

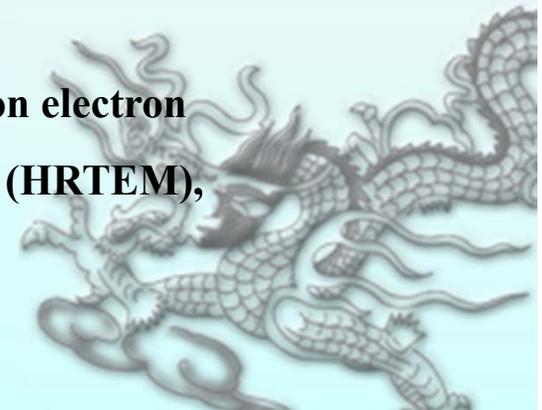
Materials Science and Engineering I

Chapter 4

Solidification and Crystalline Imperfections

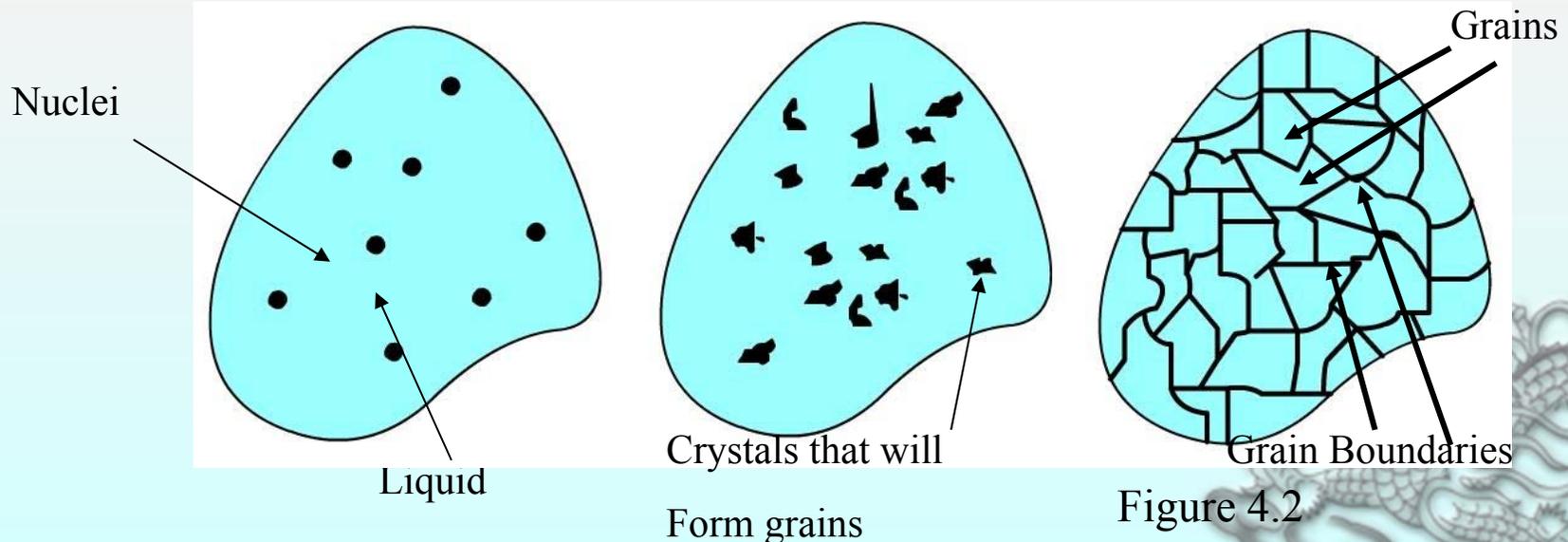
Outline of Chapter 4

- ✚ **Solidification of metals: Nuclei, growth of nuclei into crystals, Grain growth.**
- ✚ **Growth of crystalline in Liquid Metal and formation of a grain structure**
- ✚ **Grain structure of industrial casting**
- ✚ **Solidification of single crystals**
- ✚ **Metallic solid solutions: Substitutional solid solution, Interstitial solid Solution**
- ✚ **Crystalline Imperfections:**
 - Zero-dimensional defects: point defects**
 - One-dimensional defects: line defects**
 - Two-dimensional defects: external surface, grain boundaries, twins, low-angle and high-angle boundaries,**
 - Three dimensional defects: pore, cracks, and foreign inclusions.**
- ✚ **Experimental techniques for identification of microstructure and defects:**
 - Optical metallography, Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), High-Resolution Transmission Electrons Microscopy (HRTEM), Scanning probe microscopes (STM, AFM)**



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.



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

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

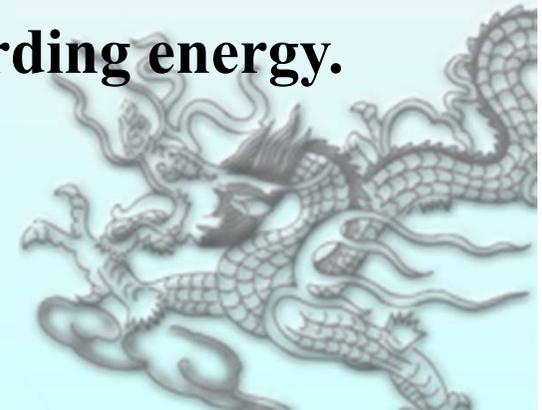
Surface energy G_s

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

Then

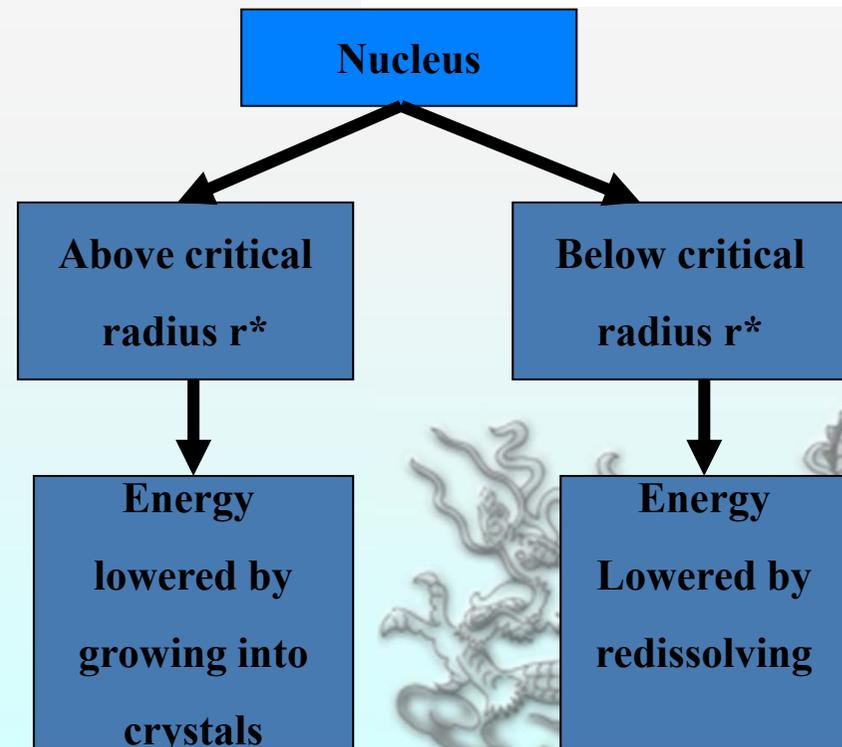
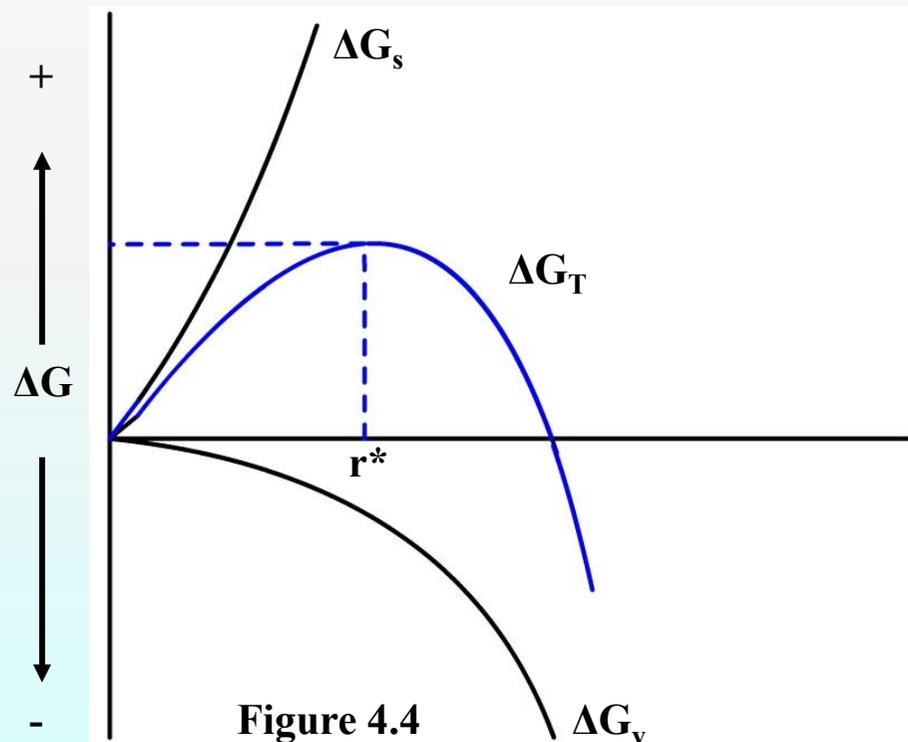
$$\Delta G_s = 4\pi r^2 \gamma$$

- ◆ 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 $r=r^*$, $d(\Delta G_T)/dr = 0$
- $$r^* = -\frac{2\gamma}{\Delta G_v}$$
- $$\frac{d(\Delta G_T)}{dr} = \frac{d}{dr} \left(\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma \right)$$
- $$\frac{12}{3}\pi r^{*2} \Delta G_v + 8\pi r^* \gamma = 0$$
- $$r^* = -\frac{2\gamma}{\Delta G_v}$$



Critical Radius Versus Undercooling

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

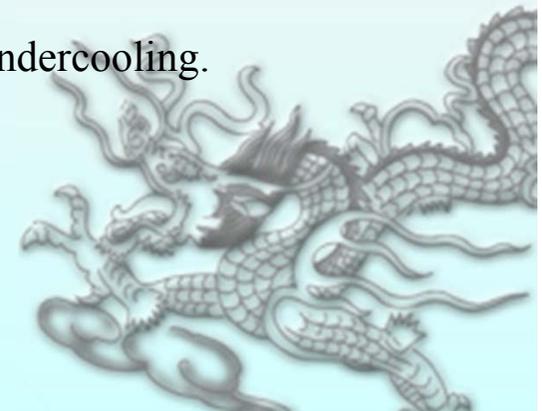
$$r^* = \frac{2\gamma T_m}{\Delta H_f \Delta T}$$

r^* = critical radius of nucleus

γ = Surface free energy

ΔH_f = Latent heat of fusion

ΔT = Amount of undercooling.



Example Problem 4.1

- Calculate the critical radius (in centimeters) of a homogeneous nucleus that forms when pure liquid copper solidifies. Assume ΔT (undercooling) = $0.2T_m$. Use data from Table 4.1.
- Calculate the number of atoms in the critical-sized nucleus at this undercooling.

■ Solution

- Calculation of critical radius of nucleus:

$$r^* = \frac{2 T_m}{\Delta H_f \Delta T} \quad (4.2)$$

$$\Delta T = 0.2T_m = (0.2 \times 1356 \text{ K}) = 271 \text{ K}$$

$$\gamma = 177 \times 10^{-3} \text{ J/m}^2 \quad \Delta H_f = 1826 \times 10^6 \text{ J/m}^3 \quad T_m = 1356 \text{ K}$$

$$r^* = \frac{2(177 \times 10^{-3} \text{ J/m}^2)(1356 \text{ K})}{(1826 \times 10^6 \text{ J/m}^3)(271 \text{ K})} = 0.97 \text{ nm} \quad \blacktriangleleft$$

- Calculation of number of atoms in critical-sized nucleus:

$$\begin{aligned} \text{Vol. of critical-sized nucleus} &= \frac{4}{3}\pi r^{*3} = \frac{4}{3}\pi (0.97 \text{ nm})^3 \\ &= 3.82 \text{ nm}^3 \end{aligned}$$

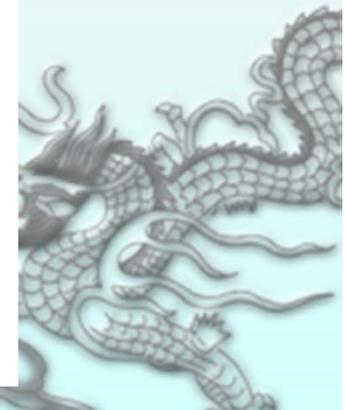
$$\begin{aligned} \text{Vol. of unit cell of Cu } (a = 0.361 \text{ nm}) &= a^3 = (0.361 \text{ nm})^3 \\ &= 0.047 \text{ nm}^3 \end{aligned}$$

Since there are four atoms per FCC unit cell,

$$\text{Volume/atom} = \frac{0.047 \text{ nm}^3}{4} = 0.012 \text{ nm}^3$$

Thus, the number of atoms per homogeneous critical nucleus is

$$\frac{\text{Volume of nucleus}}{\text{Volume/atom}} = \frac{3.82 \text{ nm}^3}{0.012 \text{ nm}^3} = 318 \text{ atoms} \quad \blacktriangleleft$$



Heterogenous Nucleation

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

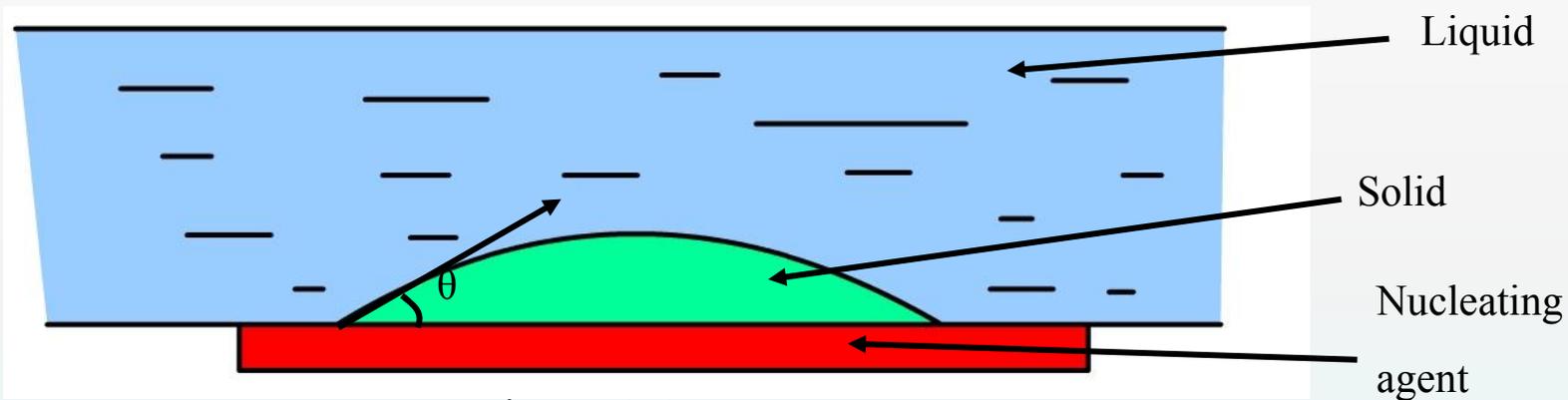
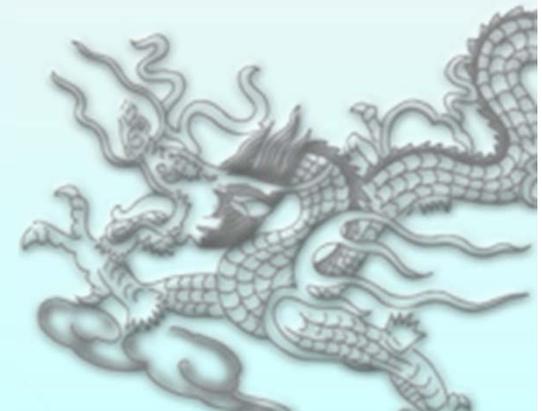


Figure 4.6

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

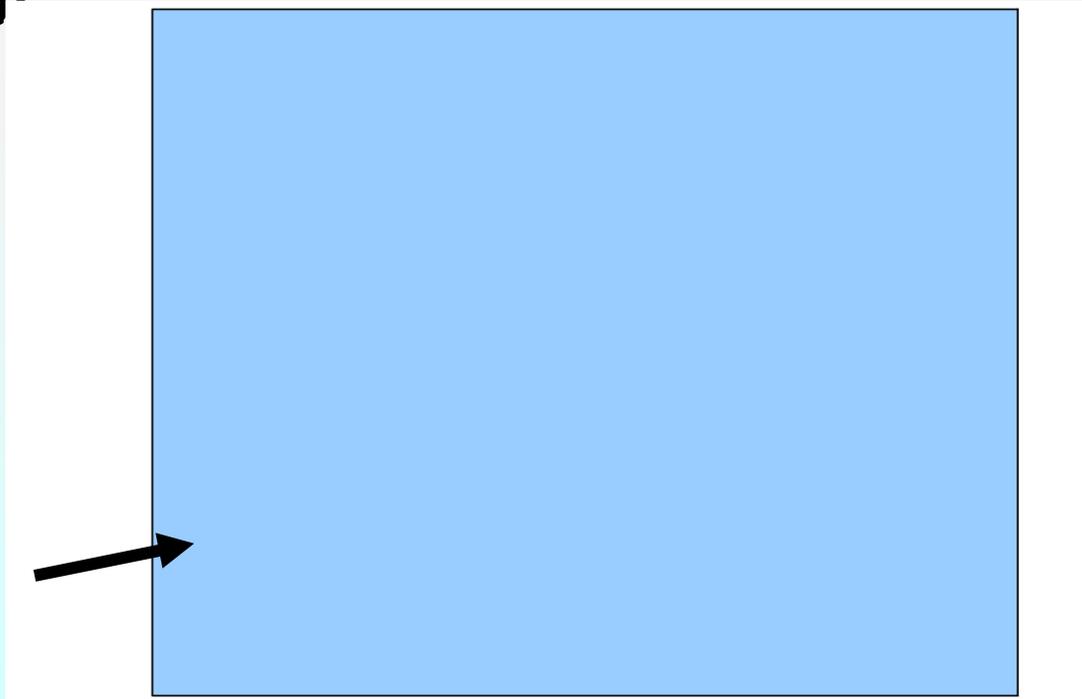


Growth of Crystals and Formation of Grain Structure

- ◆ 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 nuclei.
- 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.

Columnar Grains

Equiaxed Grains

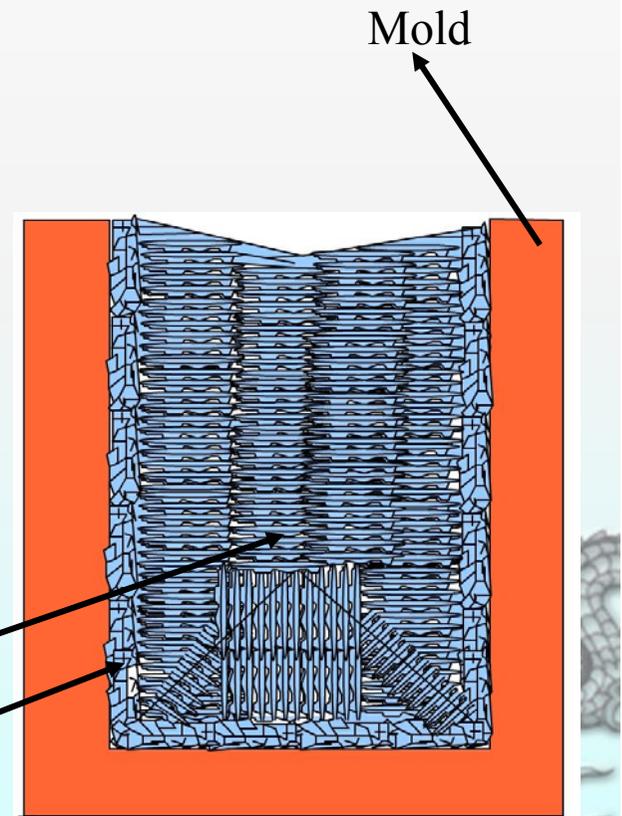


Figure 4.7a

Casting in Industries

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

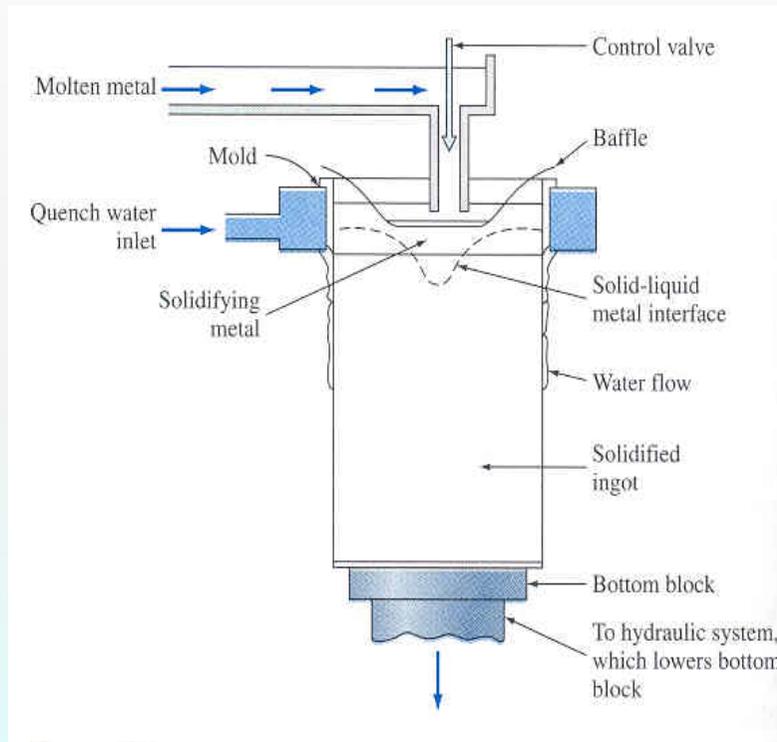


Figure 4.8

Direct-Chill semicontinuous
Casting unit for aluminum

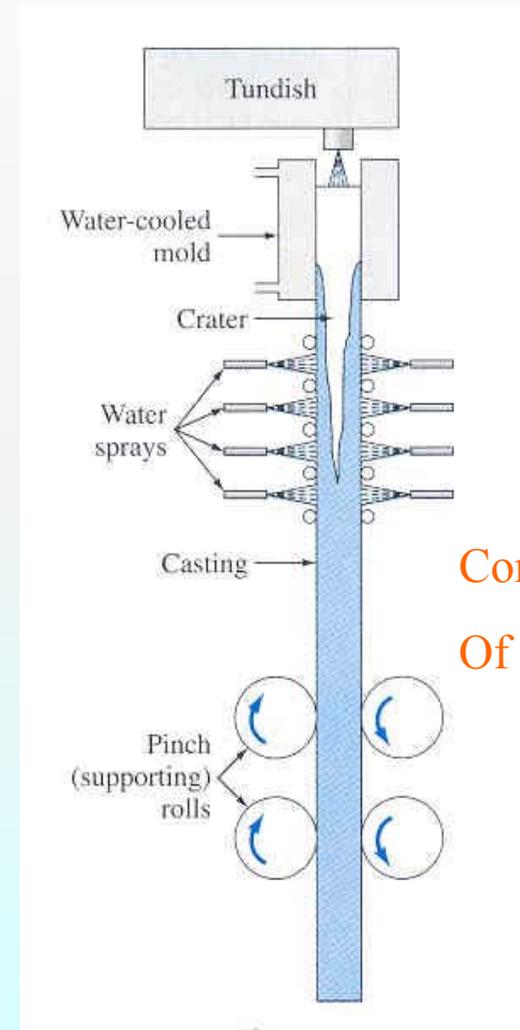
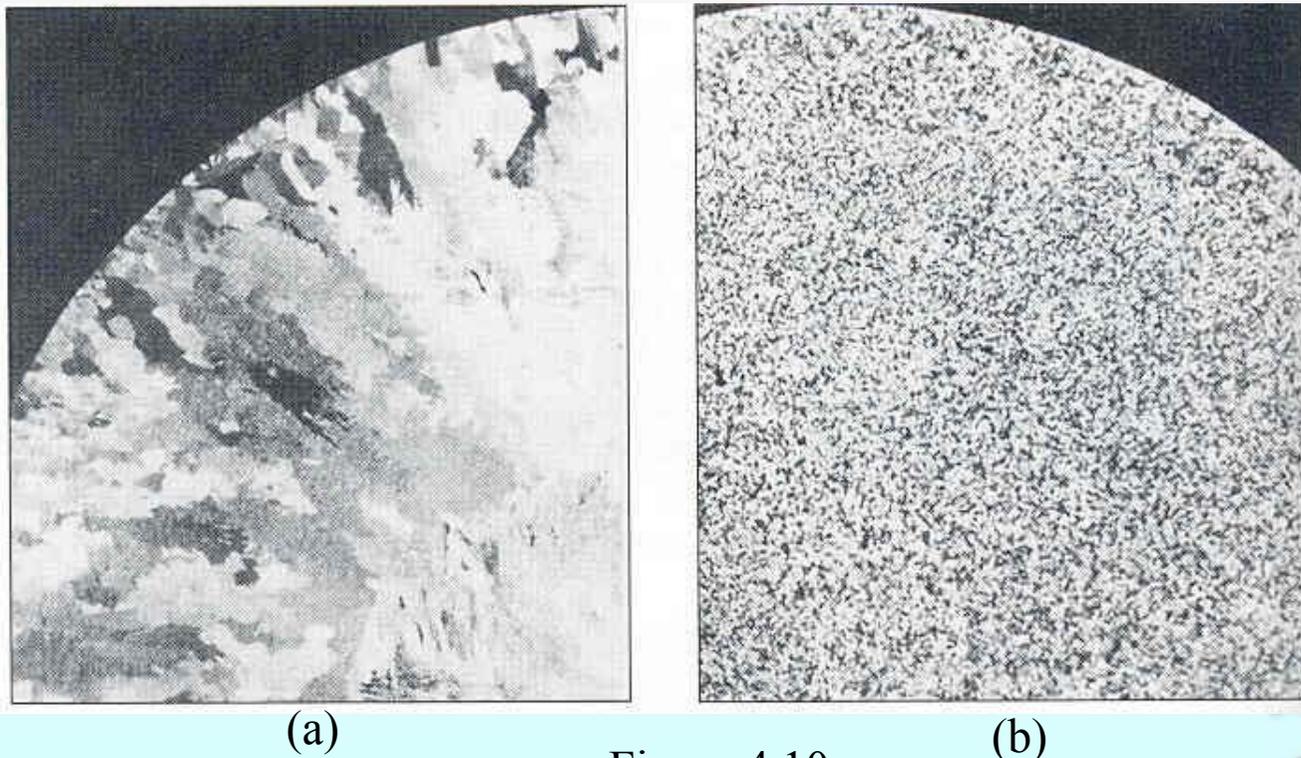


Figure 4.9b

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.



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

Figure 4.10

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 heat 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.

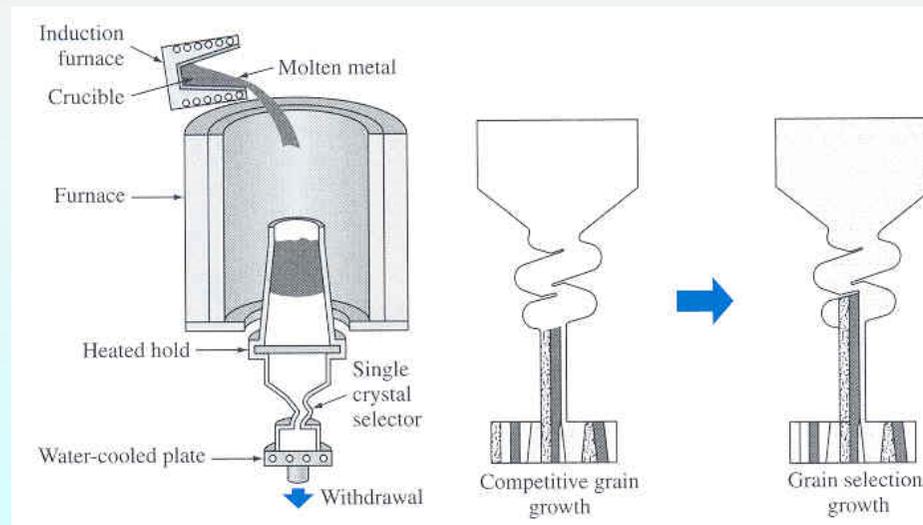


Figure 4.12

Growth of single
crystal for turbine
airfoil.

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.

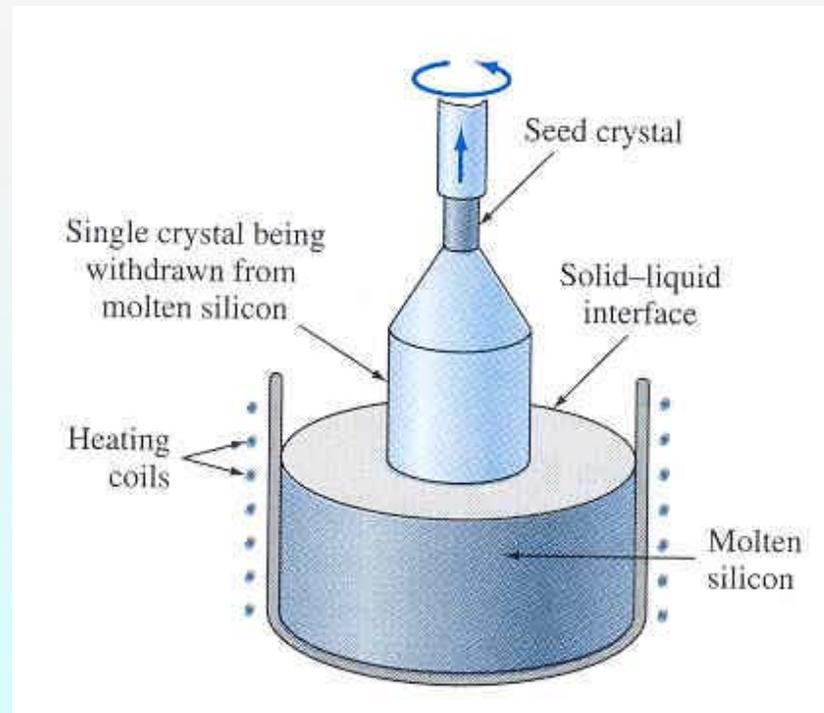
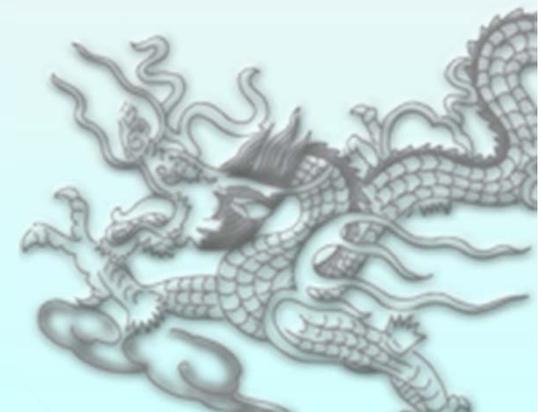
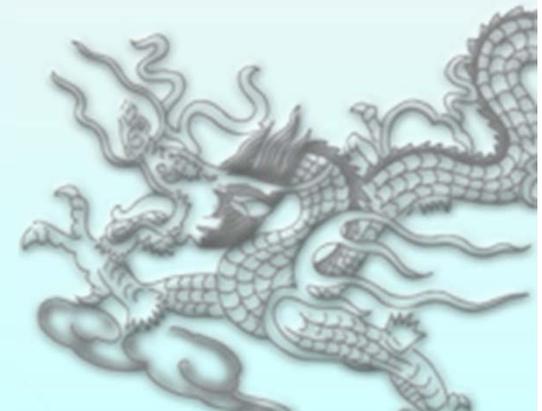


Figure 4.13



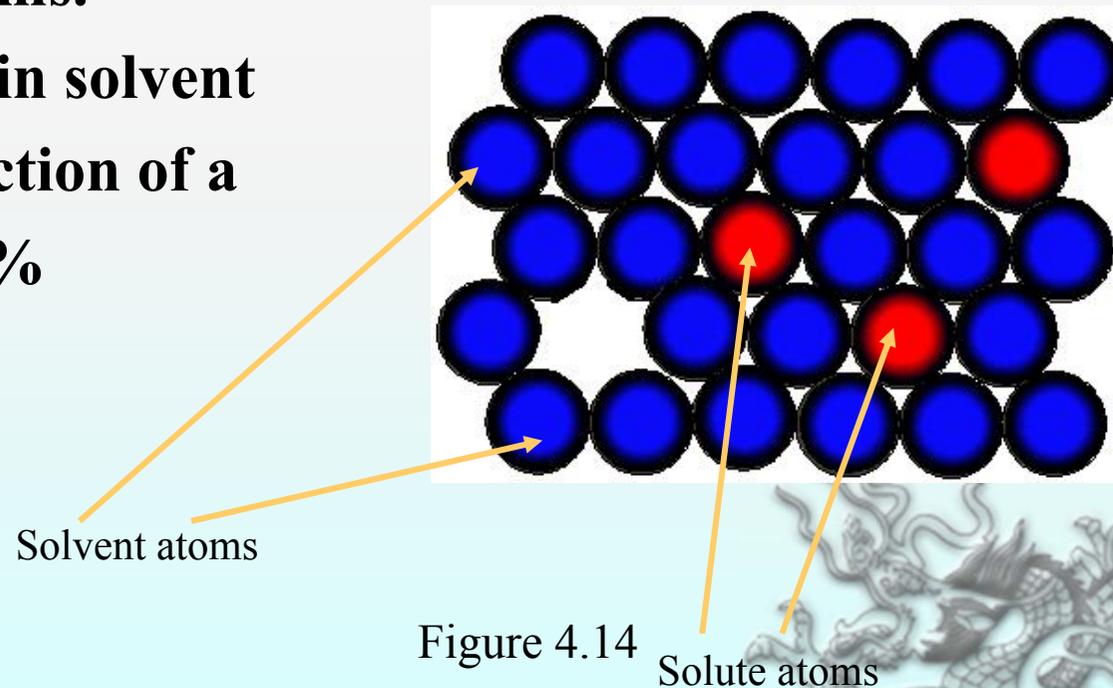
Metallic Solid Solutions

- ◆ Alloys are used in most engineering applications.
- ◆ **Alloy** is a mixture of two or more metals and nonmetals.
- ◆ **Example:**
 - **Cartridge brass** is a binary alloy of 70% Cu and 30% Zn.
 - **Inconel** 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 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%



Substitutional Solid Solution (Cont.)

- ◆ The **solubility** of solids is greater if (Hume-Rothery rules)
 - 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 same valence.

◆ Examples:-

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

Example Problem 4.2

Using the data in the following table, predict the relative degree of atomic solid solubility of the following elements in copper:

- a. Zinc
- b. Lead
- c. Silicon
- d. Nickel
- e. Aluminum
- f. Beryllium

Use the scale very high, 70%–100%; high, 30%–70%; moderate, 10%–30%; low, 1%–10%; and very low, <1%.

Element	Atom radius (nm)	Crystal structure	Electronegativity	Valence
Copper	0.128	FCC	1.8	+2
Zinc	0.133	HCP	1.7	+2
Lead	0.175	FCC	1.6	+2, +4
Silicon	0.117	Diamond cubic	1.8	+4
Nickel	0.125	FCC	1.8	+2
Aluminum	0.143	FCC	1.5	+3
Beryllium	0.114	HCP	1.5	+2

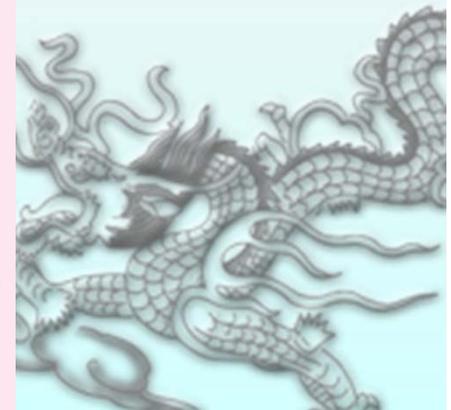
■ Solution

A sample calculation for the atomic radius difference for the Cu–Zn system is

$$\begin{aligned}\text{Atomic radius difference} &= \frac{\text{final radius} - \text{initial radius}}{\text{initial radius}} (100\%) \\ &= \frac{R_{\text{Zn}} - R_{\text{Cu}}}{R_{\text{Cu}}} (100\%) \quad (4.3) \\ &= \frac{0.133 - 0.128}{0.128} (100\%) = +3.9\%\end{aligned}$$

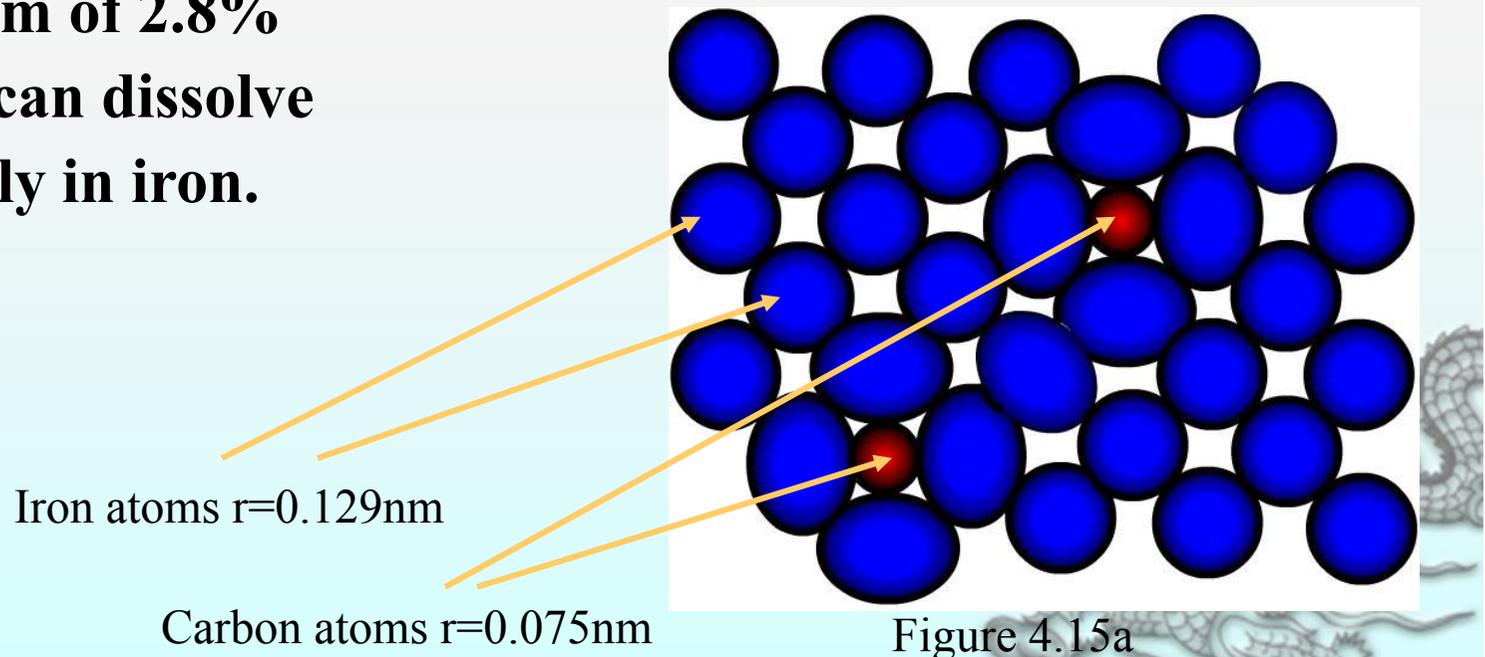
System	Atomic radius difference (%)	Electronegativity difference	Predicted relative degree of solid solubility	Observed maximum solid solubility (at %)
Cu–Zn	+3.9	0.1	High	38.3
Cu–Pb	+36.7	0.2	Very low	0.1
Cu–Si	–8.6	0	Moderate	11.2
Cu–Ni	–2.3	0	Very high	100
Cu–Al	+11.7	0.3	Moderate	19.6
Cu–Be	–10.9	0.3	Moderate	16.4

The predictions can be made principally on the atomic radius difference. In the case of the Cu–Si system, the difference in the crystal structures is important. There is very little electronegativity difference for all these systems. The valences are all the same except for Al and Si. In the final analysis, the experimental data must be referred to.



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 1394⁰C, interstitial solid solution of carbon in γ iron (**FCC**) is formed.
- ◆ A maximum of 2.8% of carbon can dissolve interstitially in iron.



Example Problem 4.3

Calculate the radius of the largest interstitial void in the FCC γ iron lattice. The atomic radius of the iron atom is 0.129 nm in the FCC lattice, and the largest interstitial voids occur at the $(\frac{1}{2}, 0, 0)$, $(0, \frac{1}{2}, 0)$, $(0, 0, \frac{1}{2})$, etc., $\frac{1}{2}$ -type positions.

■ Solution

Figure EP4.3 shows a (100) FCC lattice plane on the yz plane. Let the radius of an iron atom be R and that of the interstitial void at the position $(0, \frac{1}{2}, 0)$ be r . Then, from Fig. EP4.3,

$$2R + 2r = a \quad (4.4)$$

Also from Fig. 4.15b,

$$(2R)^2 = (a)^2 + (a)^2 = a^2 \quad (4.5)$$

Solving for a gives

$$2R = \frac{1}{\sqrt{2}}a \quad \text{or} \quad a = 2\sqrt{2}R \quad (4.6)$$

Combining Eqs. 4.4 and 4.6 gives

$$\begin{aligned} 2R + 2r &= 2\sqrt{2}R \\ r &= (\sqrt{2} - 1)R = 0.414R \\ &= (0.414)(0.129 \text{ nm}) = 0.053 \text{ nm} \blacktriangleleft \end{aligned}$$

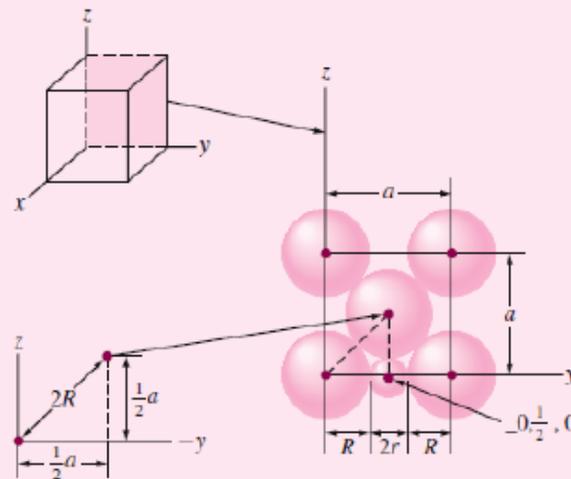
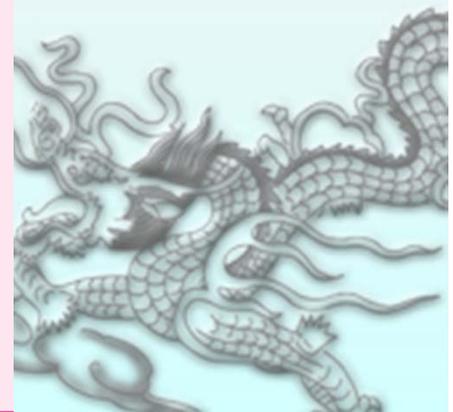


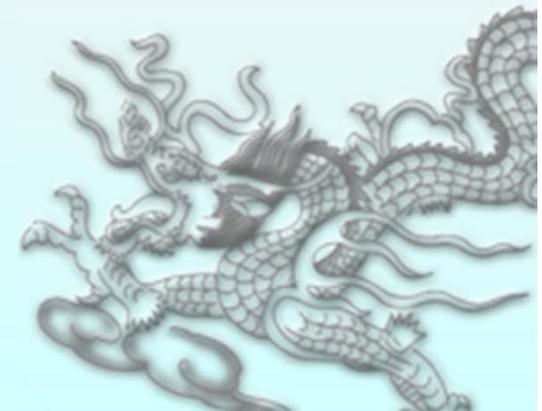
Figure EP4.3

(100) plane of the FCC lattice containing an interstitial atom at the $(0, \frac{1}{2}, 0)$ position coordinate.



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.

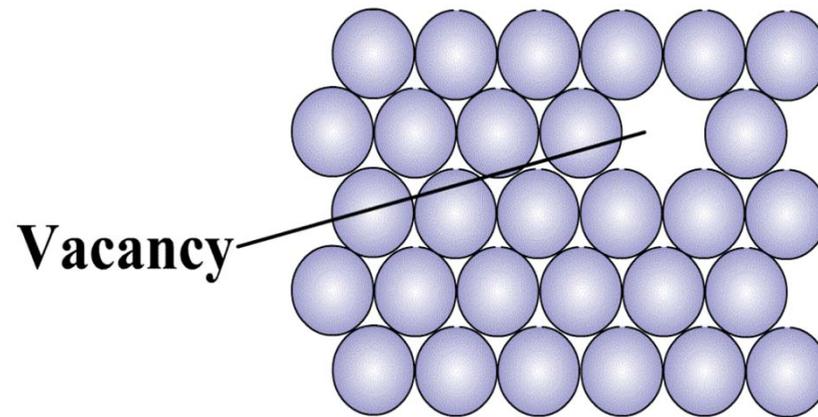


Figure: Vacancies moving to form vacancy cluster

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.

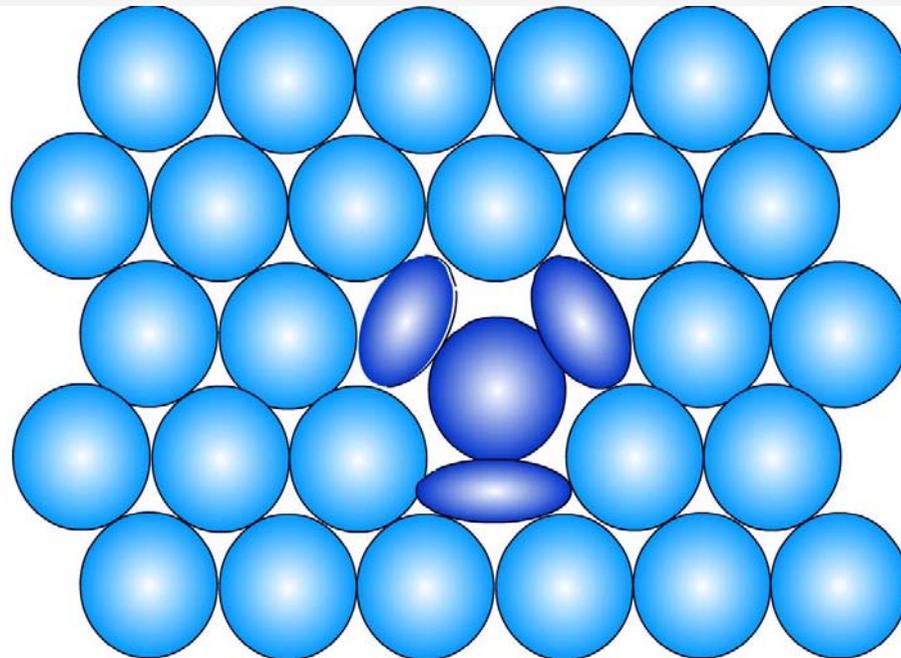
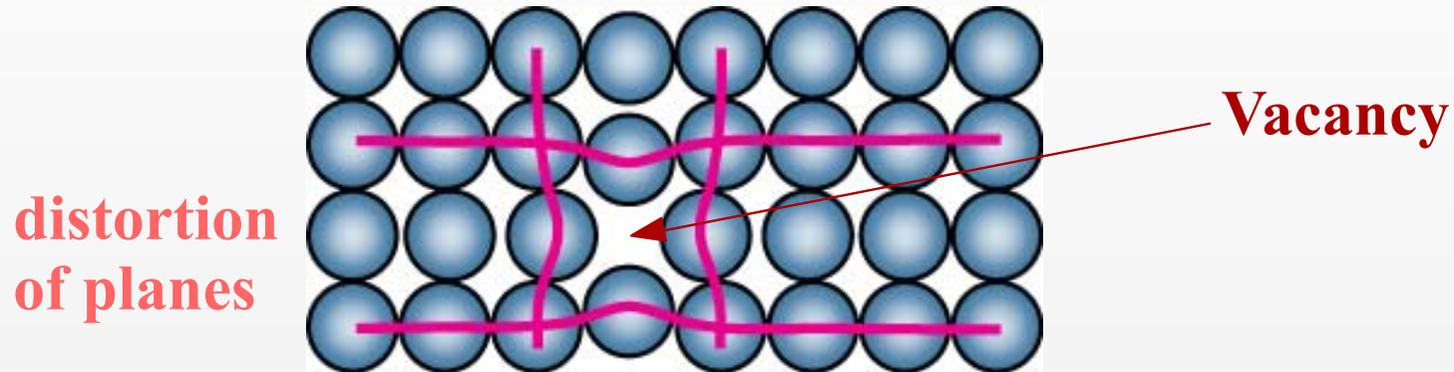


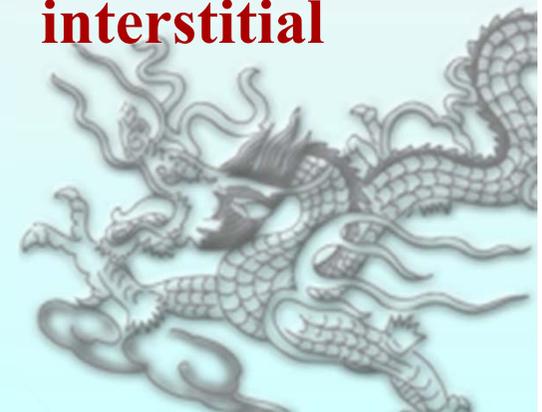
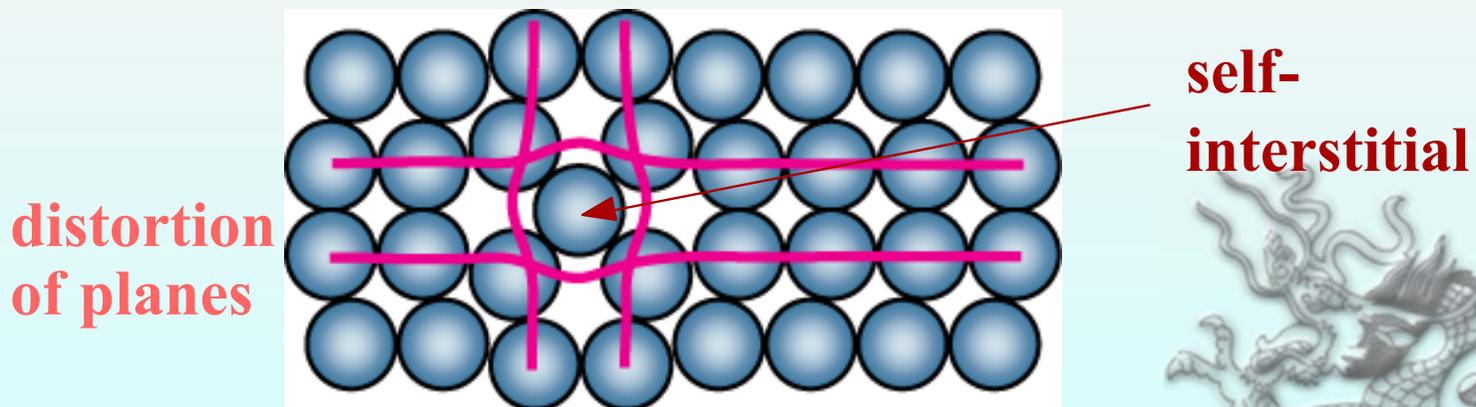
Figure 4.16b

Point Defects

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



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



Point Defects in Ionic Crystals

- ◆ Complex as electric neutrality has to be maintained.
- ◆ If two oppositely 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.

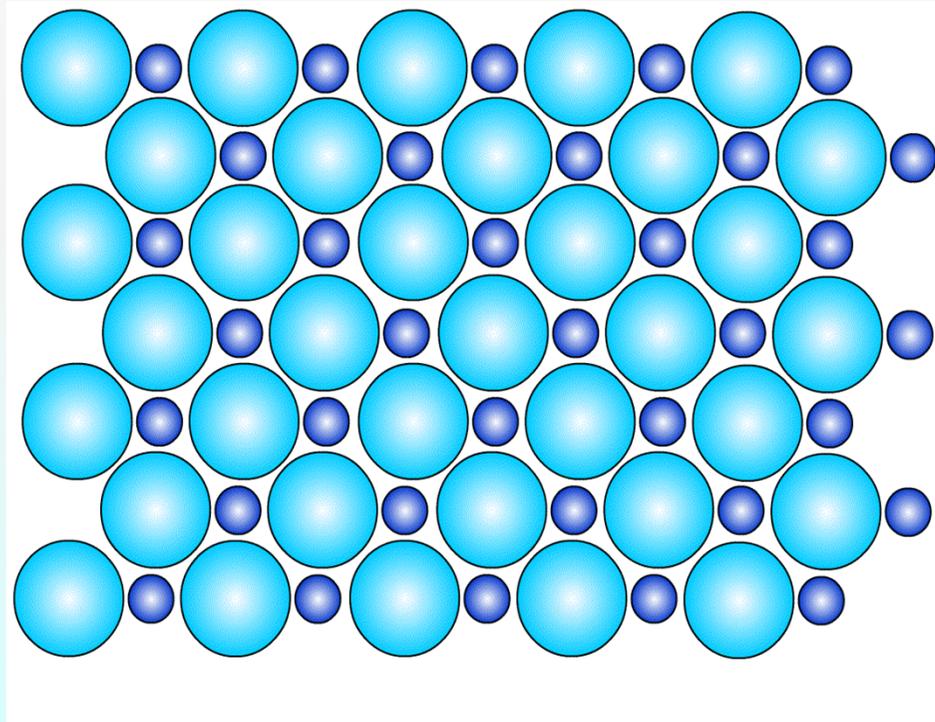
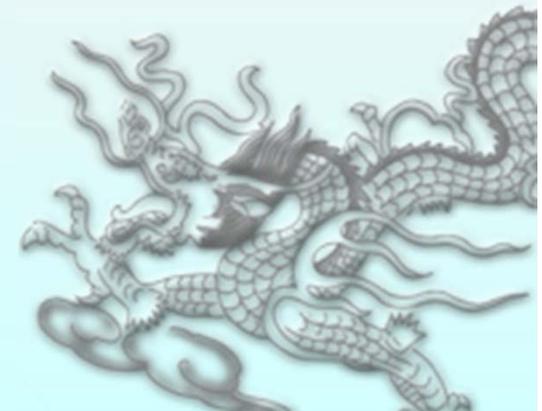


Figure 4.17

Line Defects – (Dislocations)

- ◆ **Lattice distortions are **centered** around a line.**
- ◆ **Formed during**
 - **Solidification**
 - **Permanent Deformation**
 - **Vacancy condensation**
- ◆ **Different types of line defects are**
 - **Edge dislocation (刃差排)**
 - **Screw dislocation (螺絲差排)**
 - **Mixed dislocation**



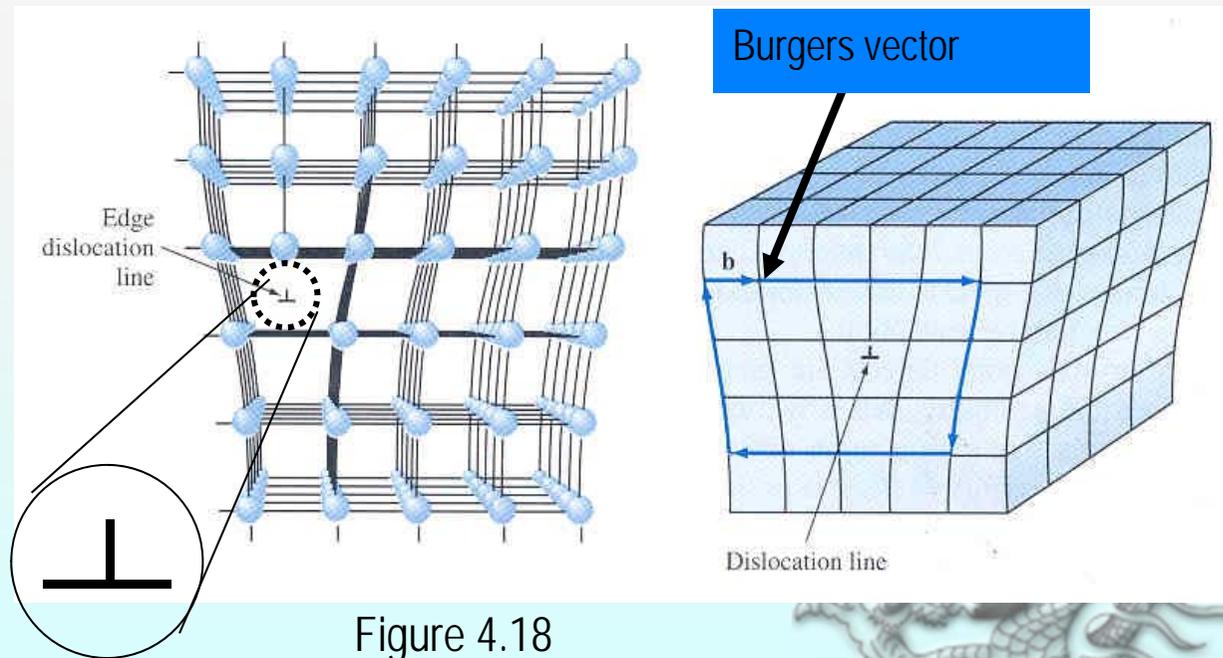
Edge Dislocation

- Created by insertion of **extra half planes** of atoms.

  **Positive edge dislocation**

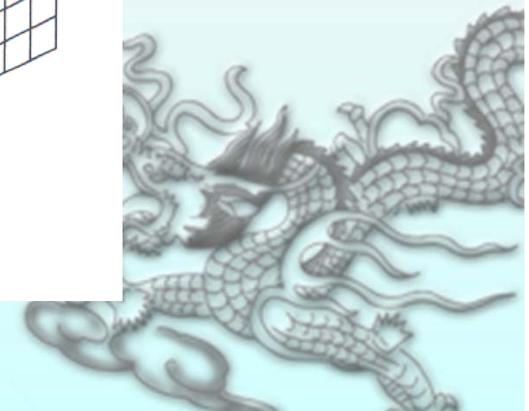
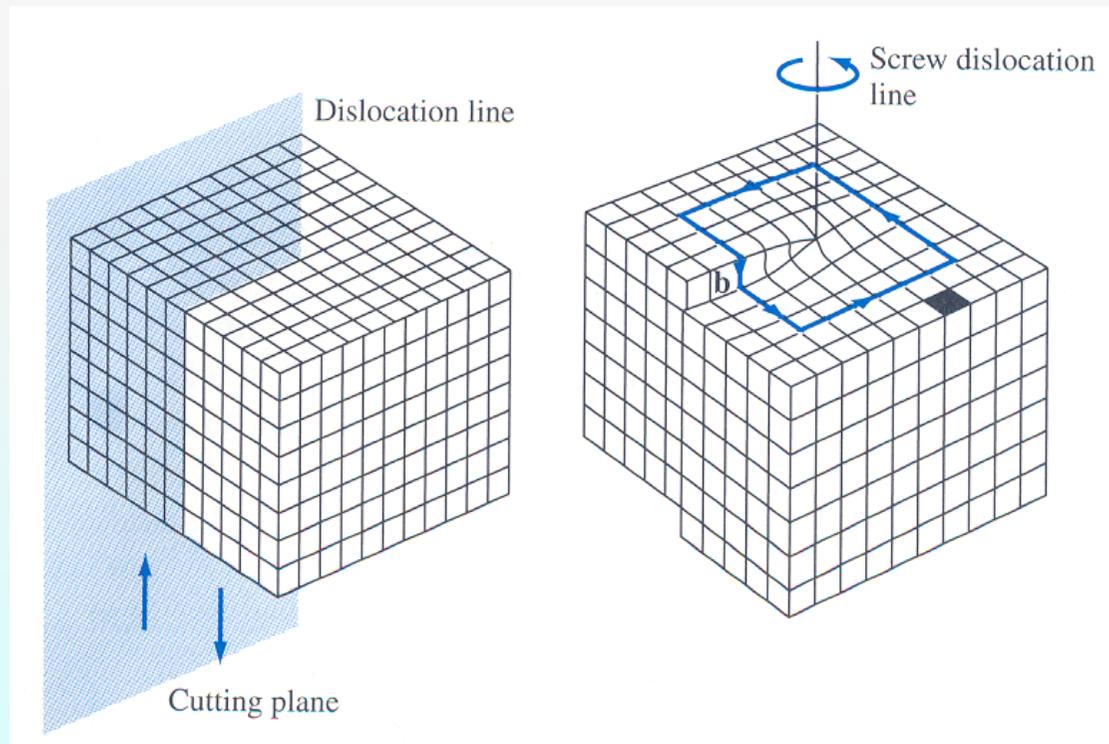
  **Negative edge dislocation**

- Burgers vector**
Shows displacement of atoms (slip).
Burger's circuit



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.



Dislocations 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:**
 - ◇ resulting from shear deformation
 - ◇ $\mathbf{b} \parallel$ to dislocation line

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



Mixed Dislocation

- ◆ Most crystals have components of **both** edge and screw dislocation.
- ◆ Dislocation, since have irregular atomic arrangement will appear as **dark lines** when observed in electron microscope.

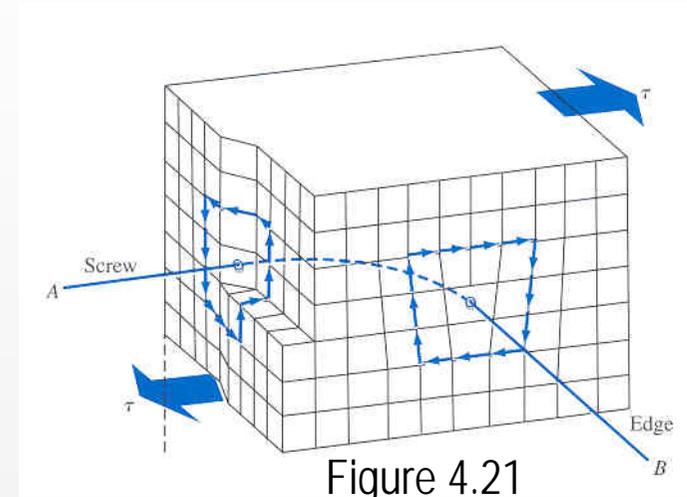


Figure 4.21

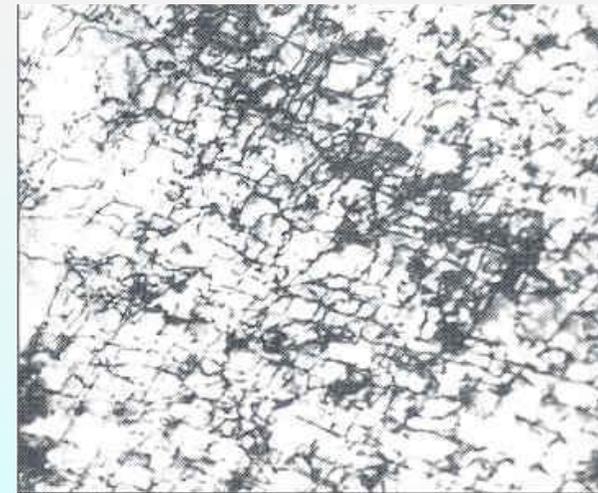
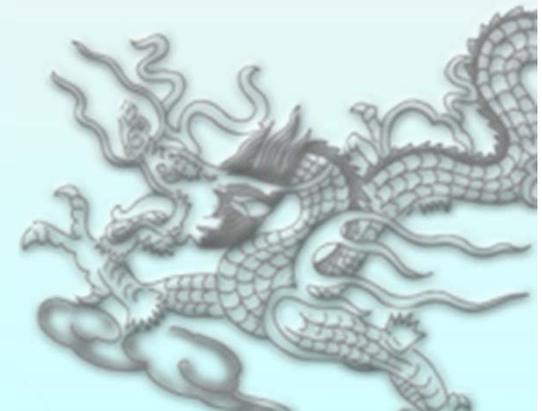


Figure 4.22

**Dislocation structure of iron deformed
14% at -195°C**

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.



Grain Boundaries

- ◆ Grain boundaries separate grains.
- ◆ Formed due to **simultaneously growing** crystals meeting each other.
- ◆ Width = 2-5 atomic diameters.
- ◆ Some atoms in grain boundaries have **higher energy**.
- ◆ Restrict plastic flow and prevent dislocation movement.

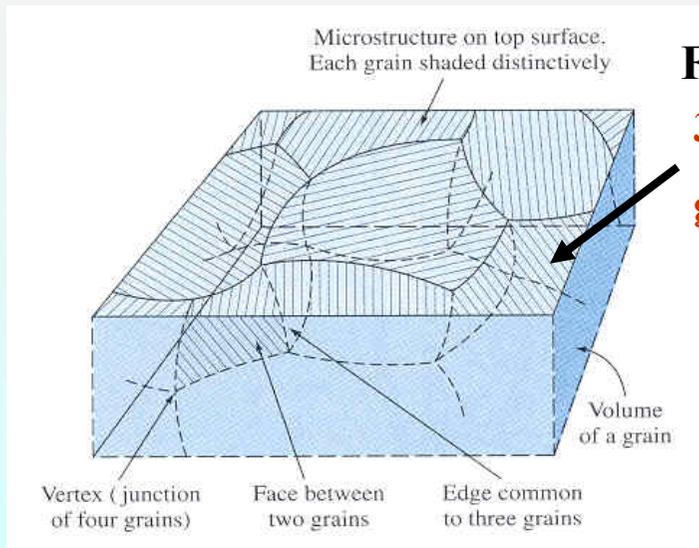
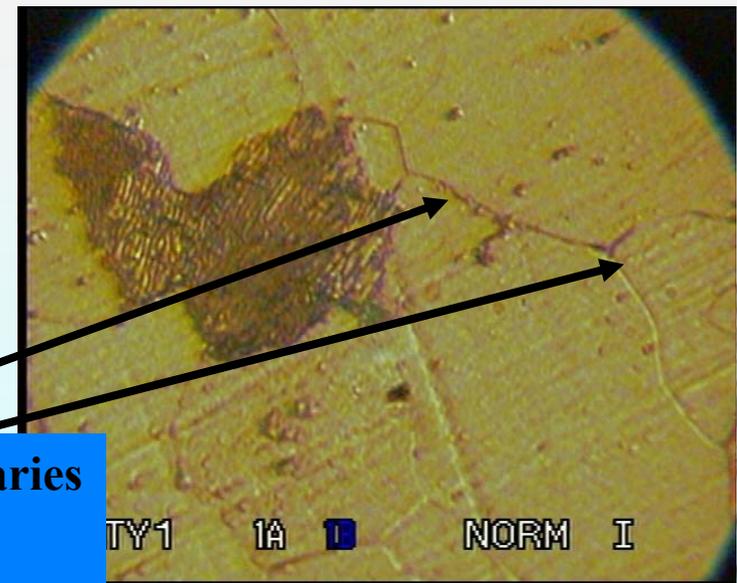


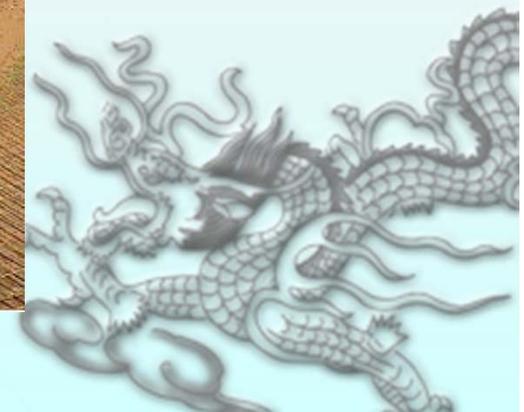
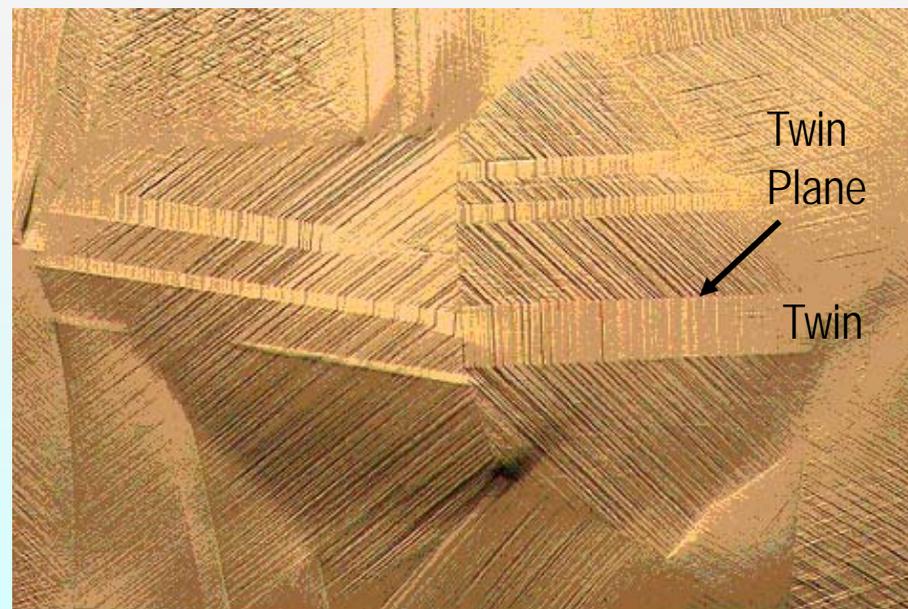
Figure 4.25
3D view of
grains

Grain Boundaries
In 1018 steel

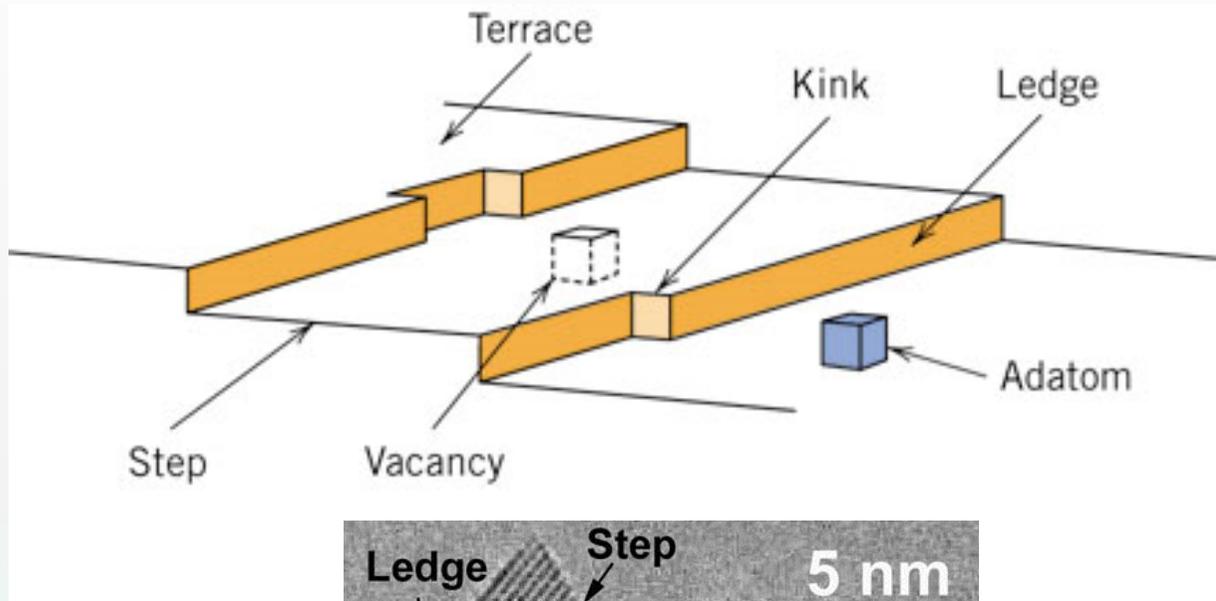


Twin Boundaries

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



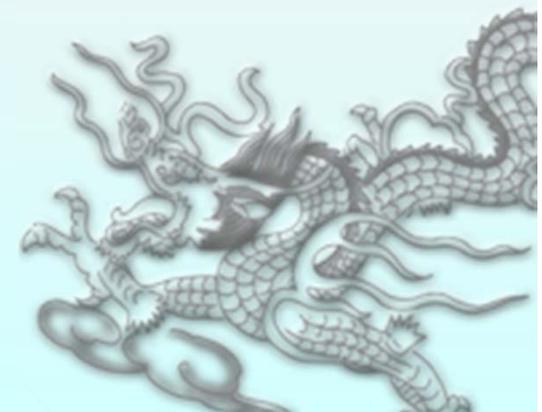
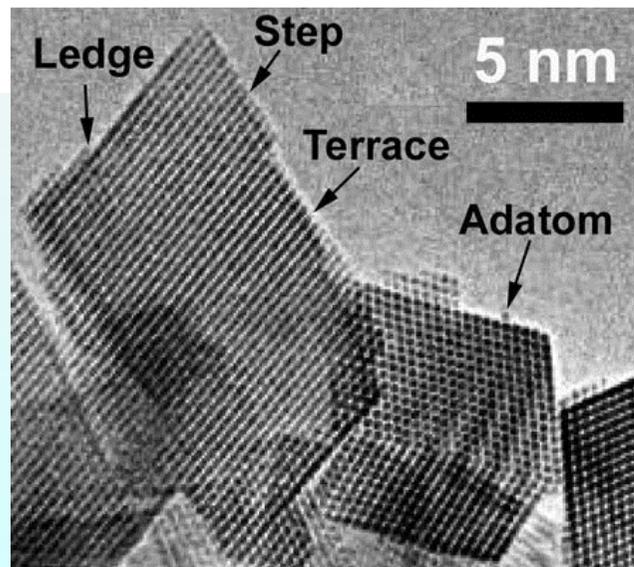
Free Surfaces



Atoms at the crystal surface possess incomplete bonding

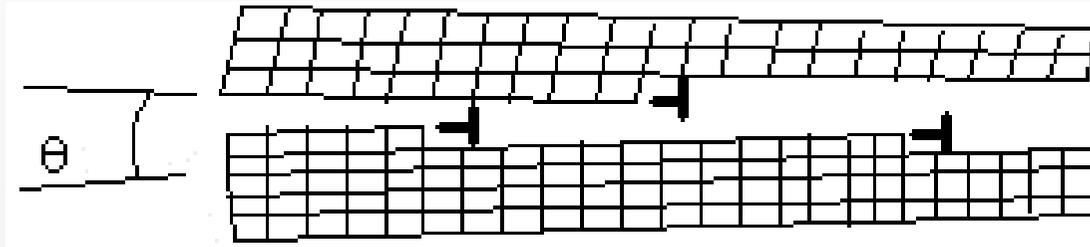
Extra energy due to unsatisfied bonds → enhanced chemical reactivity at surfaces (catalysis)

Example: Three-Way Catalytic Converter (TWC) in cars
($\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$)



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: ABCAB**A**CBABC \longrightarrow FCC fault



Observing Grain Boundaries - Metallography

- ◆ To observe grain boundaries, the metal sample must be first **mounted** for easy handling
- ◆ Then the sample should be **ground and polished** with different grades of abrasive paper and abrasive solution.
- ◆ The surface is then **etched** chemically.
- ◆ Tiny grooves are produced at grain boundaries.
- ◆ Grooves do not intensely reflect light. Hence observed by optical microscope.

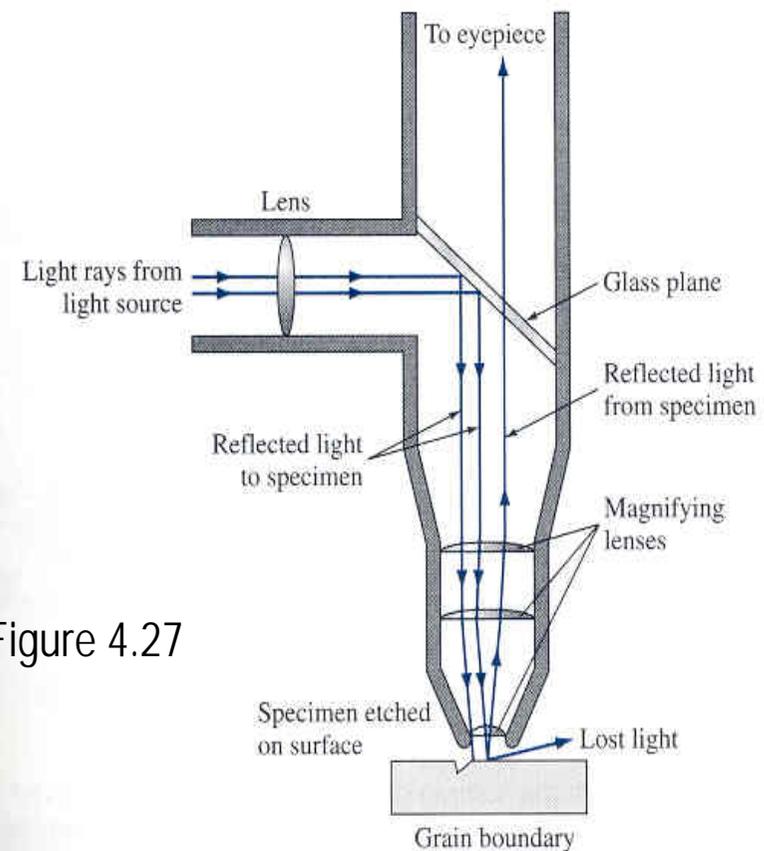


Figure 4.27

Effect of Etching

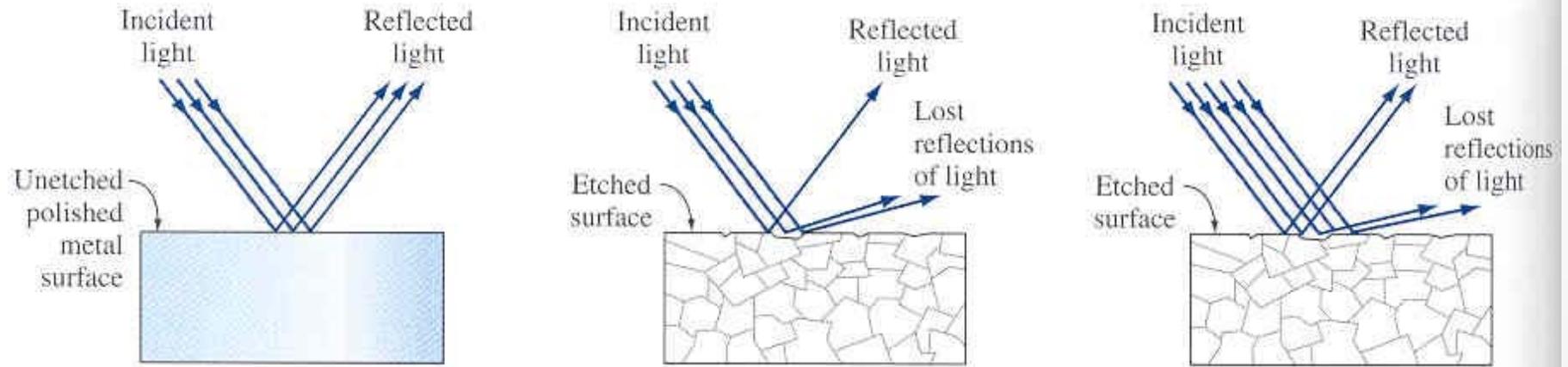
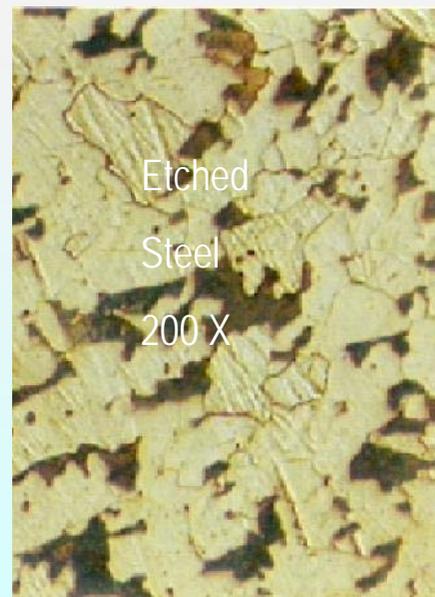


Figure 4.28



Unetched
Steel
200 X



Etched
Steel
200 X



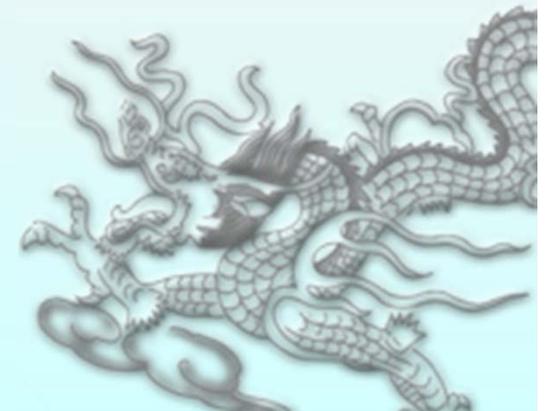
Unetched
Brass
200 X



Etched
Brass
200 X

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.**

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

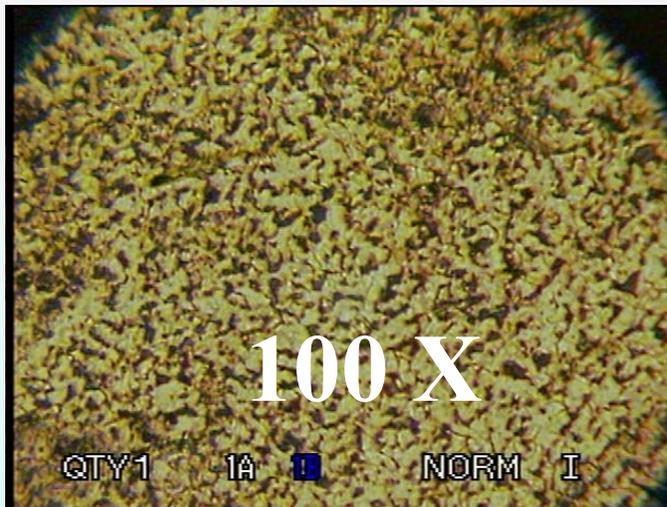
$N < 3$ – Coarse grained

$4 < n < 6$ – Medium grained

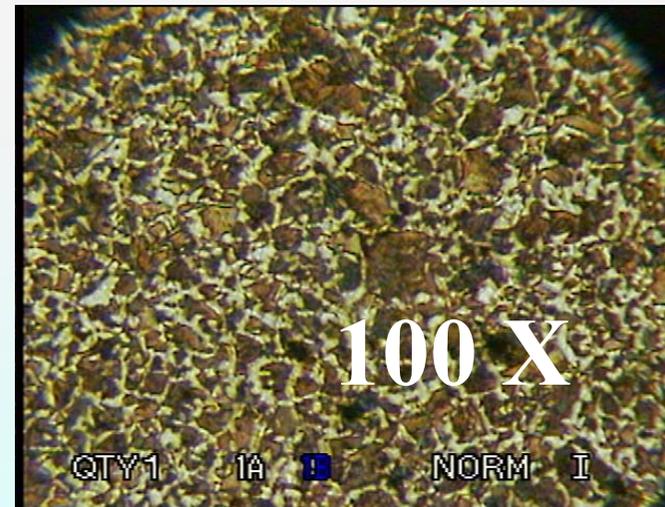
$7 < n < 9$ – Fine grained

$N > 10$ – ultrafine grained

N = Number of grains per square inch of a polished and etched specimen at 100 x.
n = ASTM grain size number per $2.54 \times 10^{-2} \text{ m}^2$



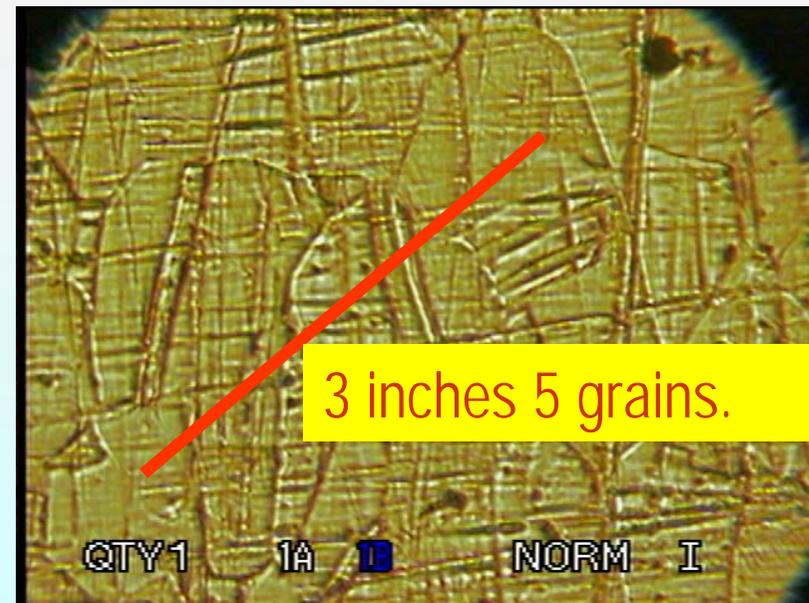
1018 cold rolled steel, $n=10$



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.



Example Problem 4.4

An ASTM grain size determination is being made from a photomicrograph of a metal at a magnification of 100 \times . What is the ASTM grain-size number of the metal if there are 64 grains per square 2.54×10^{-2} m?

■ Solution

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

where N = no. of grains per square inch at 100 \times

n = ASTM grain-size number

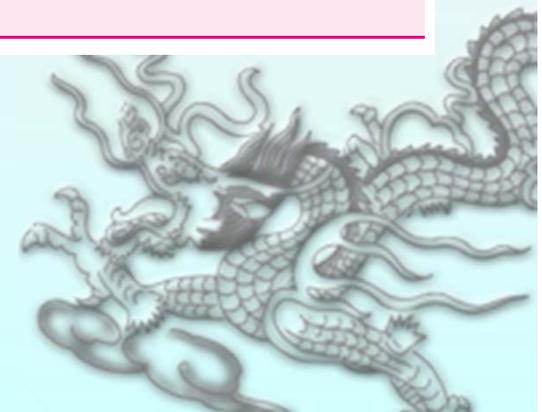
Thus,

$$64 \text{ grains}/(2.54 \times 10^{-2} \text{ m})^2 = 2^{n-1}$$

$$\log 64 = (n - 1)(\log 2)$$

$$1.806 = (n - 1)(0.301)$$

$$n = 7 \blacktriangleleft$$



Example Problem 4.5

If there are 60 grains per square 2.54×10^{-2} m on a photomicrograph of a metal at $200\times$, what is the ASTM grain-size number of the metal?

■ Solution

If there are 60 grains per square 2.54×10^{-2} m at $200\times$, then at $100\times$ we will have

$$N = \left(\frac{200}{100}\right)^2 [60 \text{ grains}/(2.54 \times 10^{-2} \text{ m})^2] = 240 = 2^{n-1}$$

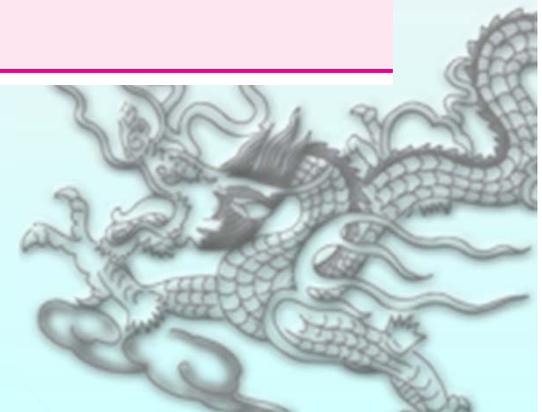
$$\log 240 = (n - 1)(\log 2)$$

$$2.380 = (n - 1)(0.301)$$

$$n = 8.91 \blacktriangleleft$$

Note that the ratio of the magnification change must be squared since we are concerned with the number of grains per square 2.54×10^{-2} m.

$$200/100=2.54^{10^{-2}/X}$$



Scanning electron microscope

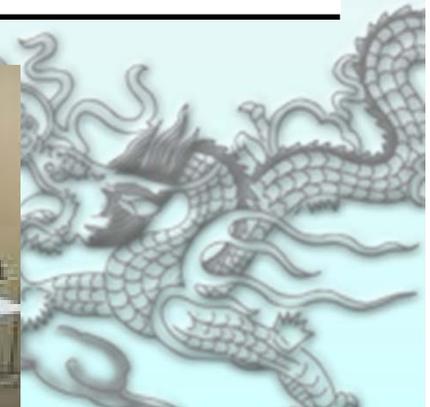


電子顯微鏡與光學顯微鏡比較

	光學顯微鏡	掃描式電鏡	穿透式電鏡
光源	可見光	電子槍	電子槍
透鏡	玻璃透鏡	電磁透鏡	電磁透鏡
放大倍率	1000~2000倍	10萬倍	100萬倍
解析度	0.2 μ m	1~10nm	0.1nm~
真空環境	不需要	需要	需要
景深	0.1~5 μ m	0.1mm	500 μ m
影像色彩	真實色彩	黑白	黑白
成分分析	無	可	可
樣品	大	大	薄,小
金屬鍍膜	不需	需	不需
影像	表面或穿透影像	表面影像	穿透影像

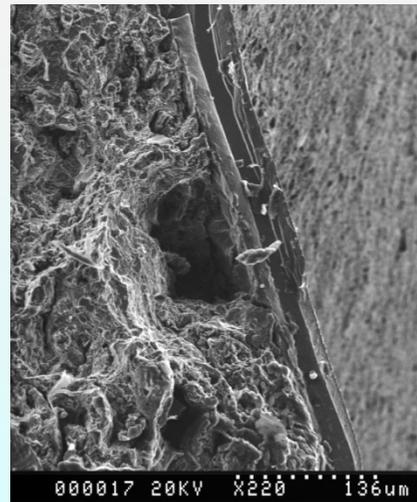


44 果蠅的複眼是由許多小眼所組成 life.nthu.edu.tw



Scanning Electron Microscope

- ◆ Electron source generates electrons.
- ◆ Electrons hit the surface and **secondary electrons** are produced.
- ◆ The secondary electrons are collected to produce the signal.
- ◆ The signal is used to produce the image.



TEM of fractured metal end

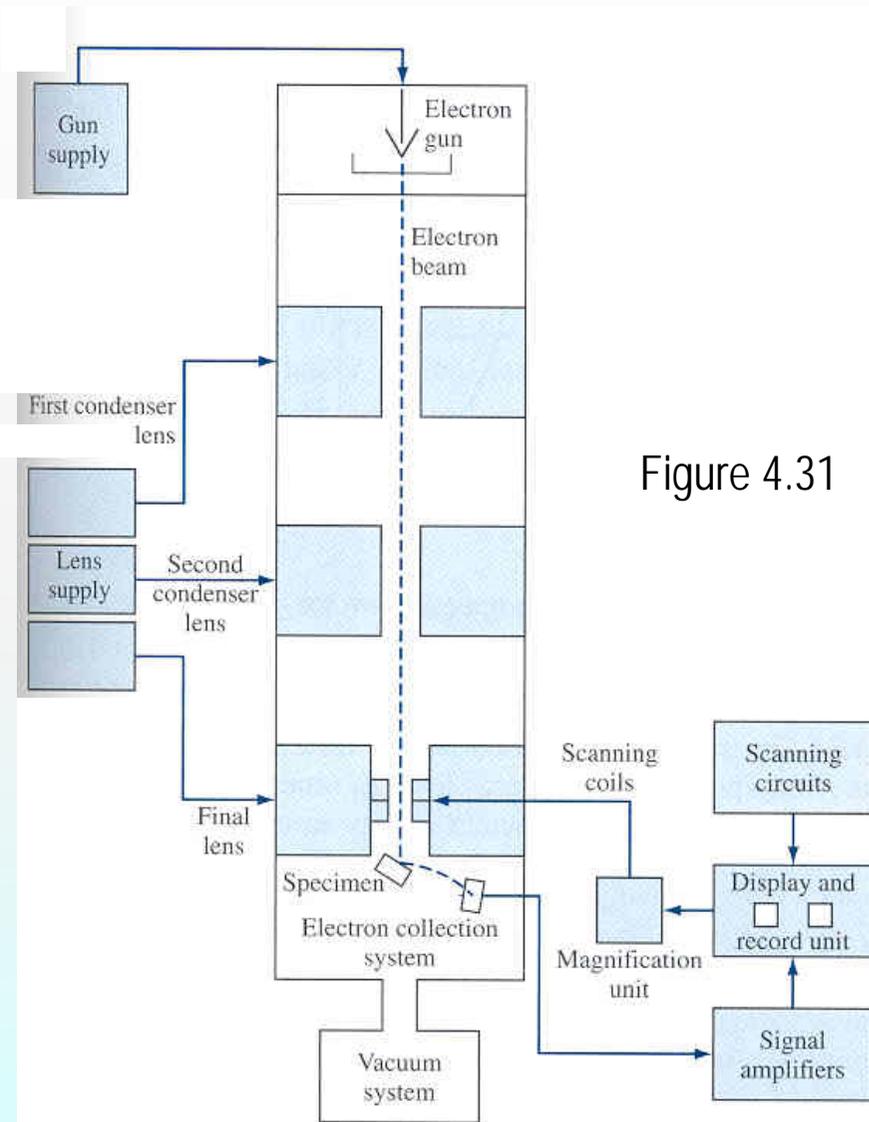
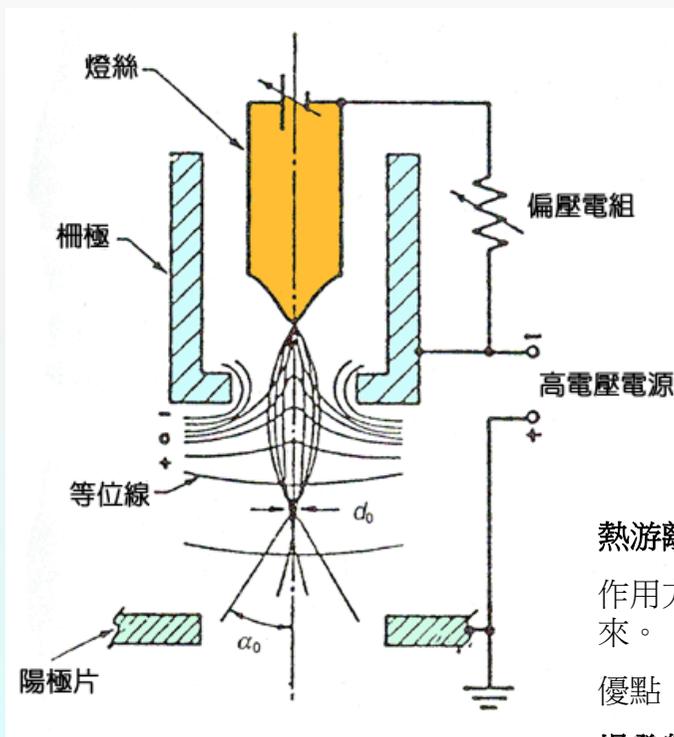


Figure 4.31

電子槍

操作的時候，燈絲會進行加熱，並通入負電壓，一般為1~50kV。另外有一柵極在燈絲的周圍，加入一個負偏壓(0~2500V)，其功能主要可以聚焦成一個如下圖所示 d_0 大小的交叉點，由此交叉點開始再進入接下來的各種聚焦透鏡，來對電子束進行壓縮。



一般的鎢燈絲設計為一個彎成V形的細線，其操作溫度大約在2700K，電流密度為 $1.75\text{A}/\text{cm}^2$ ，其使用壽命高達200小時。除了一般的鎢燈絲，還有另一種稱為場發射的電子束來源，它的陰極採用棒狀的形式，尖端的直徑小於100奈米，加入負電壓的時候，其尖端電場可達到 $10^7\text{V}/\text{cm}^2$ ，因此電子可經隧道效應，在不加熱的情況下直接離開陰極，其電流密度可達 $1000\sim 10^6\text{A}/\text{cm}^2$ 在同樣的電壓比較之下，其造成的亮度是一般熱電子槍的數百倍，不過其價格也極為昂貴

熱游離式：包含鎢燈絲、六硼化鏷燈絲。

作用方式：將燈絲加熱到高溫，讓電子的能量能克服燈絲表面的位能，從表面被游離出來。

優點：較為便宜、不需高真空環境。

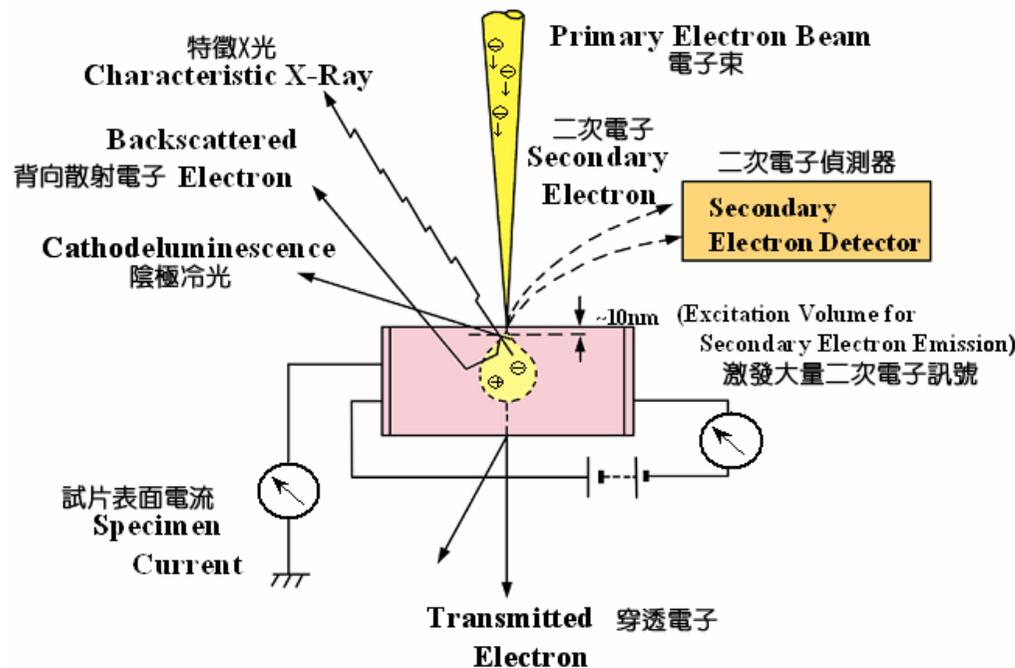
場發射式：鎢燈絲(針尖狀)。

作用方式：加上一個強電場，讓在燈絲針尖的電子受電場吸引而射出。

優點：電子能量發散小、光源亮度高，場發射式電子槍顯微鏡的解析力通常要比熱游離式的還要好。

電子束與試片的作用原理

電子束和試片的作用分為兩類，一種是彈性碰撞，幾乎沒有能量損失。另一種為非彈性碰撞，入射的電子束會將部分的能量傳遞給試片，即產生二次電子、背向散射電子、歐傑電子、與X光等等。其作用如下圖所示。

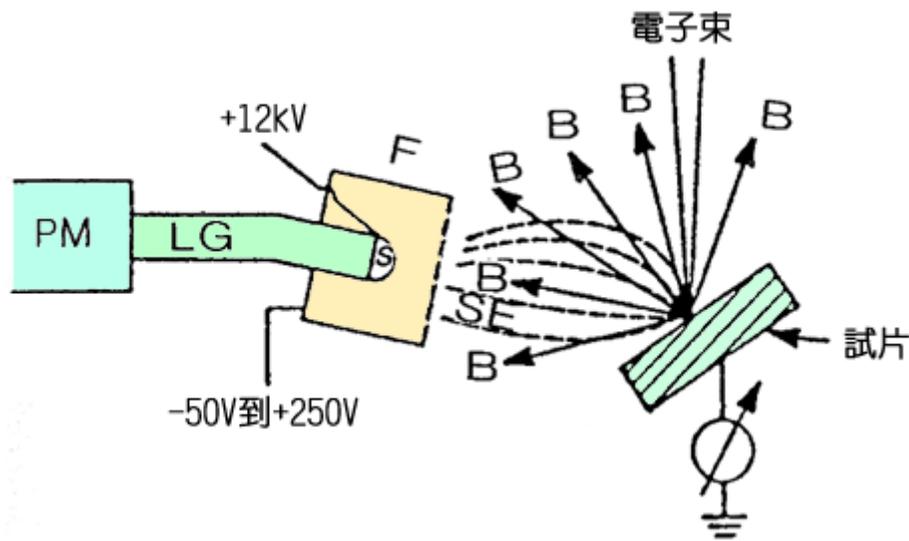


二次電子指的是，電子束將試片表面(10奈米以內)原子堆中的最外層電子打出所產生，一般利用二次電子可以看出試片表面的高低形貌。背向散射電子則是，入射電子撞擊到材料的原子核之後反彈回去，其原子量越大反彈的愈多，經過處理之後的成像就愈亮，因此可以利用它來鑑別出材料成分的差異性。

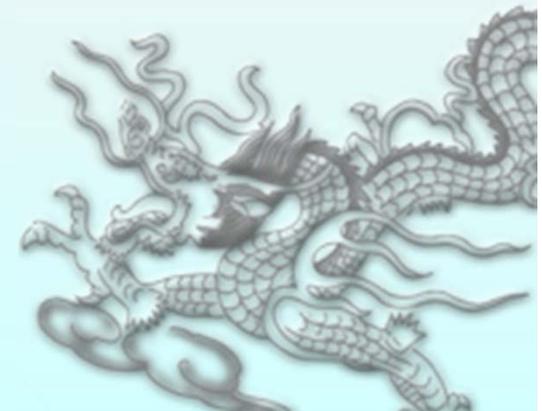
X光的原理為，當入射電子將原子核的內層電子敲出，此時外層電子會躍遷跳入內層軌道，當一個電子由能量不安定的外層跳入能量安定的內層，勢必產生能量差，而此能量差即以X光的形式放出。而歐傑電子則是，X光再將外層電子敲出所形成，也可用來判斷材料的成分差異及特性。

偵測器

偵測器有各種型式，收集不同的訊號有時需要不同的偵測器，例如閃爍計數器是由 $\text{CaF}_2 + \text{Eu}(\text{doped})$ 閃爍物質構成，當電子撞擊此材料會產生光子，此光子再經光導管進入光電倍增器，產生電子而輸出脈波，此計數器會再覆上一層Al膜，厚度約10~50奈米，加一個+10kV的偏壓來加速電子，為了避免此偏壓造成散光像差，閃爍計數器會以具有柵孔的籃子包住，稱為法拉第籠，可以在上面加上+300V的偏壓來促進二次電子的收集，或是加上-50V的偏壓排斥二次電子，讓能量高的背向電子進入。



另一固態偵測器，則是利用電子束撞擊半導體會產生電子電洞對，外加電壓時便產生電流，此電流經過放大即產生信號，此種偵測器可以以多種形式製作，其對背向電子較為敏感，如果要偵測二次電子必須設法加速電子置足夠的能量。



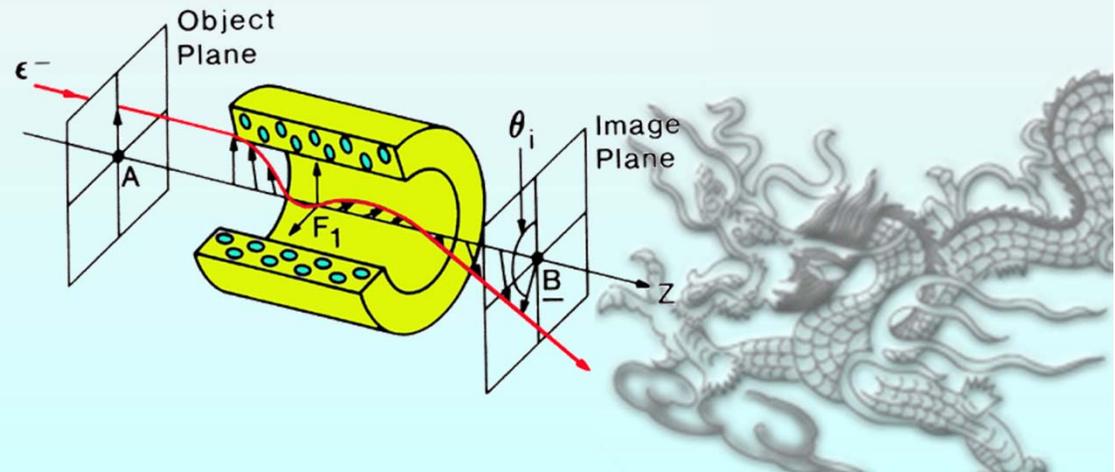
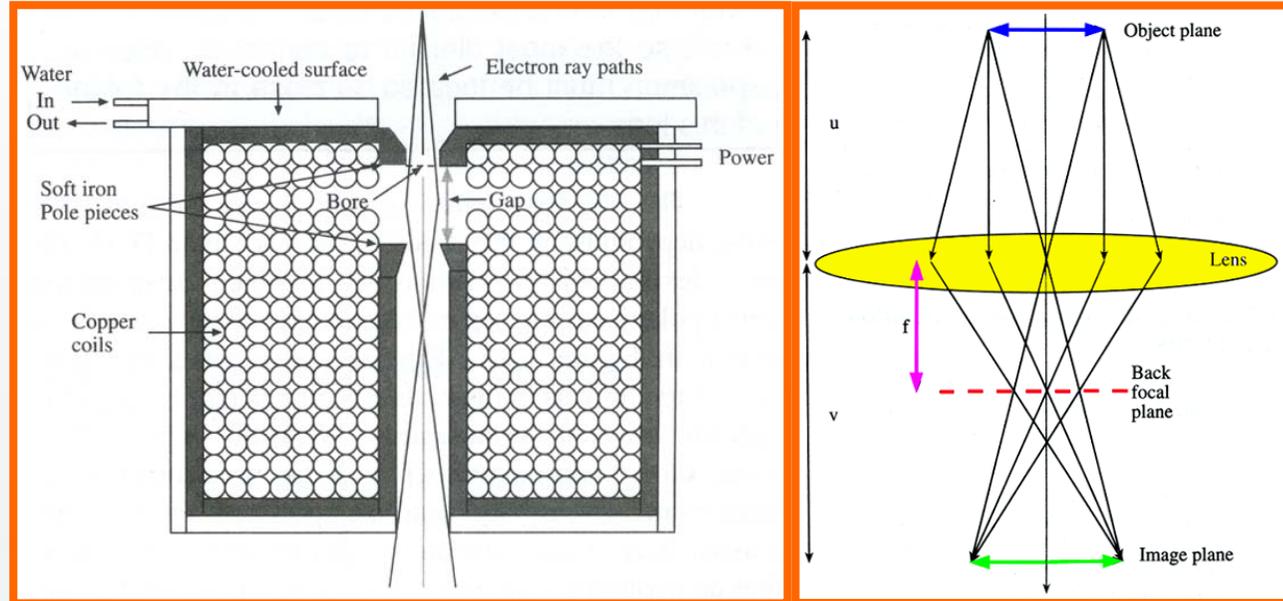
Lenses

➤ Rotational force

$$F_{\theta} = -e v_z \times B_r$$

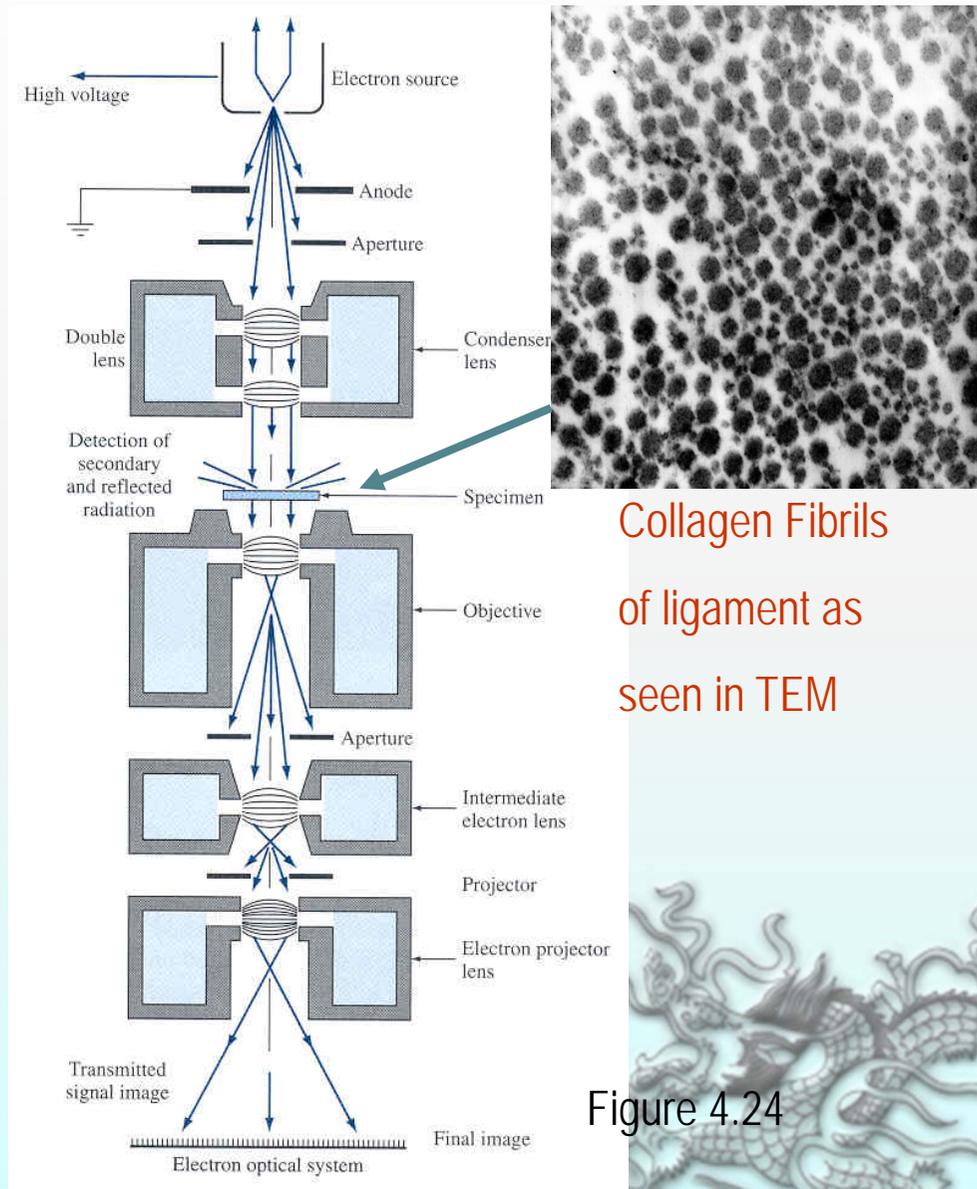
➤ Radial force

$$F_r = -e v_{\theta} \times B_z$$

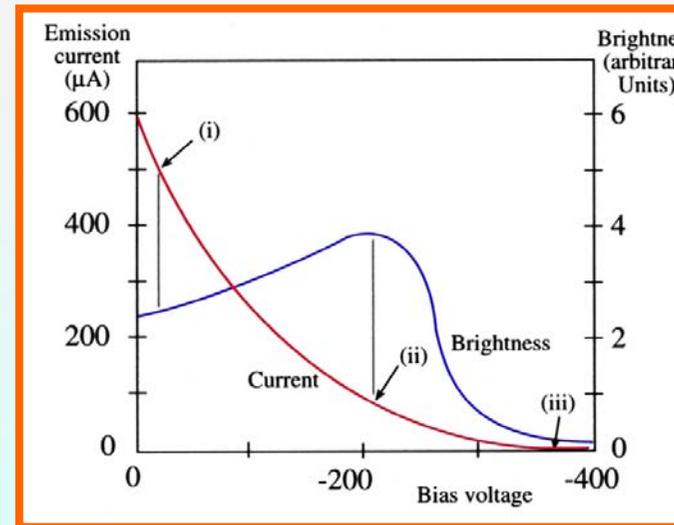
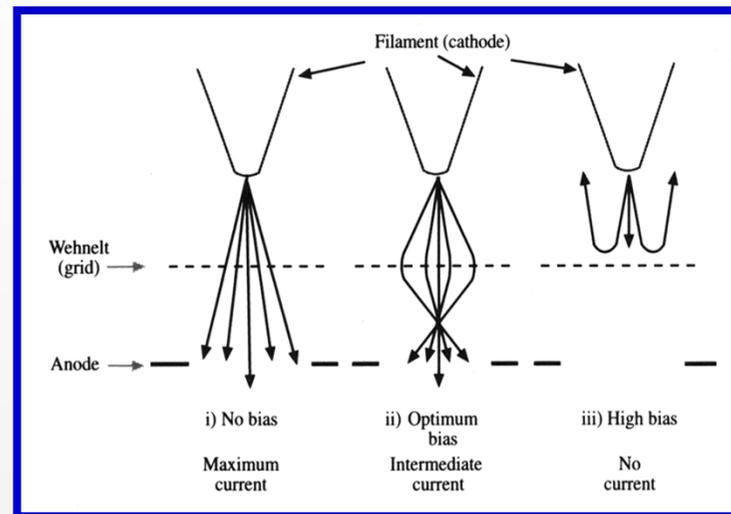
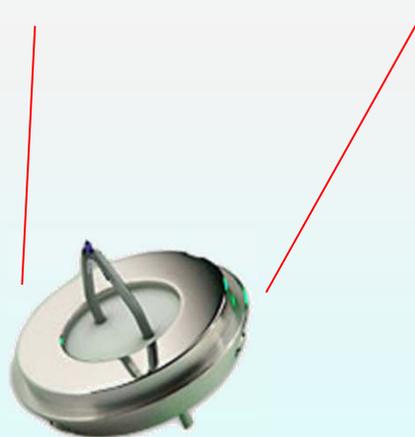
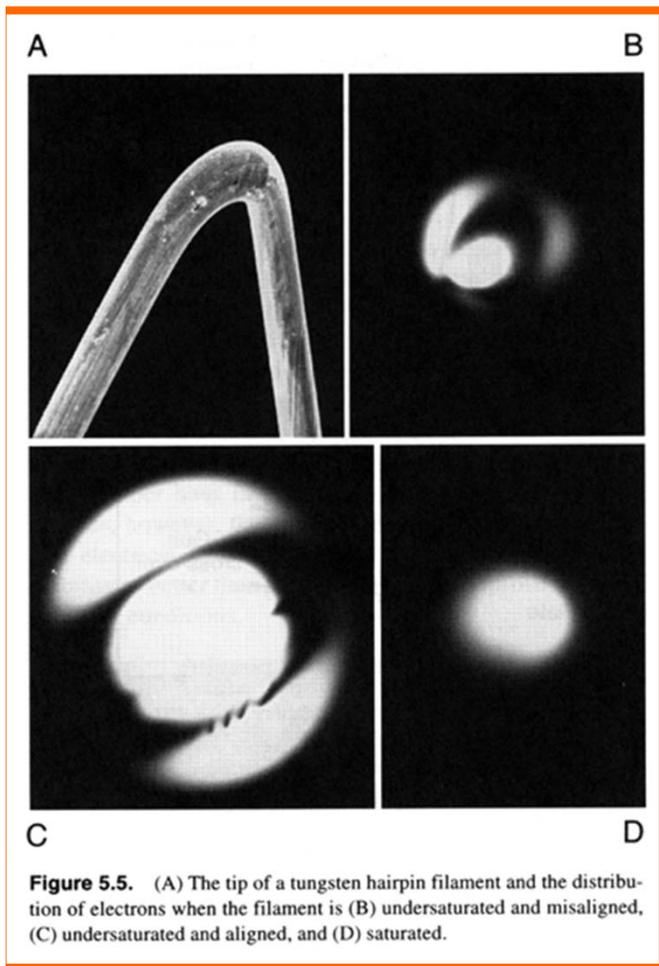


Transmission Electron Microscope

- ◆ Electron produced by heated tungsten filament.
- ◆ Accelerated by high voltage (75 - 120 KV)
- ◆ Electron beam passes through **very thin specimen**.
- ◆ Difference in atomic arrangement change directions of electrons.
- ◆ Beam is enlarged and focused on fluorescent screen.



Pictures of emission gun

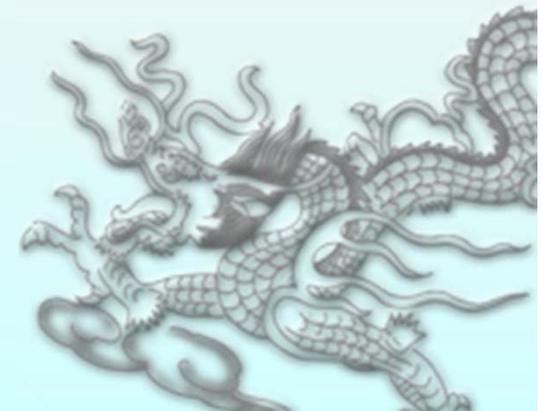


LaB₆

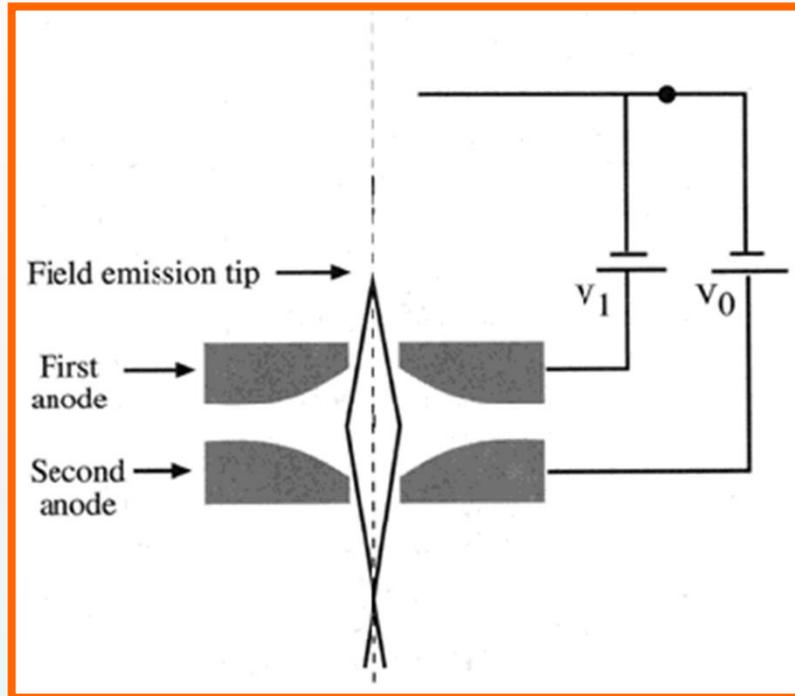
□ 價錢最便宜使用最普遍的是鎢(W)燈絲，以熱游離式來發射電子，電子能量散佈為2 eV，鎢的功函數約為4.5 eV。鎢燈絲係一直徑約100 μm，彎曲成V字形的細線，操作溫度約2700 K，使用壽命約為100小時。

□ 六硼化鏷(LaB₆)燈絲的功函數為2.4 eV，較鎢絲為低，因此同樣的電流密度，使用LaB₆只要在1500 K即可達到，而且亮度更高，因此使用壽命便比鎢絲高出許多，電子能量散佈為1 eV，比鎢絲要好。但因LaB₆在加熱時活性很強，所以必須在較好的真空環境下操作，因此儀器的購置費用較高。

□ 場發射式電子槍則比鎢燈絲和六硼化鏷燈絲的亮度又分別高出10~100倍，同時電子能量散佈僅為0.2~0.3 eV，所以目前市售的高解析度掃描式電子顯微鏡都採用場發射式電子槍，其解析度可高達1 nm以下。

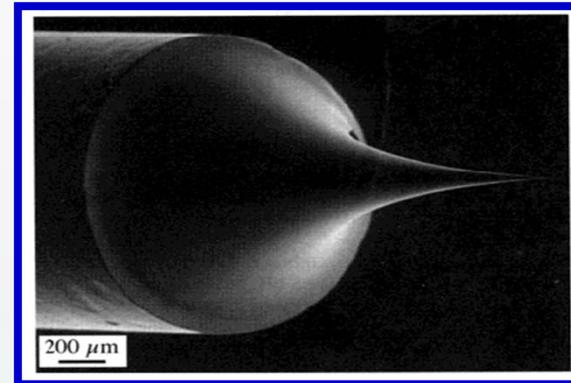


Field-Emission Guns



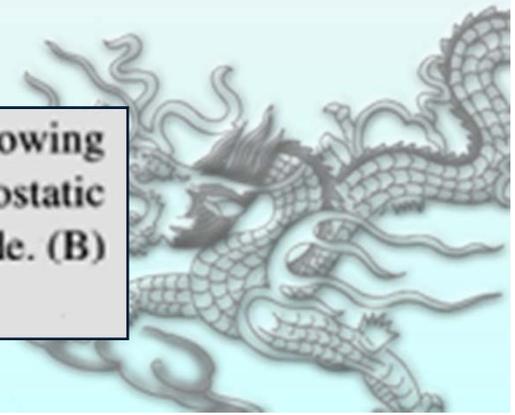
V_1 extraction voltage ~ a few kV

V_0 accelerating voltage 1-30 kV



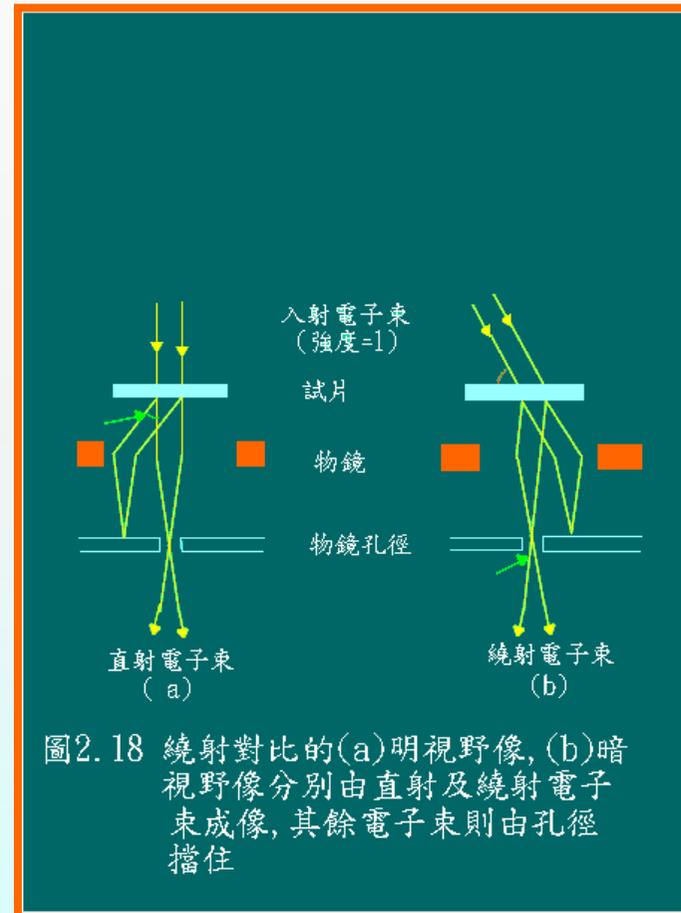
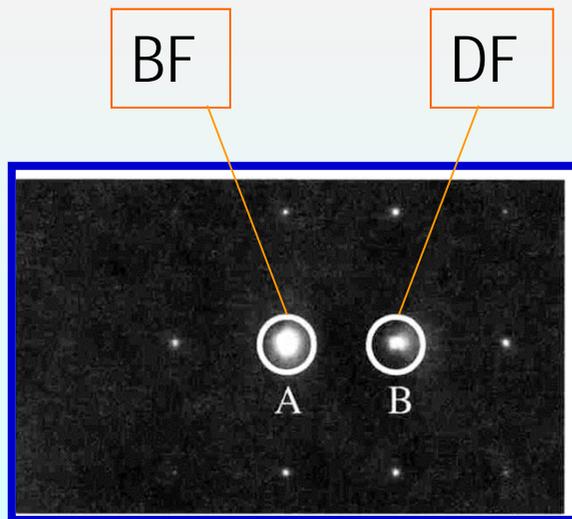
$R_{\text{tip}} \sim 0.1 \mu\text{m}$

(A) Electron paths from a field-emission source showing how a fine crossover is formed by two anodes acting as an electrostatic lens. Sometimes an extra (gun) lens is added below the second anode. (B) An FEG tip, showing the extraordinarily fine W needle.



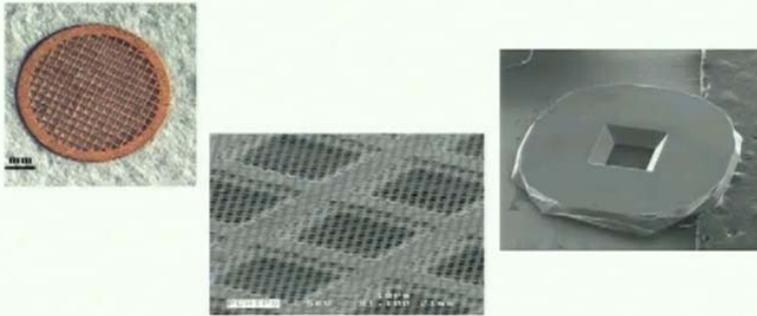
Amplitude Contrast

- BF and DF images.
 - using objective aperture



TEM sample preparation

- ❑ Grid, typically 3 mm in diameter.
- ❑ Membrane (thickness usually below 10 nm) often suspended over grid.
- ❑ Fabricate thin section by ion milling



Diamond Saw



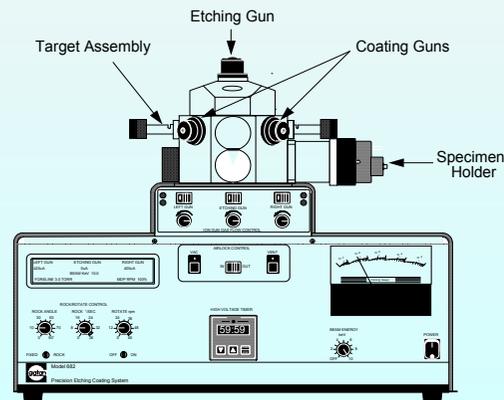
Dimpling



Grinding and polishing

Bulk, surface and small pieces :
plan-view and cross-section samples

- cutting
- prethinning
- final thinning



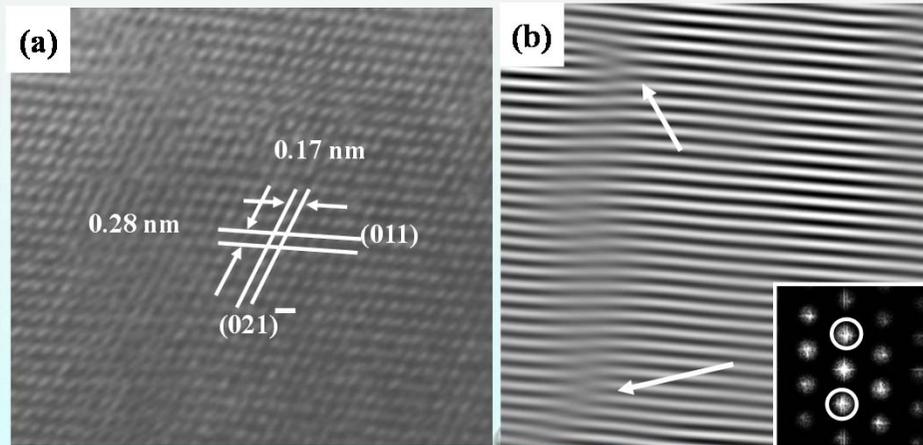
- Ion milling
- 2 –6 kV Ar ions
- 3-10 °
- Vacuum

TEM

- ◆ TEM needs complex **sample preparation**
- ◆ Very thin specimen needed (several hundred nanometers)
- ◆ **High resolution TEM (HRTEM)** allows resolution of 0.1 nm.
- ◆ 2-D projections of a crystal with accompanying defects can be observed.

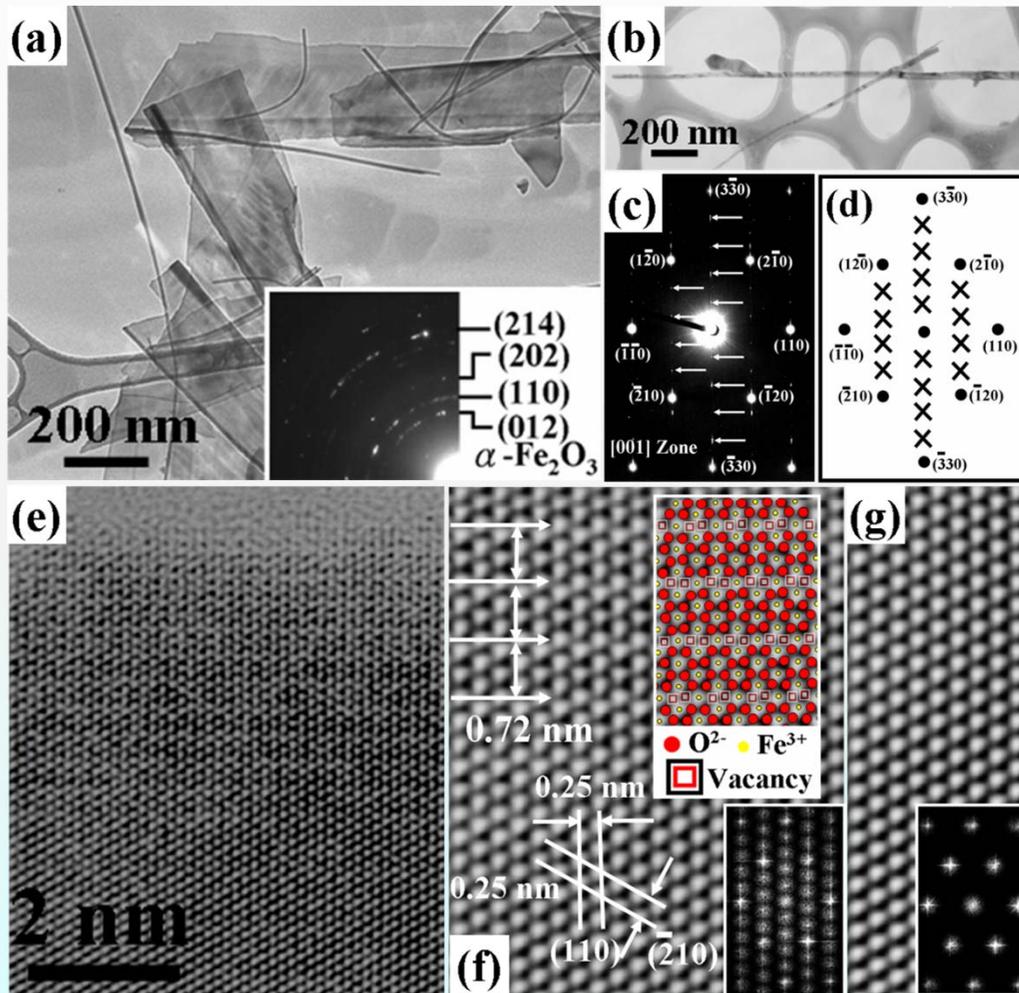


Low angle boundary As seen In HTREM



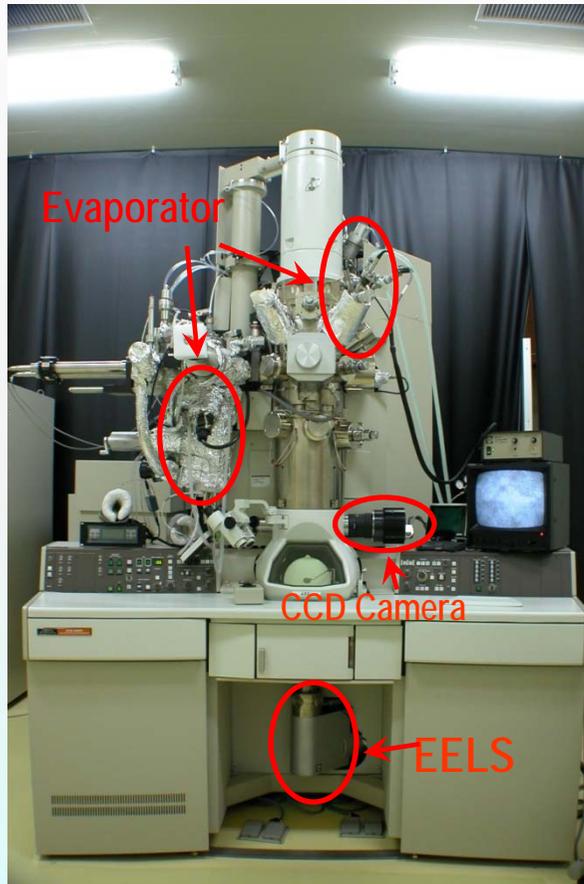
Dislocation-edge

Oxygen vacancies inside the nanowires



- The corresponding diffraction pattern is shown in the inset of Fig. (a), obviously revealing that the phase of NWs is of $\alpha\text{-Fe}_2\text{O}_3$
- Extra spots can be found in the diffraction pattern, which has five times the distance of plane, as shown by arrow heads after a detailed examination of the diffraction pattern, as presented schematically in Fig (d).
- This superstructure is suggested to be caused by oxygen vacancies inside the $\alpha\text{-Fe}_2\text{O}_3$ NWs during the growth.
- The five period distance of the Fe-O lattice plane, fits coherently with the individual sites of the corresponding high resolution TEM image

In-Situ HRTEM



Ultra High Vacuum Transmission Electron Microscope in NTHU

Ultra High Vacuum Transmission Electron Microscope

Specimen Chamber Vacuum $<5 \times 10^{-8}$ Pa

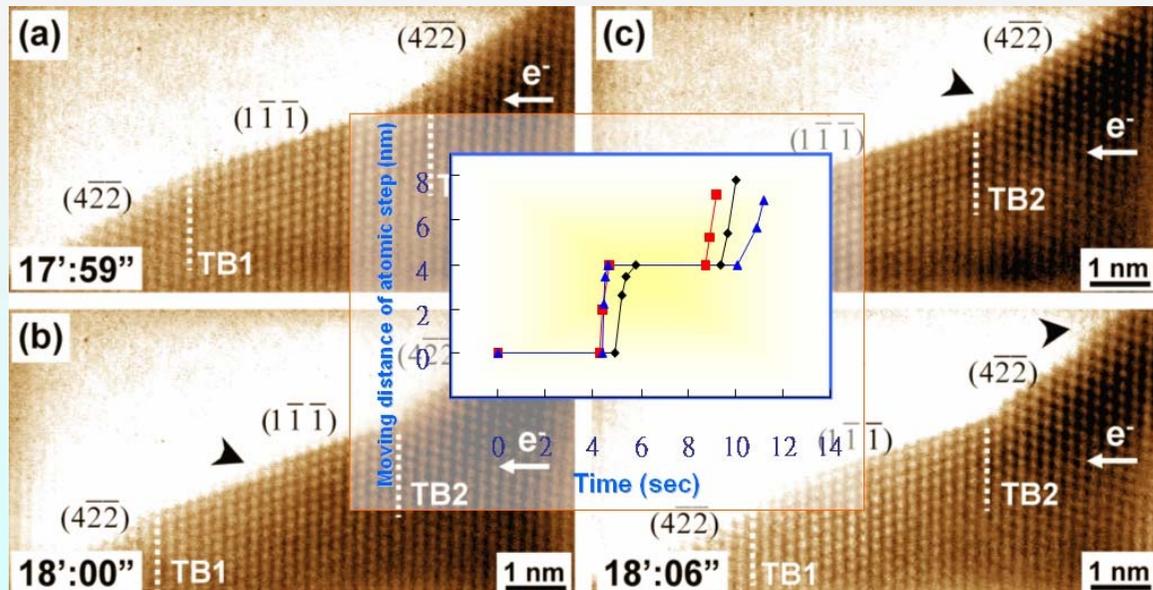
Pretreatment Chamber Vacuum $<5 \times 10^{-8}$ Pa

Point Resolution : 0.21 nm

Lattice Resolution : 0.14 nm

Accelerating Voltage : 200 KV

Double Title Direct Heating Holder ($T_{\max} = 1200$ °C)

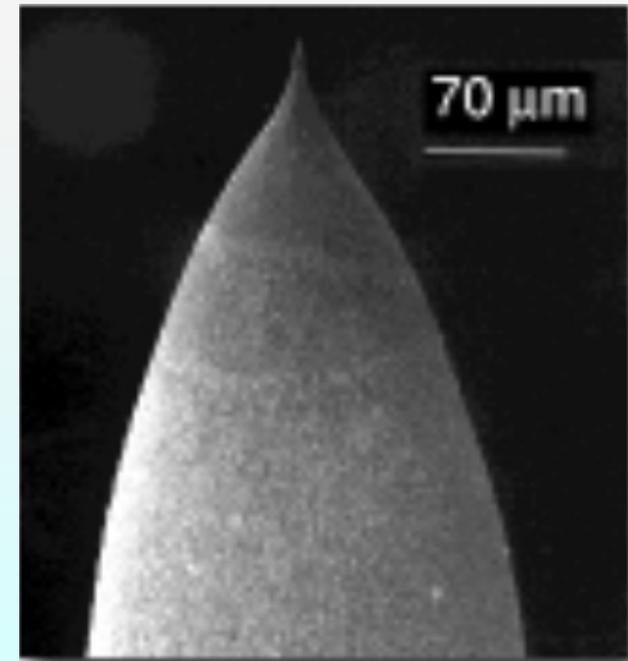


Observation of Atomic Diffusion at Twin-modified Grain Boundaries in Copper

Wen-Wei Wu et al., Science 321, 1066 (2008)

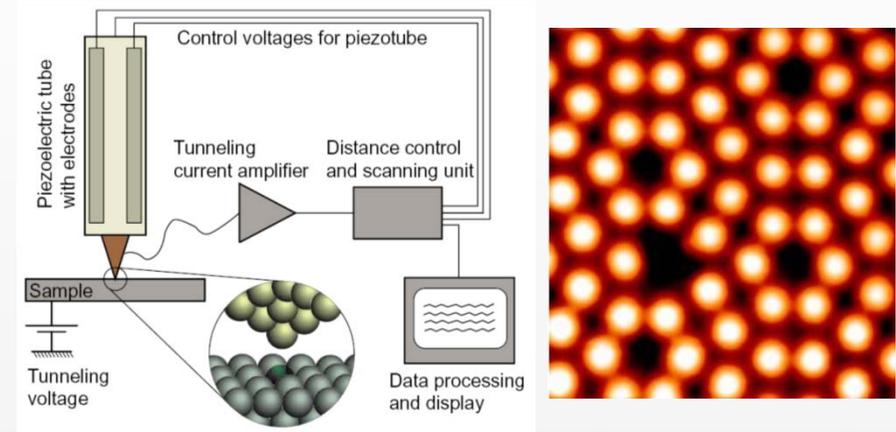
Scanning Probe Microscopy

- ◆ **Scanning Tunneling Microscope (STM)** and **Atomic Force Microscope (AFM)**.
- ◆ **Sub-nanometer magnification.**
- ◆ **Atomic scale topographic map of surface.**
- ◆ **STM uses extremely sharp tip.**
- ◆ **Tungsten, nickel, platinum**
 - **iridium or carbon nanotubes****are used for tips.**



Scanning Tunneling Microscope

- Tip placed **one atom** diameter from surface.
- Voltage applied across tip and surface.
- Electrons **tunnel the gap** and produce current.
- Current produced is proportional to change in gap.
- Can be used only for conductive materials.



Surface of platinum with defects

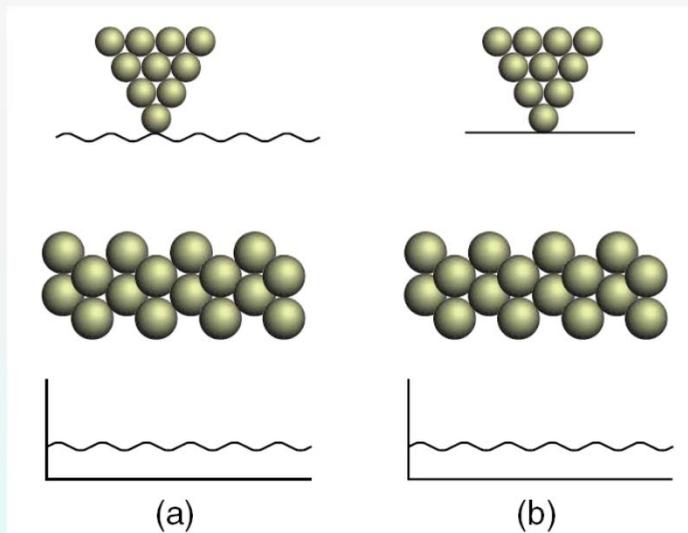
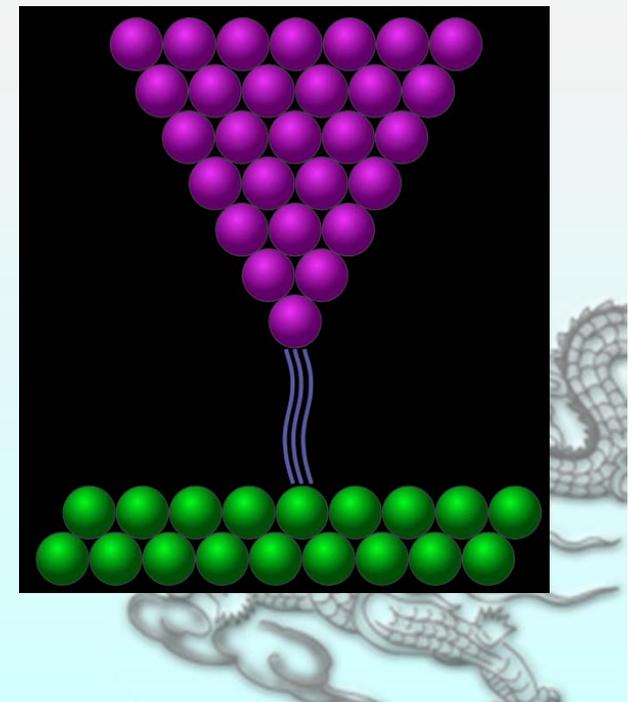


FIGURE 8.51

The two common modes of STM operation: (a) constant-current mode and (b) constant-height mode.

❖ Constant high: much sensitive to modulation of atomic level.

❖ Constant current: can measure rough surface with topographical accuracy, but data acquisition is slow.



Atomic Force Microscope

- ❑ Similar to STM but tip attached to cantilever beam.
- ❑ When tip interacts with surface, van der Waals forces deflect the beam.
- ❑ Deflection detected by laser and photo-detector.
- ❑ Non-conductive materials can be scanned.
- ❑ Used in DNA research and polymer coating technique.

