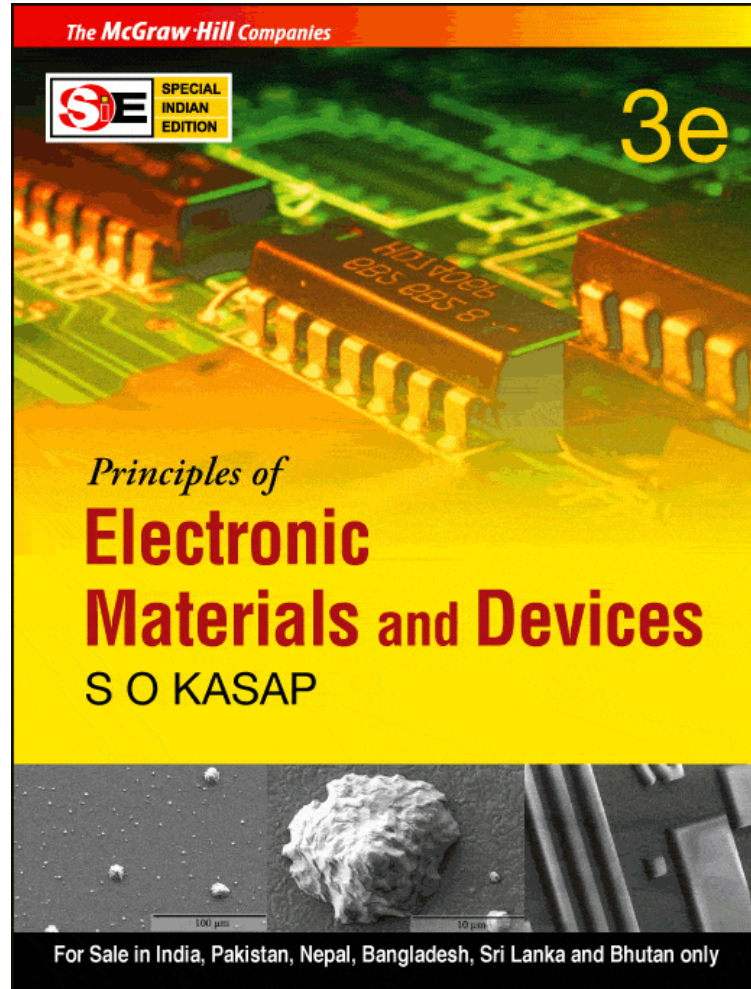# Chapter 1

Elementary Materials Science Concepts

Principles of alloy formation

Phase: substance or portion of matter, which is physically distinct, chemically homogeneous, & mechanically separable
✓ Two crystals represent different phases if their lattice structures are different

✓ Pure metals are seldom used in engineering applications. Most of the useful metallic materials are alloys

✓ Alloy is any combination of 2 or more elements that results in a substance possessing metallic properties

✓ An alloy may consist of either a single phase, 2 phases or >2 phases

✓ Element present in largest proportion is called *base metal*, & all other elements present are *alloying elements*

✓ *Mechanical Mixtures* are formed when the two elements are completely insoluble in the solid state.

✓ Intimate mixture of the components where each component retains its own identity, properties and crystal structure

✓ When two elements mix or dissolve in the solid state, the resulting phase is called a *solid solution*.

✓ If element A dissolves 10 % (by weight) of element B, then element B is said to have a solid solubility of 10% in A.

✓ The base metal A is also called as *solvent* and the alloying element B as *solute*.

✓ When solid solution forms, atoms of solute occupy certain places in the lattice structure of solvent.

Depending upon the type of places occupied by solute atoms, solid solutions could be either substitutional or interstitial
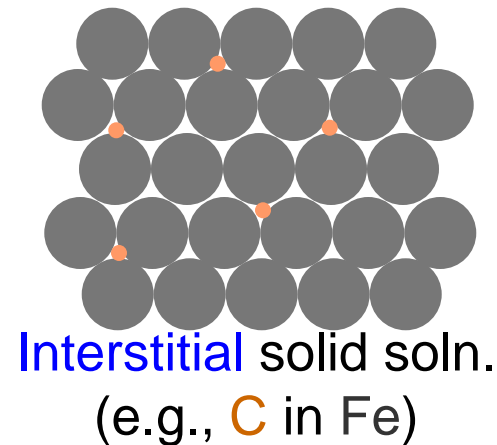
Point Defects in Alloys
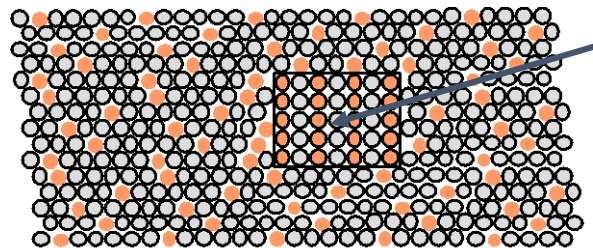
Two outcomes if impurity (B) added to host (A):
- Solid solution of B in A (i.e., random dist. of point defects)

OR

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

Interstitial solid soln.
(e.g., C in Fe)
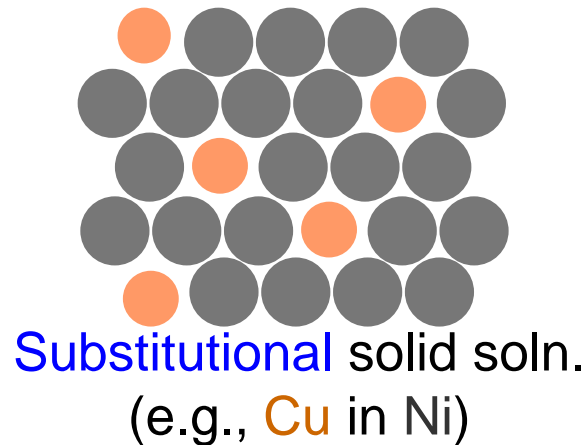
- Solid solution of B in A plus particles of a new phase (usually for a larger amount of B)

Second phase particle
--different composition
--often different structure.

Solid solutions can be disordered substitutional, ordered substitutional & interstitial
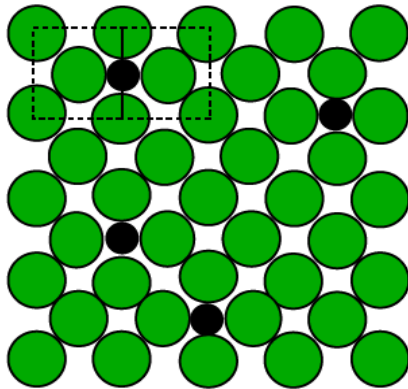*Substitution of solute atoms for solvent atoms at various lattice sites of the solvent can be either random (disordered) or ordered*
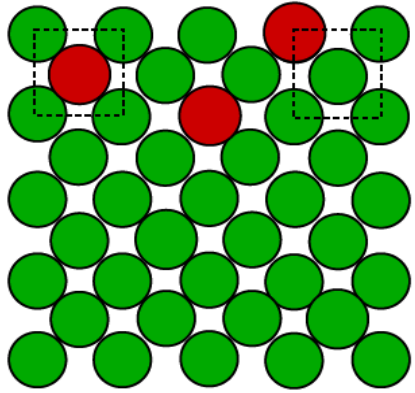
(a) Disordered Substitutional Solid Solution. Example: Cu-Ni alloys ({100} planes)
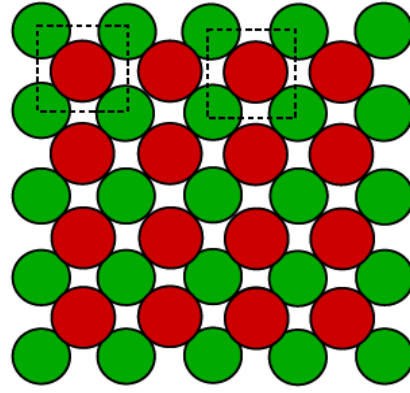
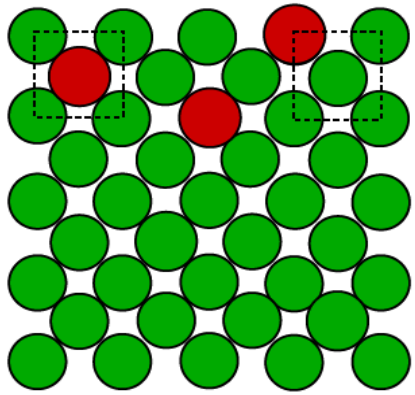(b) Ordered Substitutional Solid Solution. Example: Cu-Zn alloy of composition 50%Cu-50%Zn. ({110} planes).

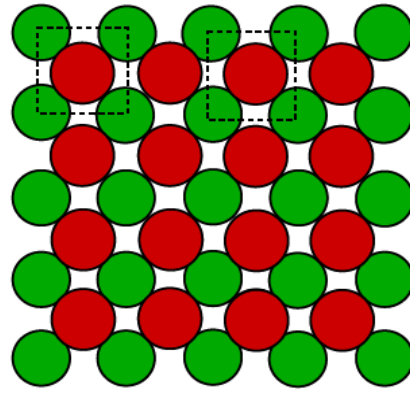(c) Interstitial Solid Solution. Example: Small number of C atoms in FCC Fe (austenite). ({100} planes)

✓ **(a) Disordered Substitutional Solid Solution:** It is formed when some of the solvent atoms are replaced by solute atoms at their normal lattice points. Solute & solvent atoms are randomly distributed on lattice sites, with a statistically uniform distribution.

✓ In the formation of substitutional solid solutions, an element A cannot dissolve any amount of element B, its limit (known as solid solubility limit) is determined by certain factors, which were first studied by William Hume-Rothery and are known as Hume Rothery Rules.

✓ **(c) Interstitial Solid Solution** (ISS): It forms when solute atoms (of small atomic radii) occupy interstitial sites, or voids between atoms, in the crystal (i.e., lattice structure of solvent atoms)

✓ Since the empty spaces of the lattice structure are limited in size, only atoms with atomic radii less than 1 Å are likely to form ISS. Elements having small radii are H, O, N, C, B.

✓ ISS normally have limited solid solubility. For e.g., interstitial solid solution of carbon in iron. γ-Fe (FCC) can dissolve upto 2%C at 1147 °C

Solid solutions can be disordered substitutional, ordered substitutional & interstitial
Substitution of solute atoms for solvent atoms at various lattice sites of the solvent can be either random (disordered) or ordered

(a) Disordered Substitutional Solid Solution. Example: Cu-Ni alloys ({100} planes)

(b) Ordered Substitutional Solid Solution. Example: Cu-Zn alloy of composition 50%Cu-50%Zn. ({110} planes).

(b) Ordered Substitutional Solid Solution:

For certain compositions, the substitution is ordered (or regular) instead of random

✓ Distinct ordering of atoms around each solute atom such that the crystal structure resembles that of a compound

✓ This can occur with 1:1 or 1:3 atom ratios.

✓ 1:1 system has BCC structure with atoms of one type on the corners of unit cell and atoms of the other type at centre.

❑ e.g. : β′ brass has composition 50 Cu – 50 Zn (at.%)
❑ Each Zn atom is surrounded by 8 Cu atoms and vice versa, as depicted in 2-D in Figure (b) above
❑ Structure is of metallic compound between Cu & Zn

Another example is $AuCu_3$, which is disordered FCC at high temperatures but becomes ordered during cooling at 400 °C, when gold atoms occupy corners & copper atoms occupy face centered positions in the lattice

➤ These regular arrangements of atoms are called *ordered solutions* or *super lattices*. These superlattices are formed upon *slow cooling of random substitutional solutions*.

➤ At elevated temperatures, there is a random distribution of solute and solvent atoms (disordered solution).

➤ During slow cooling, the atoms begin to take up preferred positions when a critical temperature is reached, and the solution becomes 'ordered'.

Crystal structures of phases that are formed in Cu—Au system

(Cu,Au)
$Fm\bar{3}m$

Au

Cu

CuAu II
$Fmmm(10\gamma)000$

CuAu₃
$Pm\bar{3}m$

CuAu
$P4/mmm$

AuCu₃
$Pm\bar{3}m$
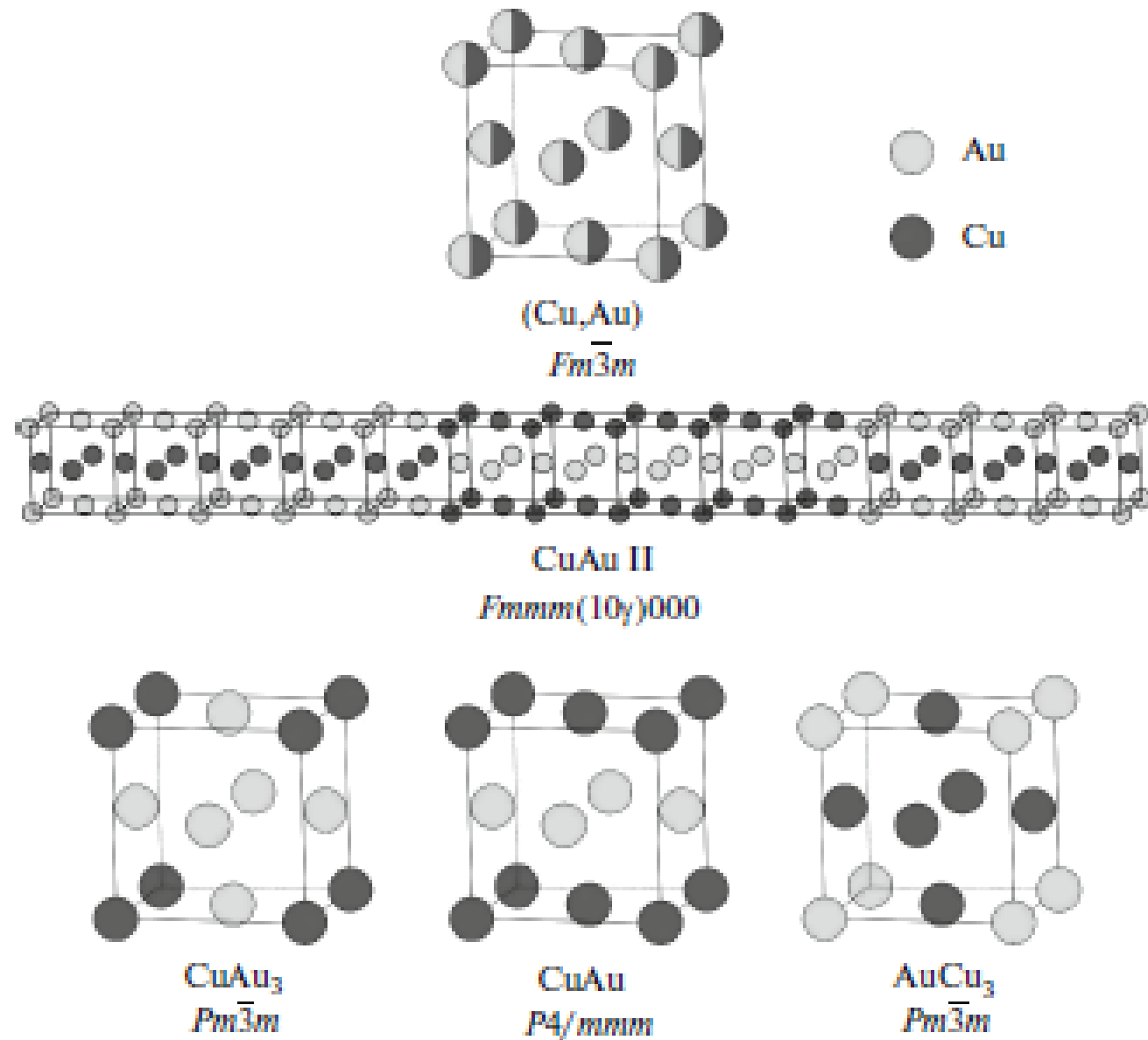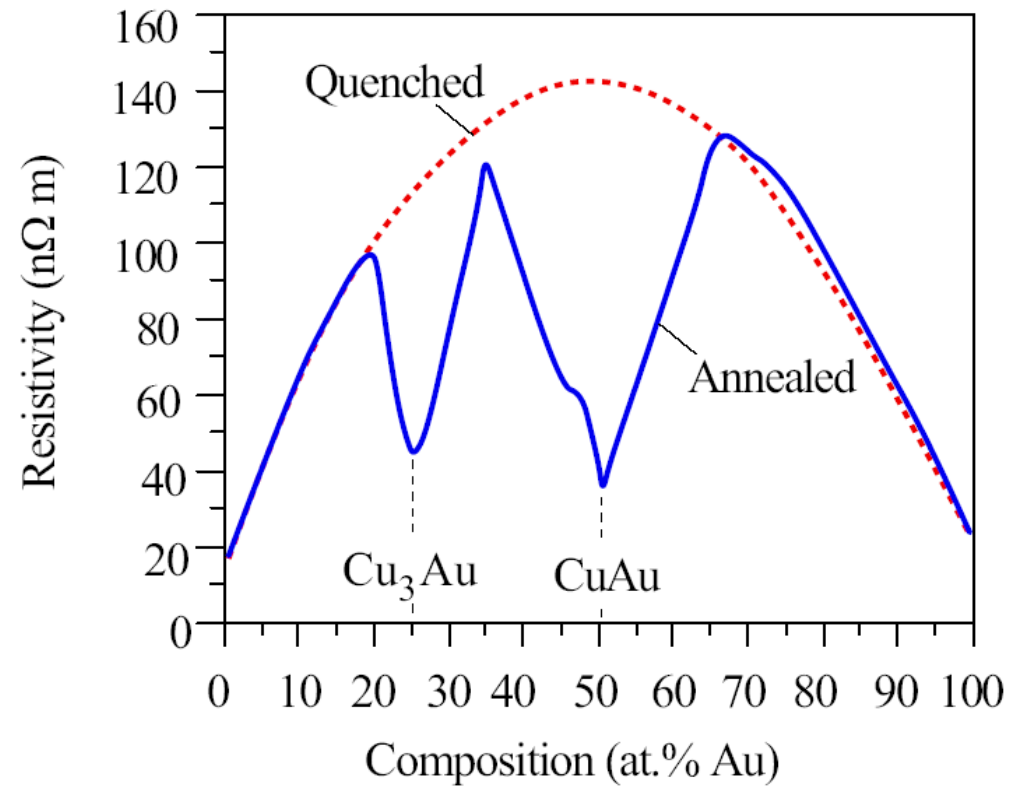
Resistivity at room temperature in Cu-Au alloys

✓ Quenched (dashed line) is obtained by quenching liquid, Cu & Au atoms are *randomly mixed*

✓ When quenched sample is annealed or liquid is *slowly cooled* (solid curve), certain compositions (Cu_3Au and CuAu) result in an ordered crystalline structure in which Cu & Au atoms are *positioned in an ordered fashion in the crystal*

Conditions for substitutional solid solution (S.S.)

- **William Hume – Rothery rules**
  - 1. Δr (atomic radius) < 15%
  - 2. Proximity in periodic table
    - i.e., similar electronegativities
  - 3. Same crystal structure for pure metals
  - 4. Valency
    - All else being equal, a metal will have a greater tendency to dissolve a metal of higher valency than one of lower valency

➤ Lattice structure of solid solution is basically that of solvent with slight changes in lattice parameter
➤ An expansion results, if solute atom is larger than solvent atom and a contraction, if solute atom is smaller

1. Would you predict more Al or Ag to dissolve in Zn?

2. More Zn or Al in Cu?

Application of Hume–Rothery rules : Solid Solutions

Element	Atomic Radius (nm)	Crystal Structure	Electro-nega-tivity	Valence
Cu	0.1278	FCC	1.9	+2
C	0.071			
H	0.046			
O	0.060			
Ag	0.1445	FCC	1.9	+1
Al	0.1431	FCC	1.5	+3
Co	0.1253	HCP	1.8	+2
Cr	0.1249	BCC	1.6	+3
Fe	0.1241	BCC	1.8	+2
Ni	0.1246	FCC	1.8	+2
Pd	0.1376	FCC	2.2	+2
Zn	0.1332	HCP	1.6	+2

Table on p. 141,
*Callister's Materials Science and Engineering,
Adapted Version.*

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Specification of composition (3ʳᵈ Edition, 1.2: Atomic Mass And Mole)

- **weight percent**

$$C_1 = \frac{m_1}{m_1 + m_2} \times 100$$

m_1 = mass of component 1

- **atom percent**

$$C_1^{'} = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100$$

n_{m1} = number of moles of component 1

Willard Gibbs - Phase Rule

Triple point of H_2O (P vs T) - Point on binary phase diagram at which 3 phases are in equilibrium, is also termed *invariant point* as its position is distinct, or fixed by definite values of composition & temperature. Any deviation from this point by change of temperature &/or composition will cause at least 1 of phases to disappear. E.g., eutectic point & at the point eutectic *invariant* reaction occurs

- Relation determines number of phases that can be in equilibrium in system
- P + F = C + 2   or   F = C – P + 2
- P = no of phases, C = no of components
- **F** (degrees of freedom) are no of such variables as temperature, pressure, or concentration/composition that can be changed independently without changing the no of phases present

✓ States and types of various phases formed in an alloy, will depend upon many variables such as temperature, pressure, and composition of alloy

✓ Existence of these different phases in an alloy system can be represented by a diagram, known as Phase diagram, Equilibrium diagram, or Constitution diagram

✓ Graphical representation of the existence (or changes) of various phases in an alloy system, with changing temperatures and compositions

✓ For phase dig., pressure is assumed to be constant at 1 atm

Ideally, the equilibrium dig. will show the phase relations under equilibrium conditions, which may be approached by extremely slow heating and cooling, so that sufficient time is allowed for the phase change to occur

Phase diagram - graphical application of Gibb's phase rule where pressure effects have been neglected and phase rule is modified,

$$P + F = C + 1 \qquad or \qquad F = C - P + 1$$

wherein the degrees of freedom are reduced to temperature and composition

Au-Cu system: images of binary phase dig

Cu-Au Phase Diagram

Liquid

(Au,Cu)+liquid

(Au,Cu)

CuAu₃

CuAu
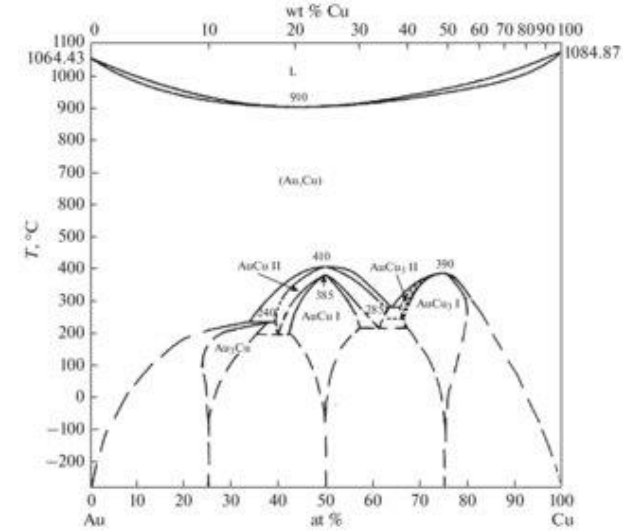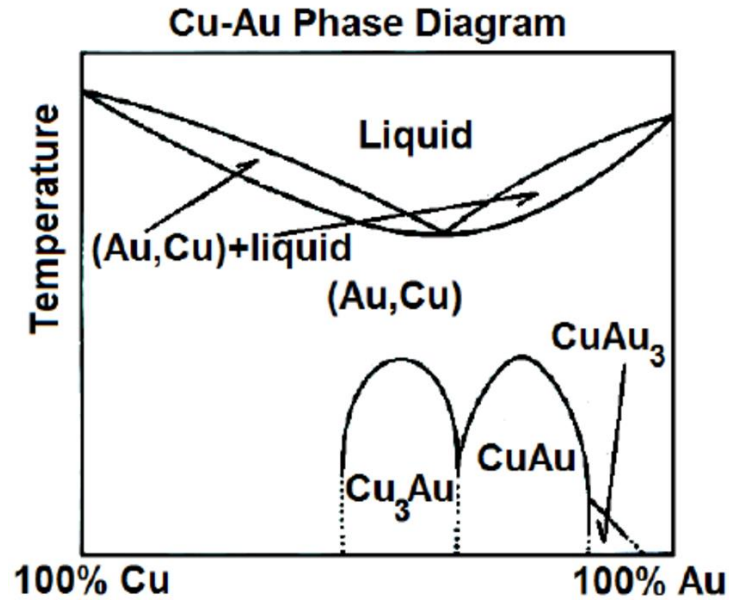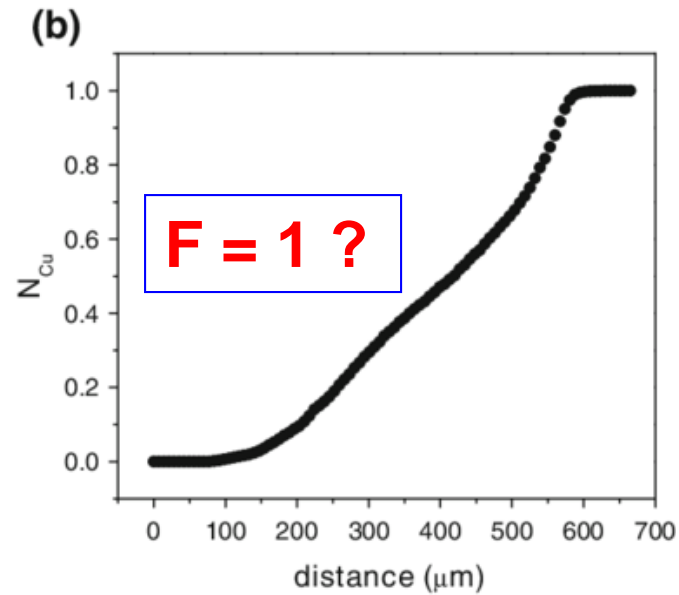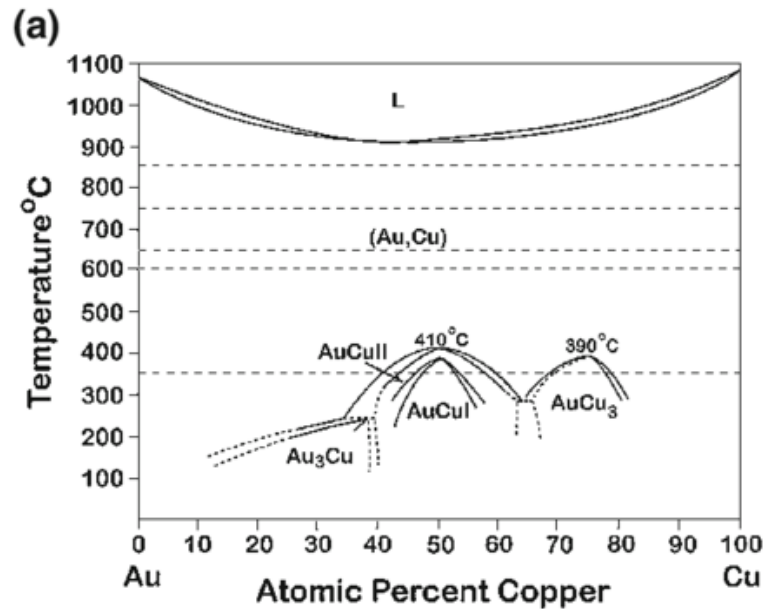
Cu₃Au

100% Cu   100% Au

wt % Cu

Fig. 1. Au—Cu phase diagram. Solid lines are borrowed from [12]; dashed lines are extrapolatic

(a)

L

(Au,Cu)

AuCuII   410°C   390°C

AuCuI   AuCu₃

Au₃Cu

(b)

F = 1 ?

Thank You

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