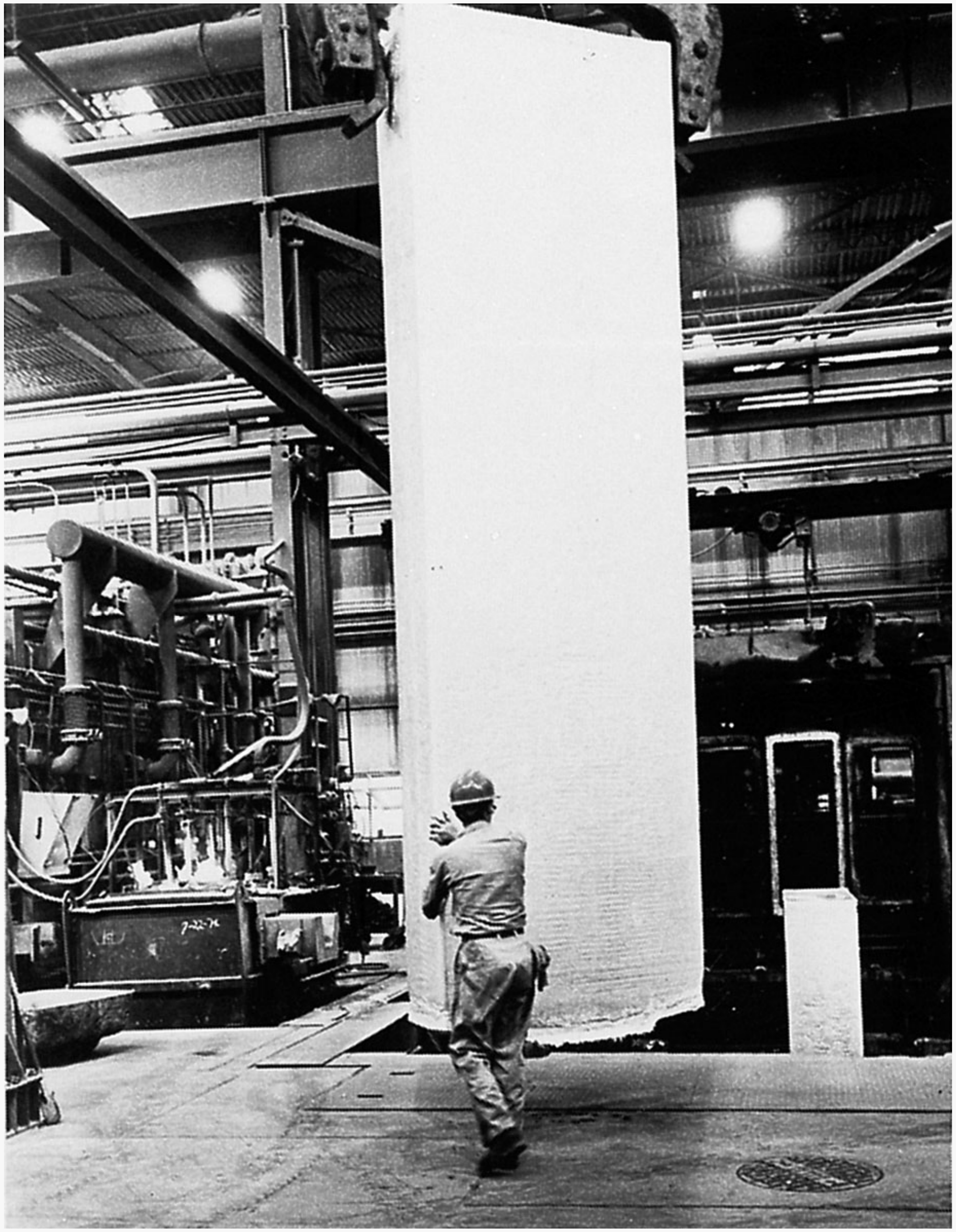
CHAPTER

4

Solidification
and
Crystalline Imperfections
in Solids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Solidification of Metals

- Metals are melted to produce finished and semi-finished parts.
- Two steps of solidification
    - ➢ **Nucleation** : Formation of stable nuclei.
    - ➢ **Growth of nuclei** : Formation of grain structure.
- Thermal gradients define the shape of each grain.

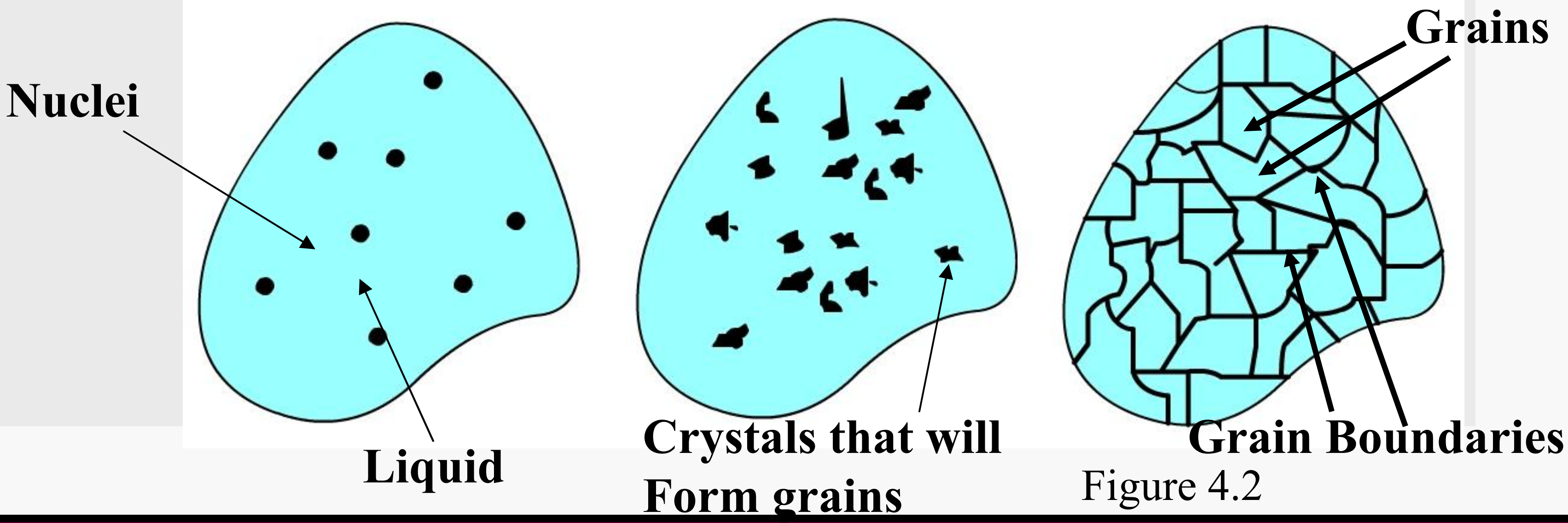


Figure 4.2

Formation of Stable Nuclei

- Two main mechanisms: Homogenous and heterogeneous.
- Homogenous Nucleation :
  - First and simplest case.
  - Metal itself will provide atoms to form nuclei.
  - Metal, when significantly undercooled, has several slow moving atoms which bond each other to form nuclei.
  - Cluster of atoms below *critical size* is called embryo.
  - If the cluster of atoms reach critical size, they grow into crystals. Else get dissolved.
  - Cluster of atoms that are grater than critical size are called nucleus.

Energies involved in homogenous nucleation.

Volume free energy G_v

- Released by liquid to solid transformation.
- ΔG_v is change in free energy per unit volume between liquid and solid.
- free energy change for a spherical nucleus of radius r is given by

$$r = \frac{4}{3}\pi r^3 \Delta G_v$$

Surface energy Gs

- Required to form new solid surface
- ΔG_s is energy needed to create a surface.
- γ is specific surface free energy.

Then $\Delta G_s = 4\pi r^2 \gamma$

- ΔG_s is retarding energy.

Total Free Energy

- **Total free energy** is given by $$\Delta G_T = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

Since when r=r*, d(ΔG_T)/dr = 0 $$r^* = -\frac{2\gamma}{\Delta G_V}$$

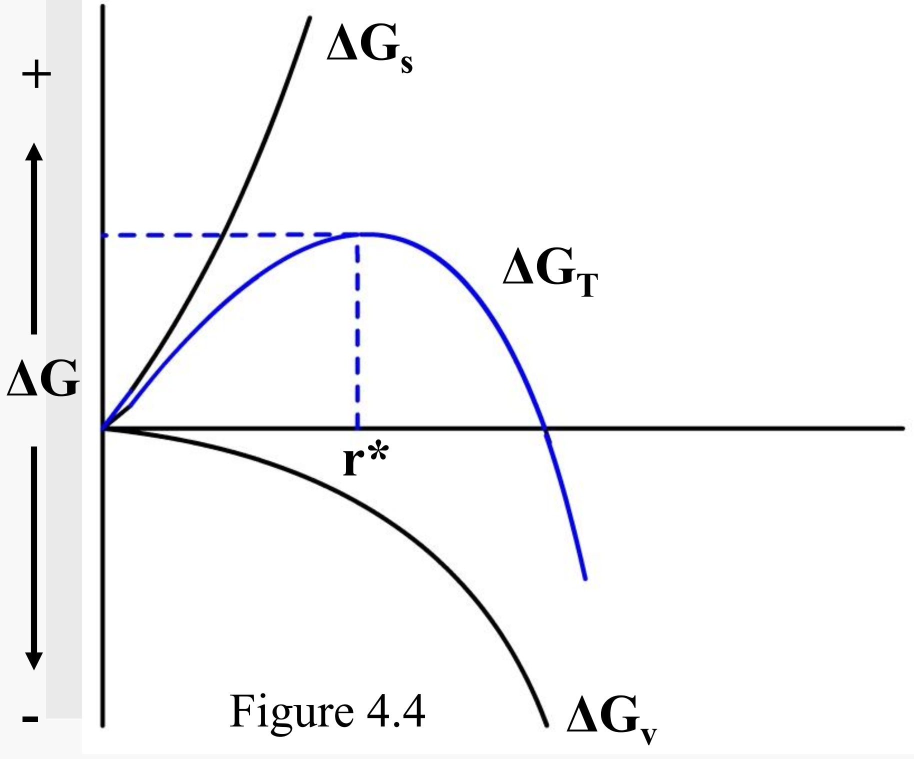
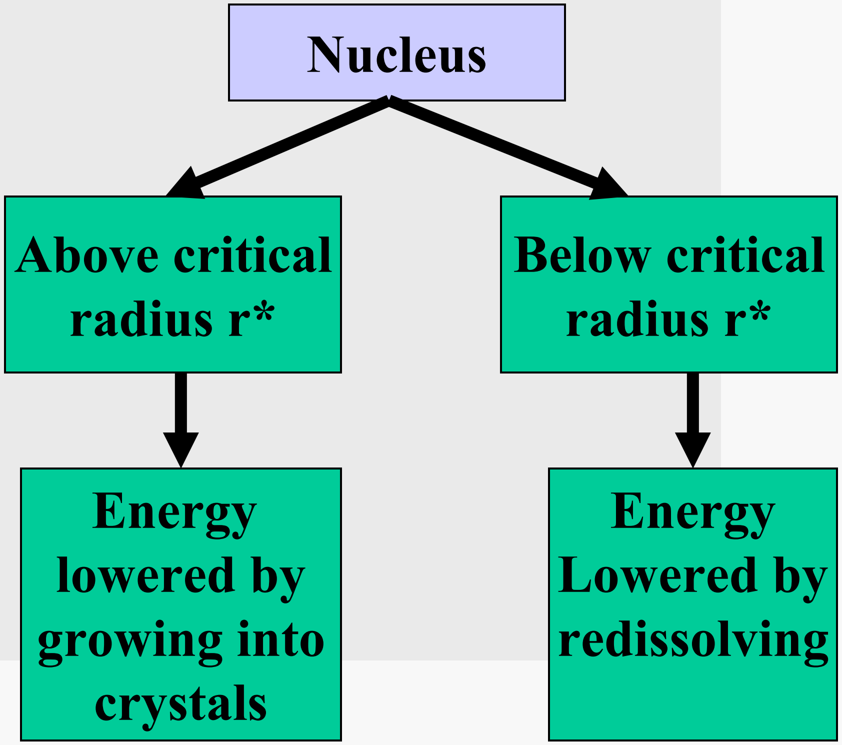


Figure 4.4



Nucleus

Above critical radius r*

Energy lowered by growing into crystals

Below critical radius r*

Energy Lowered by redissolving

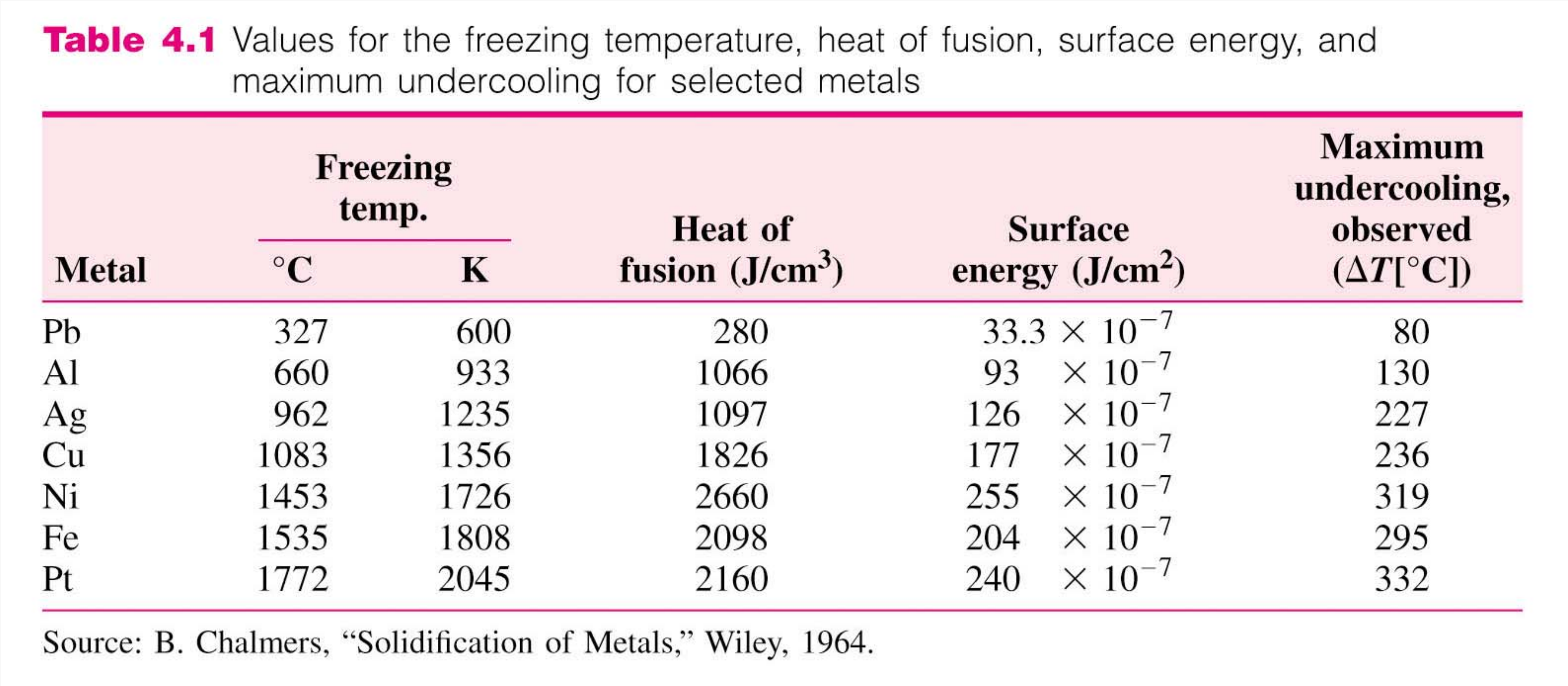
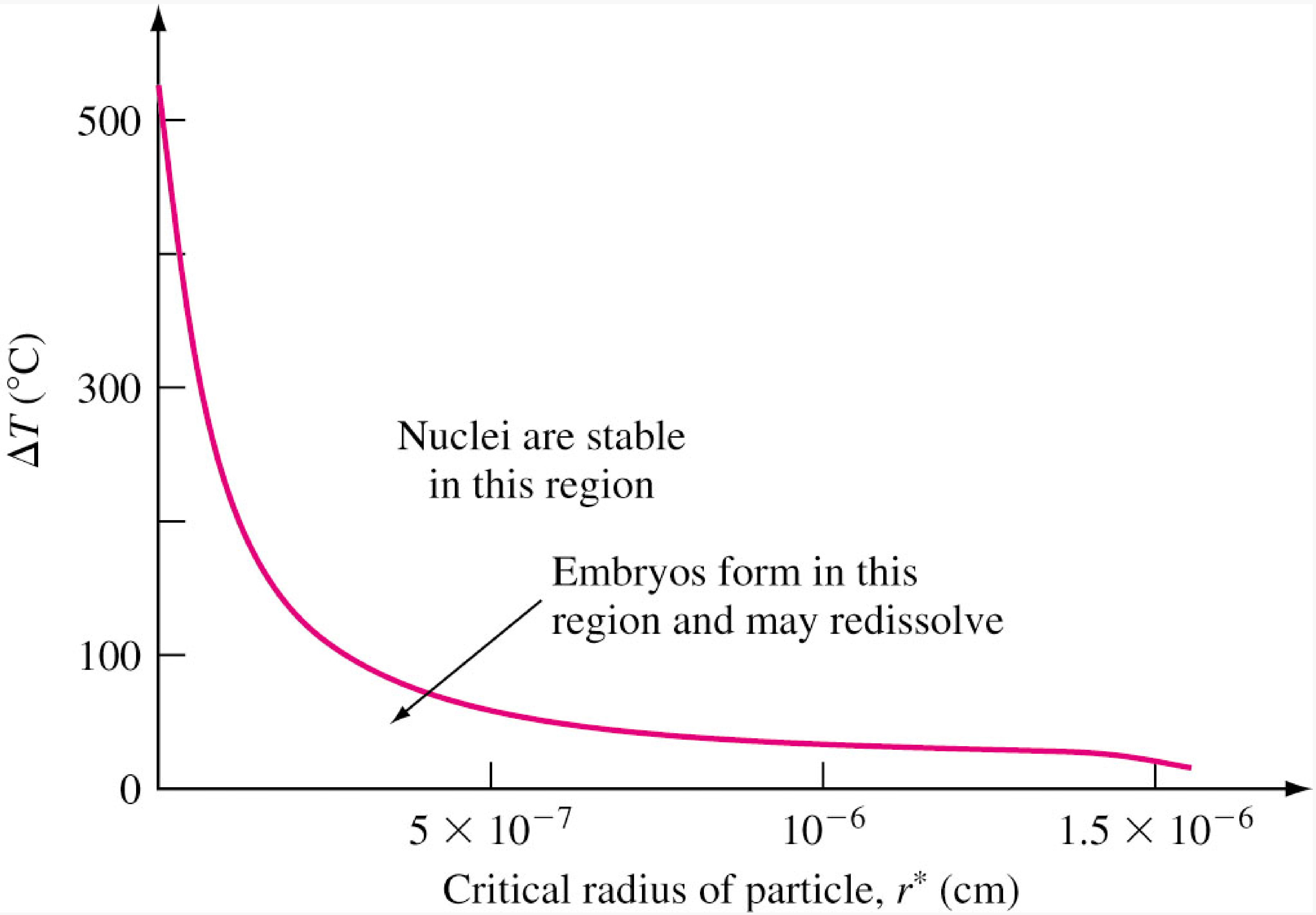


Table 4.1 Values for the freezing temperature, heat of fusion, surface energy, and maximum undercooling for selected metals

Metal	Freezing temp. °C	Freezing temp. K	Heat of fusion (J/cm^3)	Surface energy (J/cm^2)	Maximum undercooling, observed (ΔT[°C])
Pb	327	600	280	33.3×10^{-7}	80
Al	660	933	1066	93×10^{-7}	130
Ag	962	1235	1097	126×10^{-7}	227
Cu	1083	1356	1826	177×10^{-7}	236
Ni	1453	1726	2660	255×10^{-7}	319
Fe	1535	1808	2098	204×10^{-7}	295
Pt	1772	2045	2160	240×10^{-7}	332

Source: B. Chalmers, "Solidification of Metals," Wiley, 1964.


500
300
100
0
ΔT (°C)
Nuclei are stable in this region
Embryos form in this region and may redissolve
5 × 10⁻⁷
10⁻⁶
1.5 × 10⁻⁶
Critical radius of particle, r* (cm)

Critical Radius Versus Undercooling

- Greater the degree of undercooling, greater the change in volume free energy ΔG_v
- ΔGs does not change significantly.
- As the amount of undercooling ΔT increases, critical nucleus size decreases.
- Critical radius is related to undercooling by relation

$$r^* = \frac{2\gamma T_m}{\Delta H_f \Delta T}$$

r* = critical radius of nucleus
γ = Surface free energy
ΔH_f = Latent heat of fusion
Δ T = Amount of undercooling.

Heterogeneous Nucleation

- Nucleation occurs in a liquid on the surfaces of structural materials Eg:- Insoluble impurities.
- These structures, called *nucleating agents*, lower the free energy required to form stable nucleus.

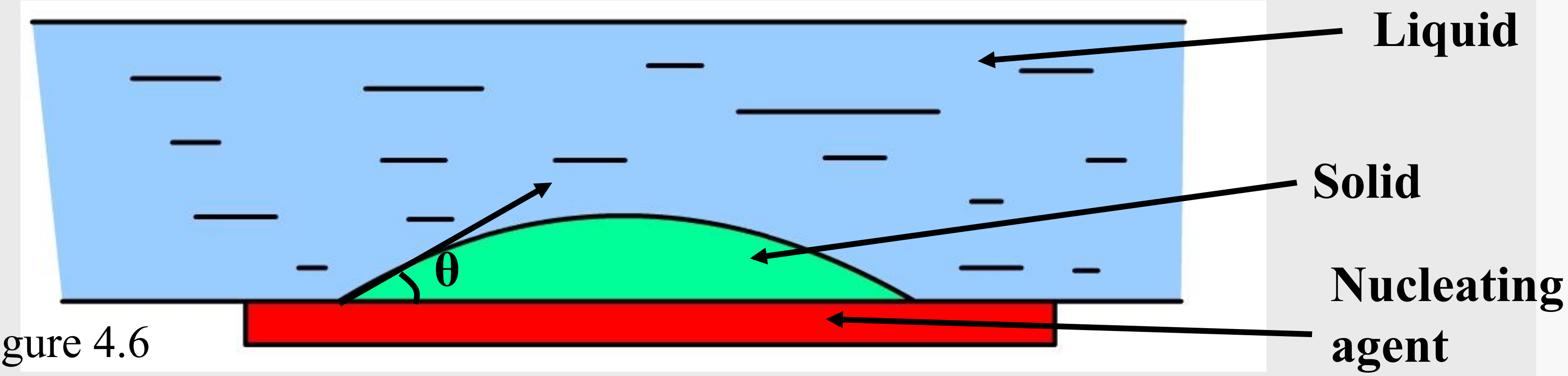


Figure 4.6

- Nucleating agents also lower the critical size.
- Smaller amount of undercooling is required to solidify.
- Used excessively in industries.

Growth of Crystals and Formation of Grain Structure

- Nucleus grow into crystals in different orientations.
- Crystal boundaries are formed when crystals join together at complete solidification.
- Crystals in solidified metals are called grains.
- Grains are separated by grain boundaries.
- More the number of nucleation sites available, more the number of grains formed.

Nuclei growing into grains
Forming grain boundaries

Types of Grains

- **Equiaxed Grains**:
  - Crystals, smaller in size, grow equally in all directions.
  - Formed at the sites of high concentration of the nuclie.
  - Example:- Cold mold wall

- **Columnar Grains**:
  - Long thin and coarse.
  - Grow predominantly in one direction.
  - Formed at the sites of slow cooling and steep temperature gradient.
  - Example:- Grains that are away from the mold wall.

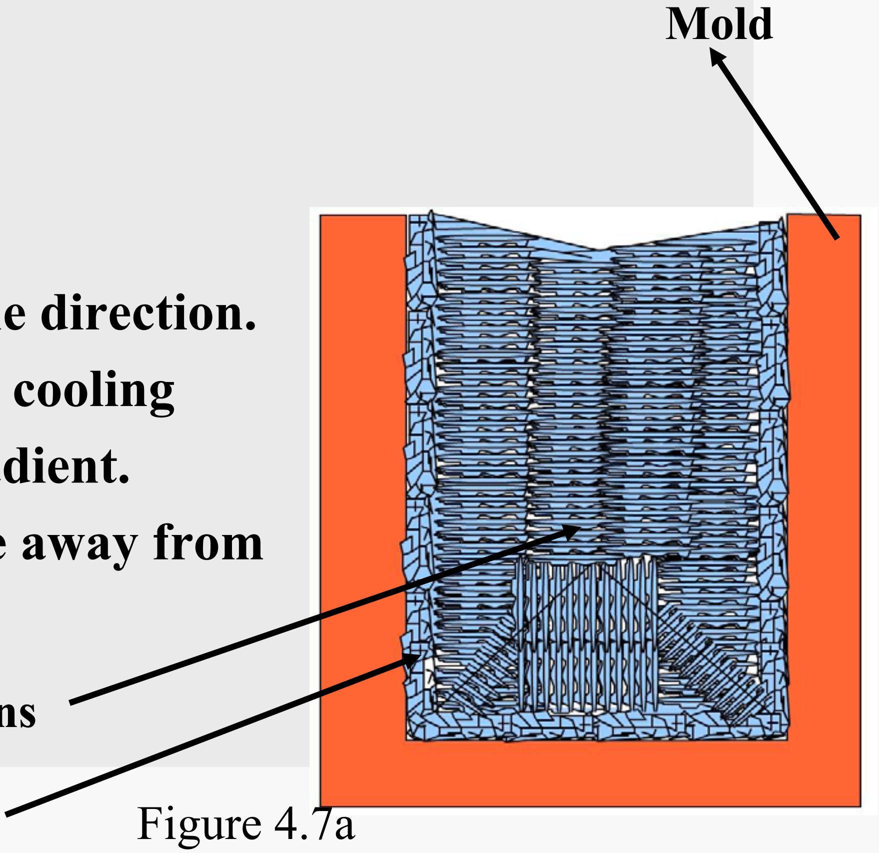


Figure 4.7a

Casting in Industries

- In industries, molten metal is cast into either semi finished or finished parts.

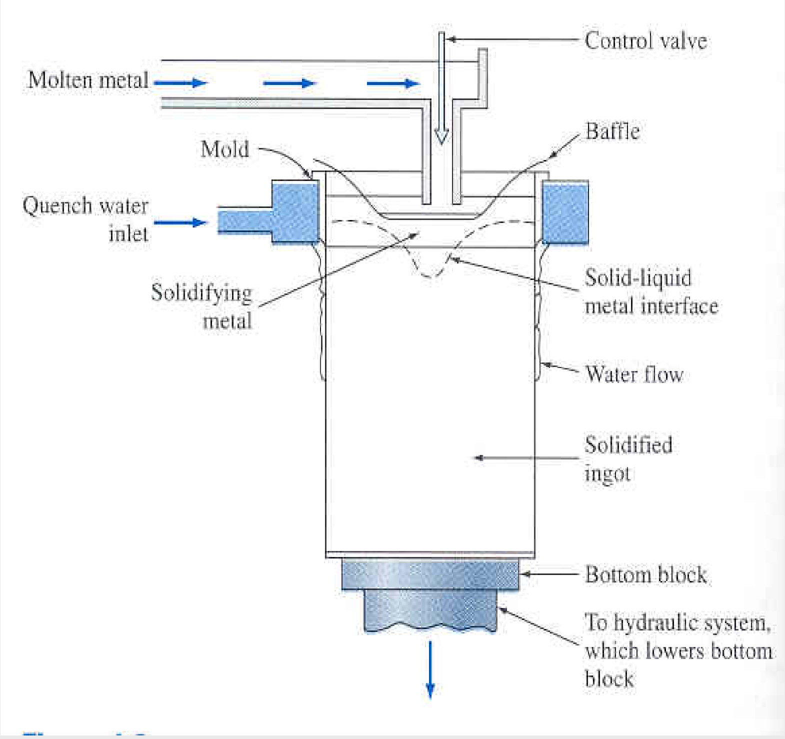


Figure 4.8

Direct-Chill semicontinuous Casting unit for aluminum

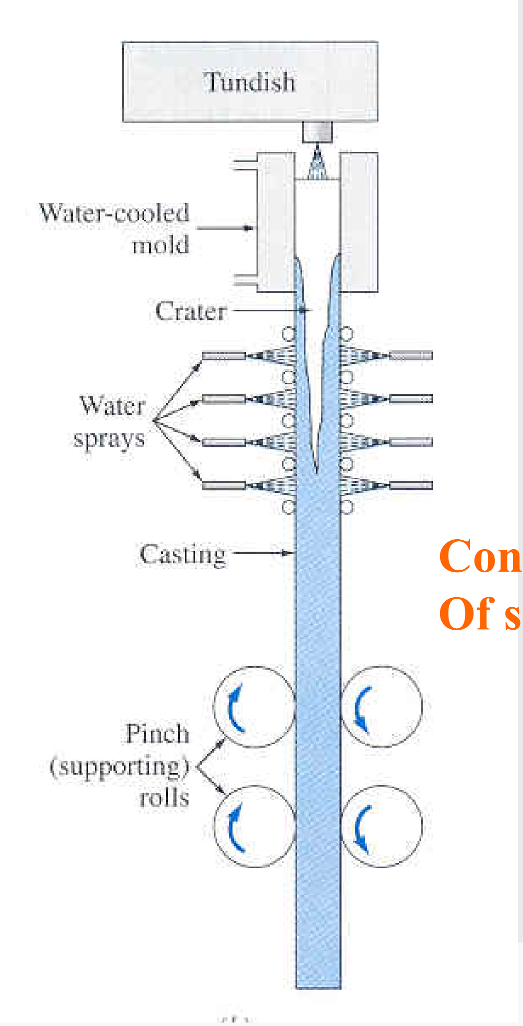
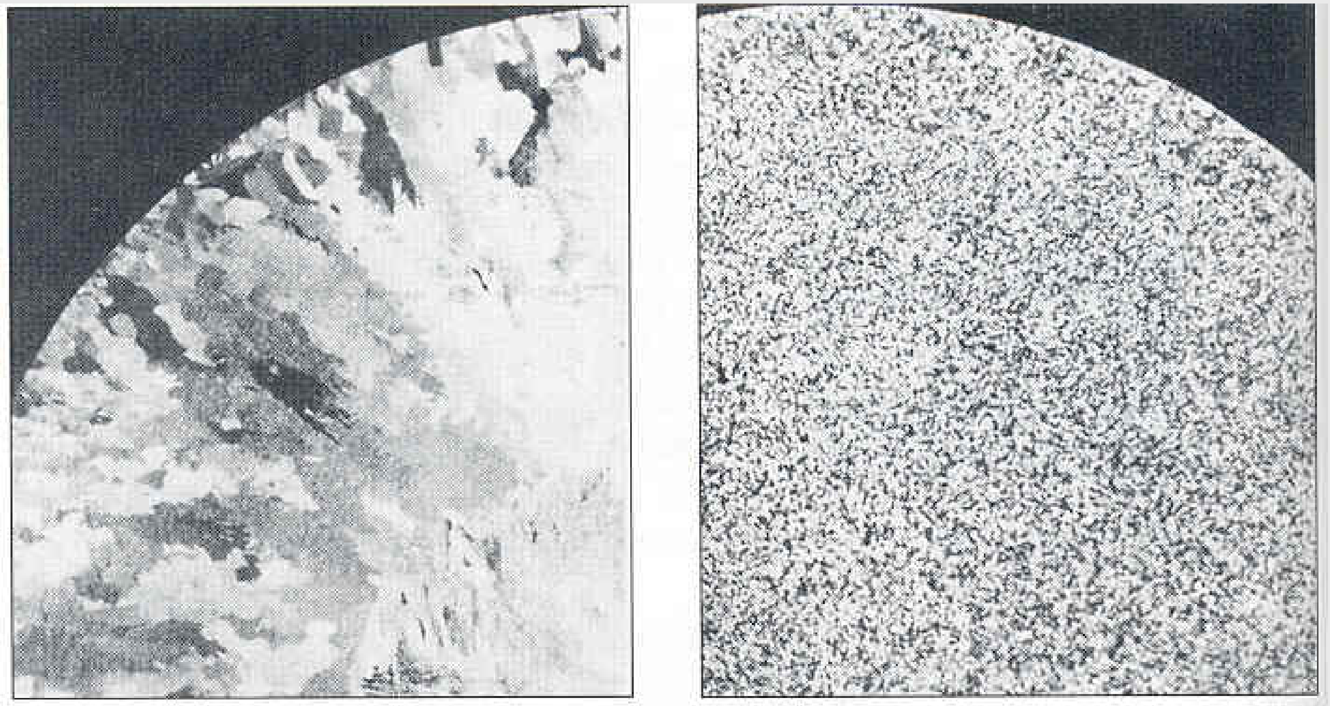


Figure 4.9b

Continuous casting Of steel ingots

Grain Structure in Industrial castings

- To produce cast ingots with fine grain size, *grain refiners* are added.
- Example:- For aluminum alloy, small amount of Titanium, Boron or Zirconium is added.



(a) (b)

Figure 4.10

Grain structure of Aluminum cast with (a) and without (b) grain refiners.

After “Metals Handbook” vol. 8, 8th ed., American Society of Metals, 1973, p.164)

Solidification of Single Crystal

- For some applications (Eg: Gas turbine blades-high temperature environment), single crystals are needed.
- Single crystals have high temperature creep resistance.
- Latent head of solidification is conducted through solidifying crystal to grow single crystal.
- Growth rate is kept slow so that temperature at solid-liquid interface is slightly below melting point.

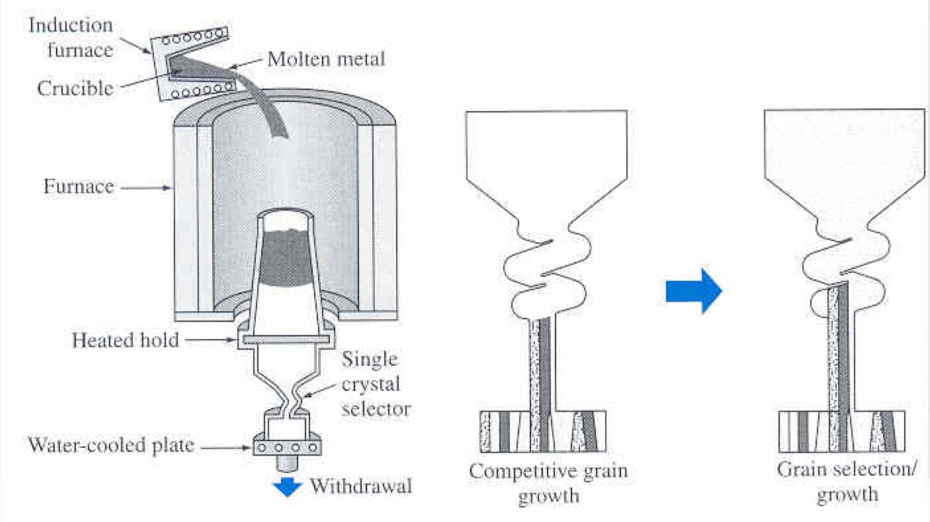


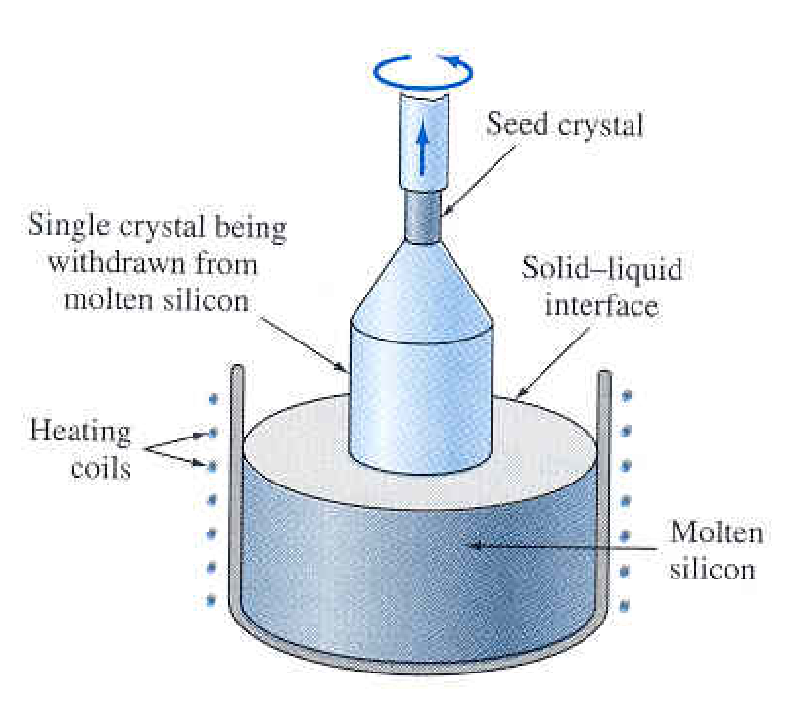
Figure 4.12

Growth of single crystal for turbine airfoil.

(After Pratt and Whitney Co.)

Czochralski Process

- This method is used to produce single crystal of silicon for electronic wafers.
- A seed crystal is dipped in molten silicon and rotated.
- The seed crystal is withdrawn slowly while silicon adheres to seed crystal and grows as a single crystal.



Metallic Solid Solutions

- Alloys are used in most engineering applications.
- **Alloy** is an mixture of two or more metals and nonmetals.
- Example:
    - **Cartridge brass** is binary alloy of 70% Cu and 30% Zinc.
    - **Iconel** is a nickel based superalloy with about 10 elements.
- Solid solution is a simple type of alloy in which elements are dispersed in a single phase.

Substitutional Solid Solution

- Solute atoms substitute for parent solvent atom in a crystal lattice.
- The structure remains unchanged.
- Lattice might get slightly distorted due to change in diameter of the atoms.
- Solute percentage in solvent can vary from fraction of a percentage to 100%

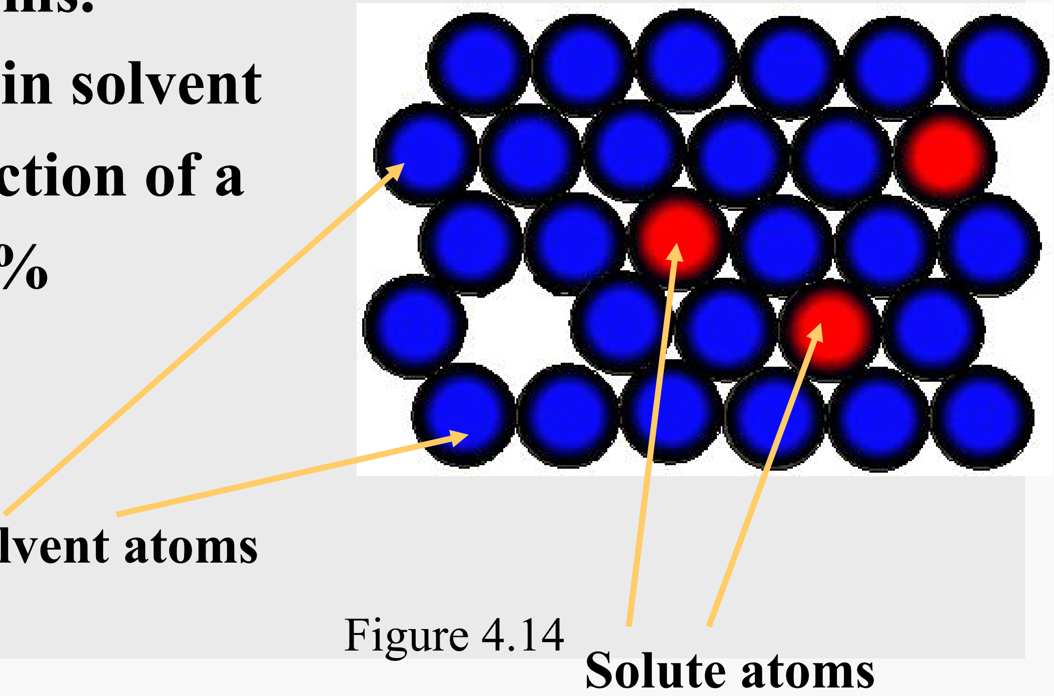


Figure 4.14

Substitutional Solid Solution (Cont..)

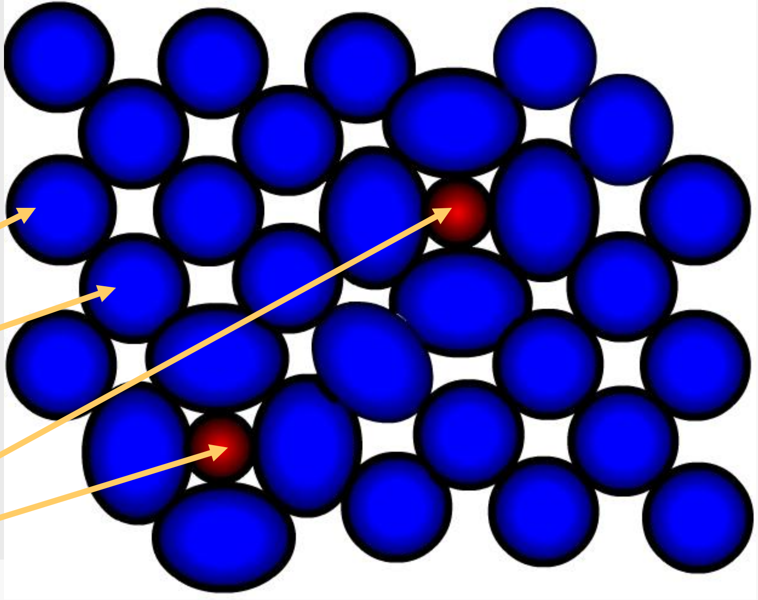
- The solubility of solids is greater if
  - The diameter of atoms not differ by more than 15%
  - Crystal structures are similar.
  - No much difference in electronegativity (else compounds will be formed).
  - Have some valence.

- Examples:-

System	Atomic radius Difference	Electron-egativity difference	Solid Solibility
Cu-Zn	3.9%	0.1	38.3%
Cu-Pb	36.7%	0.2	0.17%
Cu-Ni	2.3%	0	100%

Interstitial Solid Solution

- Solute atoms fit in between the voids (interstices) of solvent atoms.
- Solvent atoms in this case should be much larger than solute atoms.
- Example:- between 912 and 1394^{0}C, interstitial solid solution of carbon in γ iron (FCC) is formed.
- A maximum of 2.8% of carbon can dissolve interstitially in iron.



Iron atoms r00.129nm

Carbon atoms r=0.075nm

Figure 4.15a

Crystalline Imperfections

- No crystal is perfect.
- Imperfections affect mechanical properties, chemical properties and electrical properties.
- Imperfections can be classified as
    - Zero dimension point defects.
    - One dimension / line defects (dislocations).
    - Two dimension defects.
    - Three dimension defects (cracks).

Point Defects – Vacancy

- Vacancy is formed due to a missing atom.
- Vacancy is formed (one in 10000 atoms) during crystallization or mobility of atoms.
- Energy of formation is 1 ev.
- Mobility of vacancy results in cluster of vacancies.
- Also caused due to plastic deformation, rapid cooling or particle bombardment.

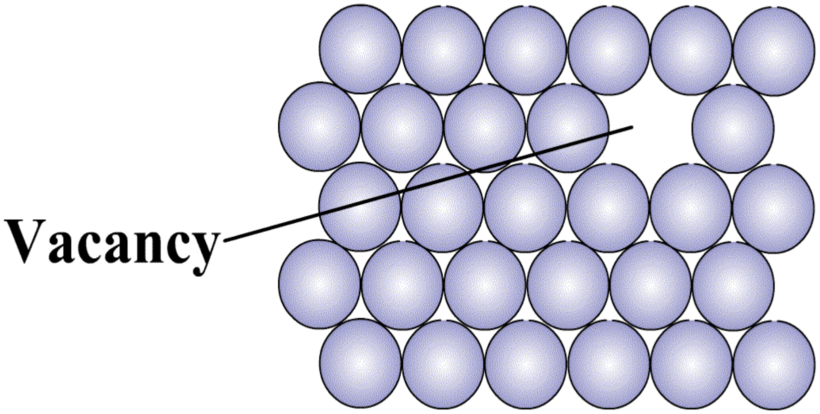


Figure: Vacancies moving to form vacancy cluster

Point Defects - Interstitially

- Atom in a crystal, sometimes, occupies interstitial site.
- This does not occur naturally.
- Can be induced by irradiation.
- This defects caused structural distortion.

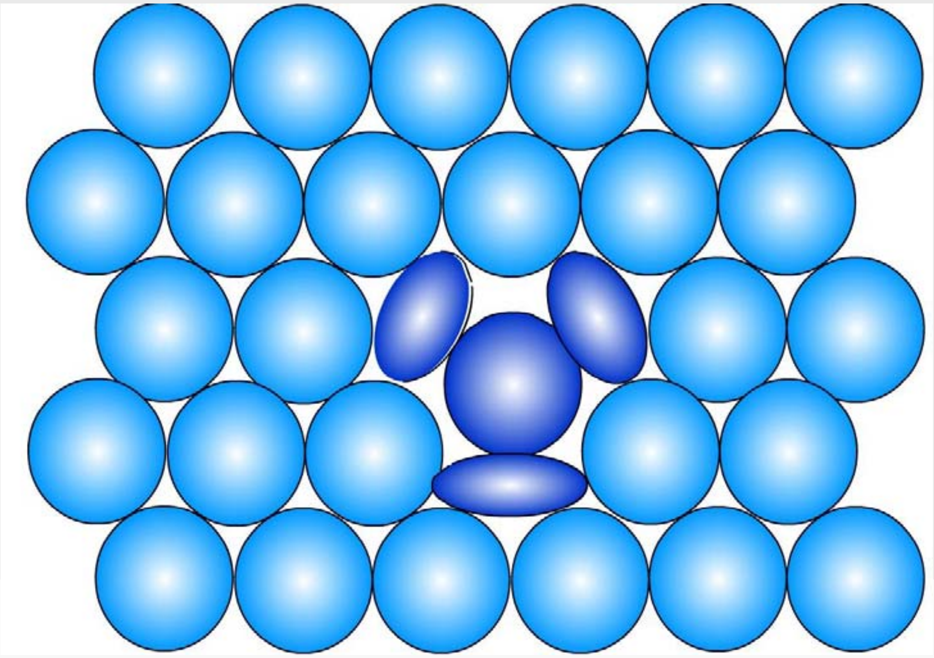


Figure 4.16b

Point Defects in Ionic Crystals

- Complex as electric neutrality has to be maintained.
- If two appositely charged particles are missing, **cation-anion divacancy** is created. This is **Schottky imperfection.**
- **Frenkel** imperfection is created when cation moves to interstitial site.
- Impurity atoms are also considered as point defects.

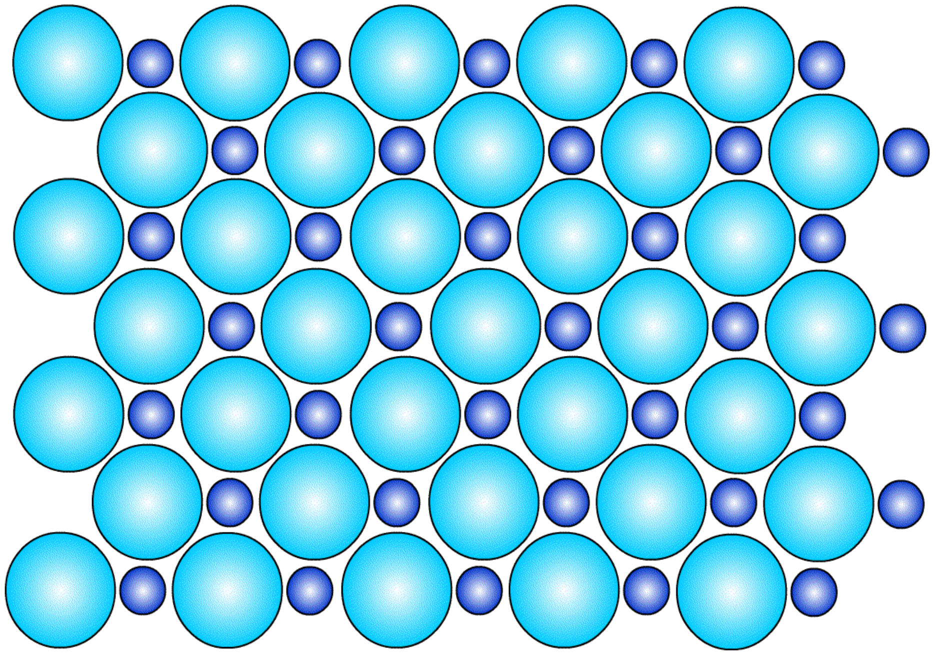
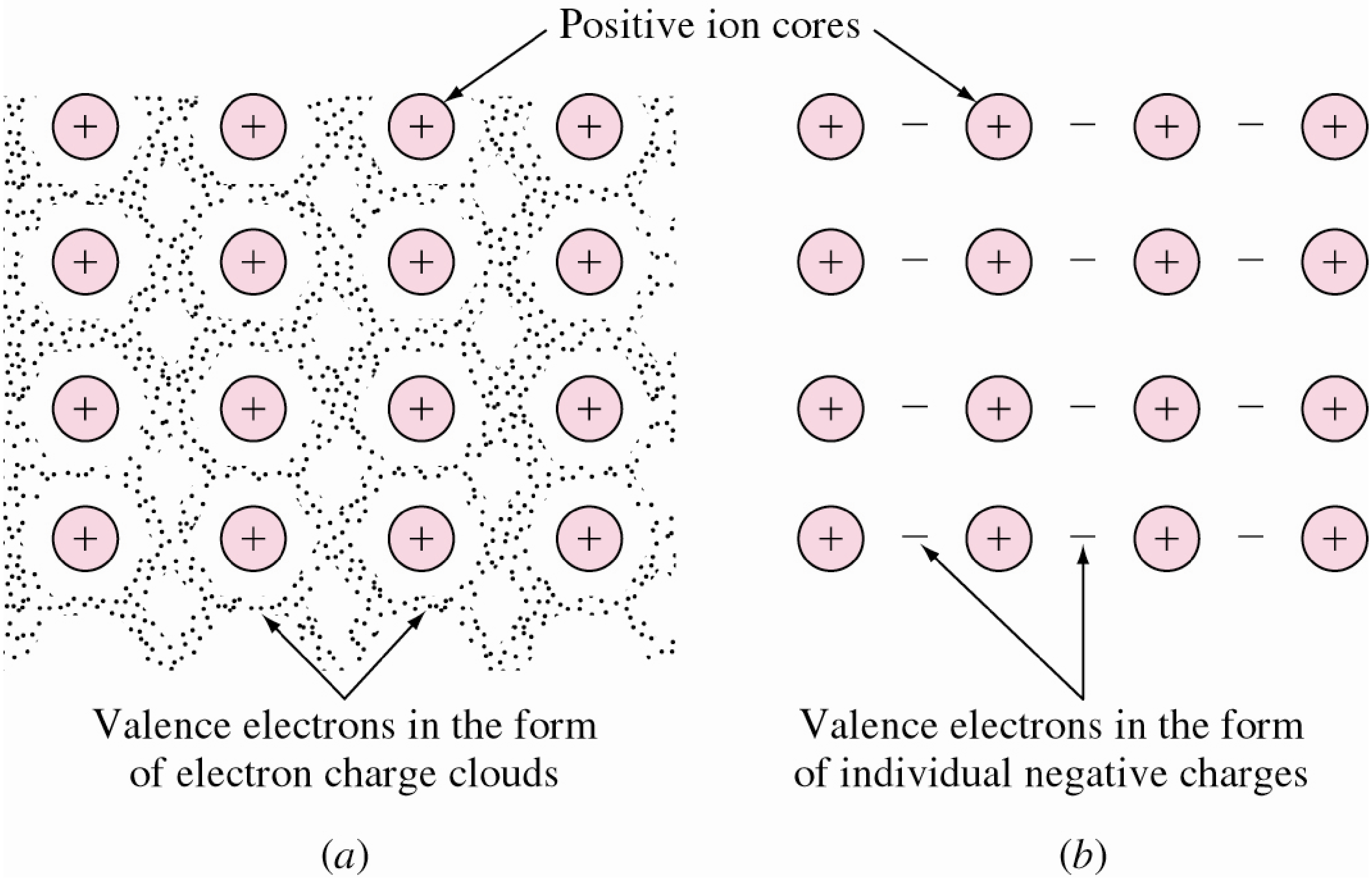
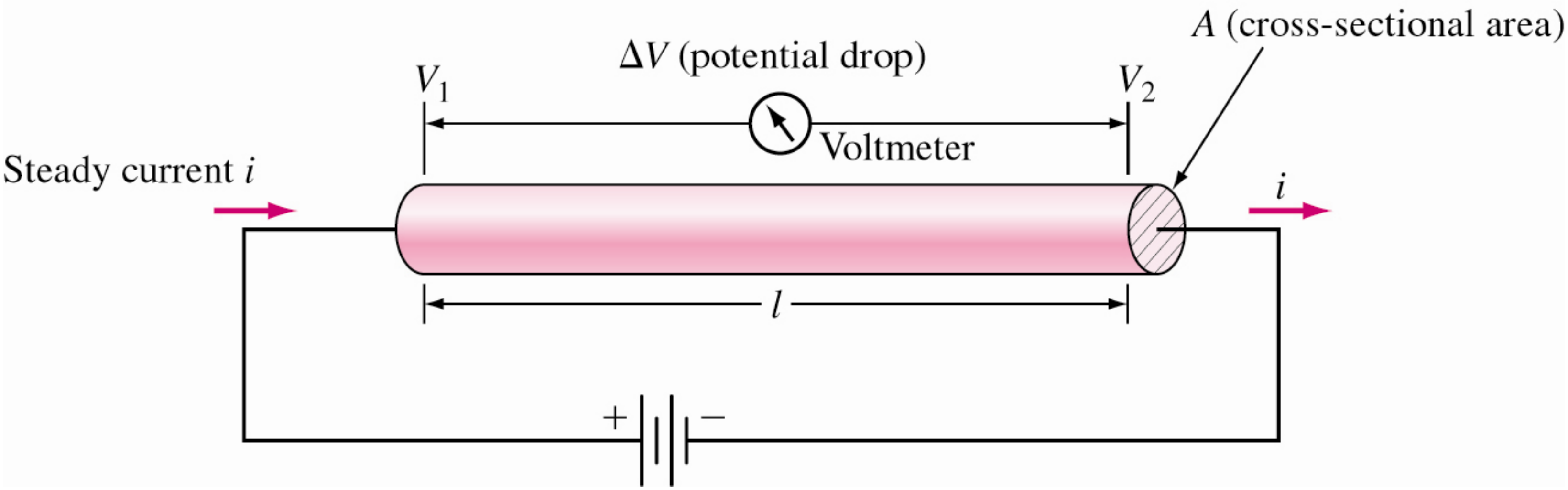


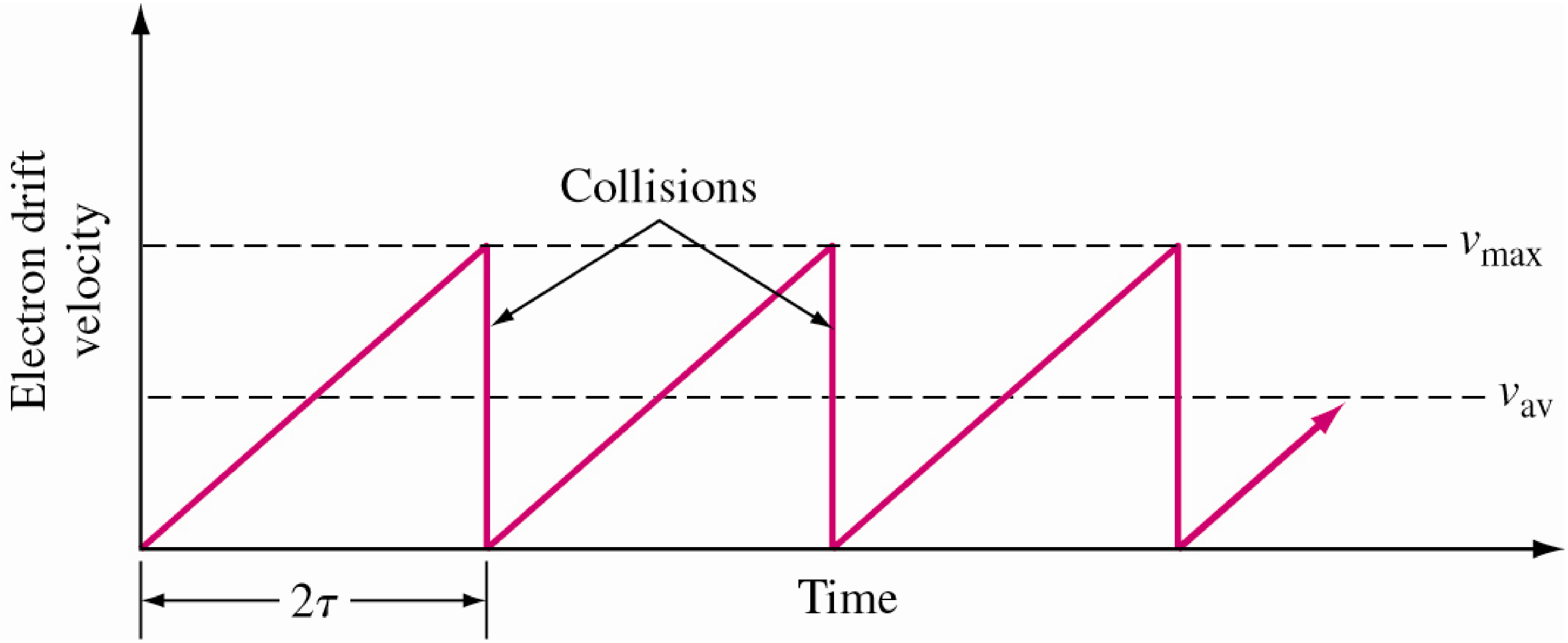
Figure 4.17

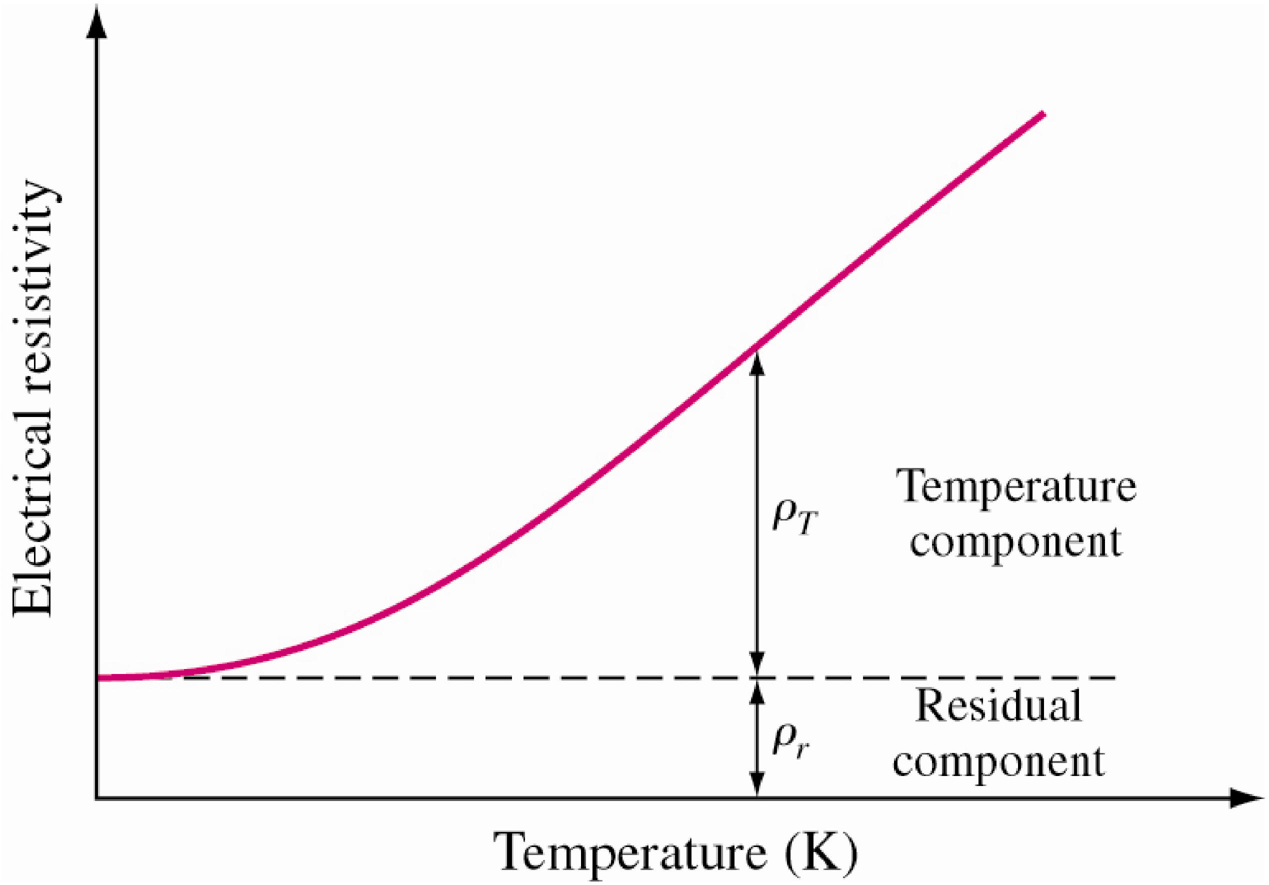
Electric Conduction – Classical Model

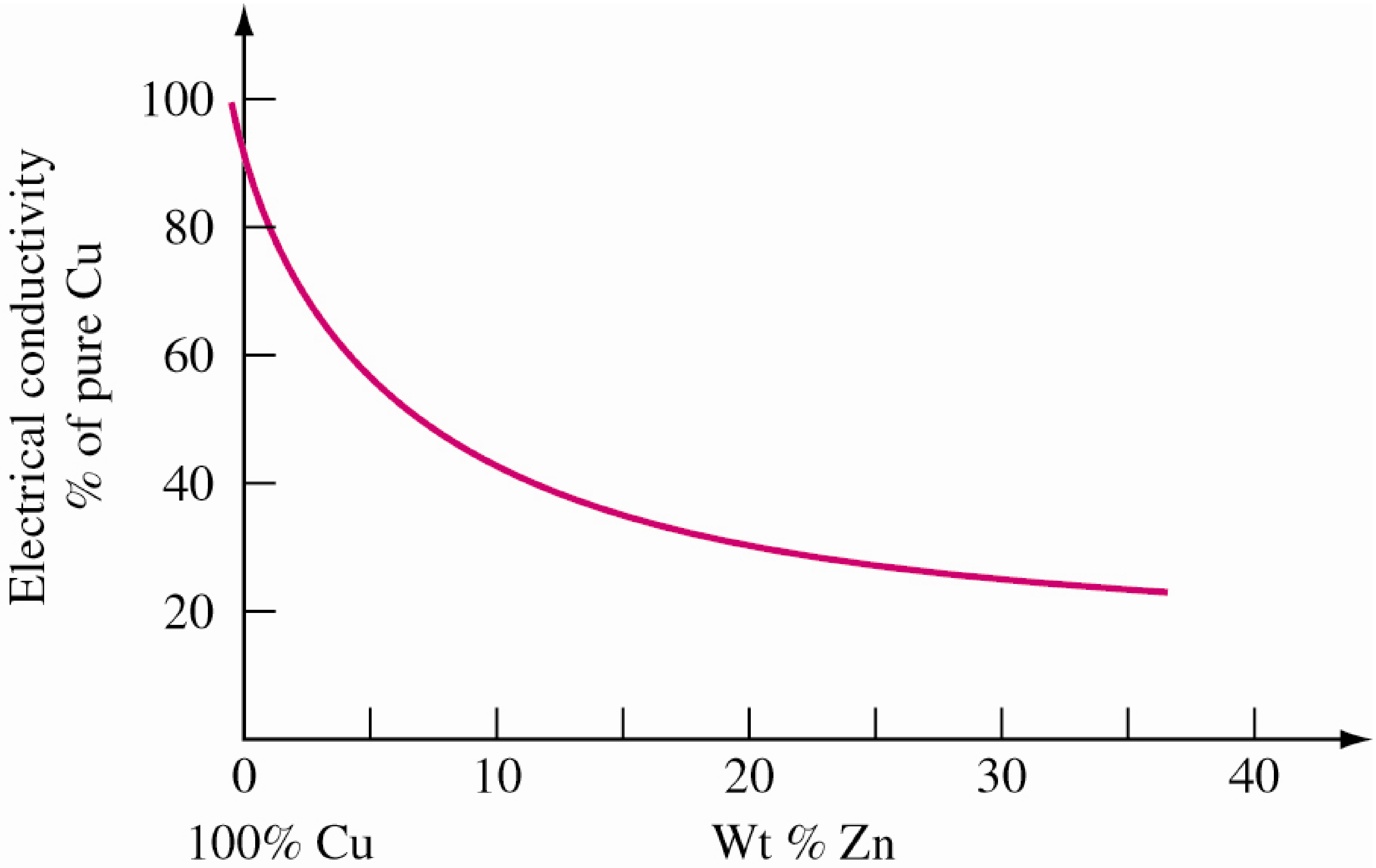
- **Metallic bonds make free movement of valence electrons possible.**
- **Outer valence electrons are completely free to move between positive ion cores.**
- **Positive ion cores vibrate with greater amplitude with increasing temperature.**
- **The motion of electrons are random and restricted in absence of electric field.**
- **In presence of electric field, electrons attain directed drift velocity.**

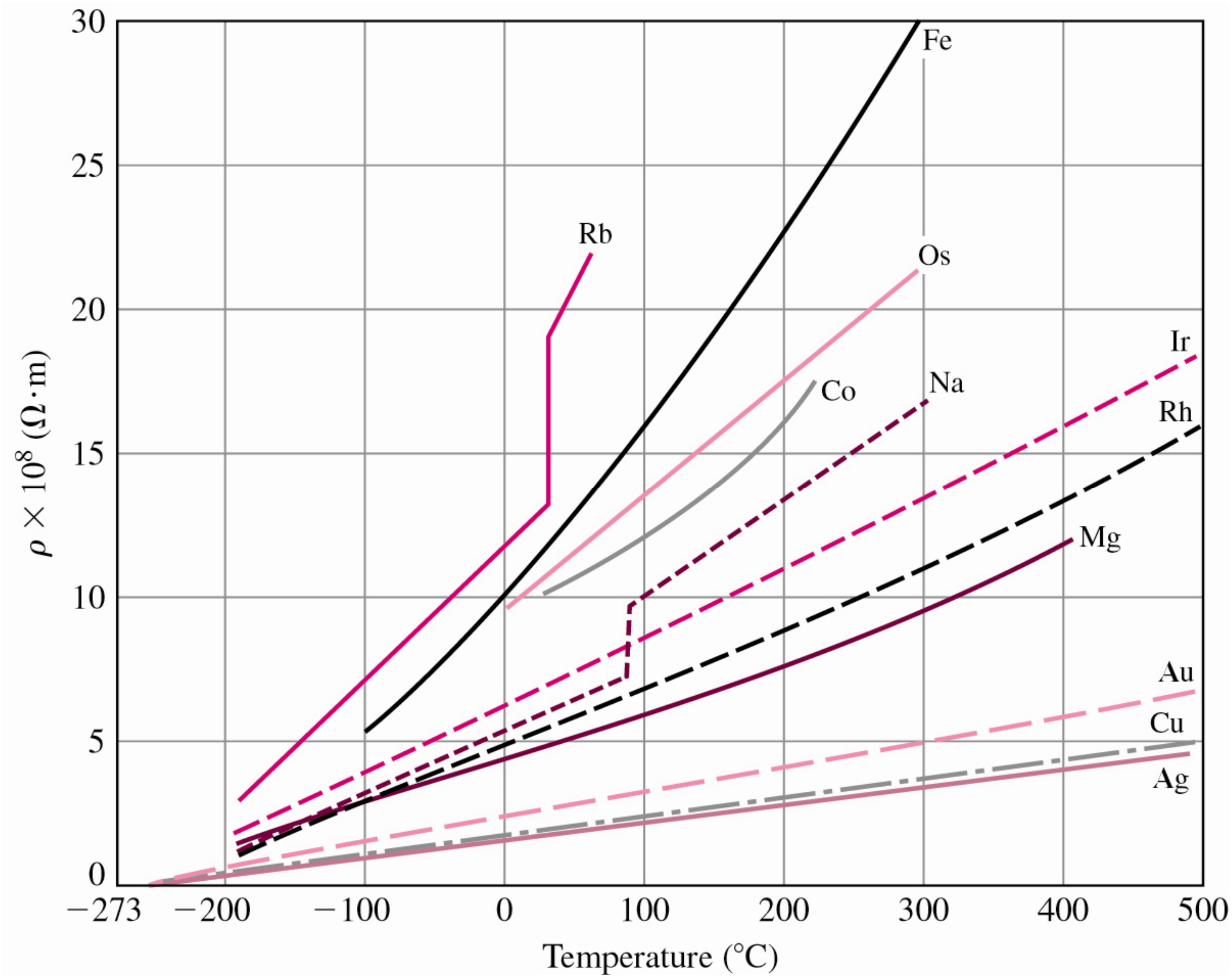

Positive ion cores
+
−
Valence electrons in the form of electron charge clouds
Valence electrons in the form of individual negative charges
(a)
(b)


A (cross-sectional area)
ΔV (potential drop)
V1
V2
Voltmeter
Steady current i
i
l
+
−

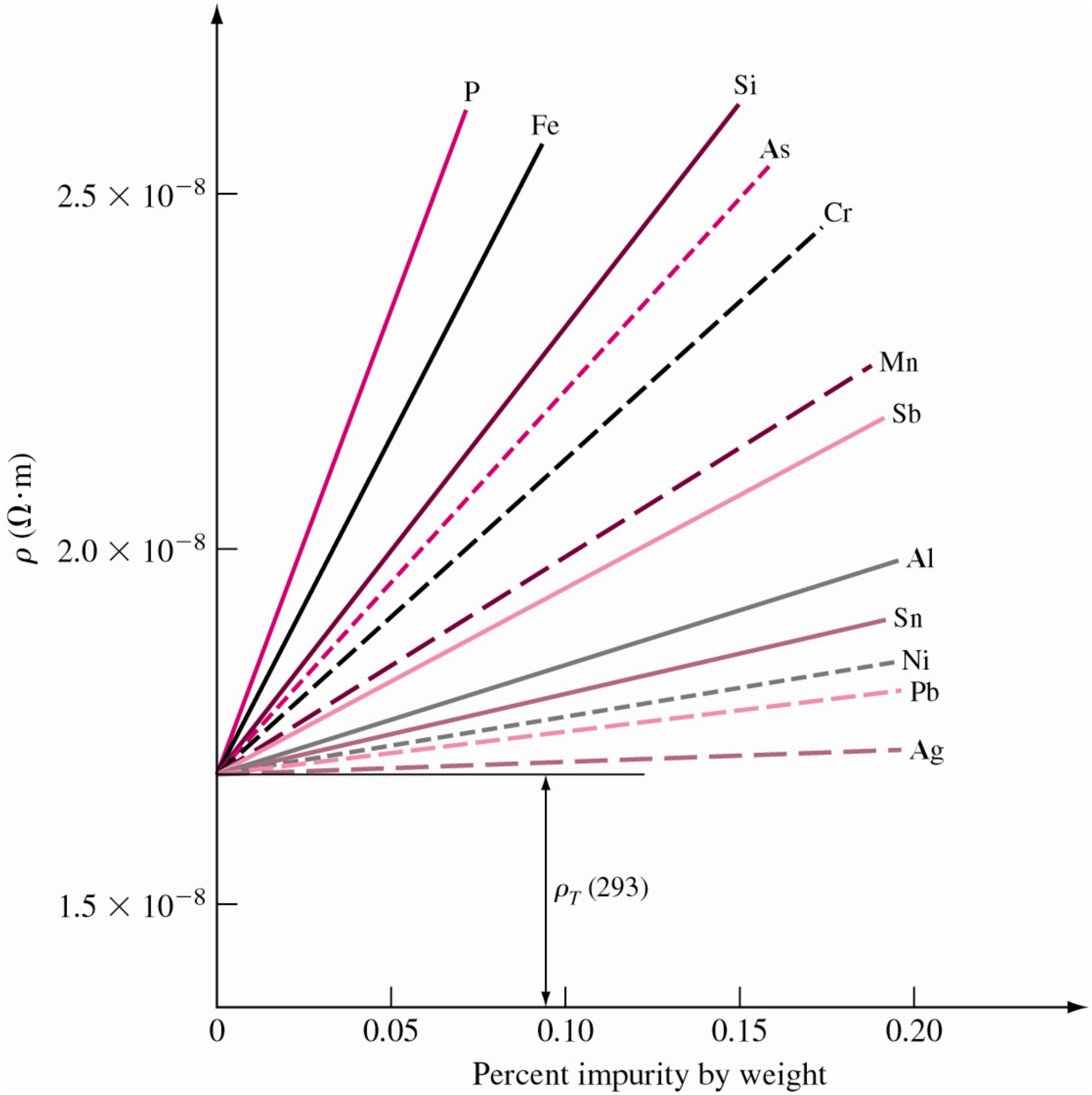

Electron drift velocity
Collisions
v_{max}
v_{av}
2τ
Time

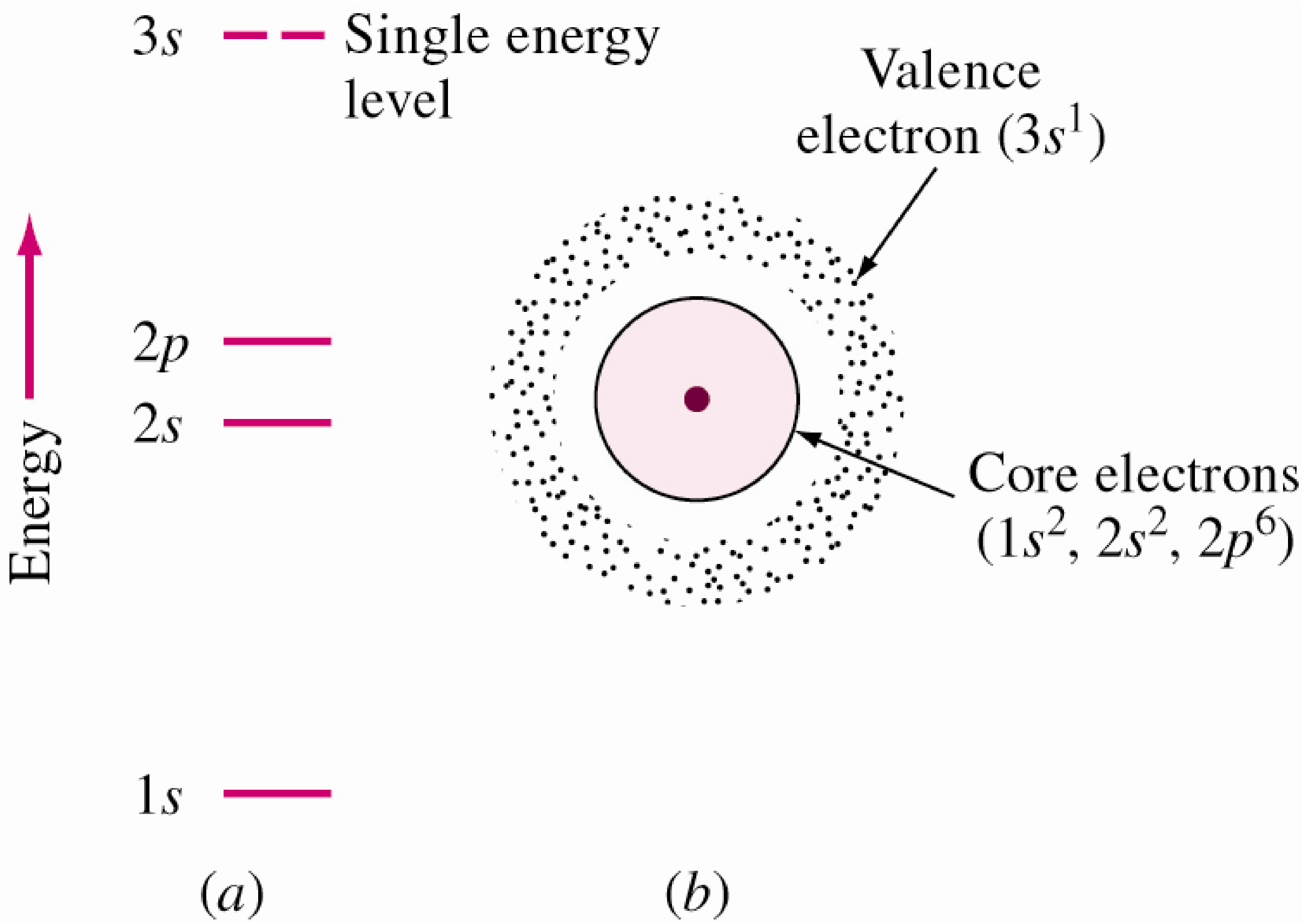

Electrical resistivity
ρ_T
Temperature component
ρ_r
Residual component
Temperature (K)


Electrical conductivity
% of pure Cu
100
80
60
40
20
0
10
20
30
40
100% Cu
Wt % Zn

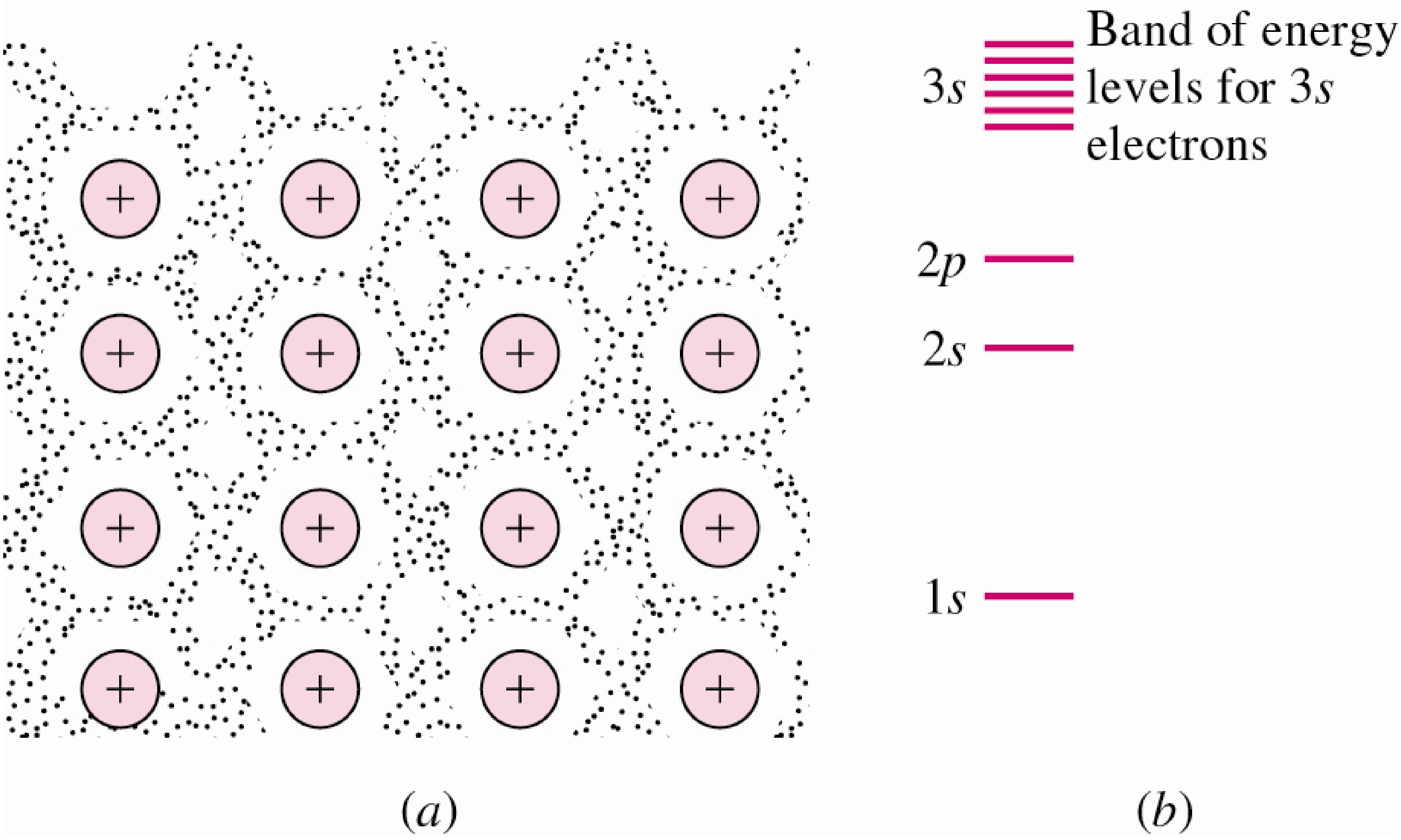


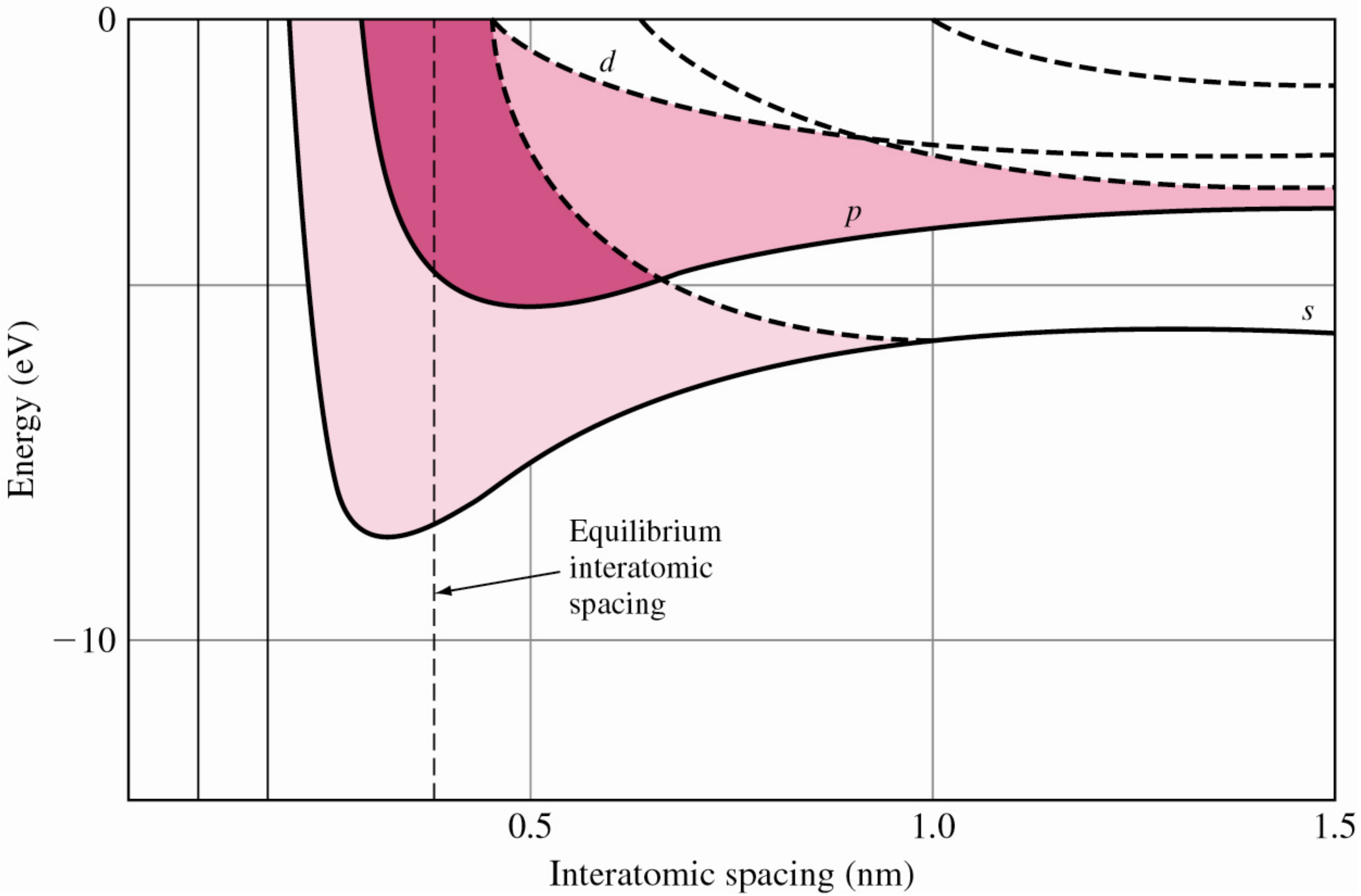
30
25
20
15
10
5
0
$\rho \times 10^8$ ($\Omega \cdot$m)
−273
−200
−100
0
100
200
300
400
500
Temperature (°C)
Fe
Rb
Os
Co
Na
Ir
Rh
Mg
Au
Cu
Ag

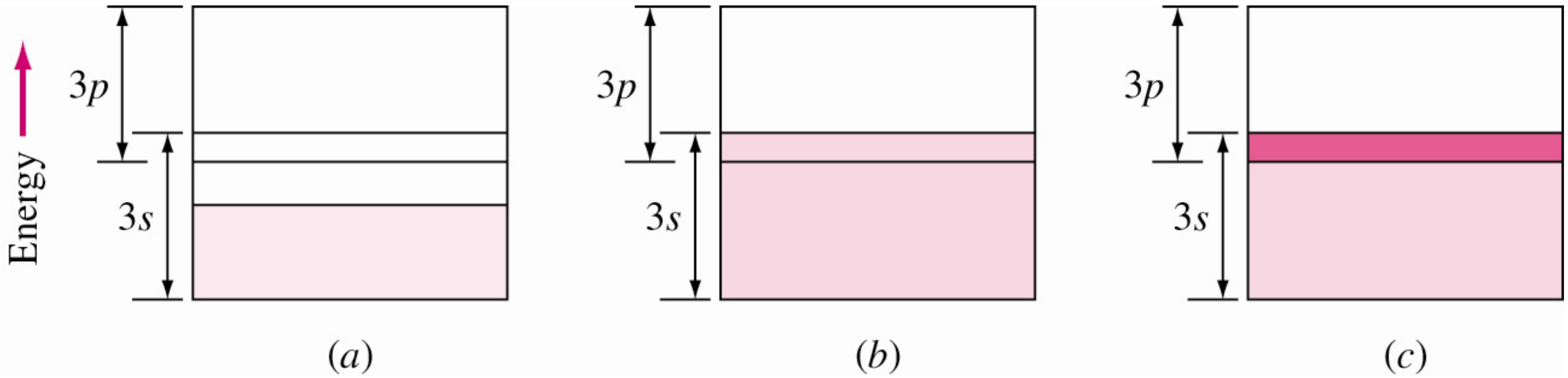

P
Fe
Si
As
Cr
Mn
Sb
Al
Sn
Ni
Pb
Ag
2.5×10^{-8}
2.0×10^{-8}
1.5×10^{-8}
ρ ($\Omega \cdot$m)
ρ_T (293)
0
0.05
0.10
0.15
0.20
Percent impurity by weight


3s
Single energy level
Energy
2p
2s
1s
(a)
Valence electron ($3s^1$)
Core electrons ($1s^2$, $2s^2$, $2p^6$)
(b)

- **Valence electrons are delocalized, interact and interpenetrate each other.**
- **Their sharp energy levels are broadened into energy bands.**
- **Example:- Sodium has 1 valence electron ($3S^1$). If there are N sodium atoms, there are N distinct $3S^1$ energy levels in 3S band.**
- **Sodium is a good conductor since it has half filled outer orbital**



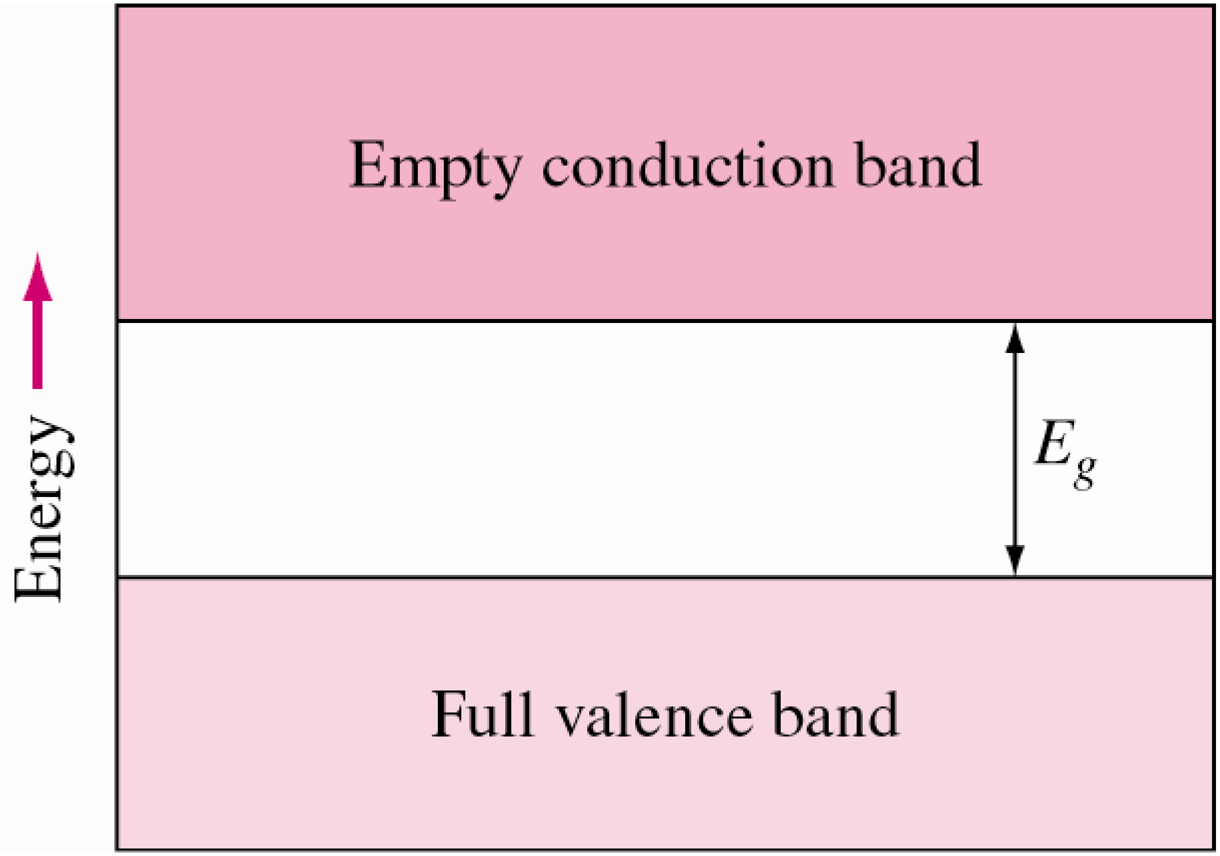

0
−10
Energy (eV)
d
p
s
Equilibrium interatomic spacing
0.5
1.0
1.5
Interatomic spacing (nm)

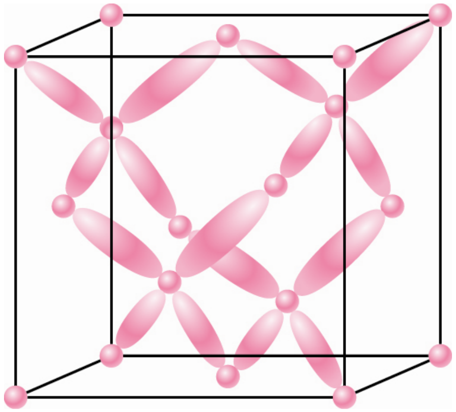

Energy
3p
3s
(a)
(b)
(c)

In insulators, electrons are tightly bound.

Large energy gap Eg Separates lower filled valence band and upper empty conduction band.

To be available for conduction, the electron should jump the energy gap.





Diamond

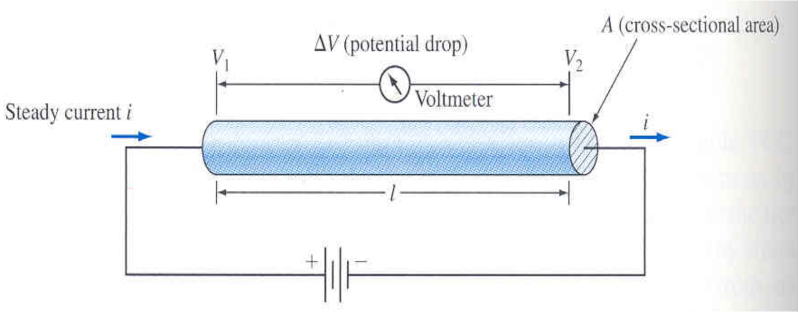
Ohm's Law

- **Ohm's law** states that electric current flow I is directly proportional to the applied voltage V and inversely proportional to resistance of the wire:

i = V/R where i = electric current (A)

V = potential difference (V)

R = resistance of wire (Ω)



- **Electric resistivity** ρ = RA/*l*

l = length of the conductor

A = cross-sectional area of the conductor

- **Electric Conductivity** σ = 1/ ρ

Conductors	Insulators	Semiconductors
Silver Copper Gold	Polyethylene Polystyrene	Silicon Germanium

Conduction in Intrinsic Semiconductors

- **Semiconductors: Conductors between good conductors and insulators.**
- **Intrinsic Semiconductors: Pure semiconductors and conductivity depends on inherent properties.**
- **Example: Silicon and Germanium – each atom contributes 4 valence electrons for covalent bond.**
- **Valence electrons are excited away from their bonding position when they are excited.**
- **Moved electron leaves a hole behind.**

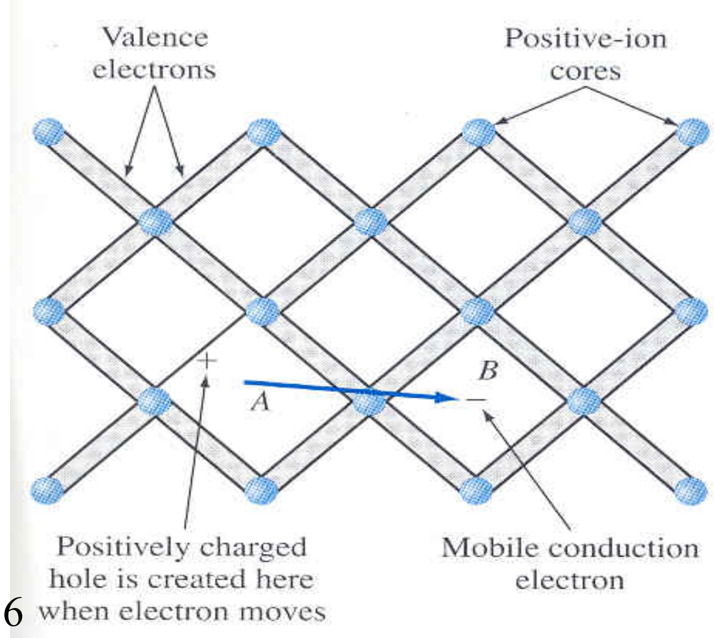


Figure 13.16

Electrical Charge Transport in Pure Silicon

- **Both electrons and holes are charge carriers.**
- **Hole is attracted to negative terminal, electron to the positive terminal**

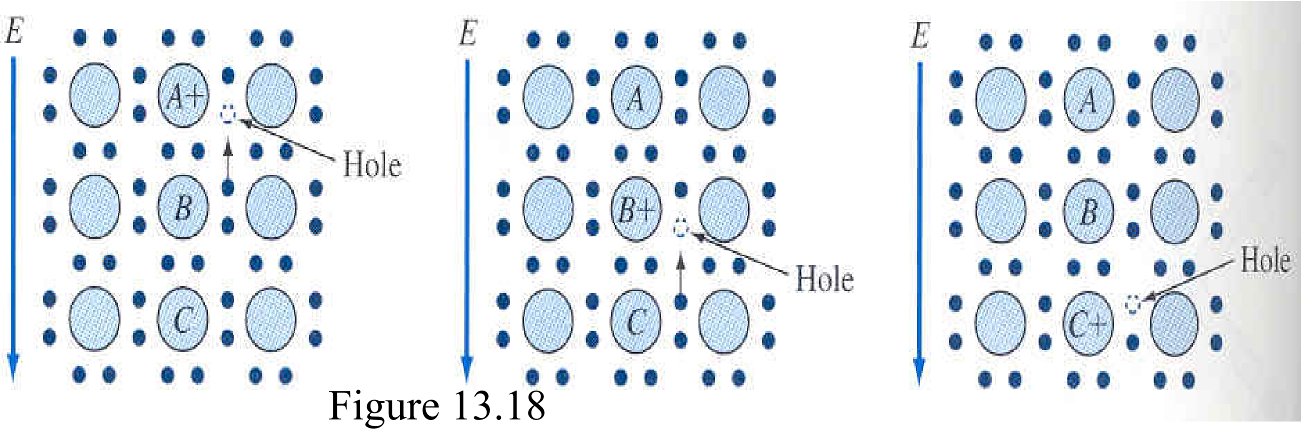


Figure 13.18

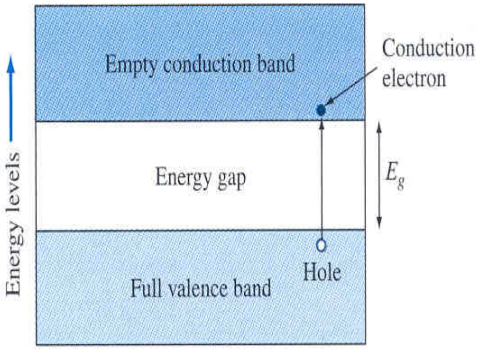
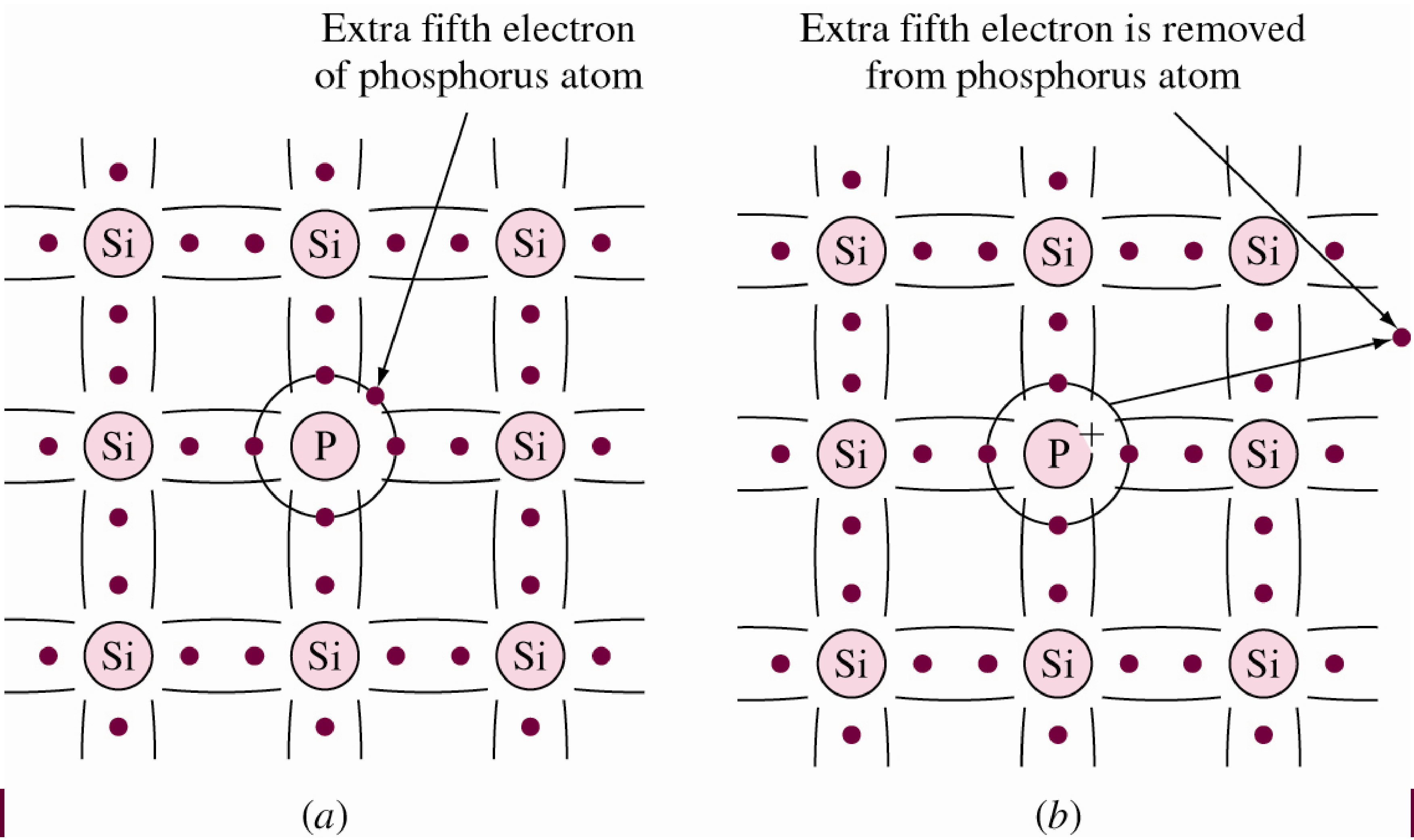


Figure 13.19

- **Valence electron 'A' is missing – Hole**
- **Valence electron 'B' moves to that spot due to the electric field leaving behind a hole.**
- **Movement of electrons is opposite to the electric field.**

Extrinsic Semiconductors

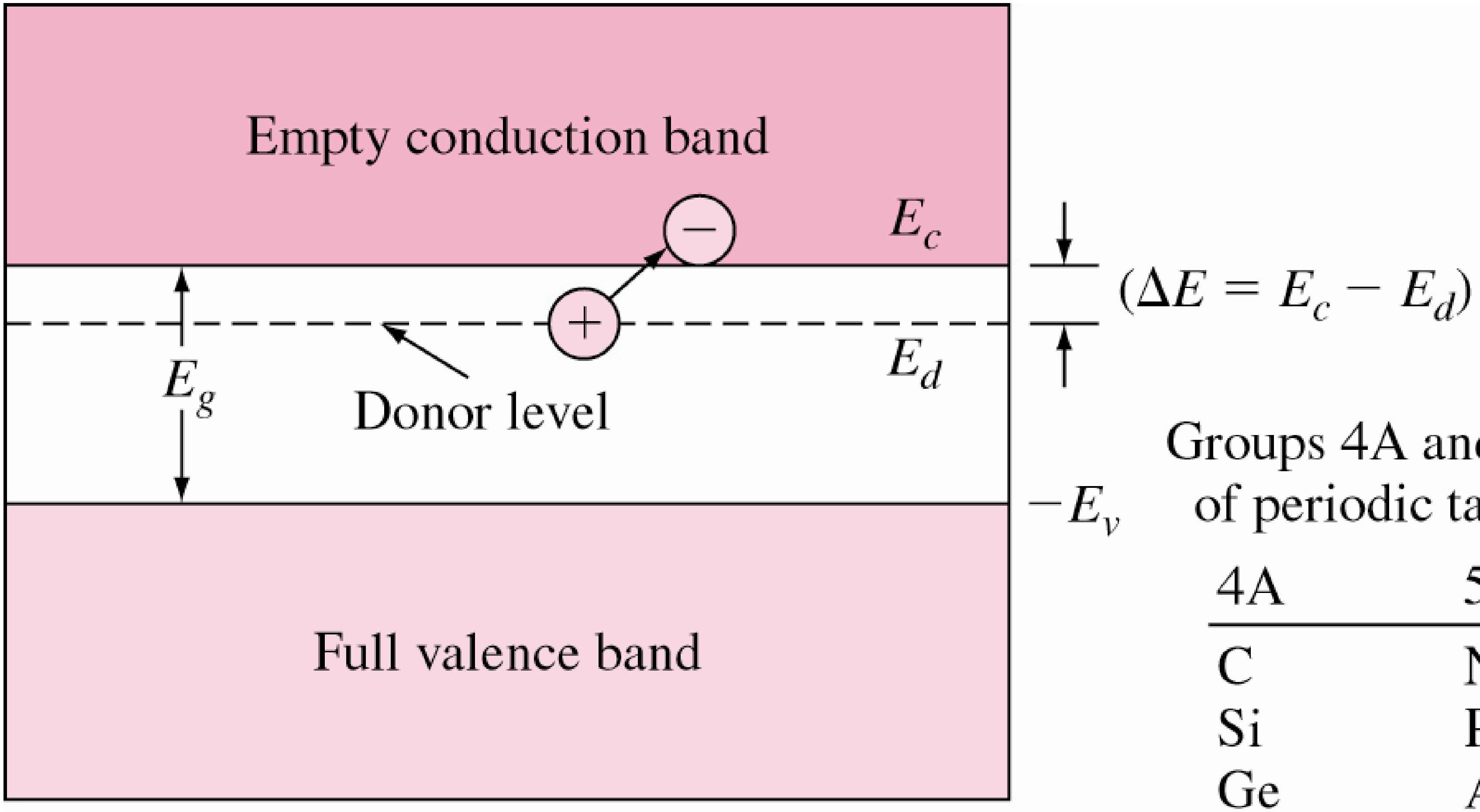
- **Extrinsic semiconductors have impurity atoms (100-1000 ppm) that have different valance characteristics.**
- **n – type extrinsic semiconductors: Impurities donate electrons for conduction.**
  - **Example:- Group V A atoms (P, As, Sb) added to silicon or Ge.**



(a)

(b)

Extrinsic Semiconductors



Groups 4A and 5A
of periodic table

4A	5A
C	N
Si	P
Ge	As
Sn	Sb

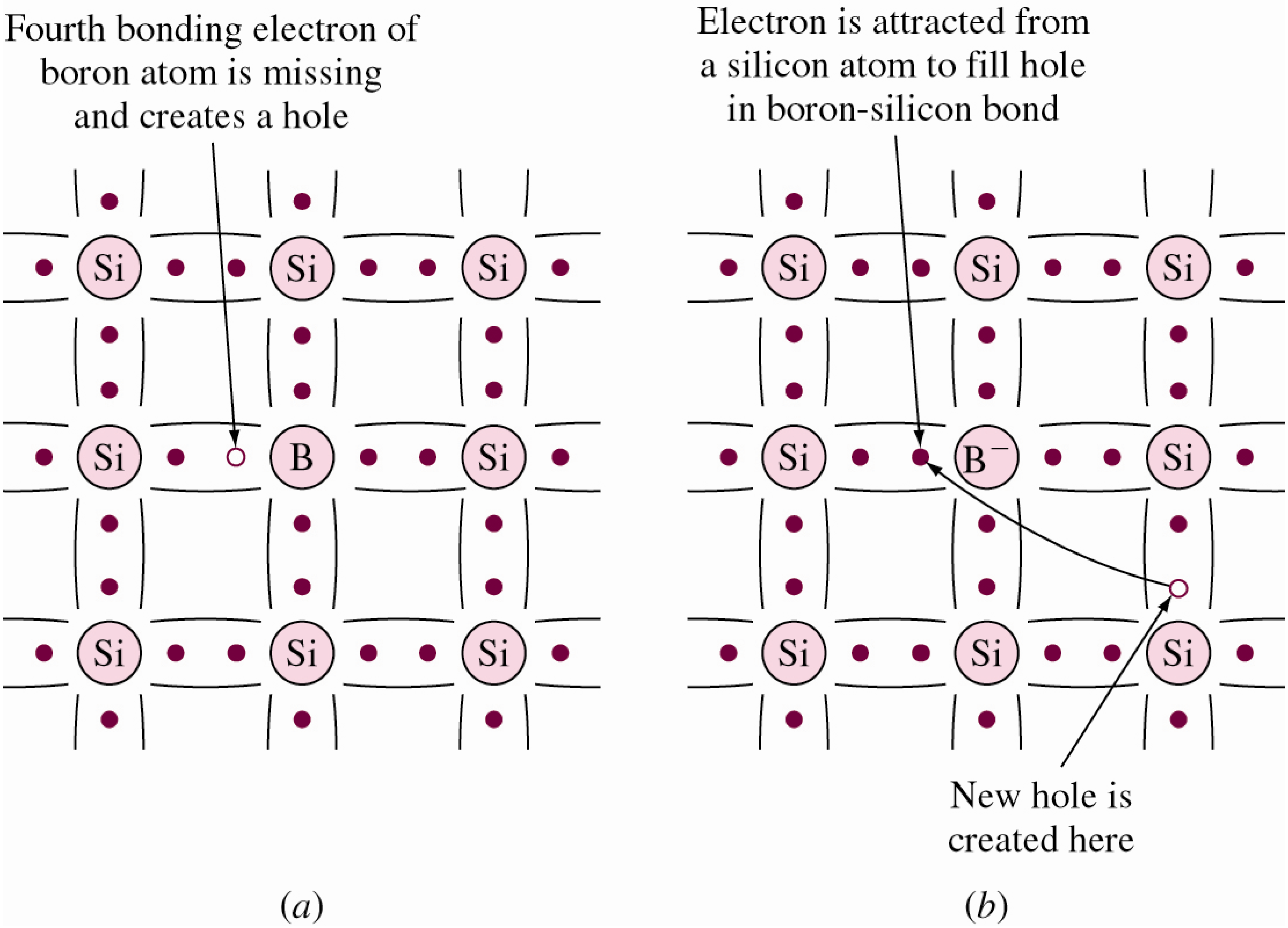
P-Type Extrinsic Semiconductors

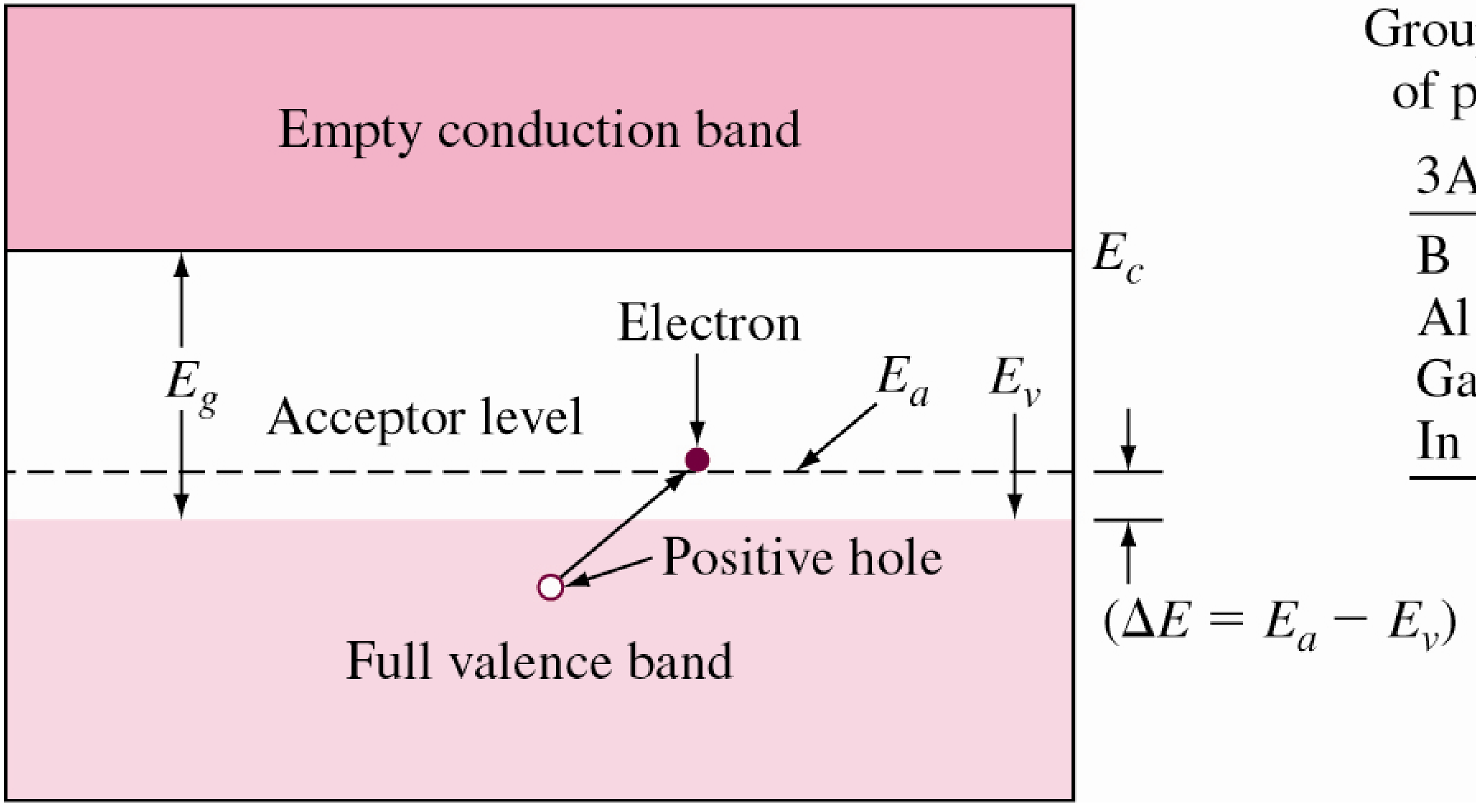
- **Group III A atoms when added to silicon, a hole is created since one of the bonding electrons is missing**

- **When electric field is applied, electrons from the neighboring bond move to the hole**

- **Boron atom gets ionized and hole moves towards negative terminal**

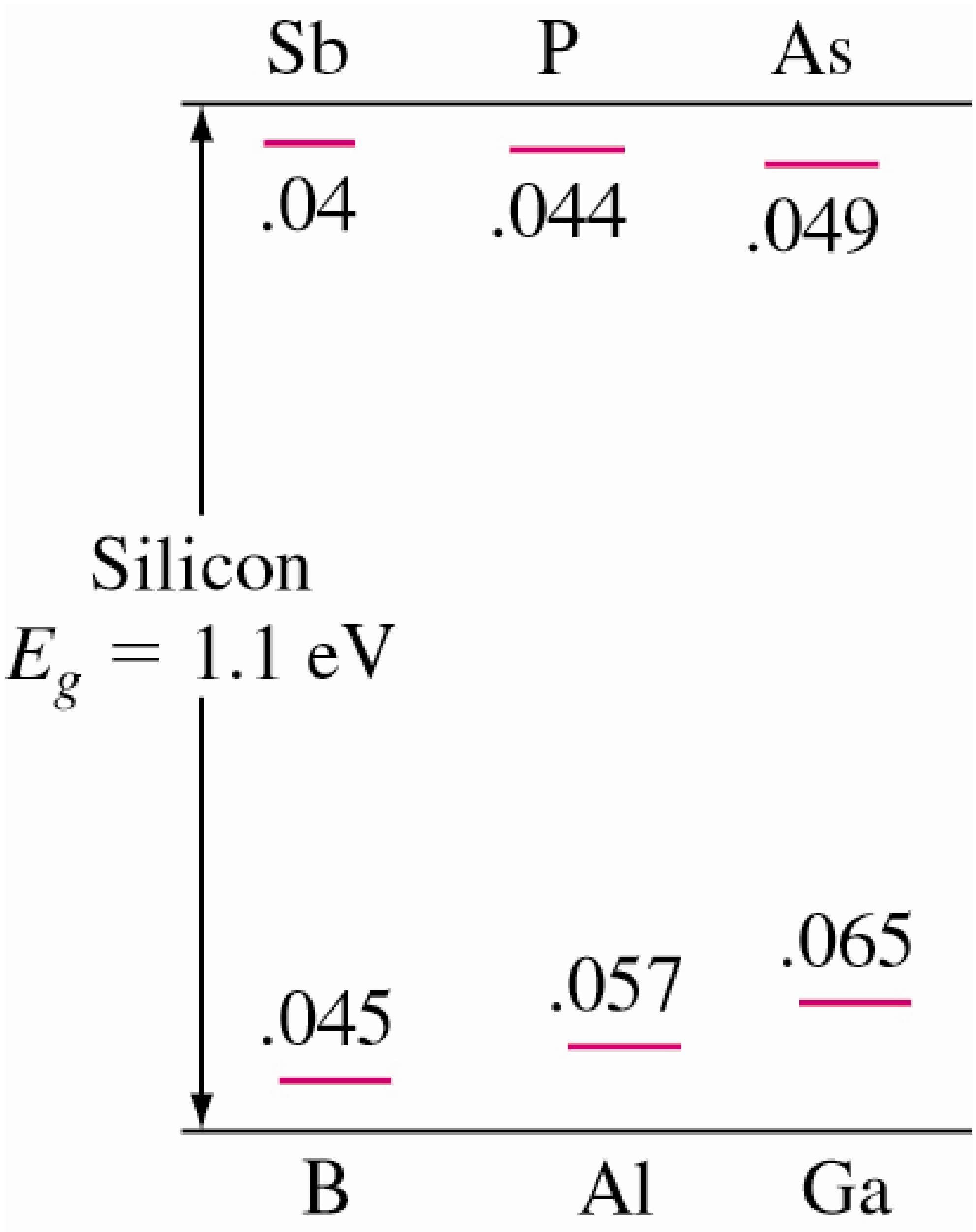
- **B, Al, provide acceptor level energy and are hence called acceptor atoms**
- **Doping: Impurity atoms (dopants) are deposited into silicon by diffusion at 1100^{0}C.**


Fourth bonding electron of boron atom is missing and creates a hole
Si
B
(a)
Electron is attracted from a silicon atom to fill hole in boron-silicon bond
B$^-$
New hole is created here
(b)



Groups 3A and 4A
of periodic table

3A	4A
B	C
Al	Si
Ga	Ge
In	Sn


Sb
P
As
.04
.044
.049
Silicon
$E_g = 1.1$ eV
.065
.057
.045
B
Al
Ga

Line Defects – (Dislocations)

- Lattice distortions are centered around a line.
- Formed during
  - Solidification
  - Permanent Deformation
  - Vacancy condensation
  - Atomic mismatch
- Different types of line defects are
  - Edge dislocation
  - Screw dislocation
  - Mixed dislocation

Edge Dislocation

- Created by insertion of **extra half planes** of atoms.
- ⊥ → **Positive edge dislocation**
- ⊤ → **Negative edge dislocation**
- **Burgers vector**
  Shows displacement of atoms (slip).

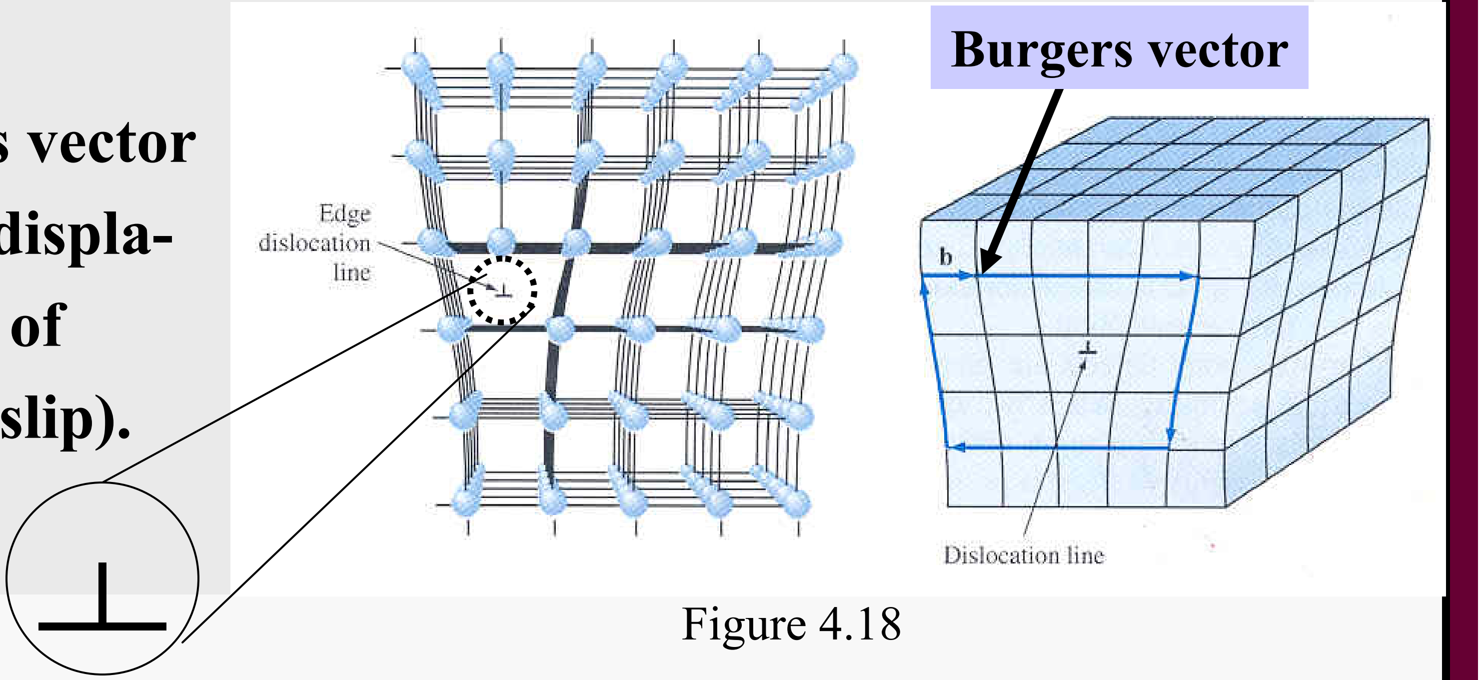
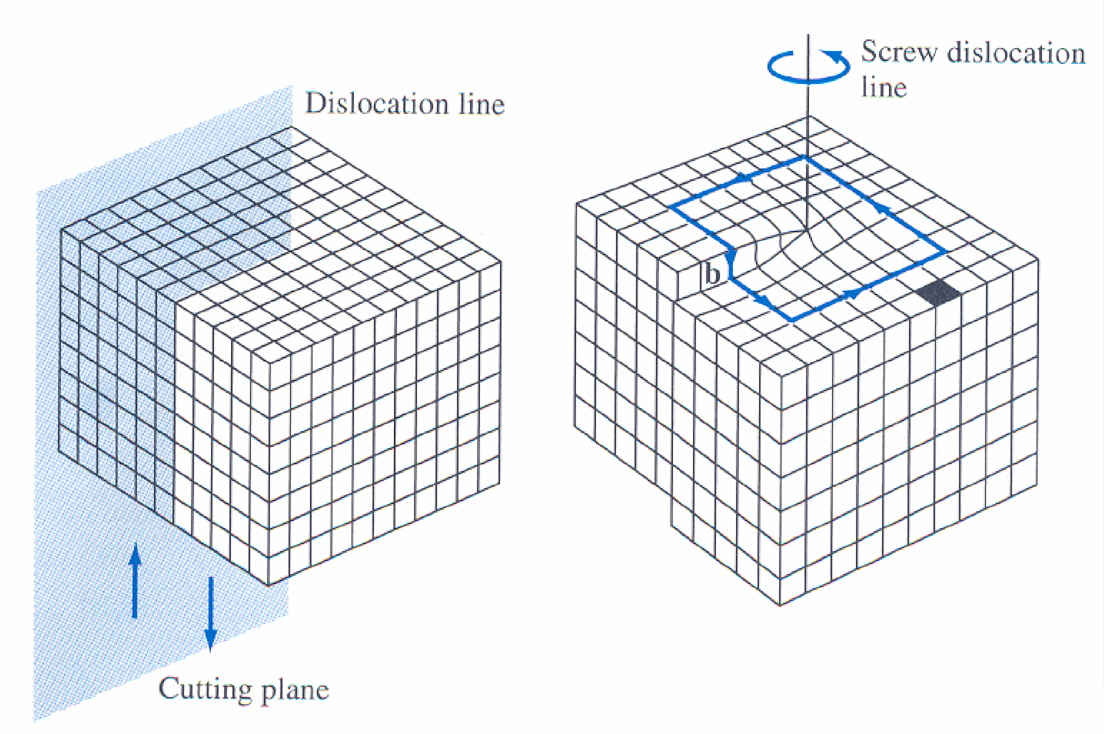


Figure 4.18

After M. Eisenstadt, “Introduction to Mechanical Properties of Materials,” Macmillan, 1971, p.117
After A.G. Guy , “Essentials of Materials Science,” McGraw-Hill, 1976, p.153

Screw Dislocation

- Created due to shear stresses applied to regions of a perfect crystal separated by cutting plane.
- Distortion of lattice in form of a spiral ramp.
- Burgers vector is parallel to dislocation line.



After M. Eisenstadt, "Introduction to Mechanical Properties of Materials," Macmillan, 1971, p.118

Mixed Dislocation

- Most crystal have components of **both** edge and screw dislocation.

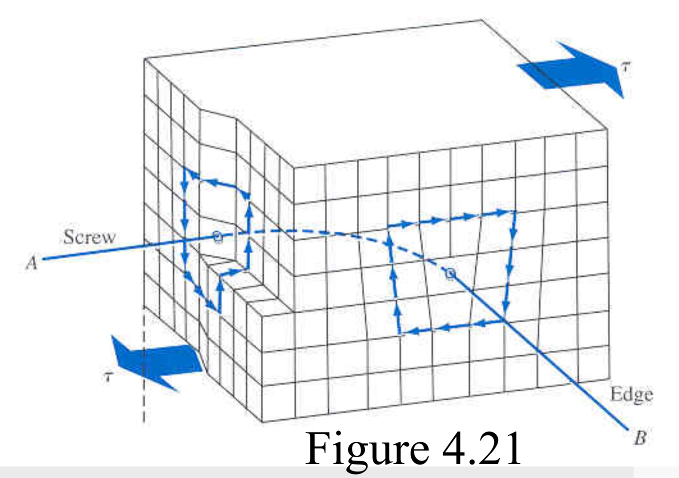
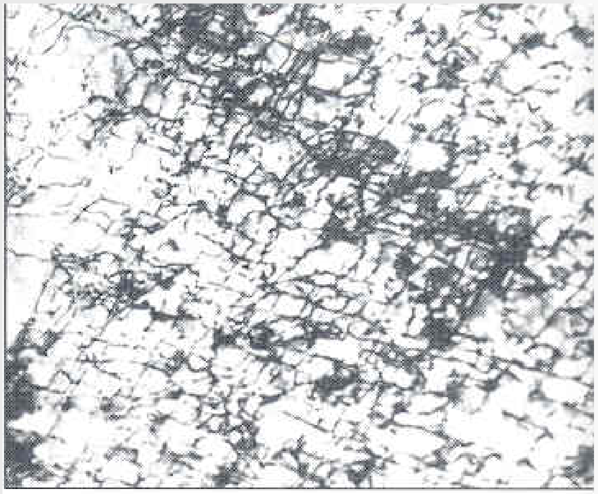


Figure 4.21

- Dislocation, since have irregular atomic arrangement will appear as **dark lines** when observed in electron microscope.

Figure 4.22



Dislocation structure of iron deformed 14% at –195^{0}C

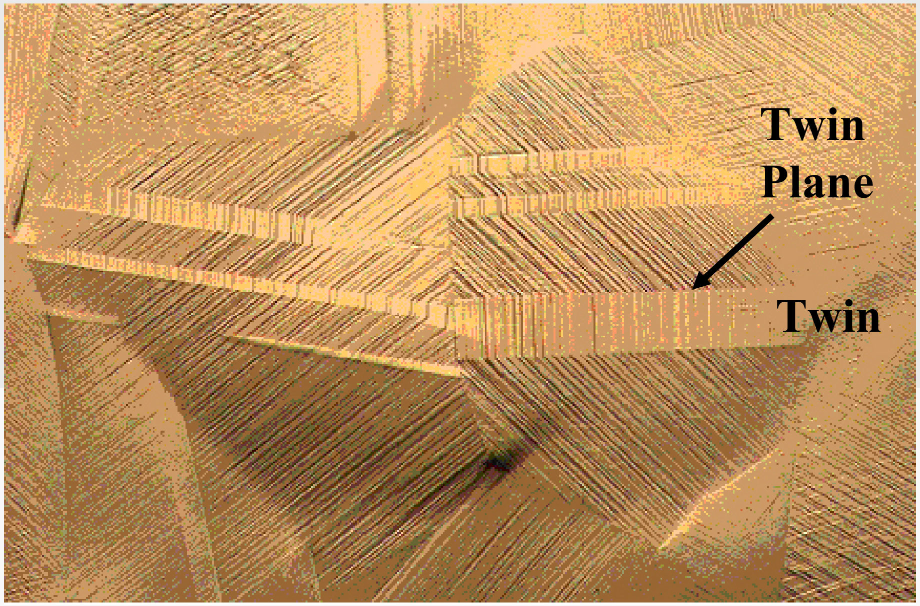
(After John Wolff et al., “Structure and Properties of Materials,” vol 3: “Mechanical Properties,” Wiley, 1965, p.65.
(After “Metals Handbook” vol. 8, 8th ed., American Society of Metals, 1973, p.164)

Planar Defects

- **Grain boundaries, twins, low/high angle boundaries, twists and stacking faults**
- **Free surface is also a defect : Bonded to atoms on only one side and hence has higher state of energy → Highly reactive**
- **Nanomaterials have small clusters of atoms and hence are highly reactive.**

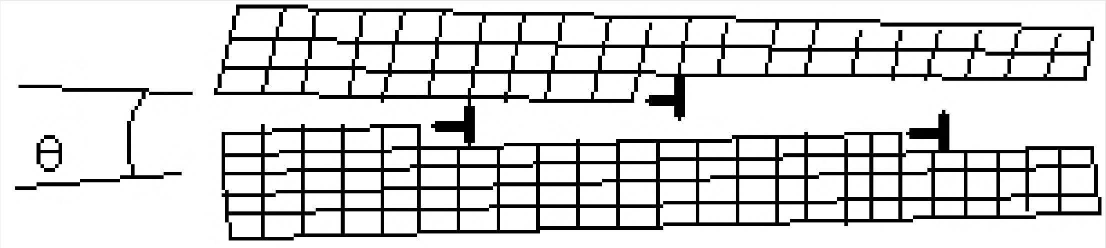
Twin Boundaries

- **Twin:** A region in which mirror image of the structure exists across a boundary.
- Formed during plastic deformation and recrystallization.
- **Strengthens** the metal.



Other Planar Defects

- **Small angle tilt boundary:** **Array of edge dislocations tilts two regions of a crystal by < 10^0**



- **Stacking faults:** **Piling up faults during recrystallization due to collapsing.**
  - **Example: ABCABAACBABC ⟶ FCC fault**

- **Volume defects: Cluster of point defects join to form 3-D void.**

Grain Size

- Affects the mechanical properties of the material
- The smaller the grain size, more are the grain boundaries.
- More grain boundaries means higher resistance to slip (plastic deformation occurs due to slip).
- More grains means more uniform the mechanical properties are.

Measuring Grain Size

- ASTM grain size number 'n' is a measure of grain size.

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

N = Number of grains per square inch of a polished and etched specimen at 100 x.

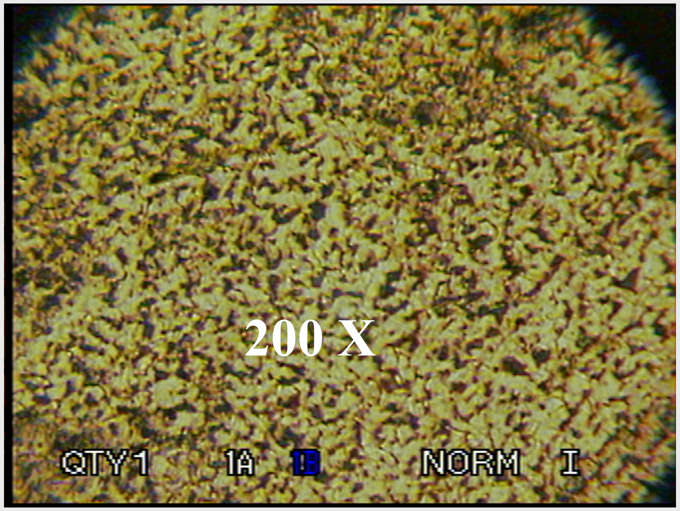
n = ASTM grain size number.

N < 3 – Coarse grained

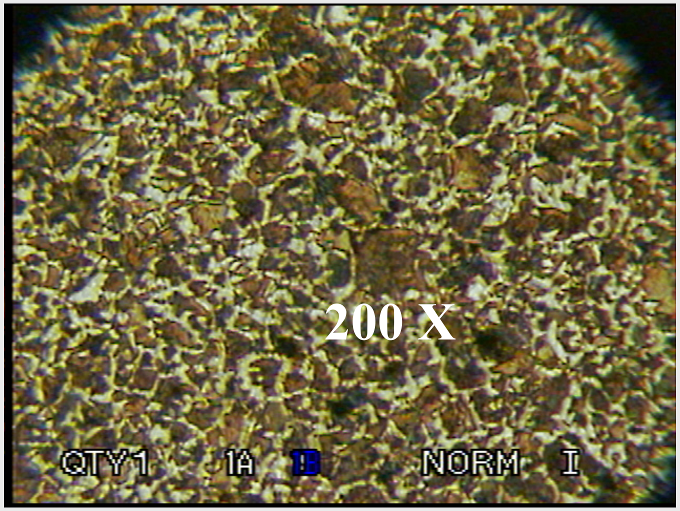
4 < n < 6 – Medium grained

7 < n < 9 – Fine grained

N > 10 – ultrafine grained



1018 cold rolled steel, n=10



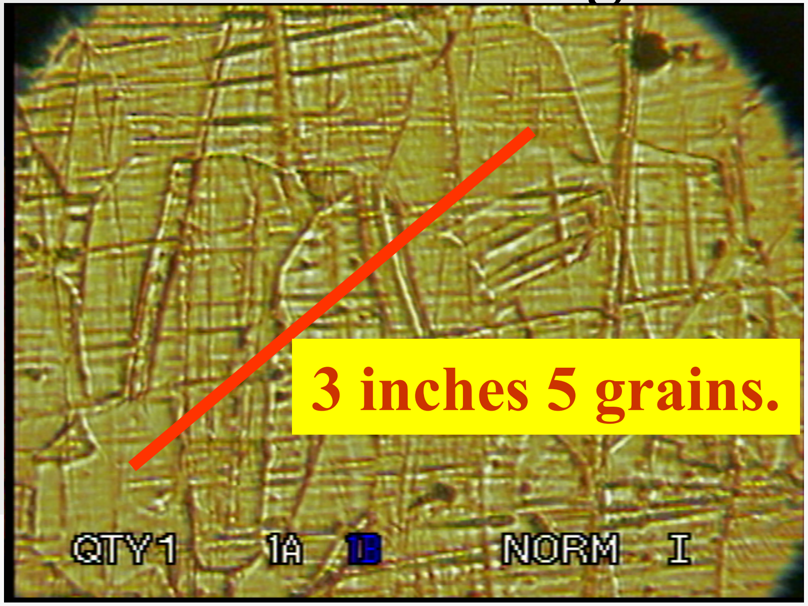
1045 cold rolled steel, n=8

Average Grain Diameter

- **Average grain diameter** more directly represents grain size.
- Random line of known length is drawn on photomicrograph.
- Number of grains **intersected** is counted.
- Ratio of number of grains intersected to length of line, n_L is determined.

$d = C/n_L M$

C=1.5, and M is magnification


3 inches 5 grains.

Effect of Etching

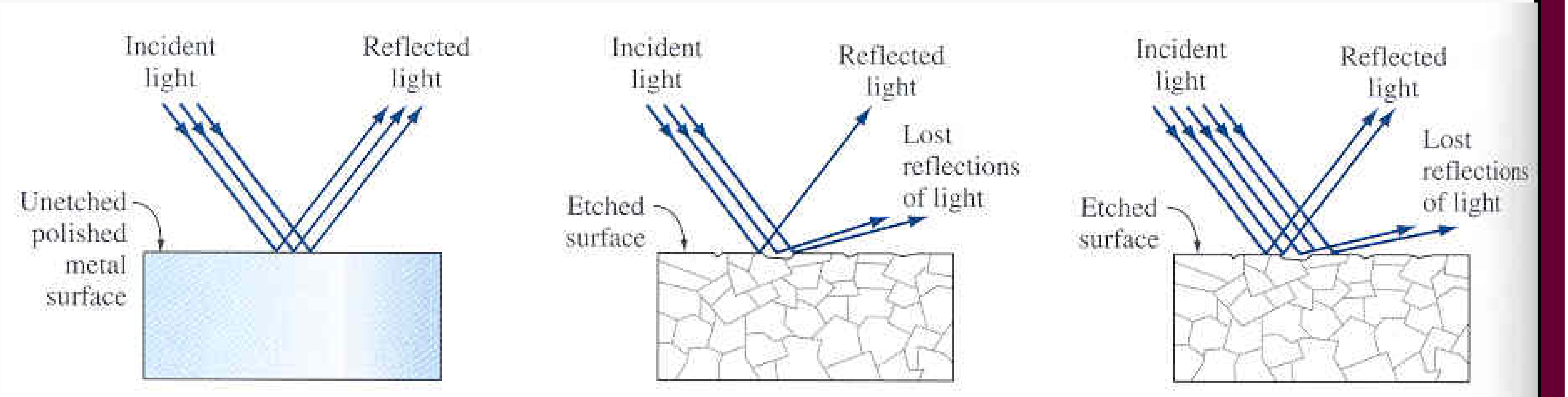
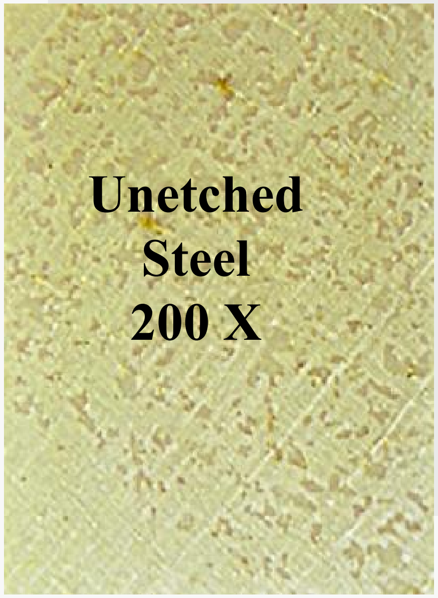
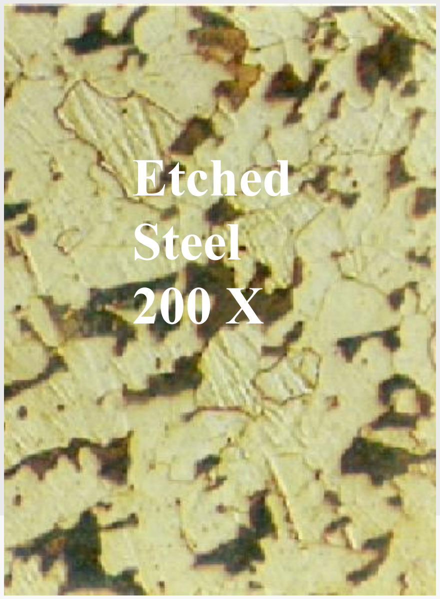


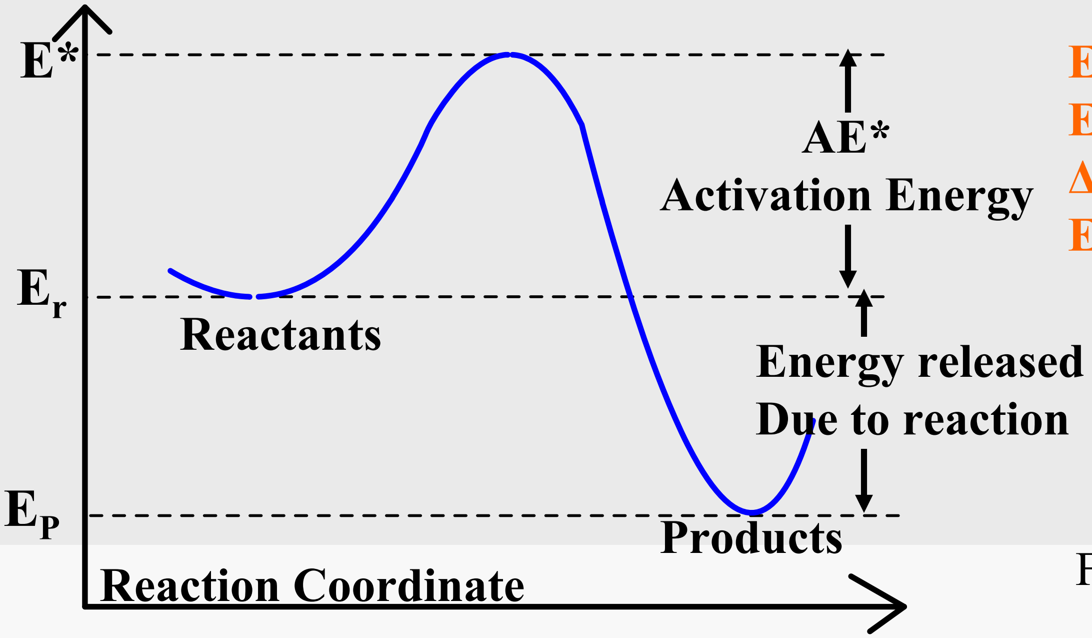
Figure 4.28





Rate Process in Solids

- Reactions occur in solid state resulting in more stable atomic arrangement.
- Reacting atoms must have sufficient energy to overcome activation energy barrier.
- At a given temperature, not all atoms have activation energy E*. It should be supplied to them.



E_r = Energy of reactants
E* = Activation Energy Level
ΔE* = Activation Energy
E_p = Energy of Products

Figure 4.33

Rate Process in Solids (Cont..)

- As **temperature** increases, more and more atoms acquire activation energy level.
- **Probability** of finding an atom/molecule with energy E* greater than average energy E of all atoms/ molecules is given by

$$\alpha e^{-(E^{*}-E)/KT}$$

K = **Boltzman's Constant** = 1.38 x 10^{-23} J/(atom.K).

T = Temperature in Kelvin.

Rate Process in Solids (Cont..)

- The fraction of atoms having energies greater than E* in a system (when E* is greater than average energy E) is given by

$$\frac{n}{N_{total}} = Ce^{\frac{-E^*}{K.T}}$$

n = Number of molecules greater than energy E*
N_{total} = Total number of molecules
K = Boltzman’s Constant
C = Constant
T = Temperature in Kelvin.

Rate Process in Solids (Cont..)

- The number of vacancies at equilibrium at a particular temperature in a metallic crystal lattice is given by

$$\frac{n_v}{N} = Ce^{\frac{-E_V}{K.T}}$$

n_v = Number of vacancies per m^3 of metal
E_v = Activation Energy to form a vacancy
T = Absolute Temperature.
K = Boltznam,s Constant.
C = Constant

Arrhenius Equation

- The rate of chemical reaction is given by **Arrhenius equation.**

  Rate of reaction = $Ce^{-Q/RT}$

  Q = Activation energy J/mol

  R = Molar gas constant J/mol.K

  T = Temperature in Kelvin

  C = Rate constant (Independent of temperature)

- Rate of reaction depends upon **number of reacting molecules.**

Solidification of Metals

- Arrhenius equation can also be written as

$$\ln(\text{rate}) = \ln(C) - Q/RT$$

Or $$\text{Log}_{10}(\text{rate}) = \text{Log}_{10}(C) - Q/2.303\,RT$$

Which is similar to

$$Y = b + mX$$

Which is equation of a straight li

With Y intercept as 'b' and slop

Y → Log$_{10}$(rate)
X → (1/T)
b → Log$_{10}$(C)
m → Q/2.303R

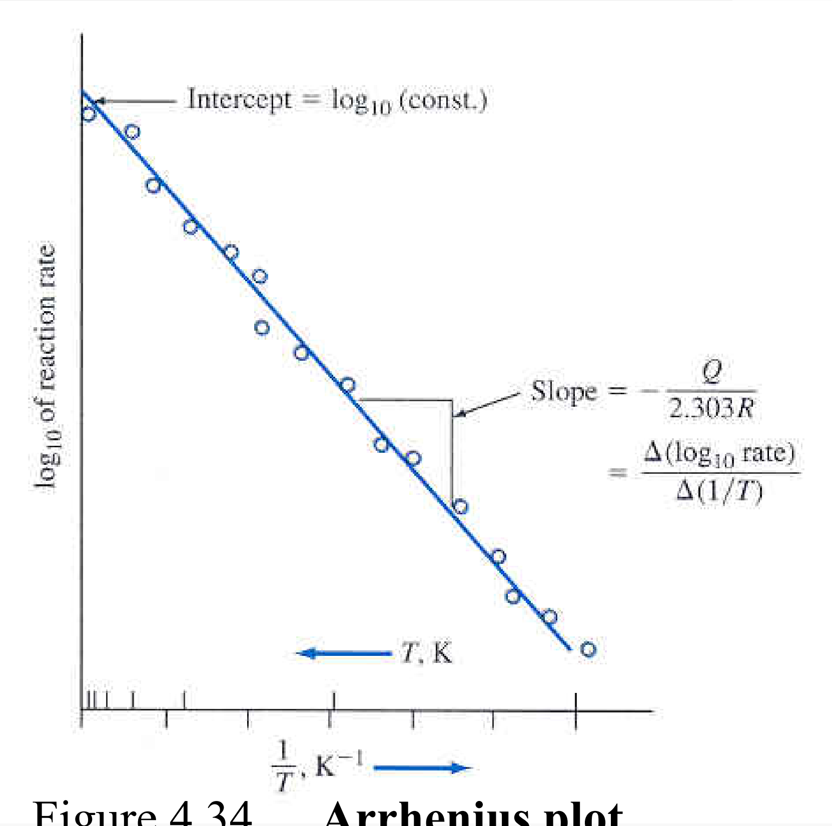


Figure 4.34 **Arrhenius plot**

(After J. Wulff et al., "Structure and Properties of Materials," vol. II: "Thermodynamics of Structure," Wiley, 1964, p.64.)

Diffusion

Atomic Diffusion in Solids

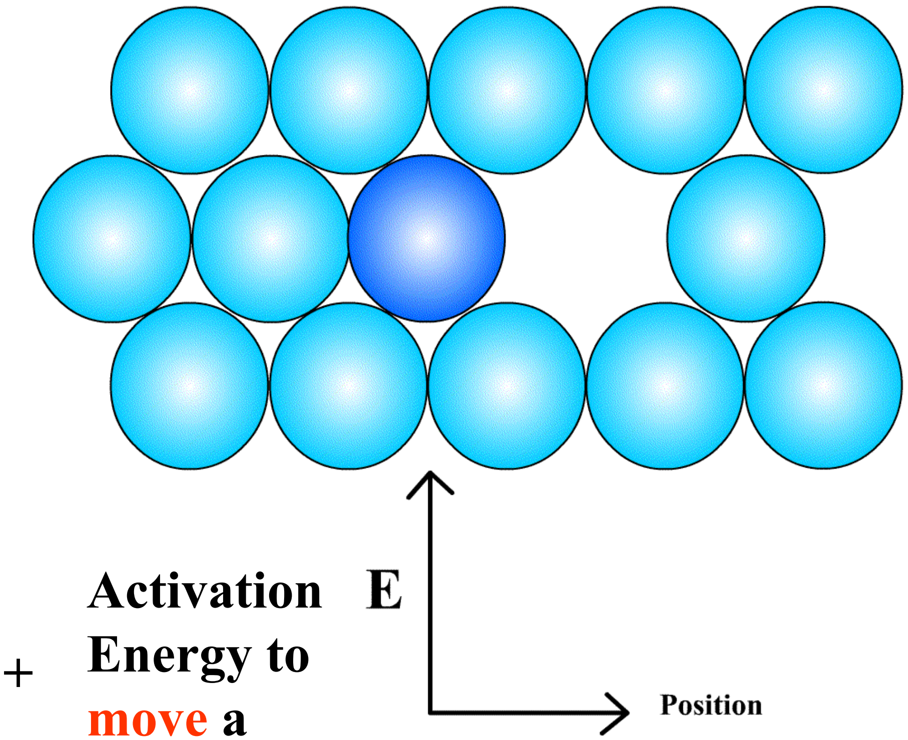
- Diffusion is a process by which a matter is transported through another matter.
- Examples:
    - ➢ Movement of smoke particles in air : Very fast.
    - ➢ Movement of dye in water : Relatively slow.
    - ➢ Solid state reactions : Very restricted movement due to bonding.

Vacancy or Substitutional Diffusion mechanism

- Atoms diffuse in solids if
  - Vacancies or other crystal defects are present
  - There is enough activation energy
- Atoms move into the vacancies present.
- More vacancies are created at higher temperature.
- Diffusion rate is higher at high temperatures.

Substitutional Diffusion

- **Example:** If atom ‘A’ has sufficient activation energy, it moves into th vacancy → self diffusion



Activation Energy of Self diffusion = Activation Energy to **form** a Vacancy + Activation Energy to **move** a vacancy

Figure 4.35

- As the melting point increases, activation energy also increases

Interstitial Diffusion mechanism

- Atoms move from one interstitial site to another.
- The atoms that move must be much smaller than the matrix atom.
- **Example:**
  Carbon interstitially diffuses into BCC α or FCC γ iron.

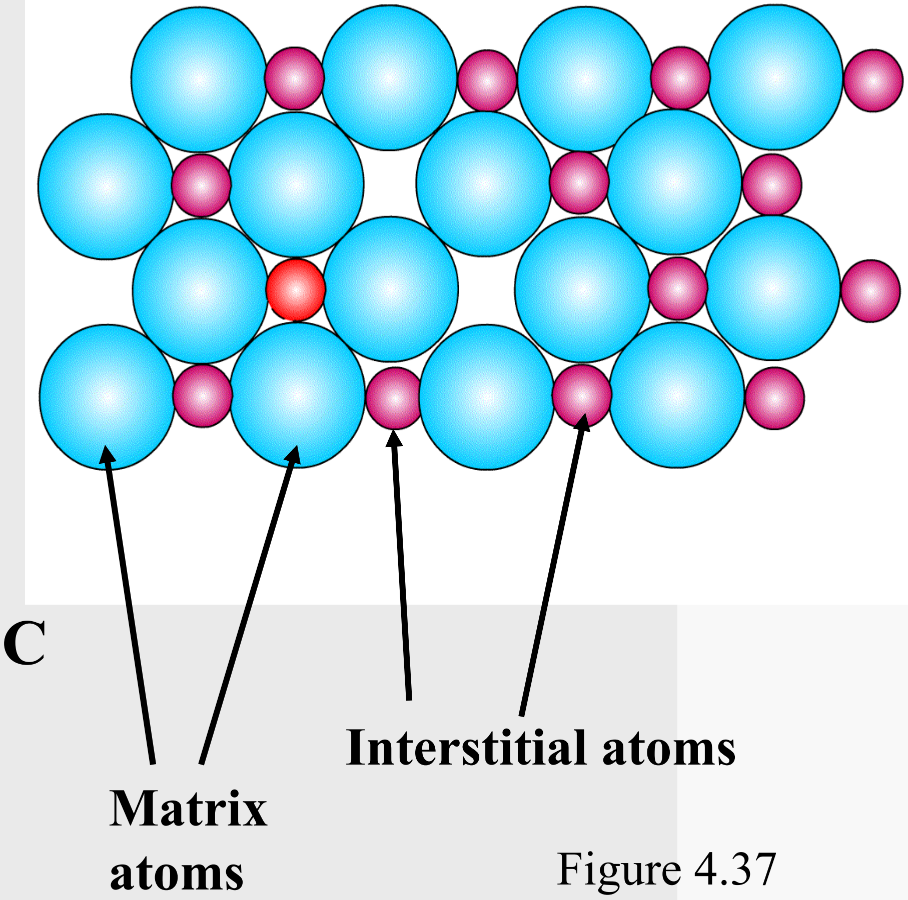
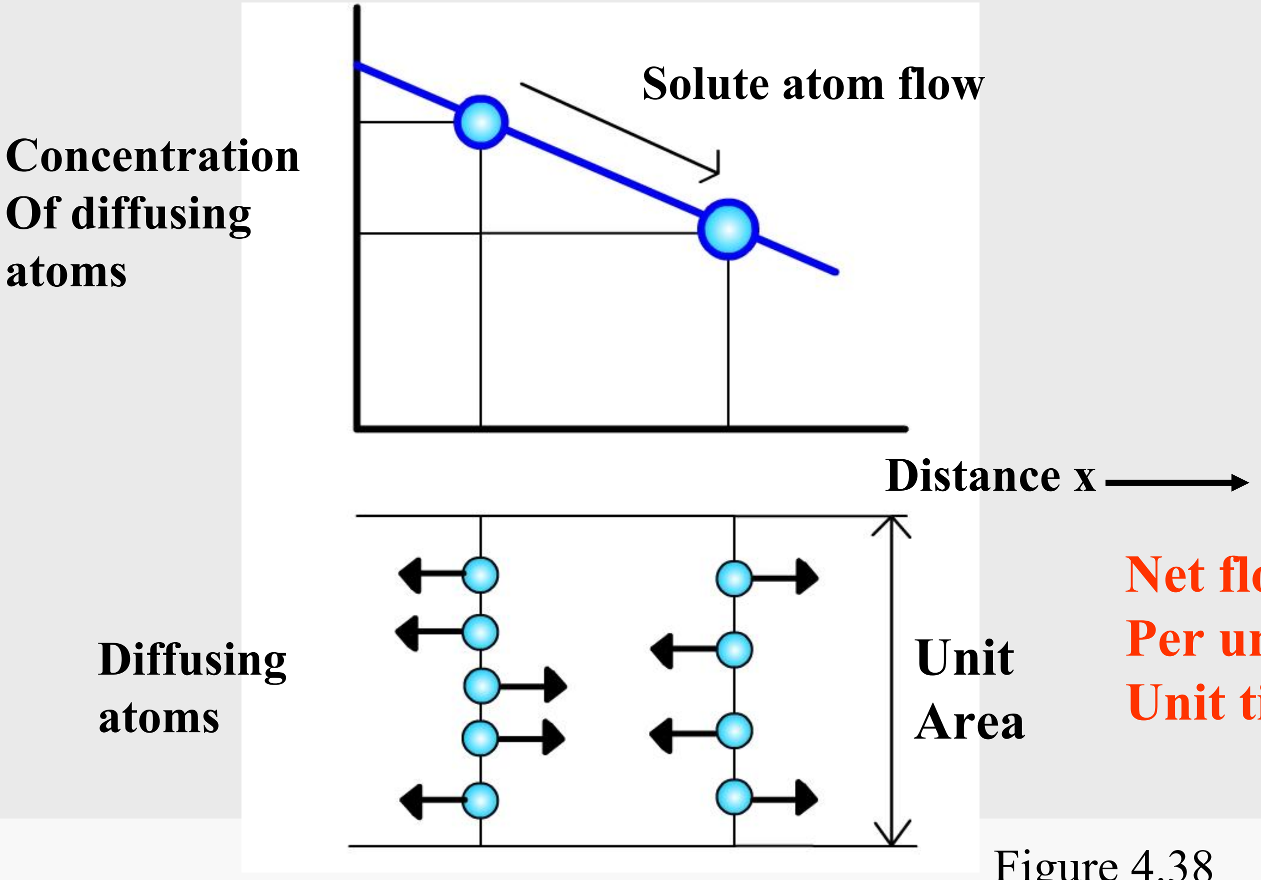


Figure 4.37

Steady State Diffusion

- There is no change in concentration of solute atoms at different planes in a system, over a period of time.
- No chemical reaction occurs. Only net flow of atoms.



Net flow of atoms
Per unit area per
Unit time = J

Figure 4.38

Fick's Law

- The flux or flow of atoms is given by

$$J = -D\frac{dc}{dx}$$

J = Flux or net flow of atoms.

D = Diffusion coefficient.

$\frac{dc}{dx}$ = Concentration Gradient.

- I.e. for steady state diffusion condition, the net flow of atoms by atomic diffusion is equal to diffusion D times the diffusion gradient dc/dx

- **Example:** Diffusivity of FCC iron at 500°C is 5×10^{-15} m^2/s and at 1000°C is 3×10^{-11} m^2/s

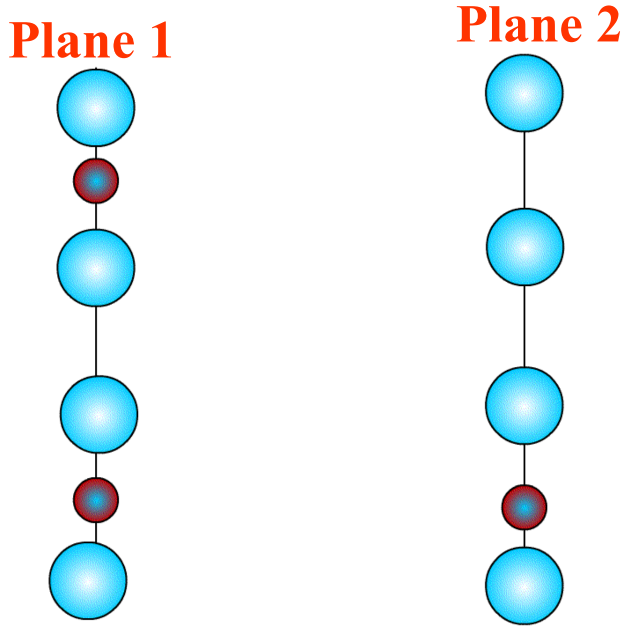
Diffusivity

- **Diffusivity depends upon**
  - **Type of diffusion : Whether the diffusion is interstitial or substitutional.**
  - **Temperature: As the temperature increases diffusivity increases.**
  - **Type of crystal structure: BCC crystal has lower APF than FCC and hence has higher diffusivity.**
  - **Type of crystal imperfection: More open structures (grain boundaries) increases diffusion.**
  - **The concentration of diffusing species: Higher concentrations of diffusing solute atoms will affect diffusivity.**

Non-Steady State Diffusion

- Concentration of solute atoms at any point in metal **changes with time** in this case.
- **Ficks second law**:- Rate of compositional change is equal to diffusivity times the rate of change of concentration gradient.

$$\frac{dC_x}{dt} = \frac{d}{dx}\left(D\frac{dc_x}{dx} \right)$$



Change of concentration of solute
Atoms with change in time in different planes

Fick’s Second Law – Solution

$$\frac{C_s - C_x}{C_s - C_0} = erf\left(\frac{x}{2\sqrt{D_t}}\right)$$

- C_s = Surface concentration of element in gas diffusing into the surface.
- C_0 = Initial uniform concentration of element in solid.
- C_x = Concentration of element at distance x from surface at time t_1.
- x = distance from surface
- D = diffusivity of solute
- t = time.

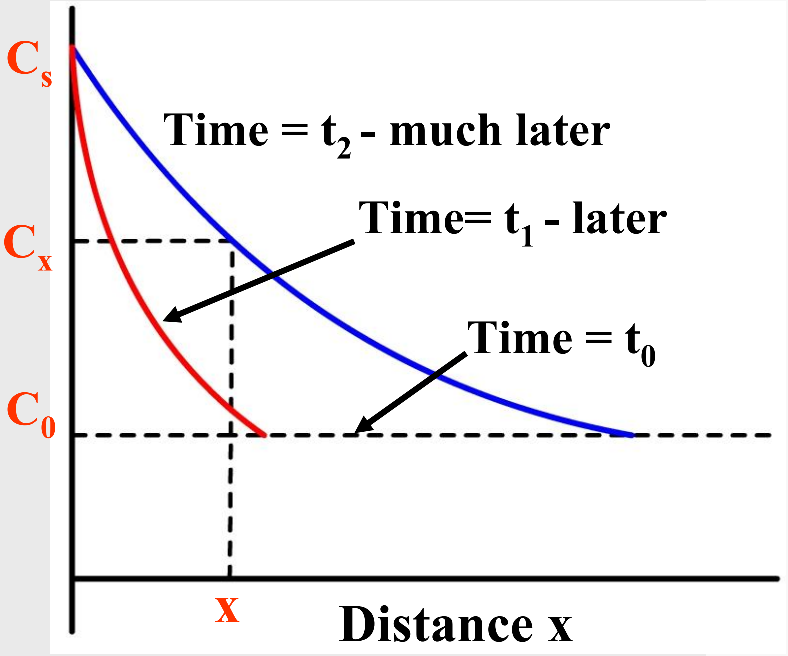
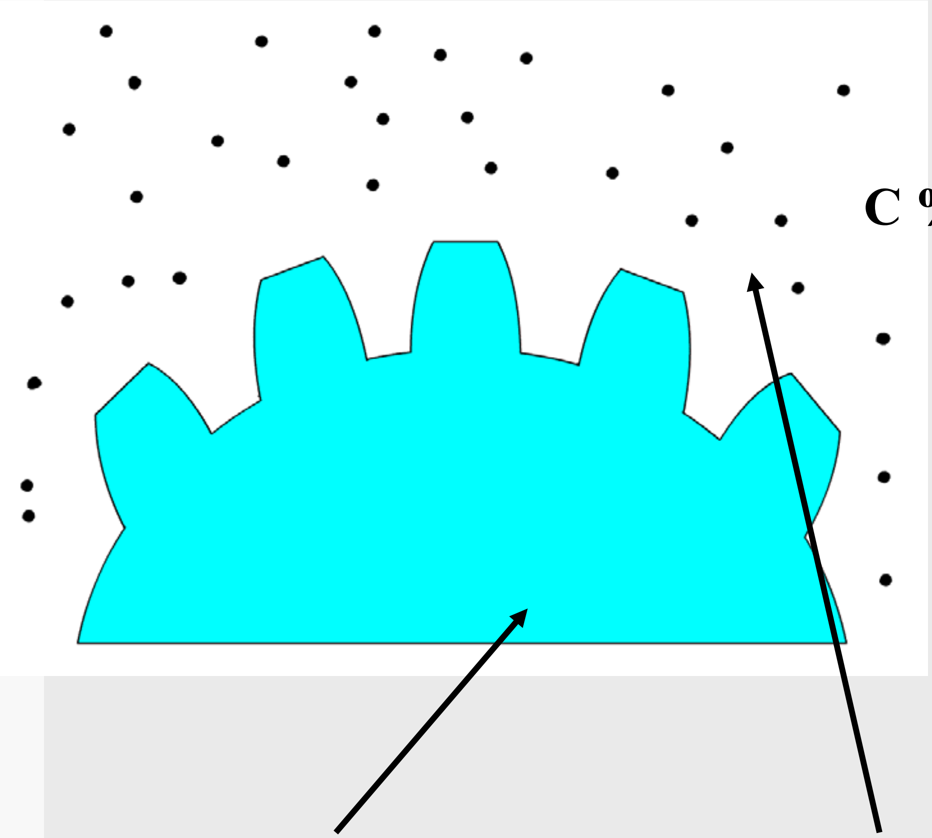


Figure 4.39

Industrial Applications of Diffusion – Case Hardening

- Sliding and rotating parts needs to have hard surfaces.
- These parts are usually machined with low carbon steel as they are easy to machine.
- Their surface is then hardened by *carburizing.*
- Steel parts are placed at elevated temperature (927^0C) in an atmosphere of hydrocarbon gas (CH_4).
- Carbon diffuses into iron surface and fills interstitial space to make it harder.

Carburizing



Low carbon Steel part

Diffusing carbon atoms

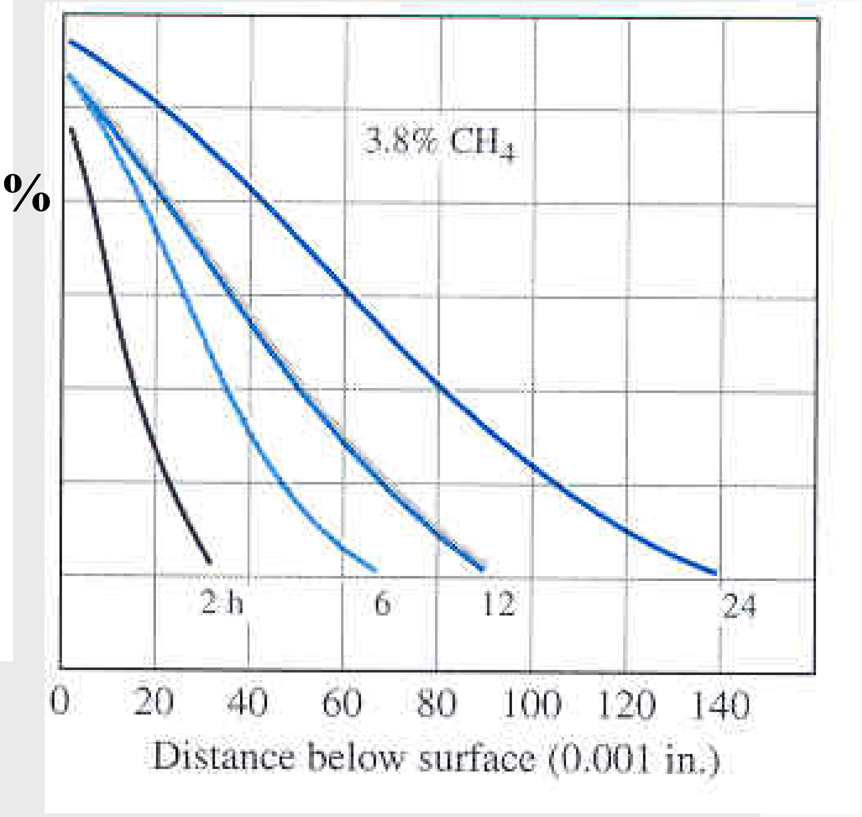


Figure 4.43 b

Carbon Gradients In Carburized metals

(After “Metals handbook,” vol.2: “Heat Treating,” 8th ed, American Society of Metals, 1964, p.100)

Impurity Diffusion into Silicon wafer

- Impurities are made to diffuse into silicon wafer to change its electrical characteristics.
- Used in integrated circuits.
- Silicon wafer is exposed to vapor of impurity at 1100^{0}C in a quartz tube furnace.
- The concentration of impurity at any point depends on depth and time of exposure.

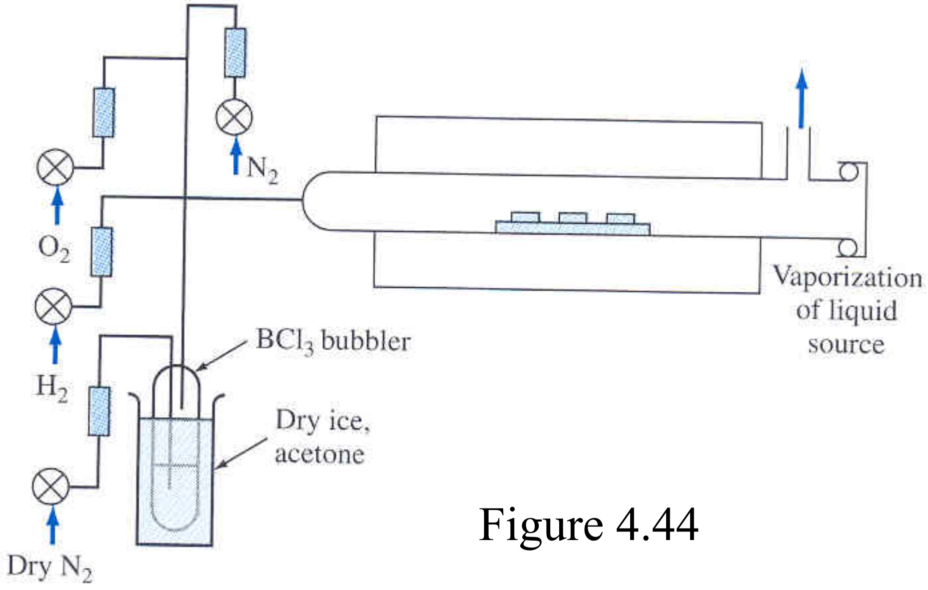


Figure 4.44

(After W.R. Runyan, " Silicon Semiconductor Technology," McGraw-Hill, 1965.)

Effect of Temperature on Diffusion

- **Dependence of rate of diffusion on temperature is given by**

$$D = D_0 e^{\frac{-Q}{RT}}$$

D = Diffusivity m²/s
D_0 = Proportionality constant m²/s
Q = Activation energy of diffusing species J/mol
R = Molar gas constant = 8.314 J/mol.K
T = Temperature (K)

or $$\ln D = \ln D_0 - \frac{Q}{RT}$$

or $$\log_{10} D = \log_{10} D_0 - \frac{Q}{2.303RT}$$

Effect of Temperature on Diffusion-Example

- If diffusivity at two temperatures are determined, two equations can be solved for Q and D_0
- **Example:-**

The diffusivity of silver atoms in silver is 1 x 10^{-17} at 500^0C and 7 x 10^{-13} at 1000^0C.

Therefore,

$$\frac{D_{1000}}{D_{500}} = \frac{\exp(-Q/RT_2)}{\exp(-Q/RT_1)} = \exp\left(\frac{-Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right)$$

$$\frac{7\times10^{-13}}{1\times10^{-17}} = \exp\left(-\frac{Q}{R}\left(\frac{1}{1273} - \frac{1}{773}\right)\right)$$

Solving for *activation energy* Q

$$Q = 183KJ/mol$$

Diffusivity Data for Some Metals

Solute	Solvent	D_0 (M^2/S)	Q KJ/mol
Carbon	FCC Iron	$2 \text{ x } 10^{-5}$	142
Carbon	BCC Iron	$22 \text{ x } 10^{-5}$	122
Copper	Aluminum	$1.5 \text{ x } 10^{-5}$	126
Copper	Copper	$2 \text{ x } 10^{-5}$	197
Carbon	HCP Titanium	$51 \text{ x } 10^{-5}$	182

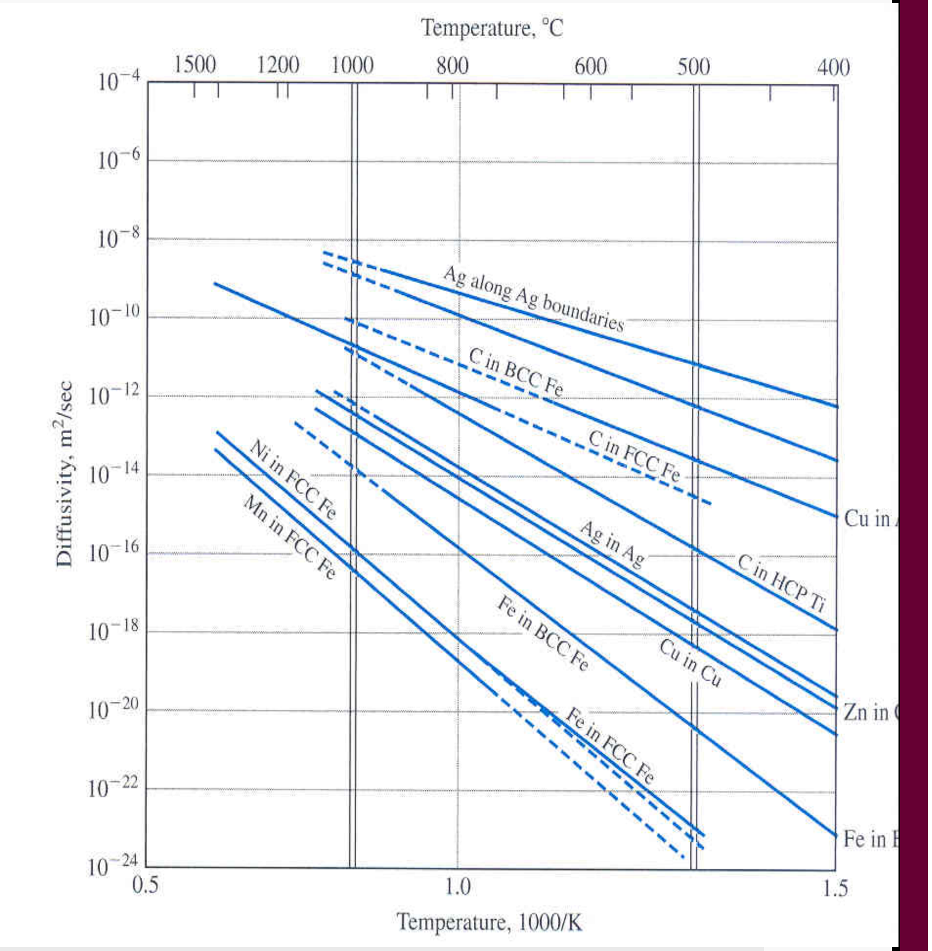


Figure 4.47

(After L.H. Van Vlack. "Elements of Materials Science and Engineering." 5th ed., Addison-Wesley, 1985. P.137.)

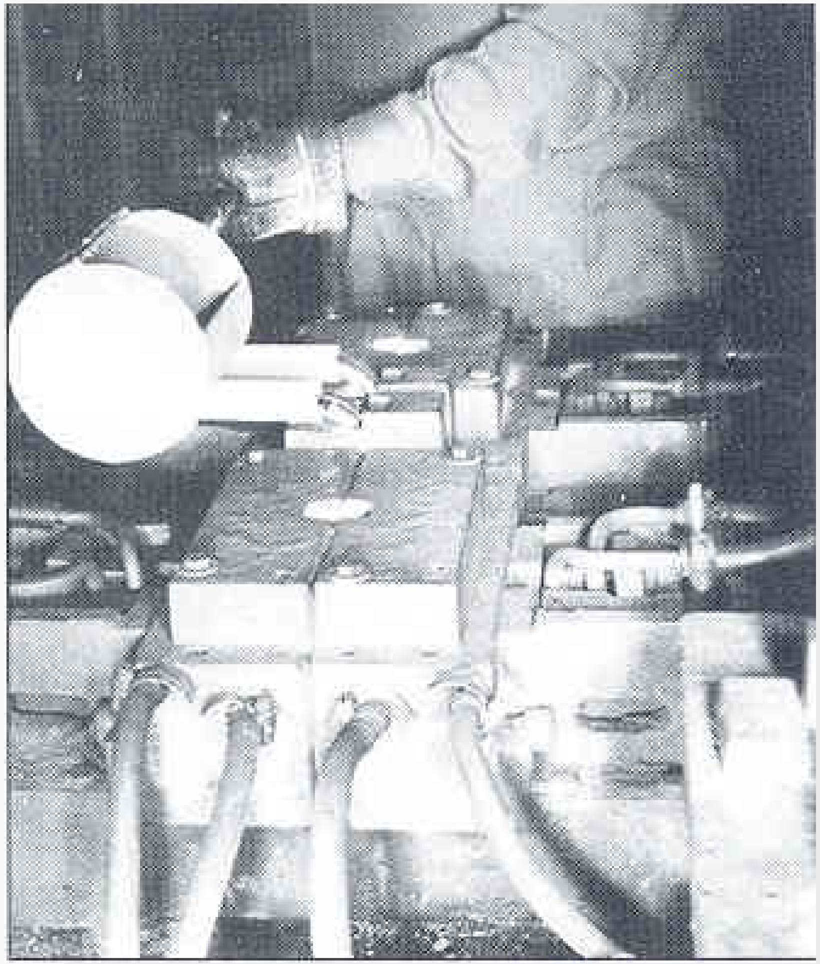
Mechanical Properties
Of
Metals - I

Processing of Metals - Casting

- Most metals are first melted in a furnace
- Alloying is done if required
- Large ingots are then cast
- Sheets and plates are then produced from ingots by rolling Wrought alloy products
- Channels and other shapes are produced by extrusion
- Some small parts can be cast as final product

Example :- Automobile Piston

Casting (Cont..)



Casting Process

Figure 5.3 a

Casting mold

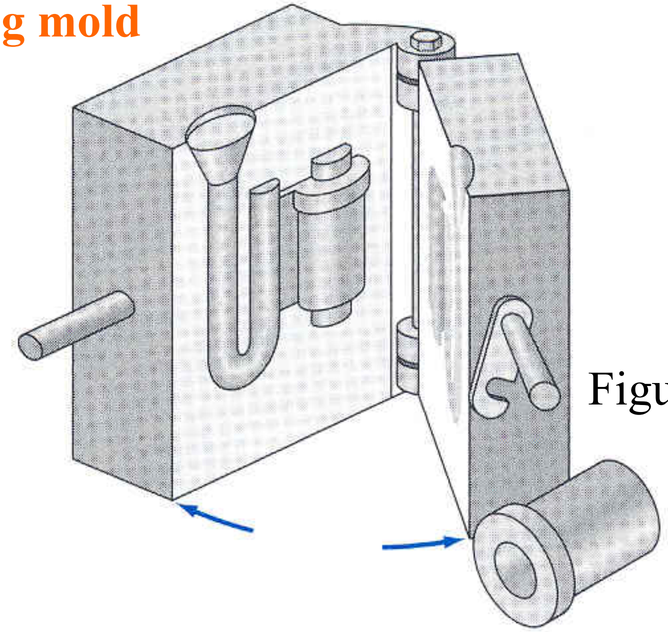
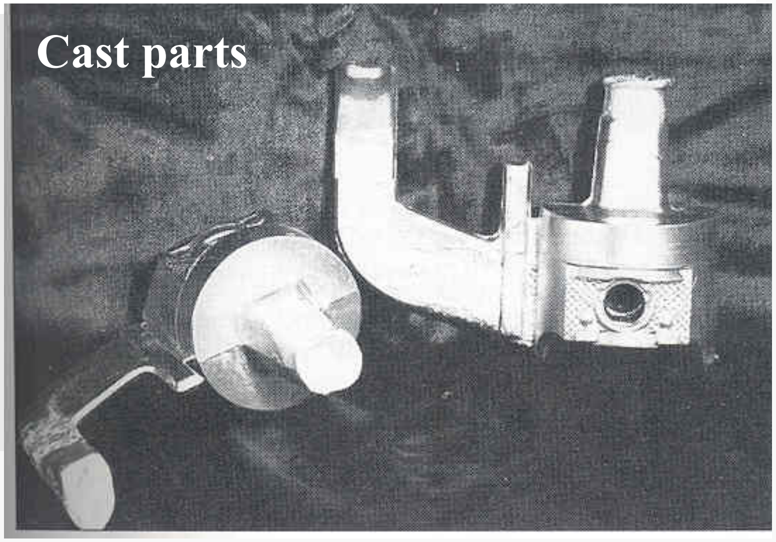


Figure 5.2

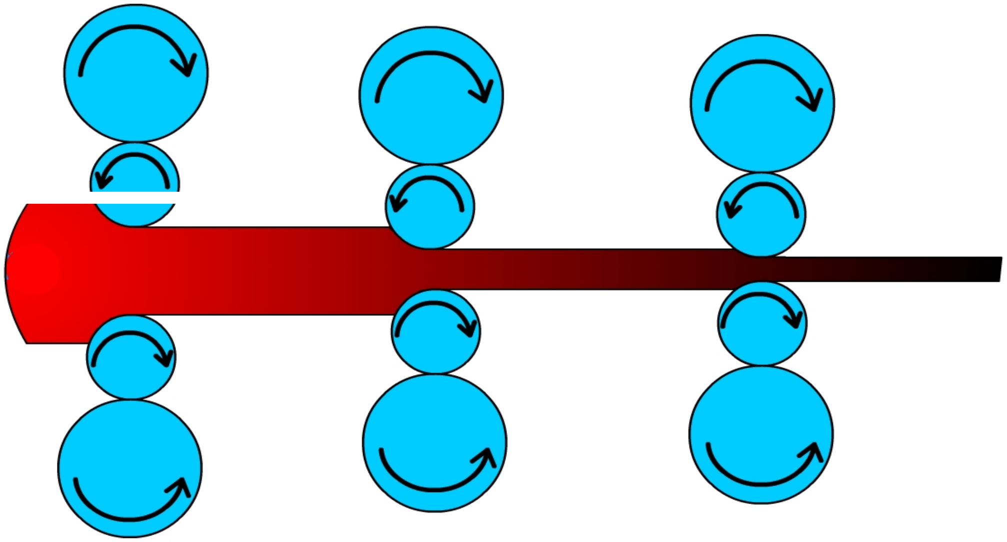


Cast parts

Figure 5.3 b

Hot Rolling of Steel

- Hot rolling → Greater reduction of thickness in a single pass
- Rolling carried out at above *recrystallization temperature*
- Ingots preheated to about 1200^{0}C. Ingots reheated between passes if required
- Usually, series of **4 high** rolling mills are used.



Cold Rolling of Metal Sheet

- Cold rolling is rolling performed below recrystallization temperature
- This results in strain hardening
- Hot rolled slabs have to be annealed before cold rolling
- Series of 4 high rolling mills are usually used.
- Less reduction of thickness
- Needs high power

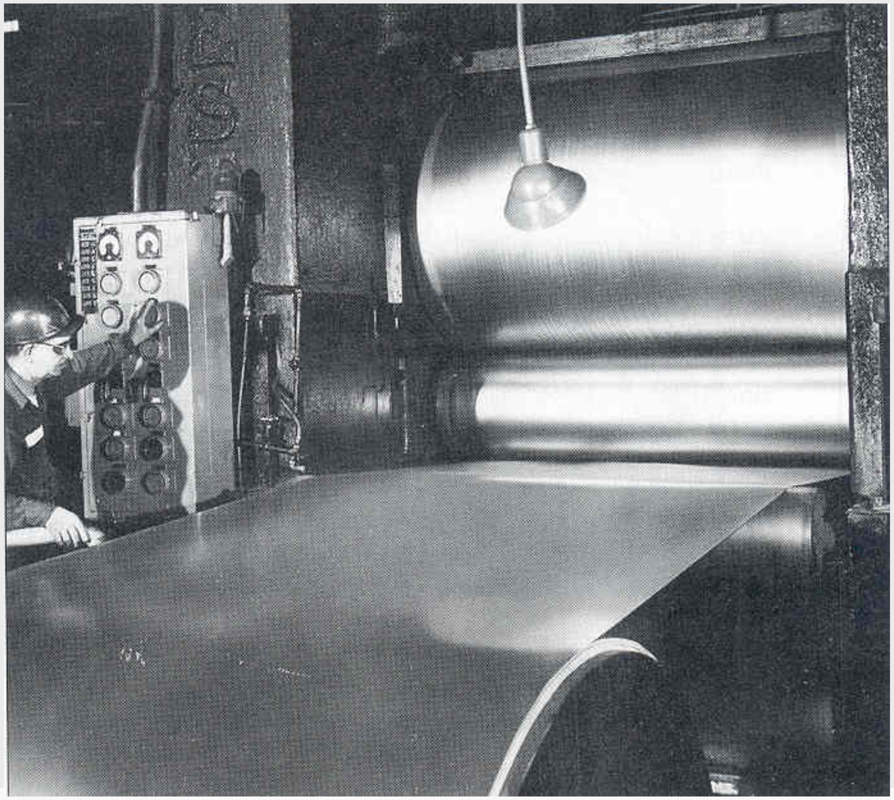


Figure 5.8

Cold Rolling (Cont..)

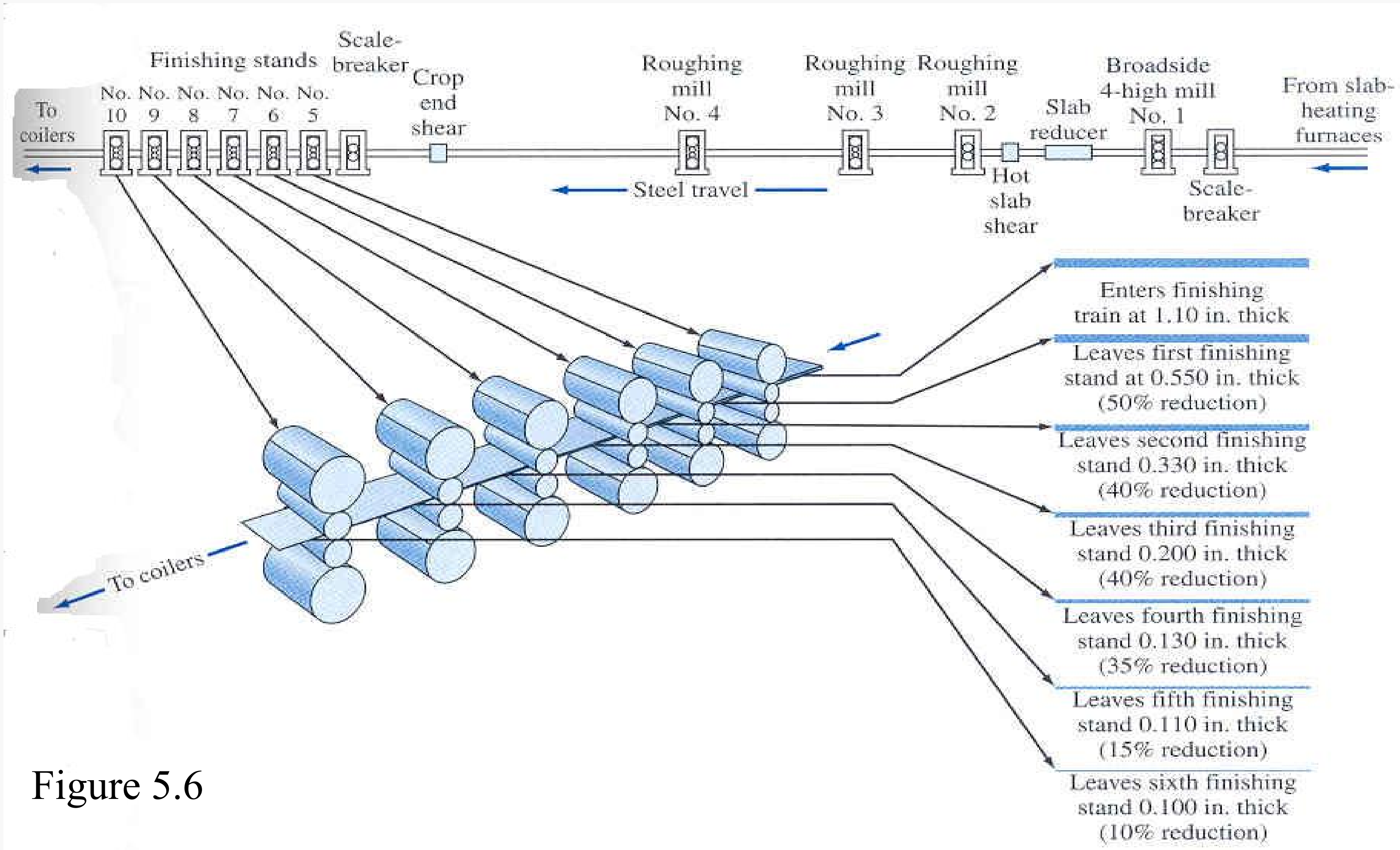
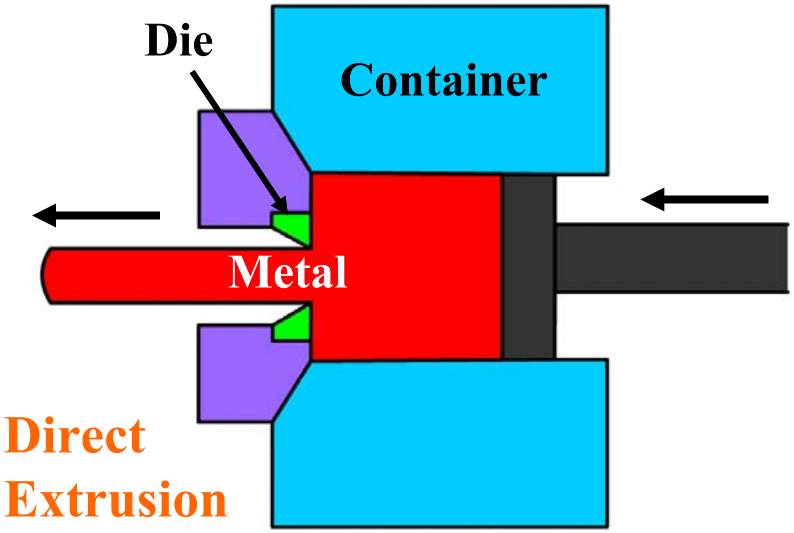


Figure 5.6

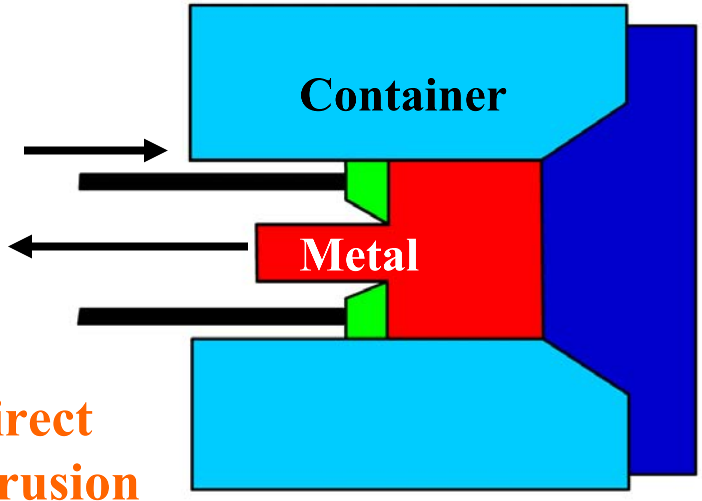
$$\%\ \text{Cold work} = \frac{\text{Initial metal thickness} - \text{Final metal thickness}}{\text{Initial metal thickness}} \times 100$$

Extrusion

- Metal under high pressure is forced through opening in a die
- Common Products are cylindrical bar, hollow tubes from copper, aluminum etc.
- Normally done at high temperature
- Indirect extrusion needs less power however has limit on load applied



Direct Extrusion



indirect Extrusion

Figure 5.9

Forging

- Metal, usually hot, is hammered or pressed into desired shape
- Types:-

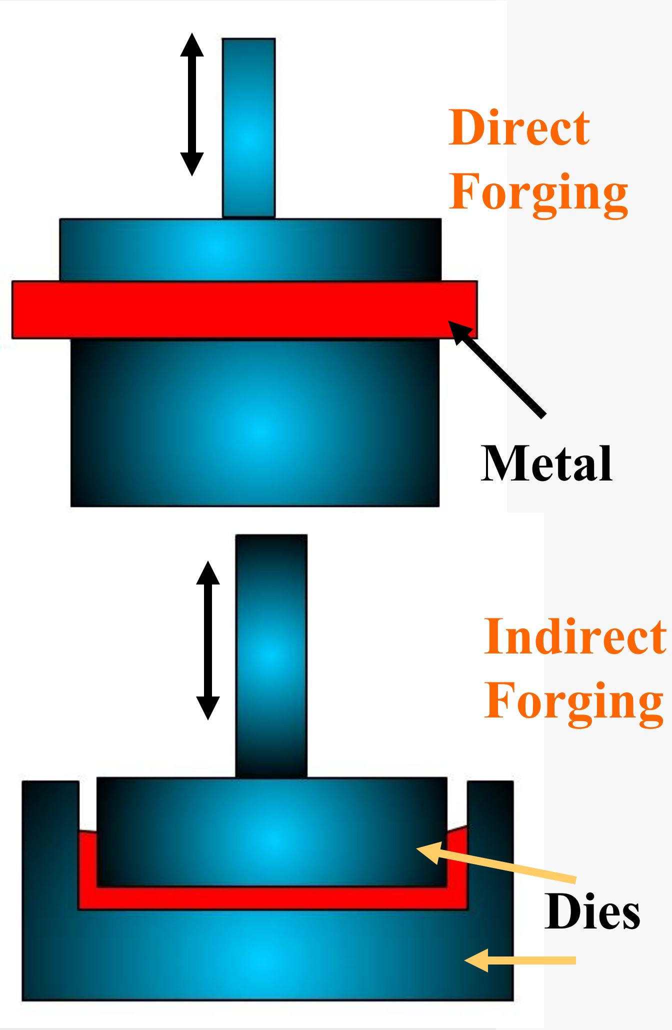
  Open die: Dies are flat and simple in shape

  * Example products: Steel shafts

  Closed die: Dies have upper & lower impression

  * Example products: Automobile engine connection rod

- Forging increases structural properties, removes porosity and increases homogeneity

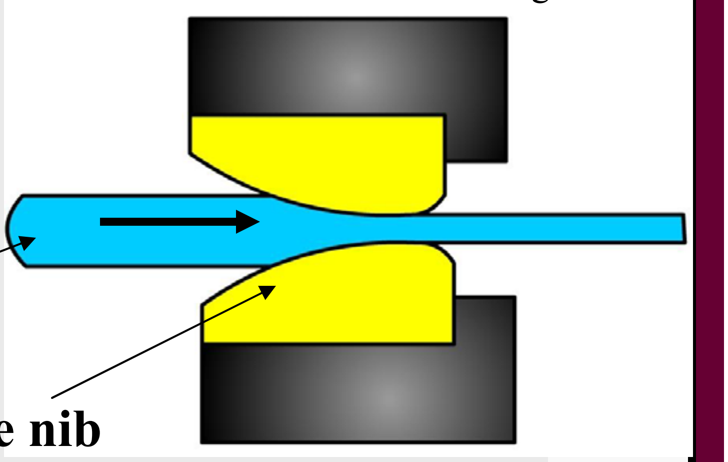


Drawing

- **Wire drawing :-** Starting rod or wire is drawn through several drawing dies to reduce diameter.

$$\% \text{ cold work} = \frac{\text{Change in cross-sectional area}}{\text{Original area}} \times 100$$

Figure 5.13



- **Deep drawing:-** Used to shape cup like articles from flats and sheets of metals

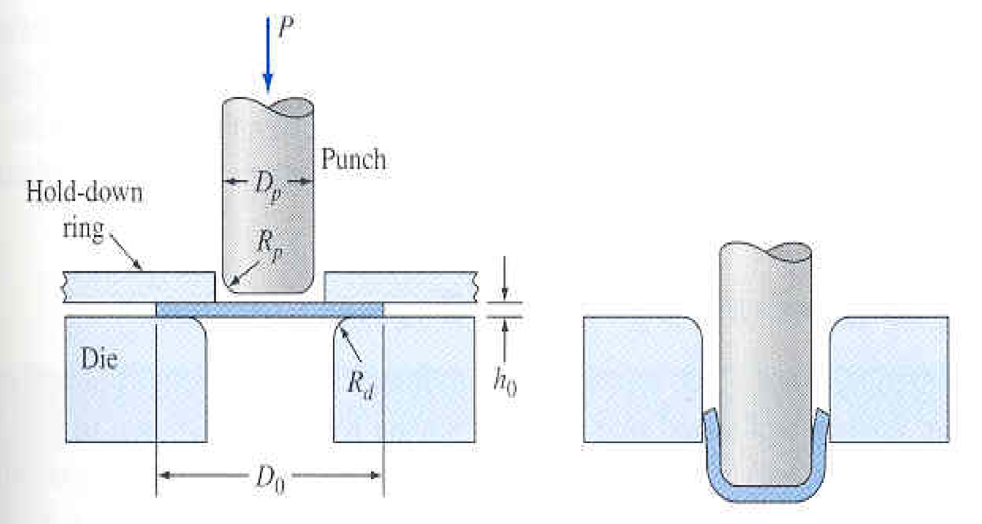
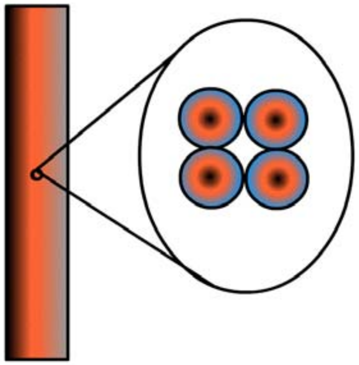


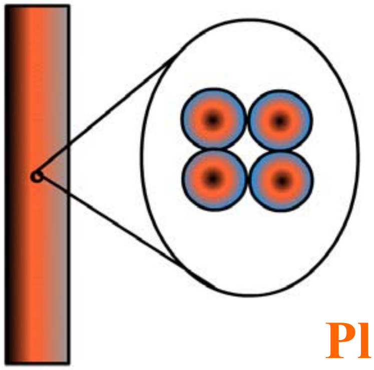
Figure 5.14

Stress and Strain in Metals

- Metals undergo deformation under uniaxial tensile force.
- **Elastic deformation:** Metal returns to its original dimension after tensile force is removed.
- **Plastic deformation:** The metal is deformed to such an extent such that it cannot return to its original dimension



Elastic deformation



Plastic deformation

Engineering Stress and Strain

Engineering stress $\sigma = \dfrac{\text{F (Average uniaxial tensile force)}}{A_0 \text{ (Original cross-sectional area)}}$

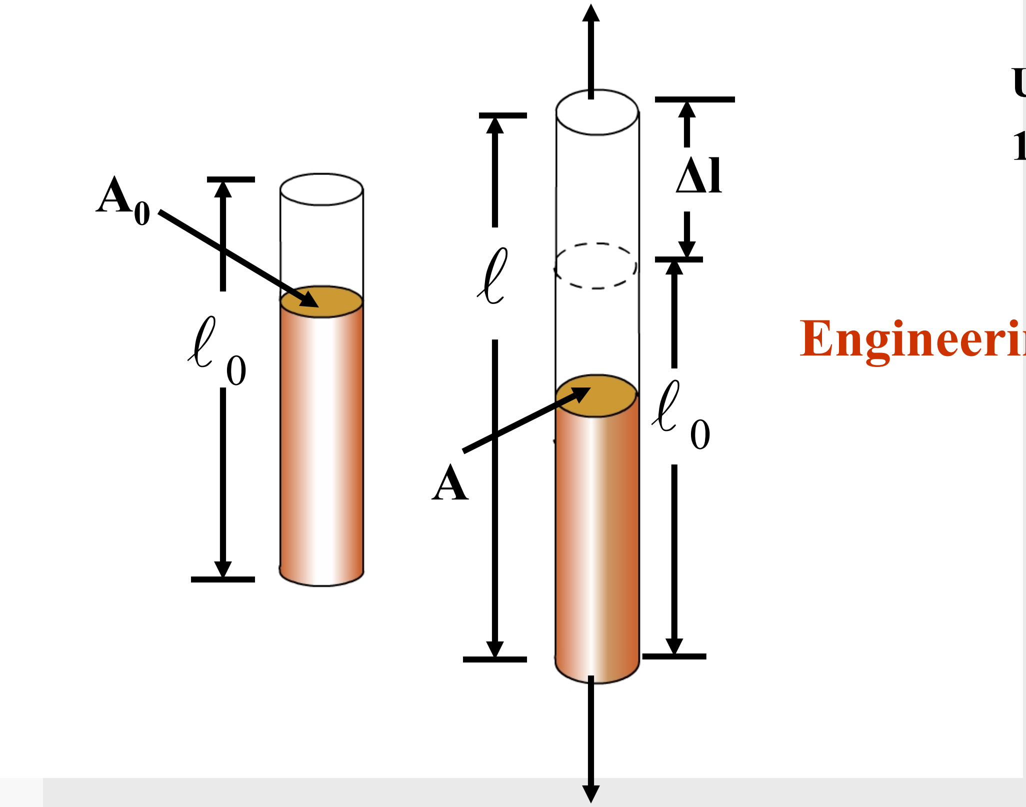


Figure 5.15

Units of Stress are PSI or N/M^2 (Pascals)

1 PSI = 6.89 x 10^3 Pa

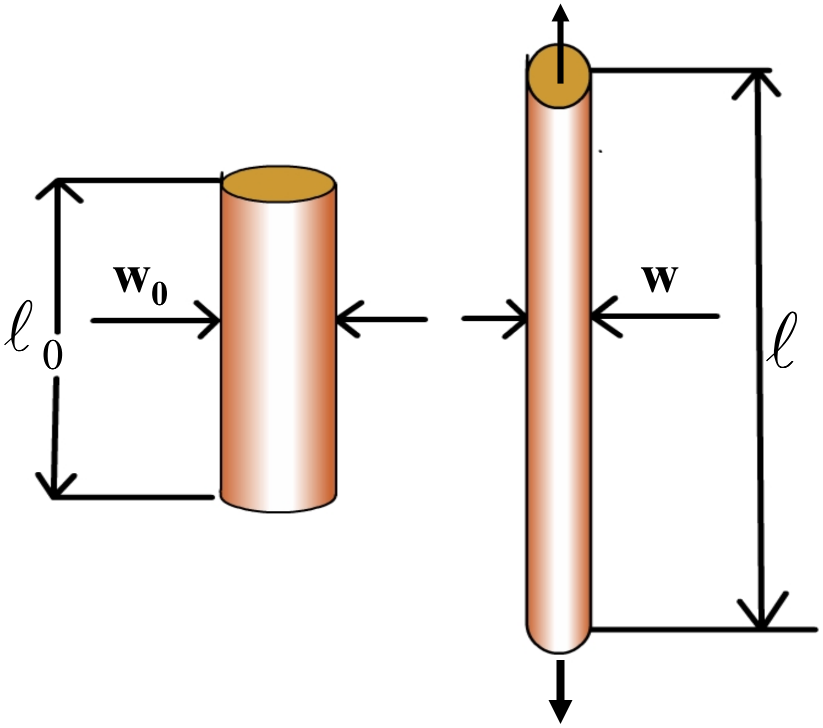
Engineering strain $= \varepsilon = \dfrac{\text{Change in length}}{\text{Original length}}$

$$= \frac{\ell - \ell_0}{\ell_0} = \frac{\Delta \ell}{\ell}$$

Units of strain are in/in, or m/m

Poisson’s Ratio

- **Poisson’s ratio** $= \nu = -\dfrac{\varepsilon(lateral)}{\varepsilon(longitudinal)} = -\dfrac{\varepsilon_y}{\varepsilon_z}$



$$\nu = -\frac{w - w_0}{\ell - \ell_0}$$

Usually poisons ratio ranges from 0.25 to 0.4.

Example: Stainless steel ➔ 0.28
Copper ➔ 0.33

Shear Stress and Shear Strain

$$\tau = \textbf{Shear stress} = \frac{\textbf{S (Shear force)}}{\textbf{A (Area of shear force application)}}$$

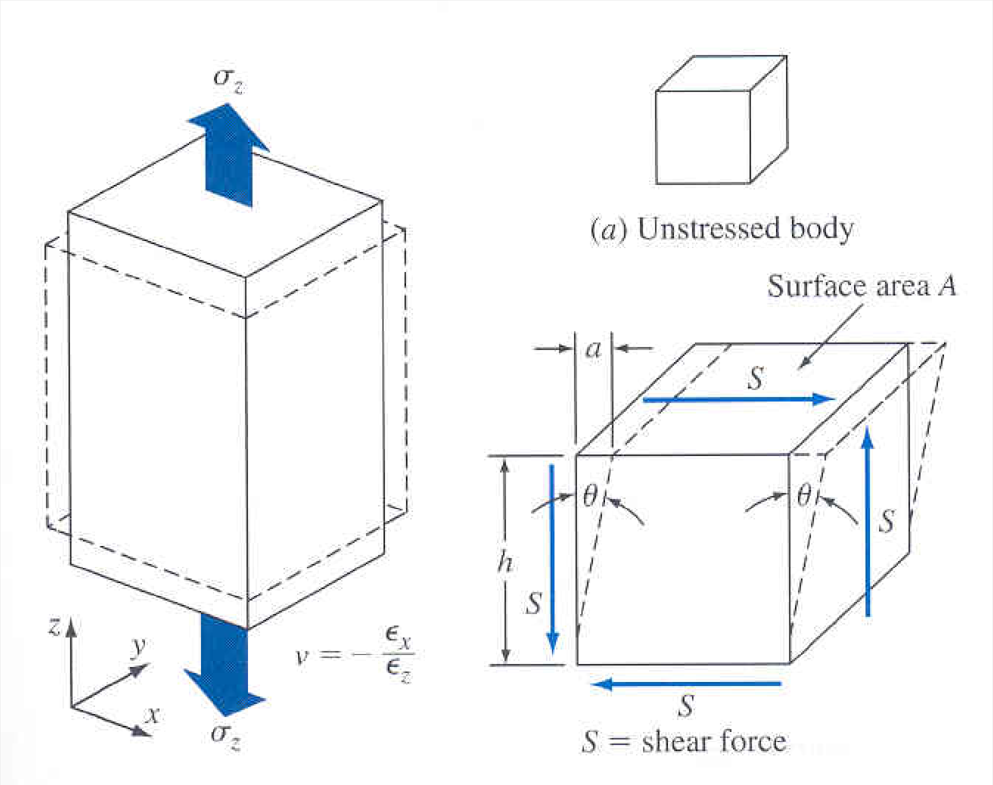


Figure 5.17

$$\textbf{Shear strain } \gamma = \frac{\textbf{Amount of shear displacement}}{\textbf{Distance ‘h’ over which shear acts.}}$$

Elastic Modulus $G = \tau / \gamma$

Tensile test

- Strength of materials can be tested by pulling the metal to failure.

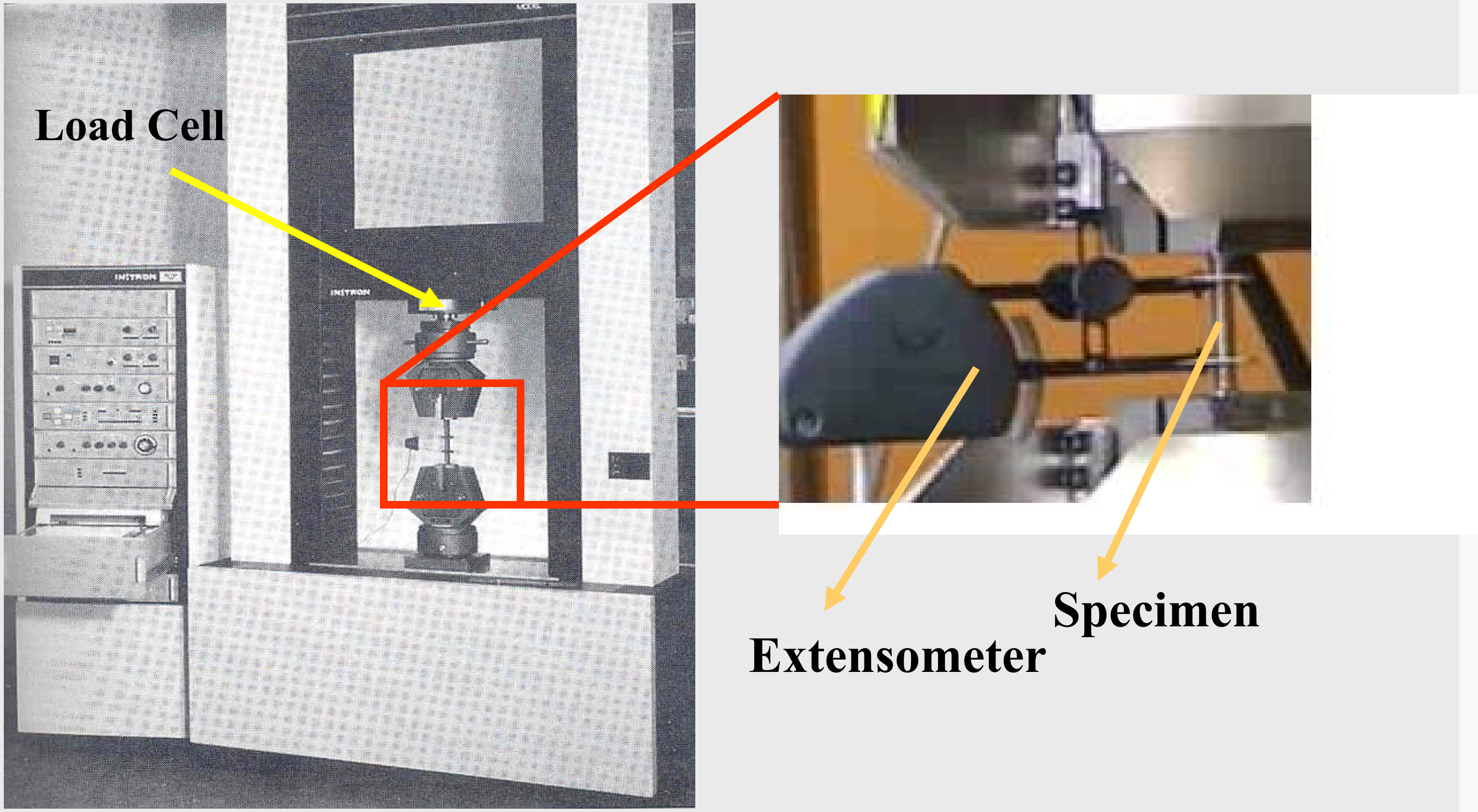


Figure 5.18

Force data is obtained from Load cell
Strain data is obtained from Extensometer.

Tensile Test (Cont)

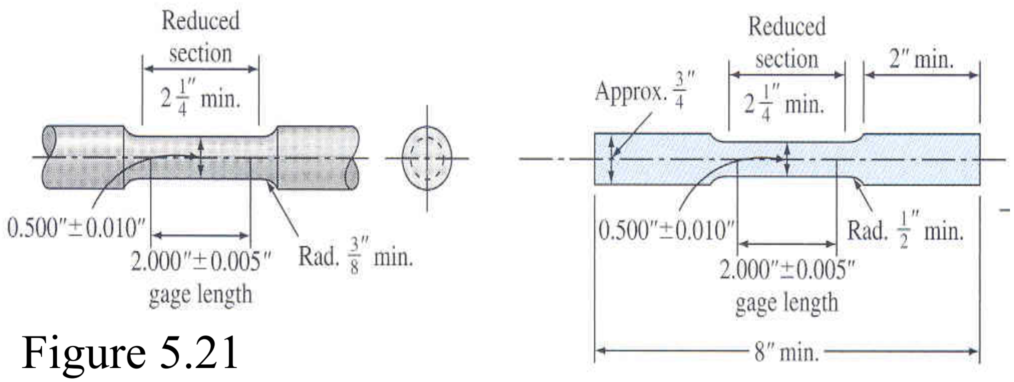
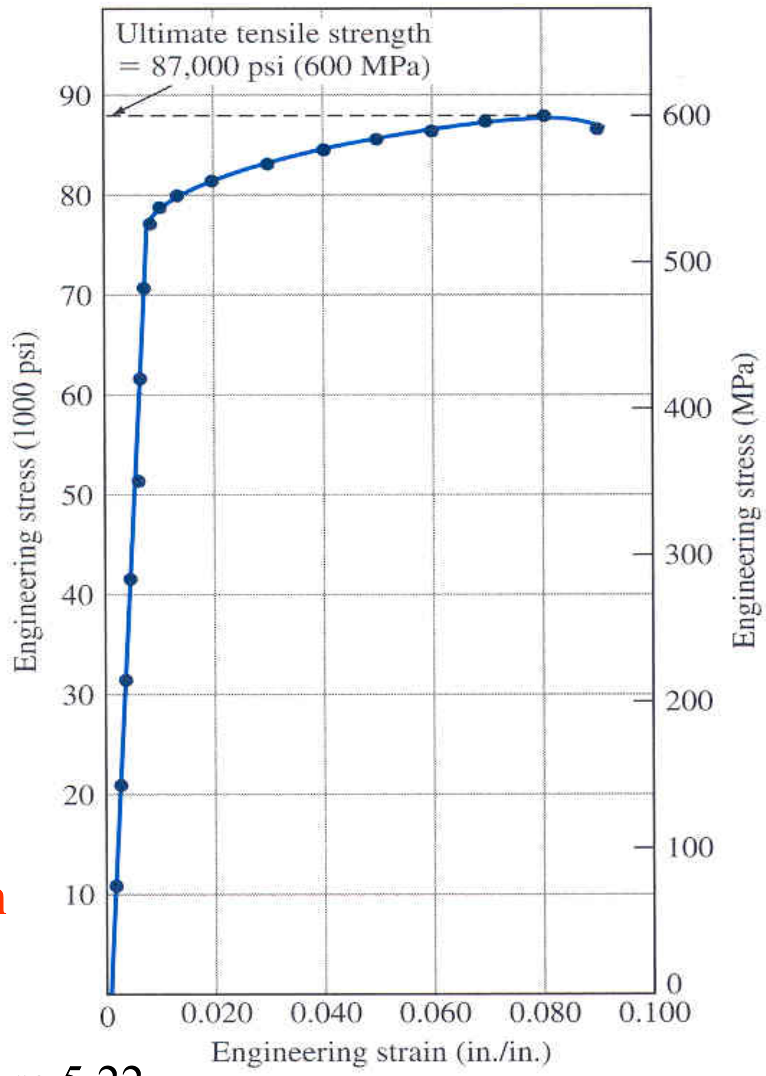


Figure 5.21

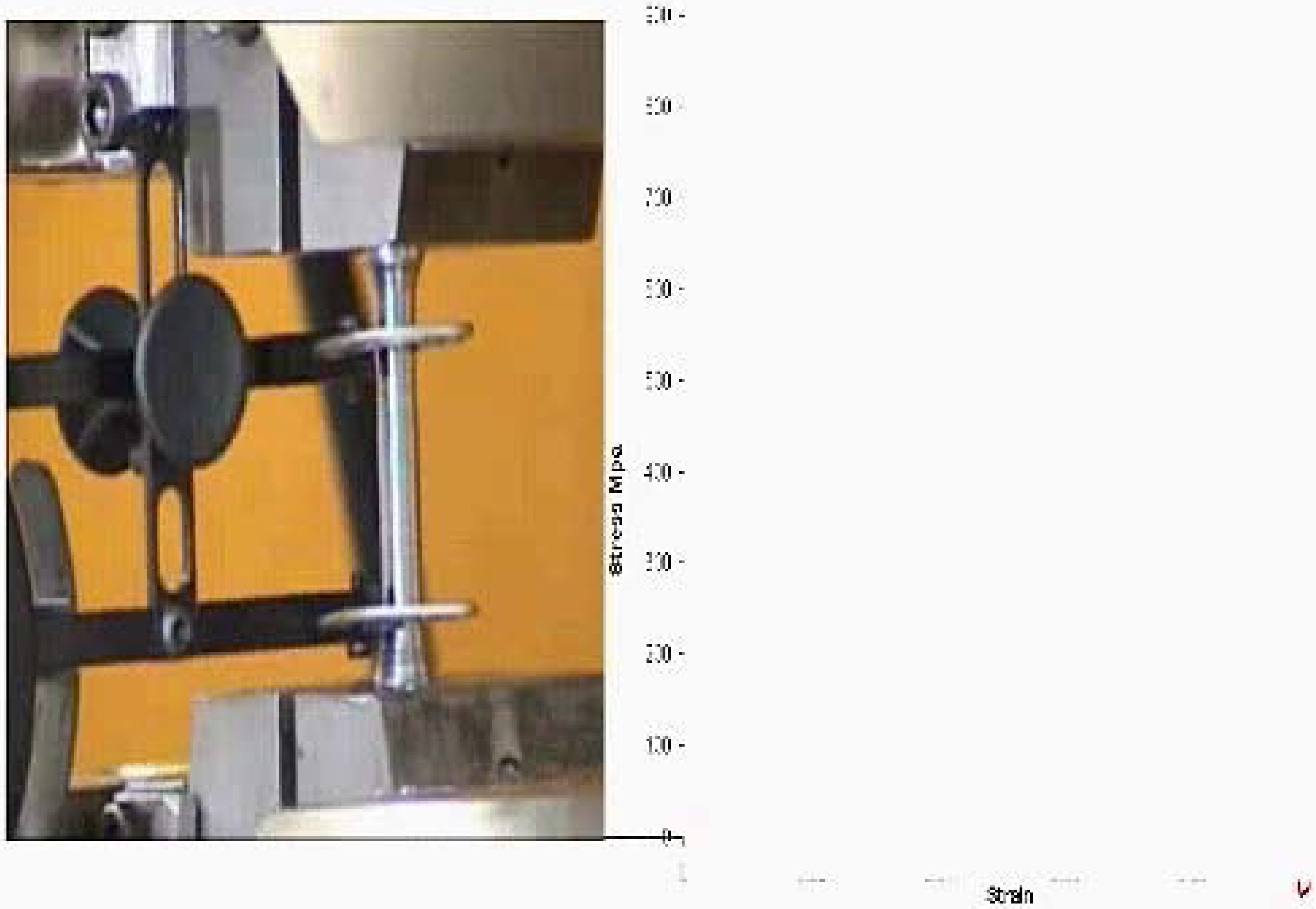
**Commonly used
Test specimen**



**Typical Stress-strain
curve**

Figure 5.22

Tensile Test –1045 Steel - Movie

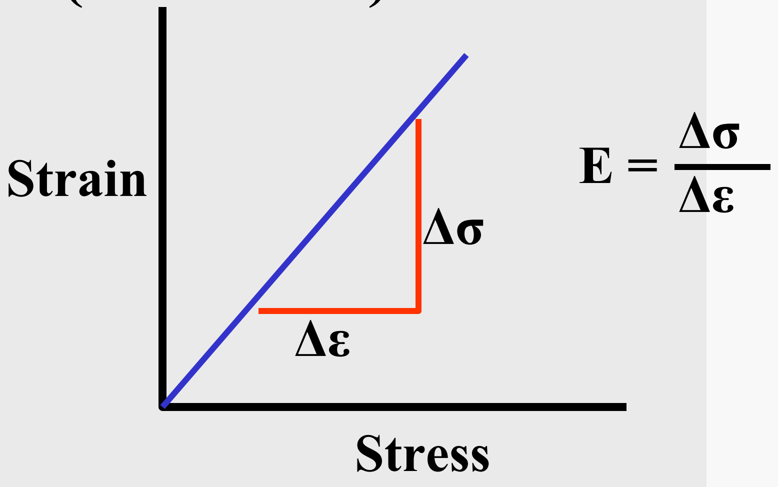


Stress-Strain Curve

Mechanical Properties

- **Modulus of elasticity (E)** : Stress and strain are linearly related in elastic region. (Hooks law)

$$E = \frac{\sigma \text{ (Stress)}}{\varepsilon \text{ (Strain)}}$$



$$E = \frac{\Delta\sigma}{\Delta\varepsilon}$$

Linear portion of the stress strain curve

- Higher the bonding strength, higher is the modulus of elasticity.

- **Examples:** Modulus of Elasticity of steel is 207 Gpa.
  Modulus of elasticity of Aluminum is 76 Gpa

Yield Strength

- Yield strength is strength at which metal or alloy shows significant amount of plastic deformation
- *0.2% offset yield strength* is that strength at which 0.2% plastic deformation takes place
- A line, starting at 0.2% strain and parallel to elastic region is drawn to obtain the 0.2% offset yield strength

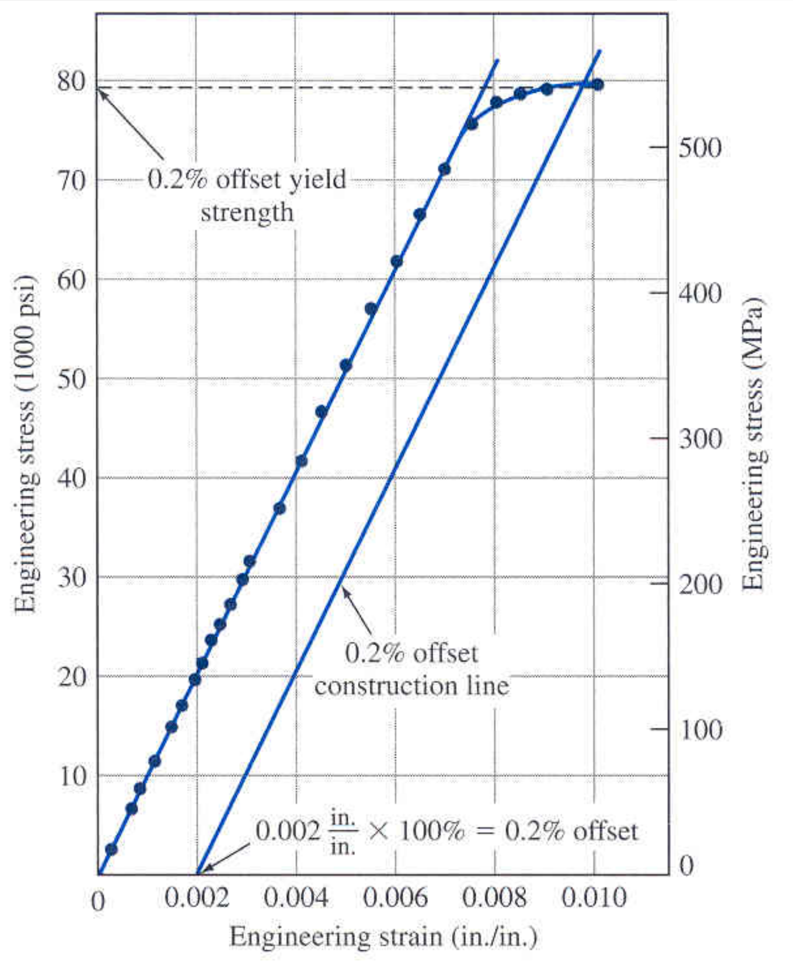


Figure 5.23

Ultimate tensile strength

- Ultimate tensile strength (UTS) is the maximum strength reached by the engineering stress strain curve.
- Necking starts after UTS is reached

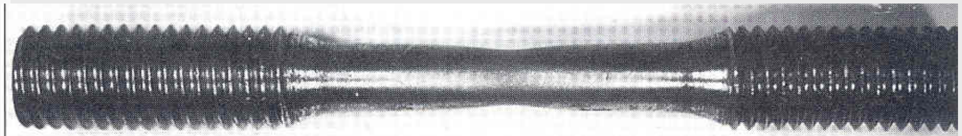
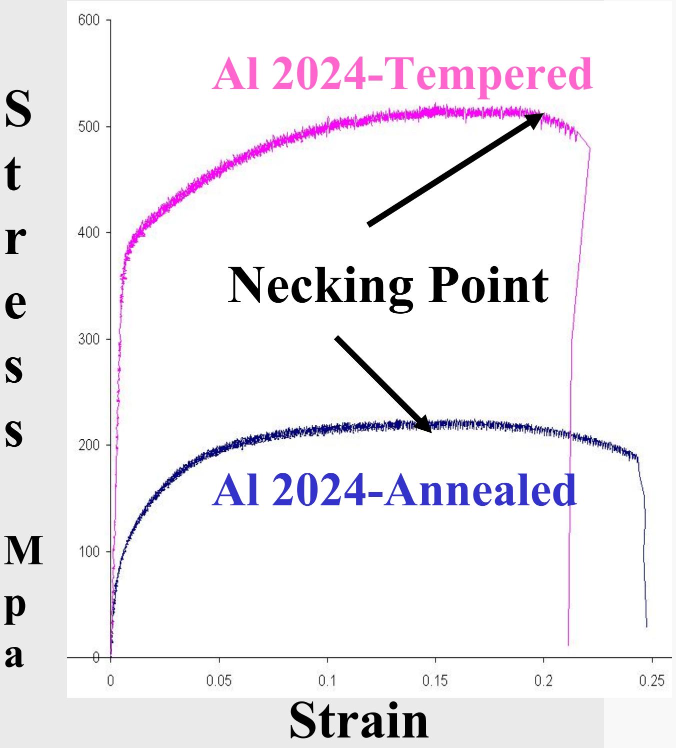


Figure 5.24

- More ductile the metal is, more is the necking before failure
- Stress increases till failure. Drop in stress strain curve is due to stress calculation based on original area.



Stress strain curves of Al 2024 With two different heattreatments. Ductile annealed sample necks more

Percent Elongation

- Percent elongation is a measure of ductility of a material.
- It is the elongation of the metal before fracture expressed as percentage of original length.

$$\% \text{ Elongation} = \frac{\text{Final length} - \text{initial Length}}{\text{Initial Length}}$$

- Measured using a caliper fitting the fractured metal together.
- Example:- Percent elongation of pure aluminum is 35%

  For 7076-T6 aluminum alloy it is 11%

Percent Reduction in Area

- **Percent reduction area** is also a measure of **ductility.**
- **The diameter of fractured end of specimen is measured using caliper.**

$$\%\ \text{Reduction Area} = \frac{\text{Initial area} - \text{Final area}}{\text{Final area}}$$

- **Percent reduction in area in metals decreases in case of presence of porosity.**

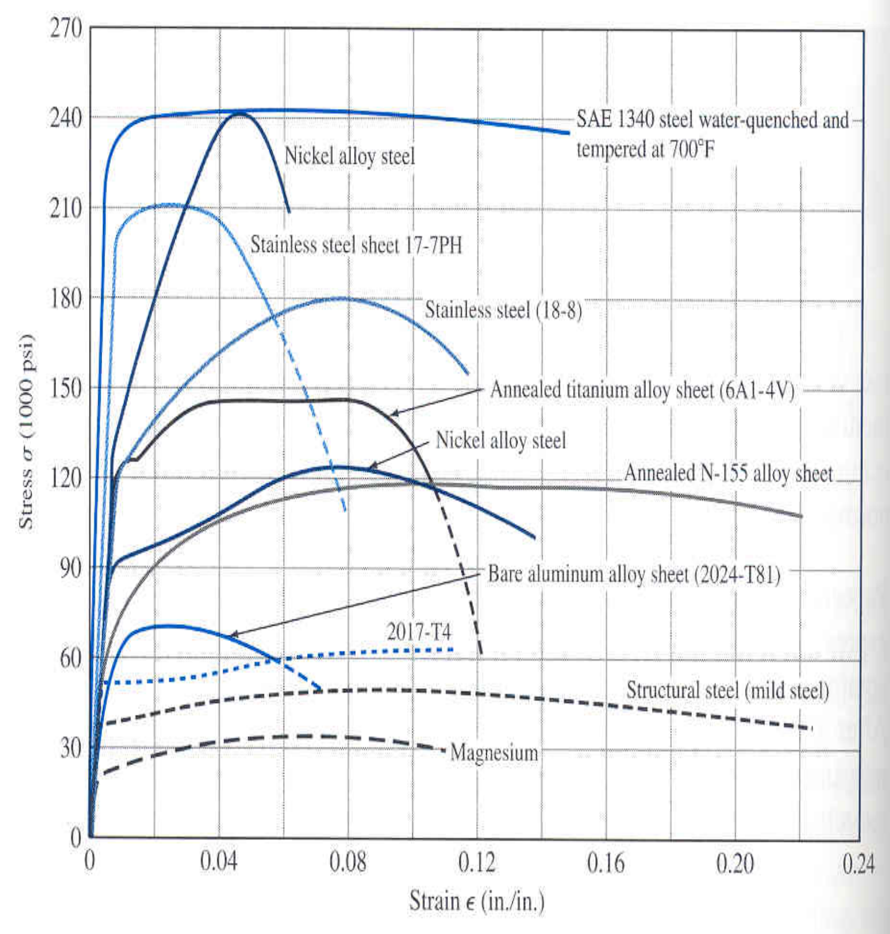
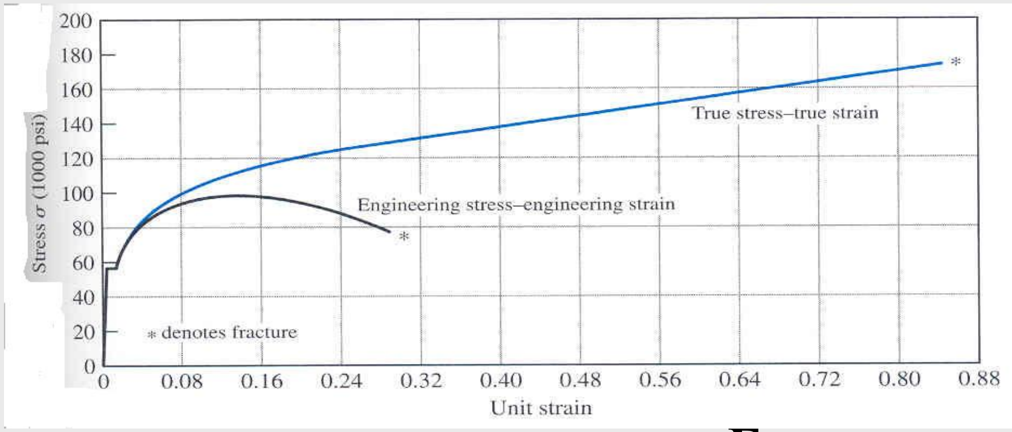


Figure 5.14

Stress-strain curves of different metals

True Stress – True Strain

- True stress and true strain are based upon instantaneous cross-sectional area and length.



- **True Stress** = $\sigma_t = \dfrac{F}{A_i \text{ (instantaneous area)}}$

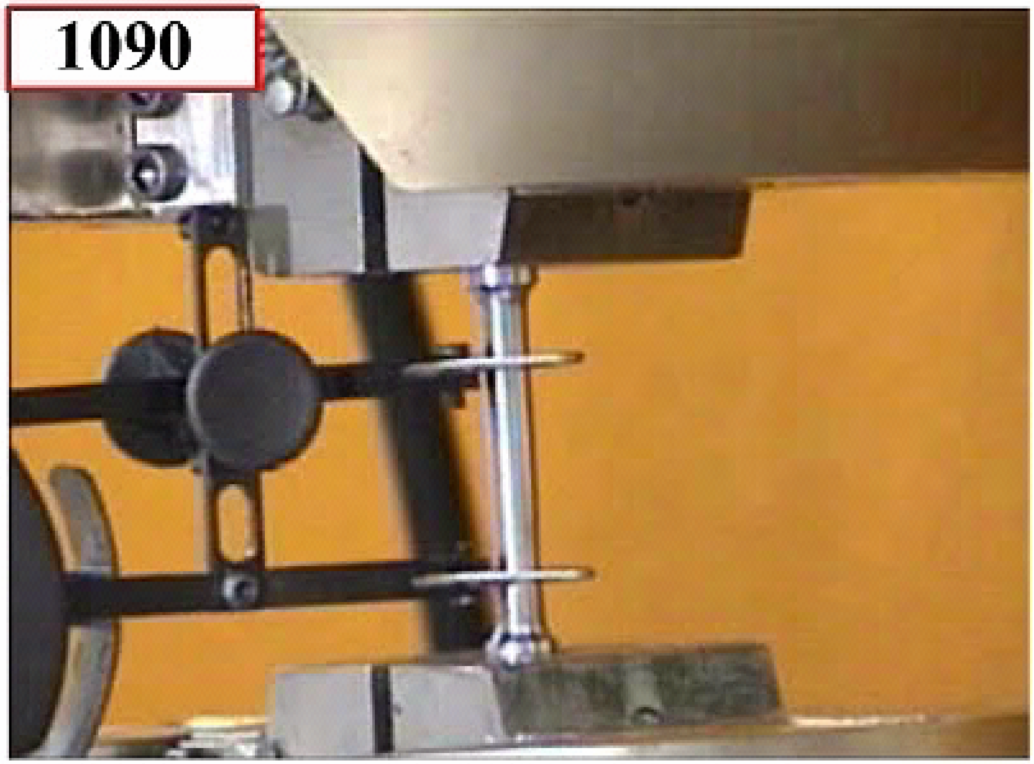
- **True Strain** = $\varepsilon_t = \displaystyle\int_{\ell_0}^{\ell_i} \frac{d\ell}{\ell} = Ln\frac{l_i}{l_0} = Ln\frac{A_0}{A_i}$

- True stress is always greater than engineering stress.

Tensile Test – 1018 Steel (Low Carbon)

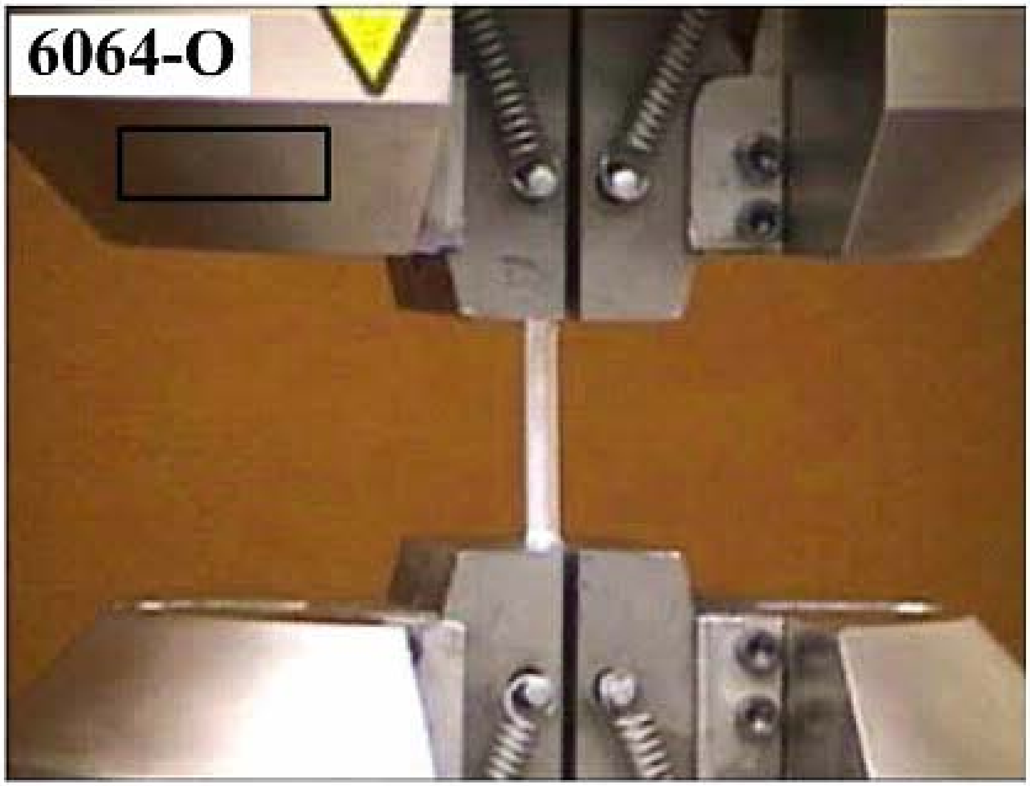
Tensile strength = 440 Mpa Modulus of Elasticity = 205 Gpa
Reduction in area = 40%, Elongation = 15%

Tensile Test 1090 Steel (High Carbon)



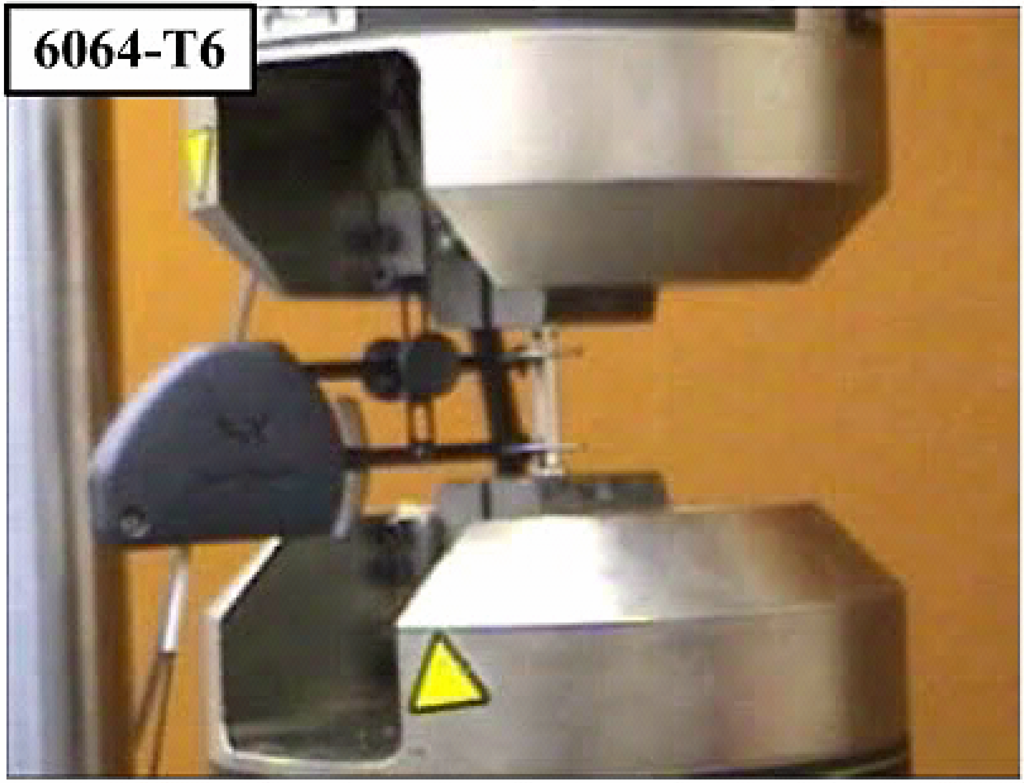
Tensile Strength = 696 Mpa, Elastic Modulus = 207 Gpa
Area reduction = 40%, Elongation = 10%

Tensile Test – 6064-O Aluminum (Annealed)



Ultimate tensile strength = 89 MPa, Modulus of elasticity = 69 Gpa
Reduction in area = 68%, Elongation = 28%

Tensile Test – 6064-T6 Aluminum (Tempered)



Ultimate tensile strength = 241 MPa, Elastic Modulus = 69 Gpa
Area reduction = 48%, Elongation = 15%

Hardness and Hardness Testing

- Hardness is a measure of the resistance of a metal to permanent (plastic) deformation.
- General procedure:

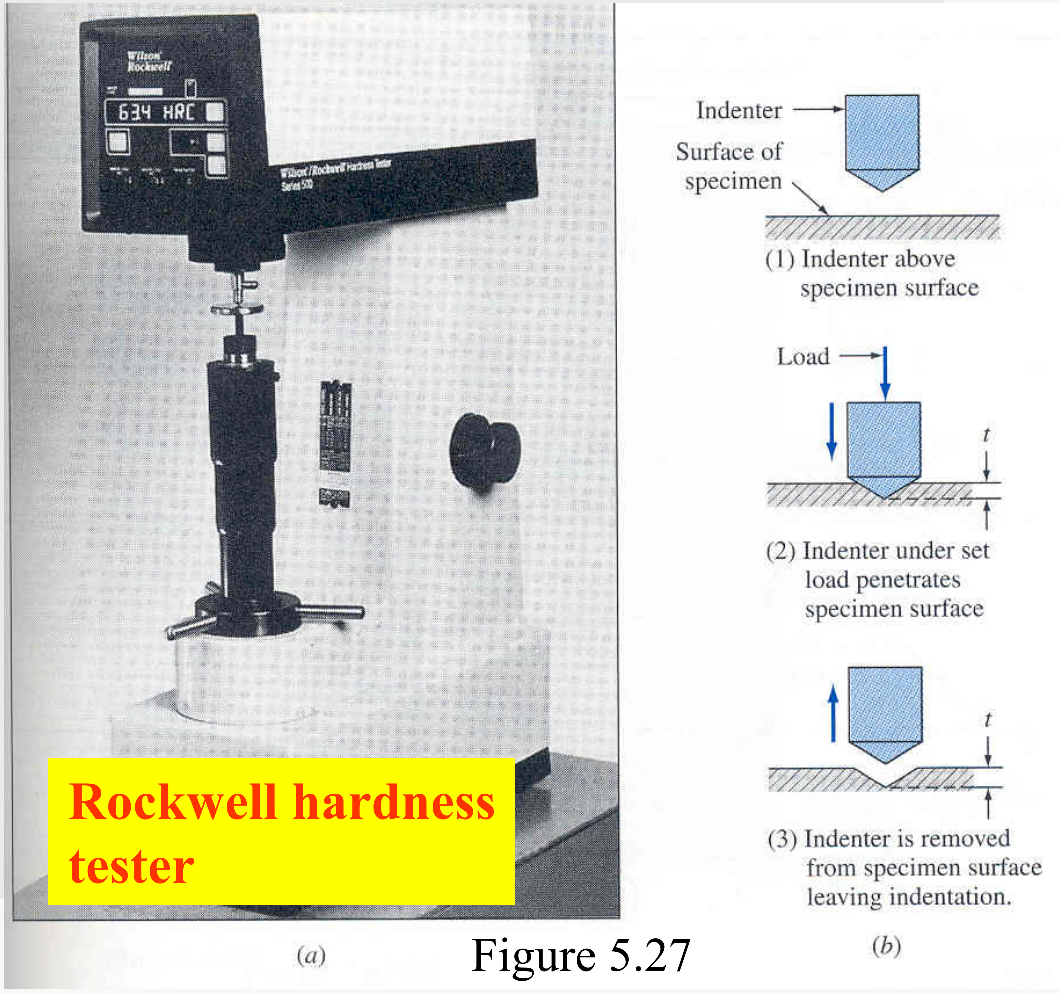
Press the indenter that is harder than the metal Into metal surface.

↓

Withdraw the indenter

↓

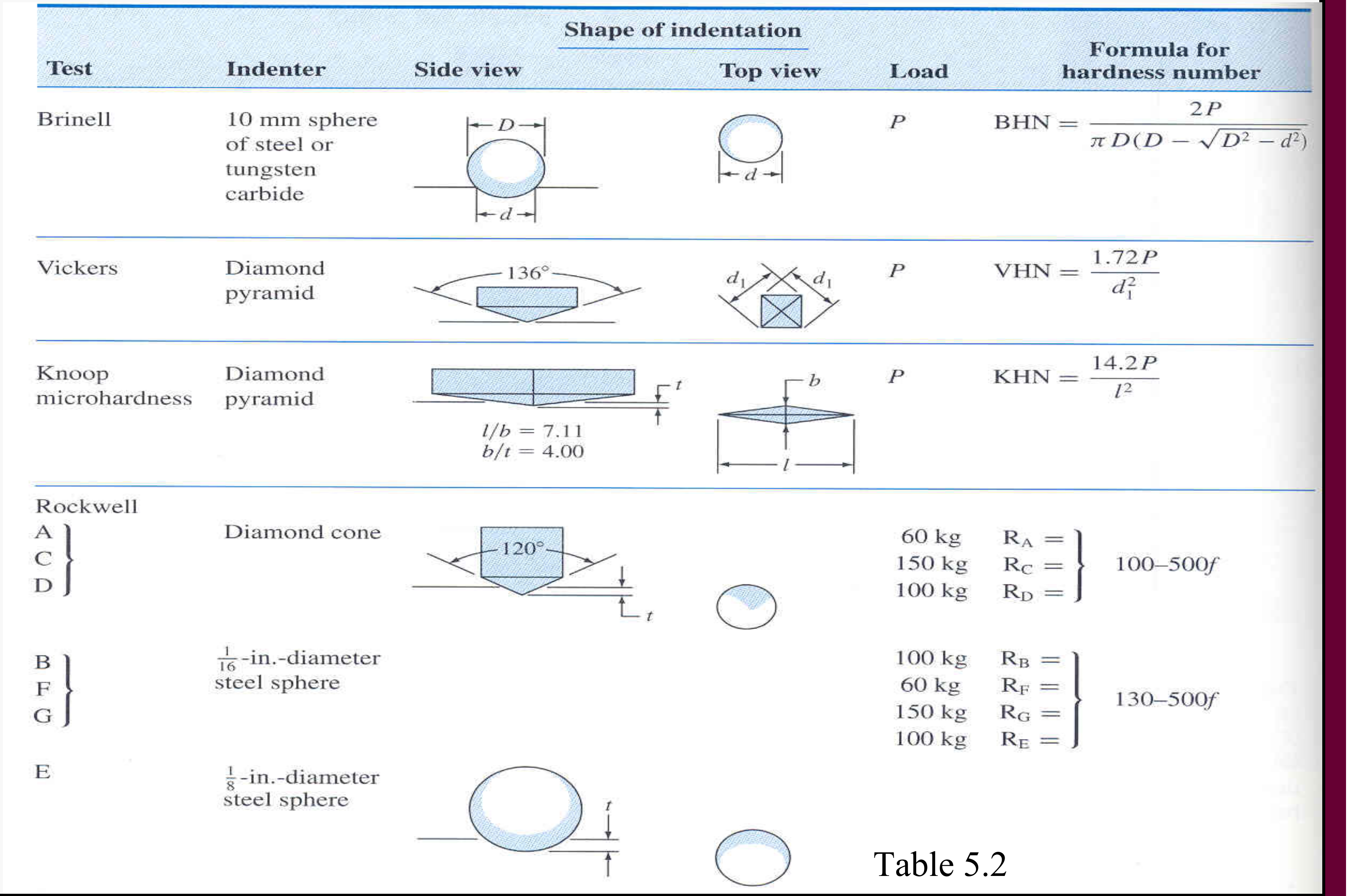
Measure hardness by measuring depth or width of indentation.



Rockwell hardness tester

Figure 5.27

Hardness Tests

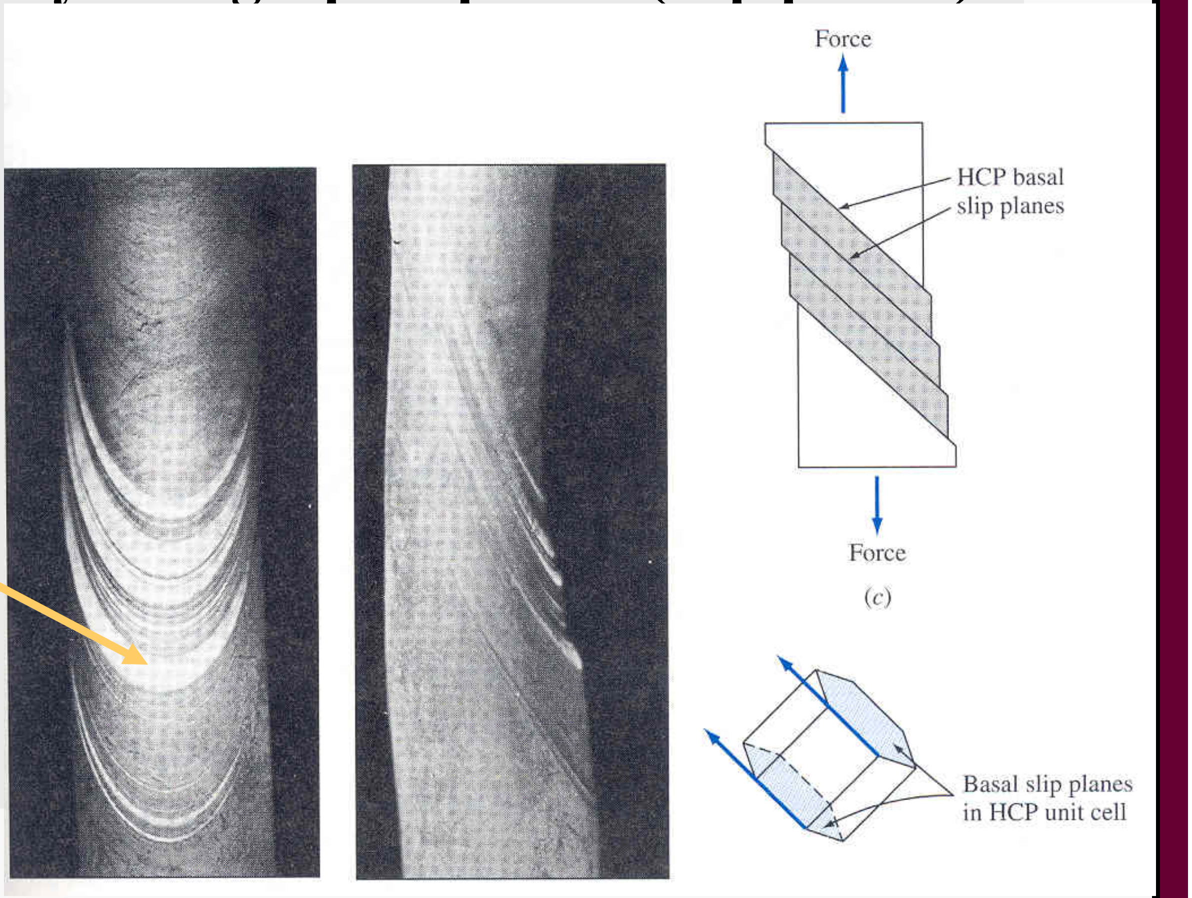


Test	Indenter	Shape of indentation: Side view	Shape of indentation: Top view	Load	Formula for hardness number
Brinell	10 mm sphere of steel or tungsten carbide			P	$\text{BHN} = \dfrac{2P}{\pi D(D - \sqrt{D^2 - d^2})}$
Vickers	Diamond pyramid			P	$\text{VHN} = \dfrac{1.72P}{d_1^2}$
Knoop microhardness	Diamond pyramid	$l/b = 7.11$ $b/t = 4.00$		P	$\text{KHN} = \dfrac{14.2P}{l^2}$
Rockwell A C D	Diamond cone			60 kg 150 kg 100 kg	$R_A =$ $R_C =$ $R_D =$ 100–500f
B F G	$\frac{1}{16}$-in.-diameter steel sphere			100 kg 60 kg 150 kg 100 kg	$R_B =$ $R_F =$ $R_G =$ $R_E =$ 130–500f
E	$\frac{1}{8}$-in.-diameter steel sphere				

Table 5.2

Plastic Deformation in Single Crystals

- Plastic deformation of single crystal results in step markings on surface → slip bands.
- Atoms on specific crystallographic planes (slip planes) slip to cause slip bands.



Slip bands

Figure 5.28

Slip Bands and Slip Planes

- Slip bands in ductile metals are uniform (occurs in many slip planes).
- Slip occurs in many *slip planes* within slip bands.
- Slip planes are about 200A thick and are offset by about 2000A

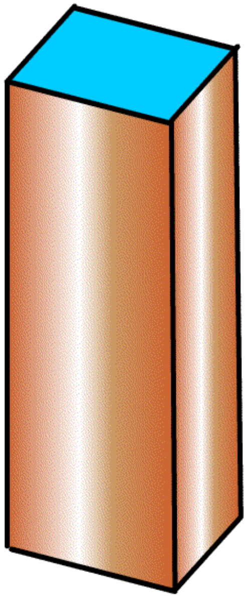


Figure 5.30

Slip Mechanism

- During shear, atoms do not slide over each other.
- The slip occurs due to movement of dislocations.

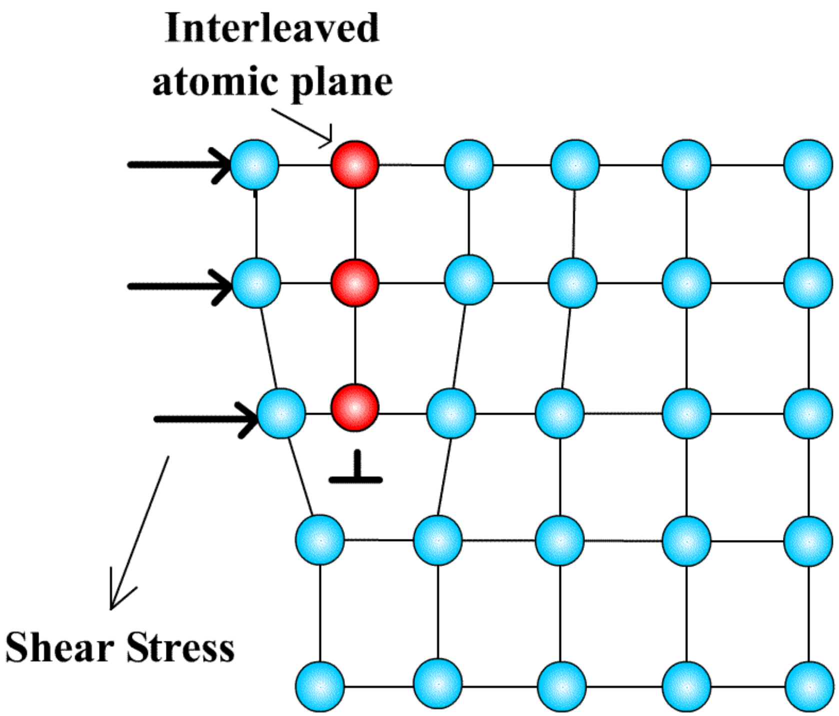


Figure 5.32

Wall of high dislocation density

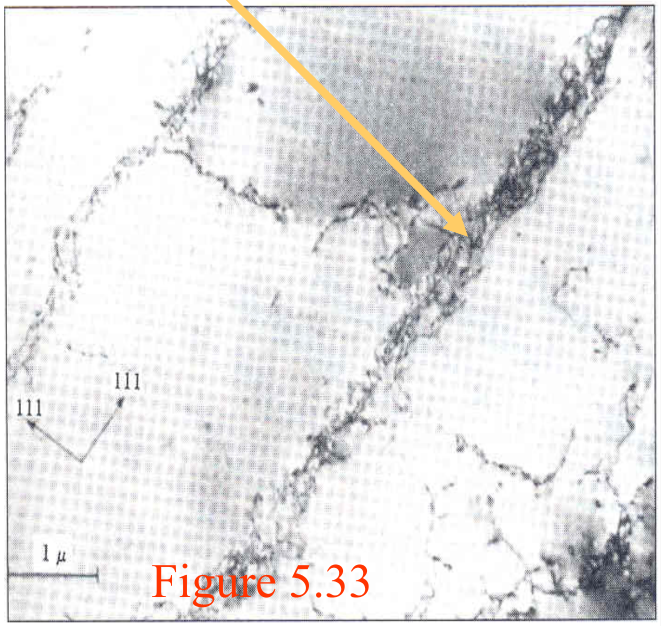


Figure 5.33

Dislocation cell structure in lightly deformed Aluminum

Slip in Crystals

- Slip occurs in densely or close packed planes.
- Lower shear stress is required for slip to occur in densely packed planes.
- If slip is restricted in close planes, then less dense planes become operative.
- Less energy is required to move atoms along denser planes.

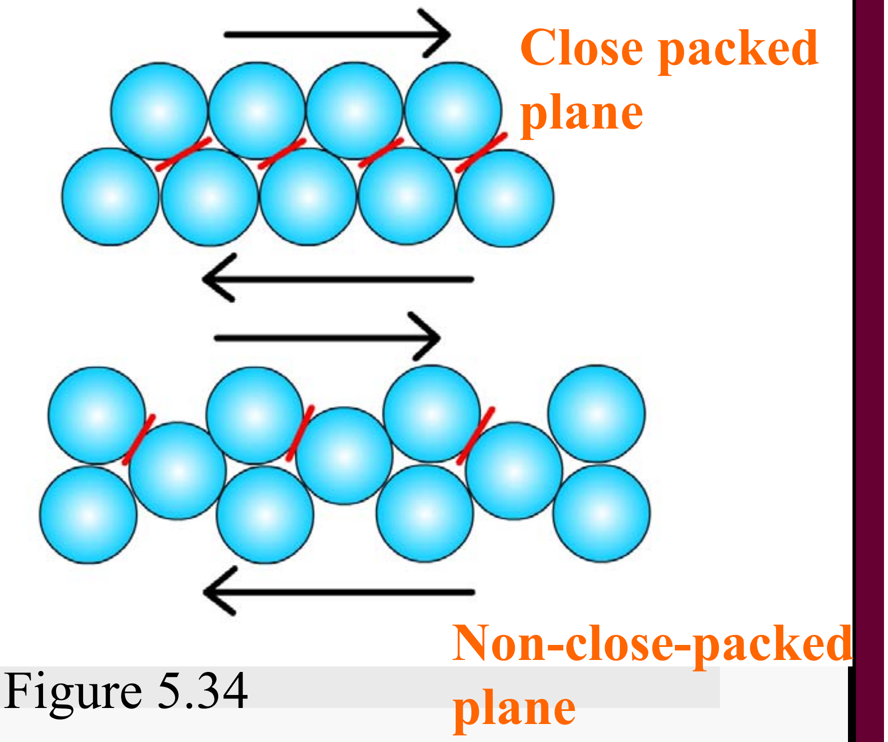
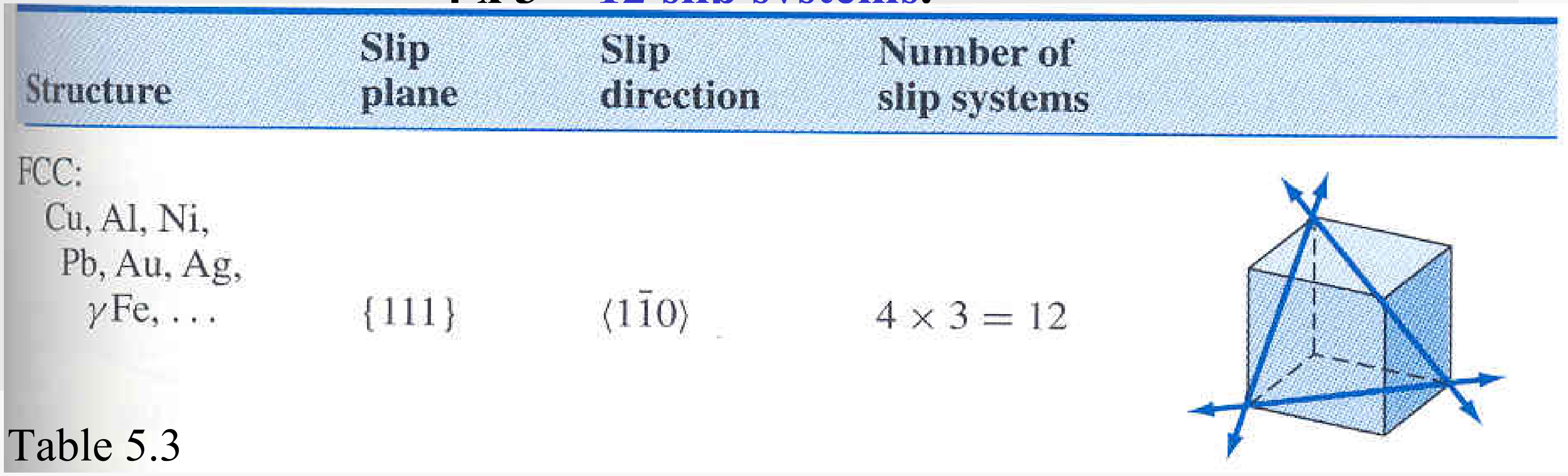


Figure 5.34

Slip Systems

- Slip systems are combination of slip planes and slip direction.
- Each crystal has a number of characteristic slip systems.
- In FCC crystal, slip takes place in {111} octahedral planes and <1$\bar{1}$0> directions.

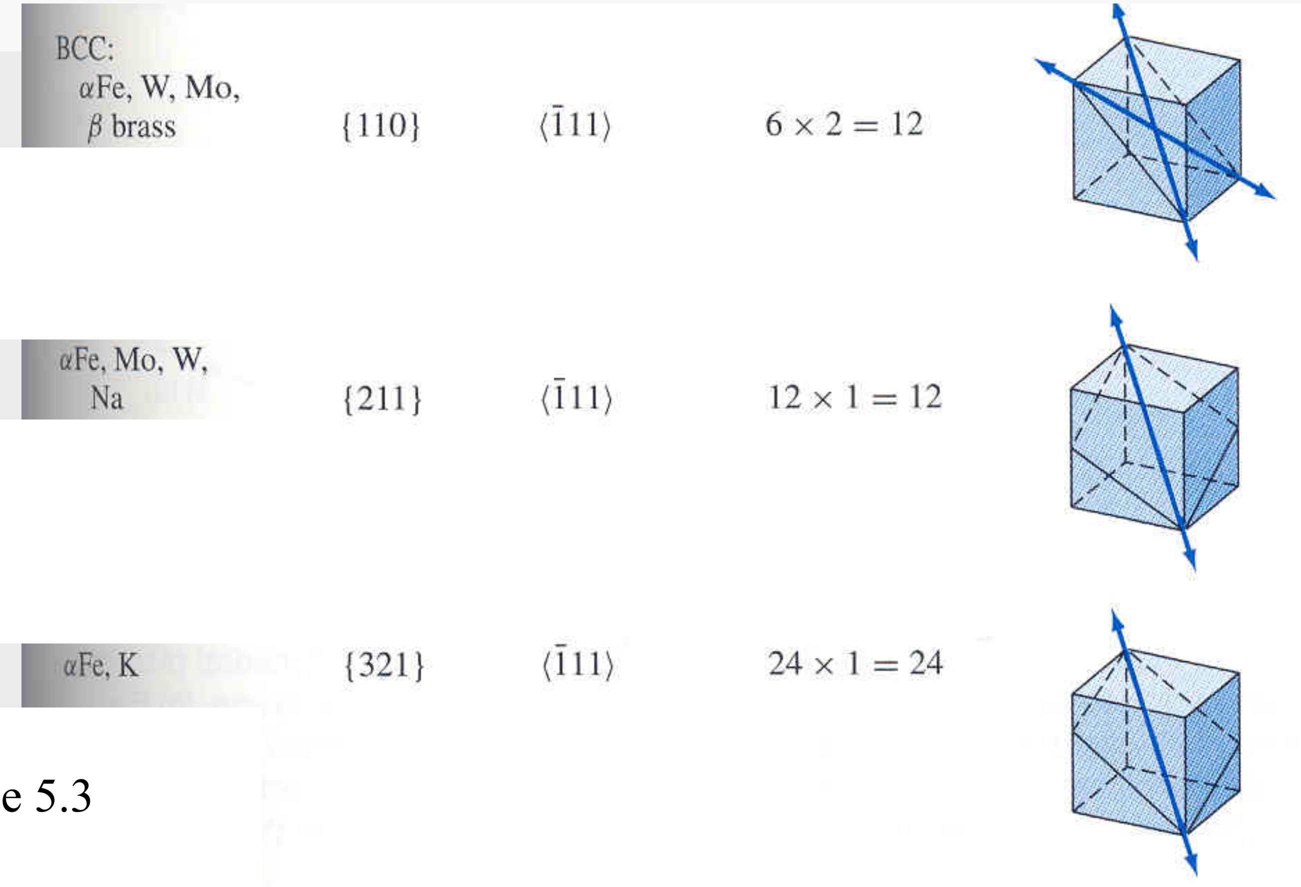
4 (111) type planes and 3 [110] type directions.
4 x 3 = 12 slip systems.



Structure	Slip plane	Slip direction	Number of slip systems
FCC: Cu, Al, Ni, Pb, Au, Ag, γFe, . . .	{111}	$\langle 1\bar{1}0\rangle$	$4 \times 3 = 12$

Table 5.3

Slip Systems in BCC Crystal

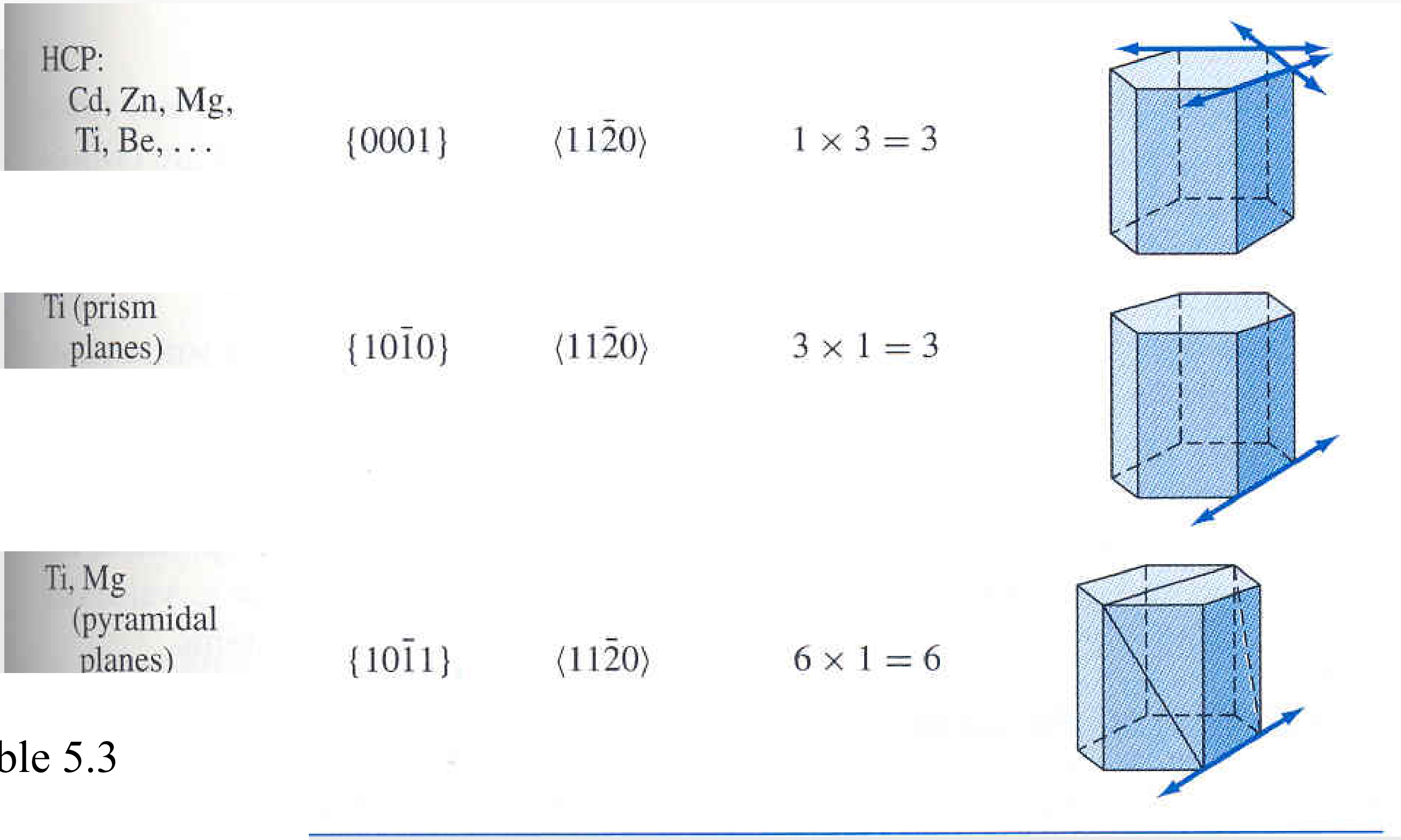


BCC: αFe, W, Mo, β brass	{110}	$\langle\bar{1}11\rangle$	$6 \times 2 = 12$
αFe, Mo, W, Na	{211}	$\langle\bar{1}11\rangle$	$12 \times 1 = 12$
αFe, K	{321}	$\langle\bar{1}11\rangle$	$24 \times 1 = 24$

Table 5.3

- BCC crystals are not close packed. The slip predominantly occurs in {110} planes that has highest atomic density.

Slip Systems in HCP Crystal



HCP: Cd, Zn, Mg, Ti, Be, . . .	$\{0001\}$	$\langle 11\bar{2}0\rangle$	$1 \times 3 = 3$	
Ti (prism planes)	$\{10\bar{1}0\}$	$\langle 11\bar{2}0\rangle$	$3 \times 1 = 3$	
Ti, Mg (pyramidal planes)	$\{10\bar{1}1\}$	$\langle 11\bar{2}0\rangle$	$6 \times 1 = 6$	

Table 5.3

- If HCP crystals have **high c/a ratio**, slip occurs along **basal planes** {0001}. For crystals with low c/a ratio, slip also occurs in {10$\bar{1}$0} and {10$\bar{1}$1} planes.

Critical Resolved Shear Stress

- **Critical resolved shear stress** is the stress required to cause slip in pure metal single crystal.
- Depends upon
    - Crystal Structure
    - Atomic bonding characteristics
    - Temperature
    - Orientation of slip planes relative to shear stress
- Slip begins when **shear stress** in slip plane in slip direction reaches critical resolved shear stress.
- This is equivalent to yield stress.
- **Example :-**

Zn	HCP	99.999%	pure	0.18MPa
Ti	HCP	99.99%	pure	13.7 MPa
Ti	HCP	99.9%	pure	90.1 MPa

Schmid’s Law

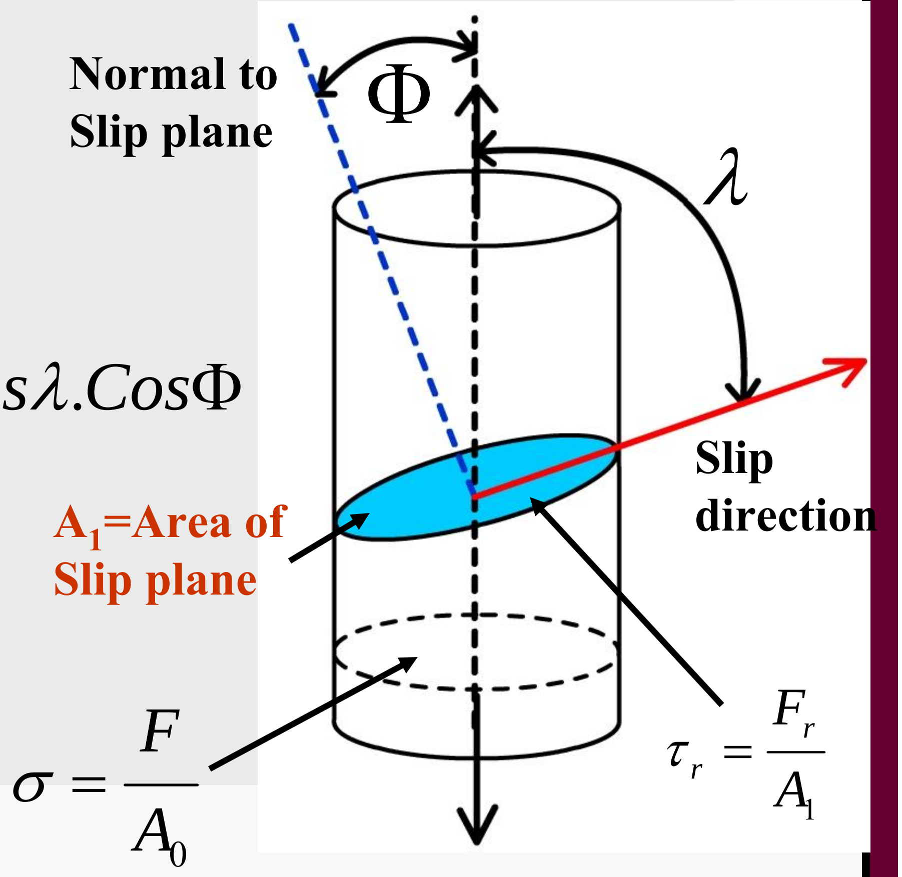
- The relationship between uniaxial stress action on a single cylinder of pure metal single crystal and resulting resolved shear stress produced on a slip system is give by

$\tau=$

$$\tau_r = \frac{\text{Shear Force}}{\text{Shear Area}}$$

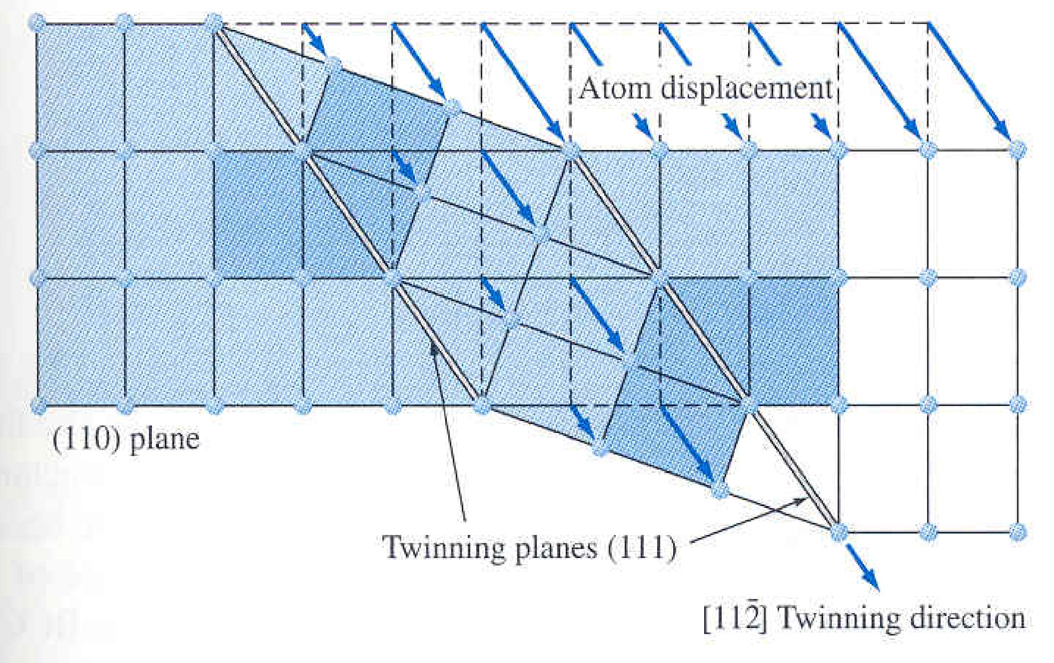
$$= \frac{F_r}{A_1} = \frac{F.Cos\lambda}{A_0 / Cos\lambda} = \frac{F}{A_0} Cos\lambda.Cos\Phi$$

$$= \sigma.Cos\lambda.Cos\Phi$$



Twinning

- In **twinning**, a part of atomic lattice is deformed and forms *mirror image* of lattice next to it
- Distance moved by atoms is proportional to their distance from twinning plane
- Deformation from twinning is small.
- Twinning **reorient** the slip system



Effects of Grain Boundaries on Strength

- Grain boundaries stop dislocation movement and hence strengthen the metals.
- Fine grain size is desirable, and hence metals are produced with finer grains.

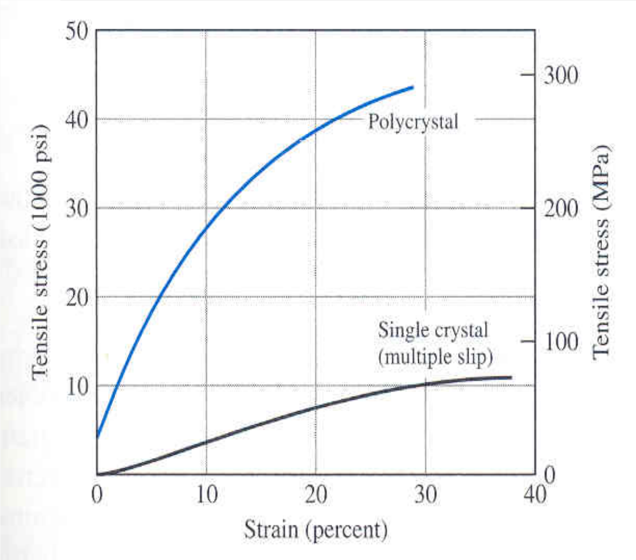


Figure 5.40
Stress-strain curve of single and polycrystalline copper

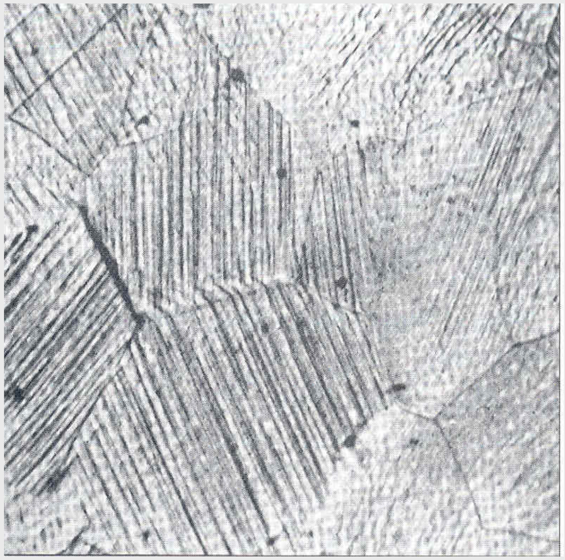


Figure 5.40
Slip bands in polycrystalline aluminum grains

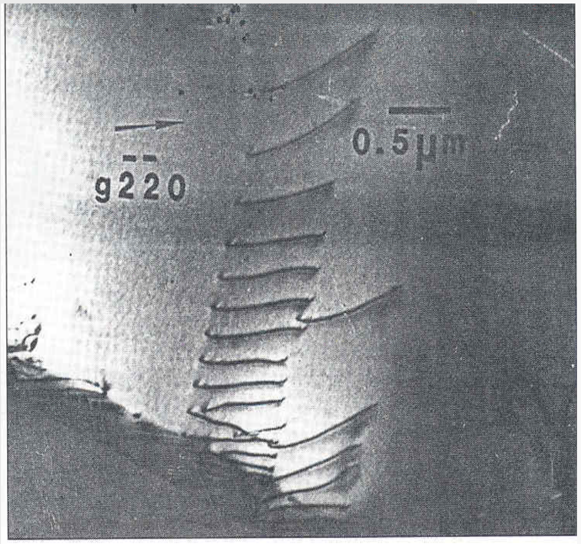


Figure 5.40
Dislocations piled up against grain boundaries in stainless steel

Hall Petch Equation

- **Finer the grains, superior are the mechanical properties (at room temperature).**
  - **More isotropic properties**
  - **Less resistant to corrosion and creep**

Hall-Petch equation - Empirical

$$\sigma_y = \sigma_o + k / (d)^{1/2}$$

$\sigma_y =$ Yield strength

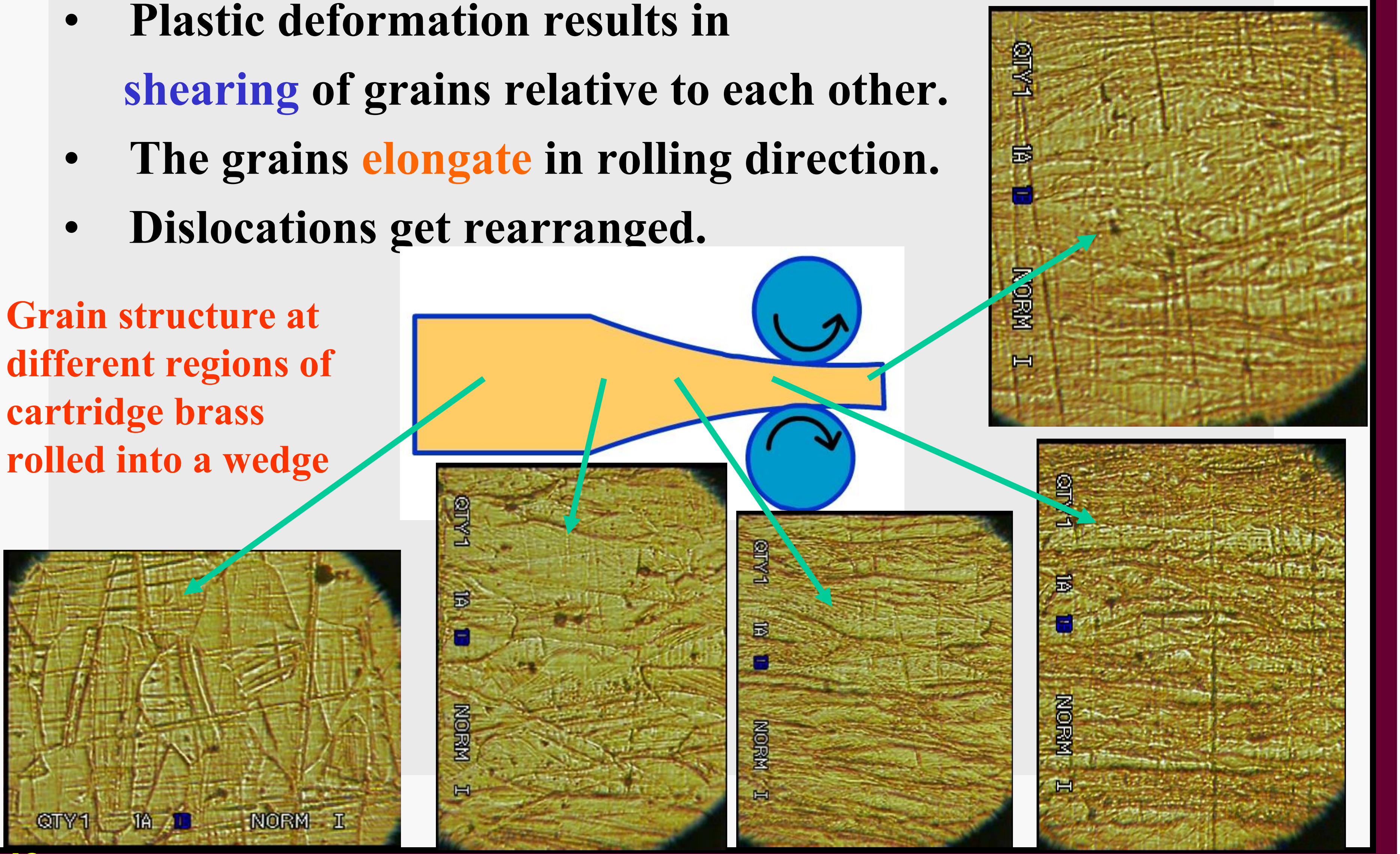
d = average grain diameter

σ_o and k are constants for a metal.

$\sigma_o = 70$ Mpa and $k = 0.74$ Mpam$^{1/2}$ for mild steel.

Effects of Plastic Deformation

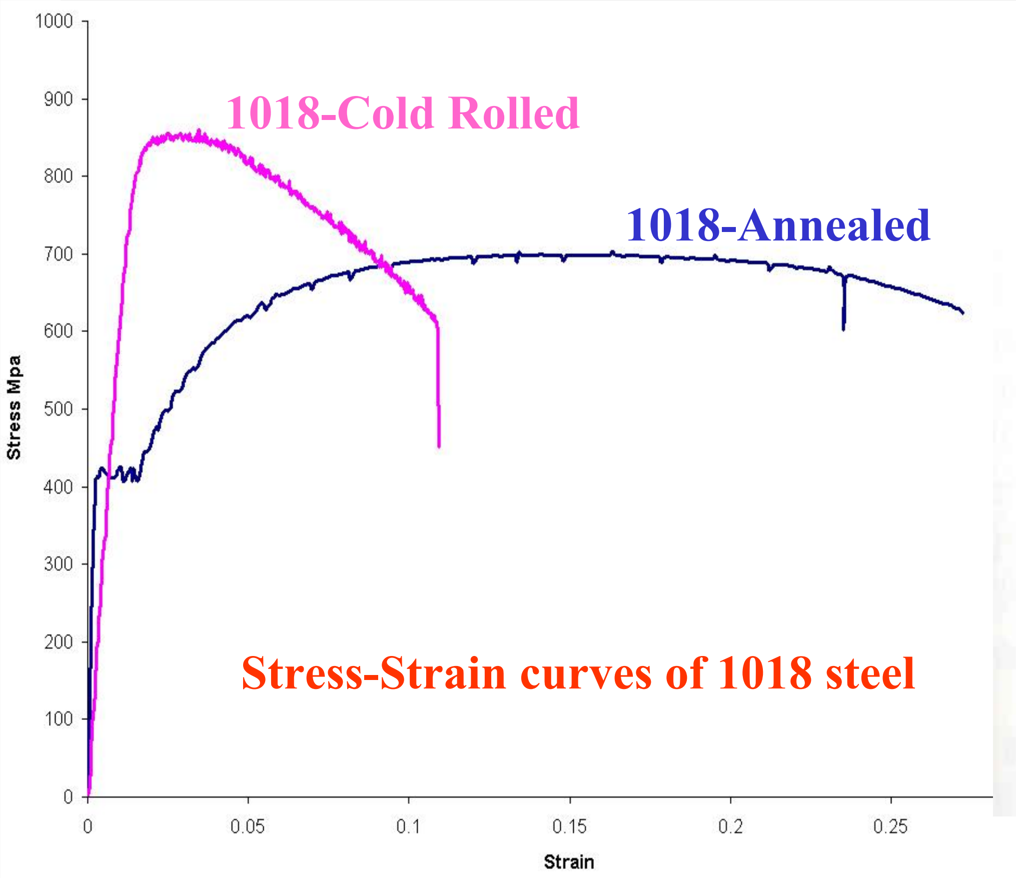
- Plastic deformation results in shearing of grains relative to each other.
- The grains elongate in rolling direction.
- Dislocations get rearranged.



Grain structure at different regions of cartridge brass rolled into a wedge

Effect of Cold Work on Tensile Strength

- Number of dislocations are increased by cold work.
- Dislocation movements are hindered by both grain boundaries and other dislocations → **Strain Hardening**



Stress-Strain curves of 1018 steel

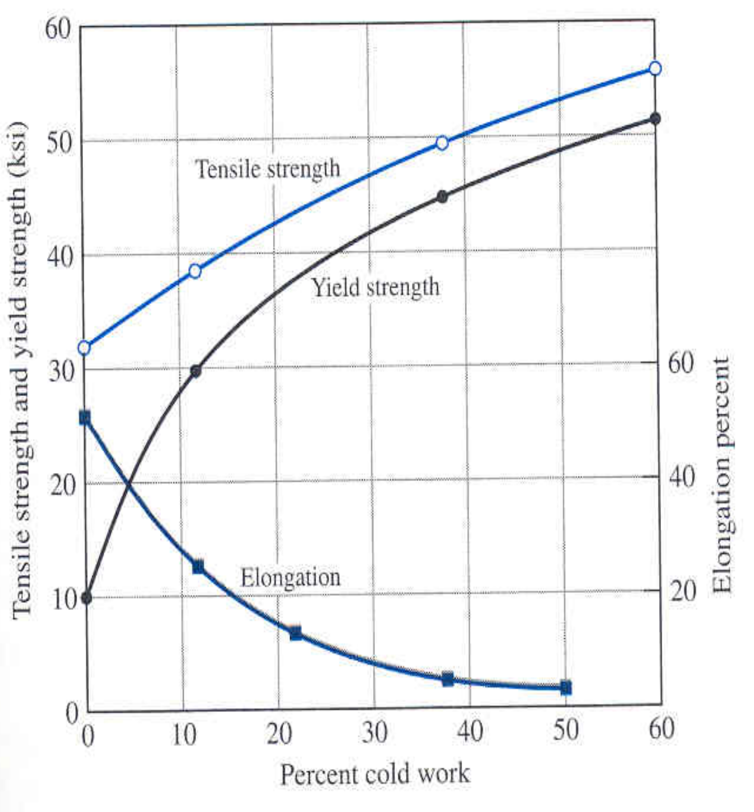


Figure 5.45

Solid Solution Strengthening

- Addition of one or more metals can increase the strength of metals.
- Solute atoms, on case of substitutional solid solution, create *stress fields* around themselves and hinder the dislocation movement.
- Distortion of lattice and clustering of like atoms also impede dislocation movement.
- **Example:** Solid solution of 70 wt % Cu & 30 wt % Zn (cartridge brass) has tensile strength of 500 MPa. Tensile strength of unalloyed copper is 330 MPa

Superplasticity in Metals

- At elevated temperature and slow loading, some alloys deform 2000%.
- Annealed Ti alloy
    - ➢ Elongates 12% at room temperature
    - ➢ Elongates up to 1170% at 870°C and $1.3\text{x}10^{-4}$/s loading rate.

- Conditions: very fine grain size (5-10 microns)

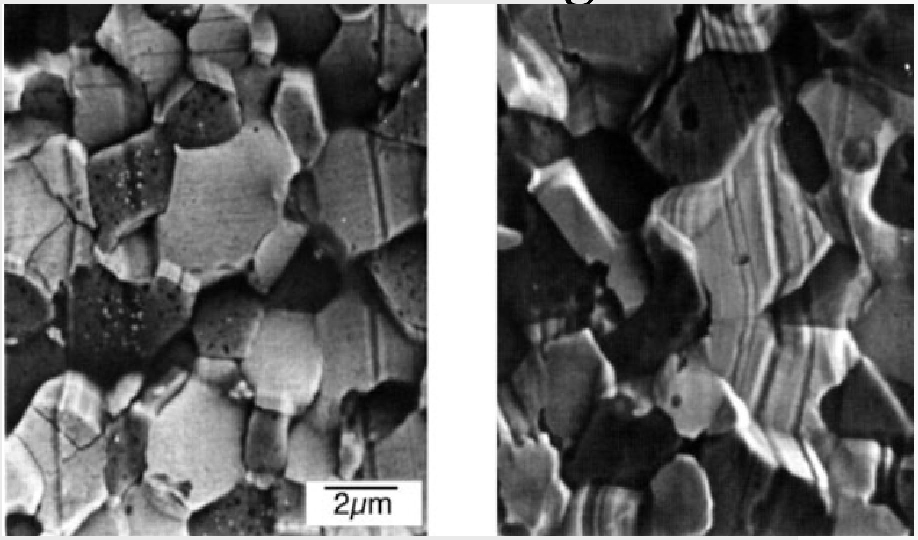
    * Highly strain sensitive

    * Temperature above 0.5 Tm

    * Slow strain rate

Mechanism of Superplasticity

- Very limited dislocation activity
- Deformation mechanism:
  - Grain boundary sliding
  - Grain boundary diffusion
  - Sliding and rotation of individual grains.
- Applications: Metal forming operations.
  - Blow forming to produce automobile hoods.



Grains before and after deformation

Nanocrystalline Metals

- Average grain diameter < 100 nm
- Results in high strength and hardness, and Superplasticity
- If grain diameter reduces from 10 microns to 10 nm, yield strength of copper increases 31 times.
- Very difficult to produce nanocrystalline metals.
- If d < 5 nm, elastic modulus drops as more atoms are in grain boundary
- Hall-Petch equation is invalid in lower nanocrystalline range.
- Negative Hall-Petch effect might take place