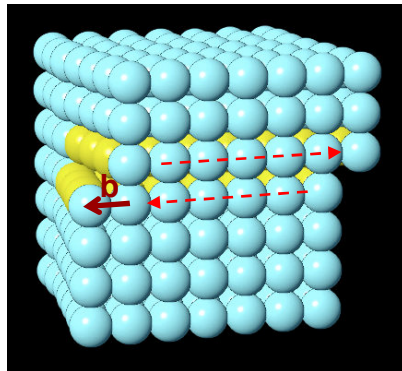


Adapted from Fig. 4.4, Callister & Rethwisch 8e.

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Screw Dislocation:

- The upper front region of the crystal is shifted one atomic distance to the right relative to the bottom portion.

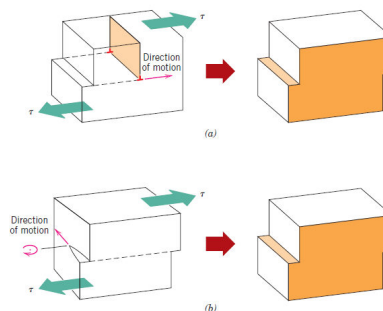


- The atomic distortion associated with a screw dislocation is also linear and along a dislocation line.
- The positions of “dislocation line” and “burger vector” are parallel.

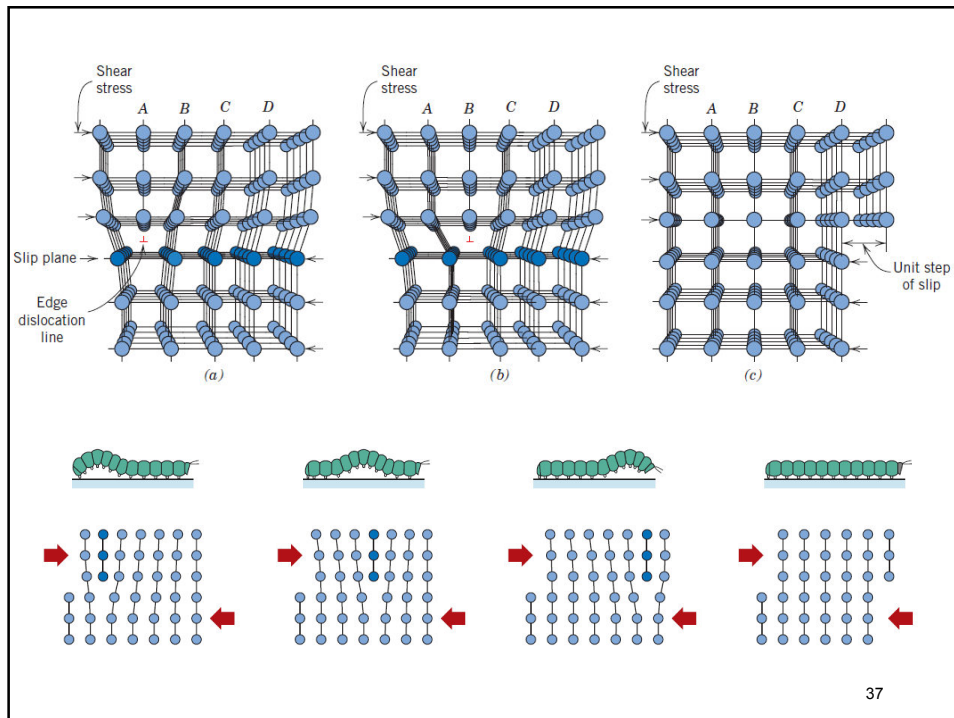
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How plastic deformation occurs?

- Plastic deformation corresponds to the motion of large numbers of dislocations.
- An edge dislocation moves in response to a shear stress applied in a direction perpendicular to its line.
- The process by which plastic deformation is produced by dislocation motion is termed as **slip**.



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Imperfections in Solids

Dislocations are visible in electron micrographs

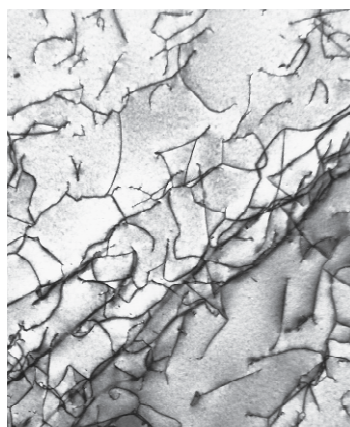


Fig. 4.6, Callister & Rethwisch 8e.

0.2 μm

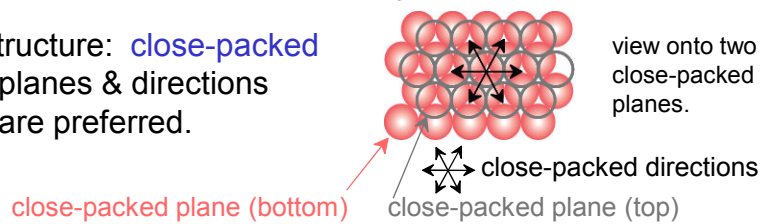
•Virtually all crystalline materials contain some dislocations that were introduced during

- Solidification,
- Plastic deformation, and
- as a consequence of thermal stresses that result from rapid cooling.

•Dislocations are involved in the plastic deformation of crystalline materials, both metals and ceramics.

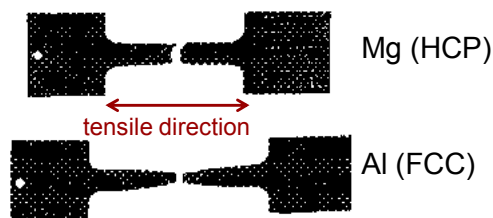
Dislocations & Crystal Structures

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



- Comparison among crystal structures:
FCC: many close-packed planes/directions;
HCP: only one plane, 3 directions;

- Specimens that were tensile tested.



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Interfacial Defects:

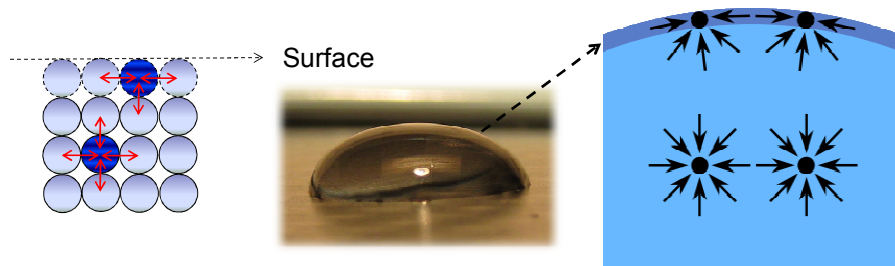
- Interfacial defects are boundaries that have two dimensions and normally separate regions of the materials that have different crystal structures and/or crystallographic orientations.

- These imperfections include:
 - External surfaces,
 - Grain boundaries,
 - Twin boundaries,
 - Stacking faults.

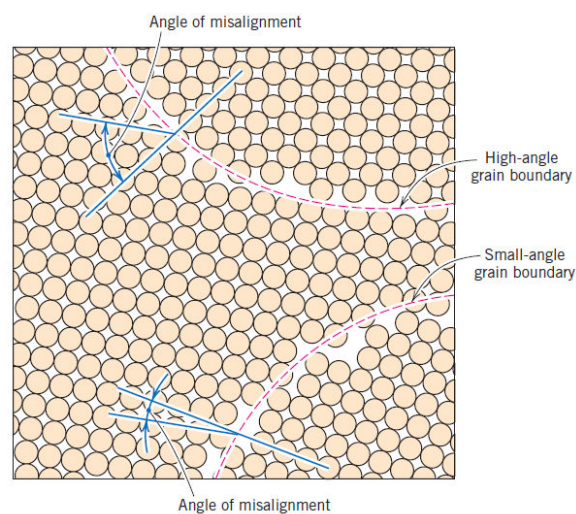
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External Surfaces:

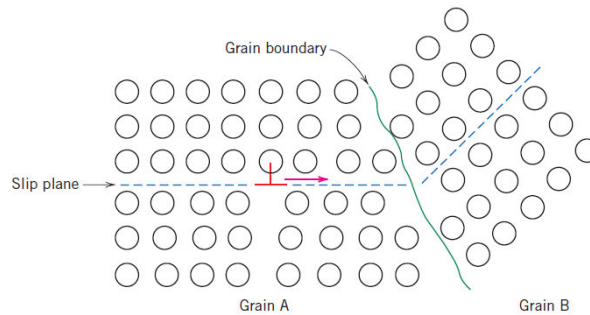
- Surface atoms are **not** bonded to the maximum number of nearest neighbors, and are therefore in a higher energy state than the atoms at interior positions.
- The bonds of these surface atoms that are not satisfied give rise to a **surface energy**.
- To reduce this energy, materials tend to minimize the total surface area.
- For example, liquids assume a shape having a minimum area: the droplets become spherical. This is not possible with solids, which are mechanically rigid.



Grain Boundaries: Discussed previously.....



Strengthening by Grain Size Reduction:



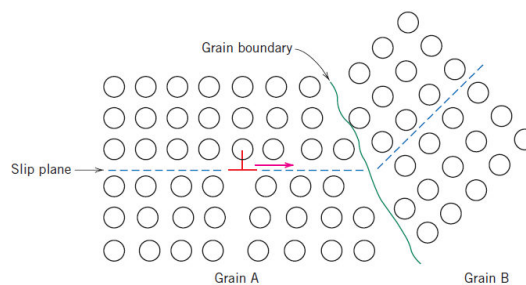
- The size of the grains, or average grain diameter, in a polycrystalline metal influences the mechanical properties.
- Adjacent grains normally have different crystallographic orientations and, of course, a common grain boundary.
- During plastic deformation, slip or dislocation motion must take place across this boundary (from grain A to grain B)

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Strengthening by Grain Size Reduction:

The grain boundary acts as a barrier to dislocation motion for two reasons:

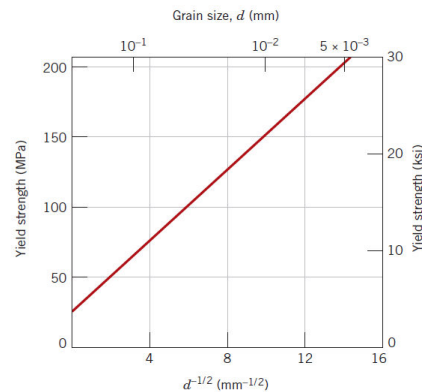
1. **Since the two grains are of different orientations**, a dislocation passing into grain B will have to change its direction of motion; this becomes more difficult as the crystallographic misorientation increases.
2. **The atomic disorder within a grain boundary region** will result in a discontinuity of slip planes from one grain into the other.



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Strengthening by Grain Size Reduction:

- A fine-grained material (one that has small grains) is harder and stronger than one that is coarse grained, since the former has a greater total grain boundary area to impede dislocation motion.



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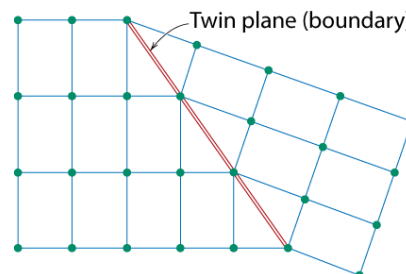
Twin Boundaries:

Essentially a reflection of atom positions across the **twin plane**.

- A twin boundary is a special type of grain boundary across which there is a specific mirror lattice symmetry.
- Atoms on one side of the boundary are located in mirror-image positions of the atoms on the other side.

Twins result from atomic displacements that are produced from:

- applied mechanical shear forces (mechanical twins), and
- during annealing heat treatments following deformation (annealing twins).



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

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Stacking faults:

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

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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.)

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