

Lecture 21: Types of Interfaces: *coherent, semi-coherent, and incoherent*

Today's topics

- Basics of the three types of interfaces: coherent, semi-coherent, and incoherent, and the major differences between them regarding the chemical and structural (strain) contribution to the surface energy: $\gamma_{\text{interface}} = \gamma_{\text{ch}} + \gamma_{\text{st}}$.
- Comparison of the phase growth (diffusion kinetics) at the three interfaces.
- Becker's model for description of the coherent interface: surface energy is proportional to the square of the composition (concentration) gradient: $\gamma_{\text{interface}} \sim \left(\frac{dC}{dx}\right)^2$.

General consideration of interface (say between α and β phase)

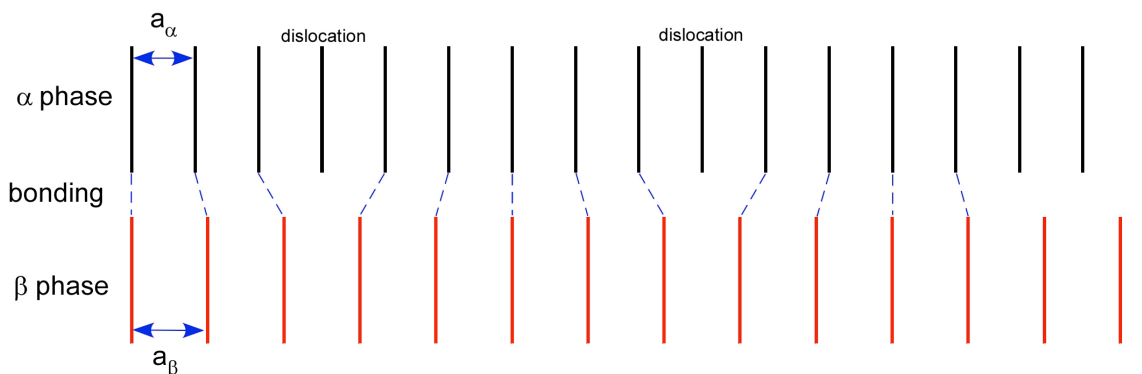
When β particle precipitates from α phase, a new interface forms. For a spherical particle of radius r , the total surface energy is the sum of the two sources: surface energy, $4\pi r^2 \gamma_{\alpha\beta}$ (i.e., γ_{ch} contributed by chemical

bonding at interface), and the strain energy, $\frac{4}{3}\pi r^3 \cdot c \epsilon^2$ (i.e., γ_{st}) --- $\gamma_{\text{interface}} = \gamma_{\text{ch}} + \gamma_{\text{st}}$ --- see Lecture 11

where c is elastic constant, and ϵ is the relative strain due to misfit of lattice:

$$\epsilon \approx \frac{|a_\alpha - a_\beta|}{a_\alpha} \approx \frac{|a_\alpha - a_\beta|}{a_\beta}$$

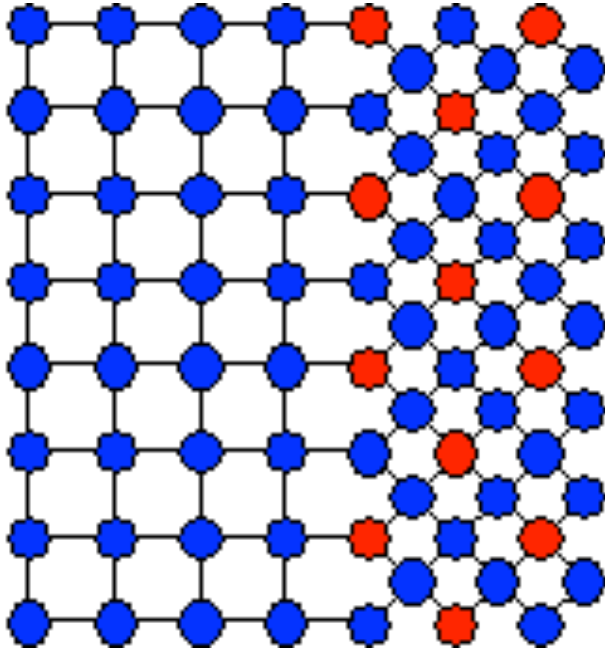
Where a_α and a_β are the unstressed interplanar spacings of the matching planes in the α - and β -phase, respectively.



For example for the above dislocation (a type of misfit), if $a_\alpha = 1.0 \text{ \AA}$, $a_\beta = 1.2 \text{ \AA}$, then $\epsilon = 20\%$ (i.e. every 5 continuous planes in the β phase will take a dislocation to accommodate the misfit of the two lattice). However, if $a_\alpha = 1.0 \text{ \AA}$, $a_\beta = 1.01 \text{ \AA}$, i.e., no significant difference between the two phase lattice, then $\epsilon = 1\%$ (i.e. the dislocation density decreases to every 100 planes in the β phase, approaching to the case of *coherent interface*;

on the other hand, if the two phases differ dramatically in lattice, say $a_\alpha = 1.0 \text{ \AA}$, $a_\beta = 1.5 \text{ \AA}$, then $\epsilon = 50\%$ (i.e., now every 2 continuous planes in the β phase will take a dislocation, very worse for the two phases to match or fit, thus falling to the category of *incoherent interface*.) for the interface with intermediate $\epsilon < 25\%$, usually called *semicoherent interface*.

Coherent interface: see the figure below



A coherent interface arises when two crystals match perfectly at the interface plane so that the two lattices are continuous across the interface, as shown in the Figure above. This can only be achieved if, disregarding chemical species, the interfacial plane has the *same atomic configuration* (orientation, interplane distance) in both phases, and this requires the two crystals to be oriented relative to each other in a special way.

One such example: in Cu-Si alloy, a coherent interface can be formed between the hexagonal close-packed (hcp) si-rich κ -phase and the fcc Cu-rich α -matrix. The lattice parameters of these two phases are such that the (111)fcc plane is identical to the (0001)hcp plane --- both planes are hcp, and in this particularly case the interatomic distances are also identical. Therefore when the two crystals are joined along the hcp planes, the resultant interface is completely coherent.

Other coherent interface examples:

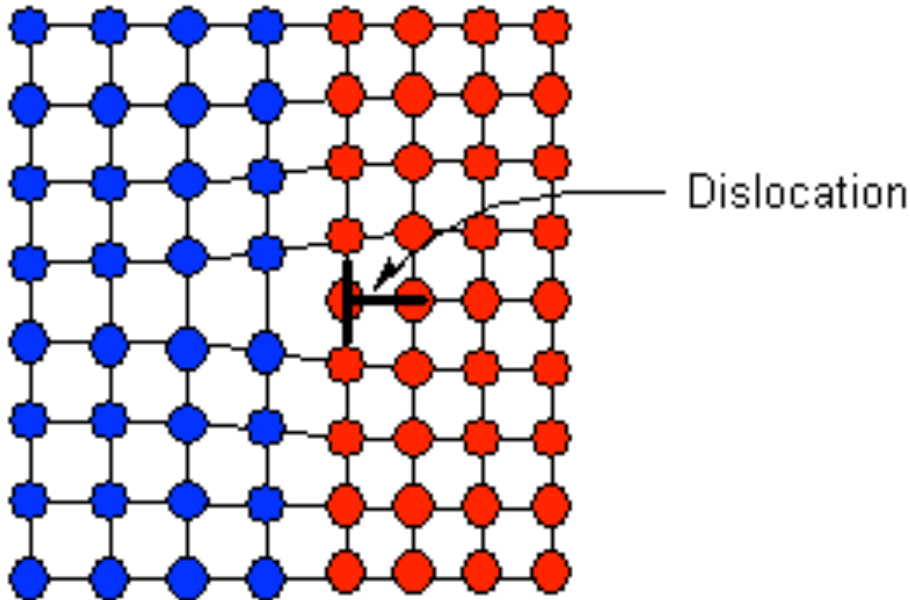
GaAs/AlAs, InAs/GaAs, Ge/Si

Surface energy of coherent interface:

- formation of new interface leads to formation of mismatching chemical bond (AA or BB \rightarrow AB), and such chemical contribution is the only source of surface energy for coherent interface: $\gamma_{\text{coherent}} = \gamma_{\text{ch}}$ (since γ_{st} is usually negligible)
- coherent interfacial energy ranges 0 – ca. 200 mJ/m². For the Cu-Si alloys mentioned above the interfacial energy is only 1 mJ/m².

- For very small particles (though still larger than r^*), the term of strain energy $\frac{4}{3}\pi r^3 \cdot c\varepsilon^2$ is smaller than the surface energy $4\pi r^2\gamma_{\alpha\beta}$ (chemical contribution), and total interfacial energy is small (due to the limited surface area, and thus the limited number of interface chemical bondings), thereby it is energetically favorable to maintain coherent.

Semicoherent Interfaces: see the figure below



The strains associated with a coherent interface raise the total energy of the system, and for sufficiently large atomic misfit, or interfacial area, it becomes energetically more favorable to replace the coherent interface with a semicoherent interface in which the disregistry is periodically taken up by misfit *dislocations*, see the Figure above.

Surface energy of semicoherent interface:

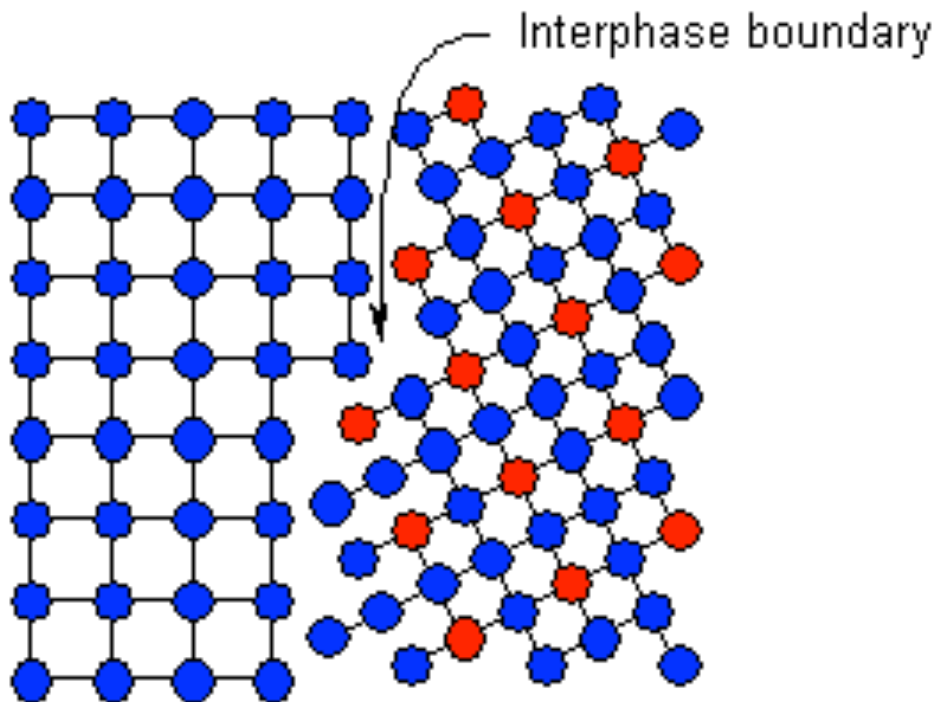
- The interfacial energy of a semicoherent interface can be approximately considered as the sum of the chemical contribution and strain (misfit) contribution: $\gamma_{\text{semicoherent}} = \gamma_{\text{ch}} + \gamma_{\text{st}}$.
- Semicoherent interfacial energy ranges 200 – 500 mJ/m².
- As shown in the Figure above, as the misfit ε increases, the dislocation spacing diminishes. For small values of ε , the structural contribution to the interfacial energy is roughly proportional to the density of the dislocations in the interface: $\gamma_{\text{st}} \propto \varepsilon$. However, γ_{st} increases less rapidly as ε becomes larger and it levels out when $\varepsilon \rightarrow 0.25$. the reason for such behavior is that as the misfit dislocation spacing decreases, the associated strain field increasingly overlap and annul each other.
- When $\varepsilon > 0.25$, i.e., one dislocation for every four interplanar spacings, the regions of poor fit around the dislocation cores overlap and the interface cannot be considered as coherent, now turns to be incoherent.

Incoherent Interfaces: see the figure below

When the interface plane has a very different atomic configuration in the two adjacent phases, there is no possibility of good matching across the interface. The *pattern of atoms* may either be very different in the two phases or, if it is similar, the *interatomic distances* may differ by more than 25%. In both cases the interface is defined as *incoherent*. See Figure below.

Surface energy of incoherent interface:

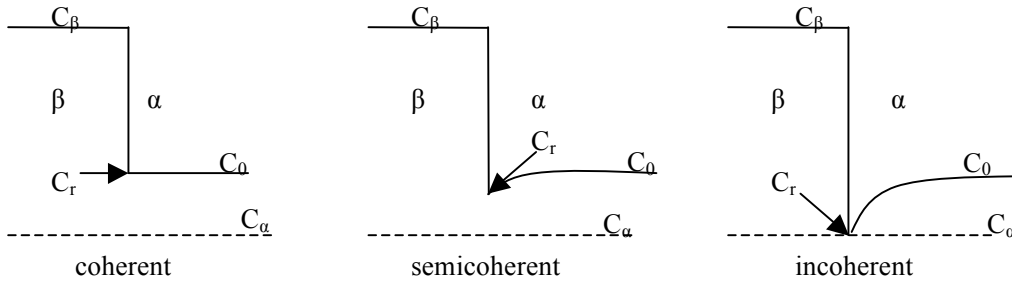
- Incoherent interfacial energy ranges $\sim 500 - 1000 \text{ mJ/m}^2$, where the structural contribution is really large.
- Very little is known about the detailed atomic structure of incoherent interfaces.



The nature of interfaces and the growth of precipitates:

Diffusion normally occurs by a vacancy mechanism in substitutional solid solutions (see Lecture 6). In the case of the formation of a precipitate, a reconstruction of the lattice occurs, where involves the *creation and annihilation of vacancies*, if the interface is semicoherent or incoherent. However, if the interface is coherent, no such vacancies processes involved.

The concentration profile across precipitate/matrix interface for the three different interfaces are shown below:



In terms of the interface transfer parameter, M , it is easily seen that:

$$M (\text{coherent}) < M (\text{semicoherent}) < M (\text{incoherent})$$

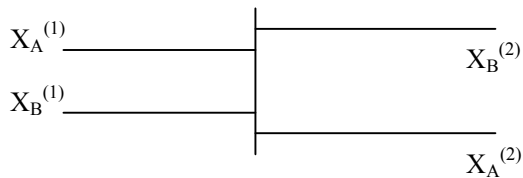
Thus, for a given diffusion coefficient, the incoherent interface moves fastest, while the coherent one moves the slowest.

--- this can be understood by considering the oil/water interface: when oil droplet (β phase) forms in a water matrix (α phase containing small amount of oil), the interface around the droplet represents a typical incoherent interface (oil/water don't like each other). When oil molecules diffuse from the water matrix, reaching the droplets, they will migrate across the interface and deposit onto the droplet rapidly (just because these oil molecules like to be part of the oil phase, rather than the water phase). In other words, the cross interface diffusion is fast!

Becker's Model of Coherent Interfaces:

The model is based on the regular solution theory. It is applicable to the coexistence of two phases of identical crystal structures provided the interface is *coherent*.

Consider a binary solution A-B, let there be an abrupt change in composition along some direction as shown below (resulting in formation of a new interface).



Consider a lattice site just to the left of the interface, where the probability that it is occupied by an A atom is $X_A^{(1)}$. It has Z' nearest neighbors on the right hand side, just across the interface. Of these, $Z' X_A^{(2)}$ are A atoms and $Z' X_B^{(2)}$ are B atoms. Thus, the number of AA bonds formed is equal to $X_A^{(1)} Z' X_A^{(2)}$ and the number of AB bonds formed is equal to $X_A^{(1)} Z' X_B^{(2)}$.

Similarly, the probability that a site on the left side is occupied by a B atom is $X_B^{(1)}$. Thus, the number of BB bond is $X_B^{(1)} Z' X_B^{(2)}$ and the number of BA bonds is $X_B^{(1)} Z' X_A^{(2)}$

The **number of sites/unit area** is $N = N_V a$, where N_V is the number of sites **per unit volume**, a is the interplanar spacing.

Thus, number of AA bonds/unit area of the interface, $P_{AA} = NZ' X_A^{(1)} X_A^{(2)}$

number of BB bonds/unit area of the interface, $P_{BB} = NZ' X_B^{(1)} X_B^{(2)}$

number of AB bonds/unit area of the interface, $P_{AB} = NZ' X_A^{(1)} X_B^{(2)} + NZ' X_B^{(1)} X_A^{(2)}$

If h_{AA} , h_{AB} , and h_{BB} are **bond enthalpies**,

$$H \text{ (per unit interface area)} = h_{AA}P_{AA} + h_{BB}P_{BB} + h_{AB}P_{AB} \quad (1)$$

If the interface region (in the original solution) had been of a uniform composition of A and B with concentrations:

$$X_A = \frac{X_A^{(1)} + X_A^{(2)}}{2} \quad \text{and} \quad X_B = \frac{X_B^{(1)} + X_B^{(2)}}{2}$$

Then:

$$\text{number of AA bonds/unit area: } P_{AA}^0 = NZ' \left(\frac{X_A^{(1)} + X_A^{(2)}}{2} \right)^2;$$

$$\text{number of BB bonds/unit area: } P_{BB}^0 = NZ' \left(\frac{X_B^{(1)} + X_B^{(2)}}{2} \right)^2$$

$$\text{number of AB bonds/unit area: } P_{AB}^0 = 2NZ' \left(\frac{X_A^{(1)} + X_A^{(2)}}{2} \right) \left(\frac{X_B^{(1)} + X_B^{(2)}}{2} \right)$$

The corresponding enthalpy/unit area is

$$H^0 = h_{AA}P_{AA}^0 + h_{BB}P_{BB}^0 + h_{AB}P_{AB}^0 \quad (2)$$

Thus, the excess enthalpy associated with the interface is

$$\Delta H \text{ (per unit area)} = H - H^0$$

After some algebra, we have

$$\Delta H = \frac{NZ'}{2} \left[h_{AB} - \frac{1}{2}(h_{AA} + h_{BB}) \right] (X_A^{(1)} - X_A^{(2)})^2 \quad (3)$$

The above is the **excess enthalpy per unit area** due to the existence of an interface. Such an interface can form only if $h_{AB} - \frac{1}{2}(h_{AA} + h_{BB}) > 0$. That is, the deviation from ideality must be positive.

Equation (3) gives the interfacial energy (net gain of enthalpy by formation of the interface):

$$\gamma = \frac{NZ'}{2} \left[h_{AB} - \frac{1}{2}(h_{AA} + h_{BB}) \right] (X_A^{(1)} - X_A^{(2)})^2$$

now, let's have $\Omega = N_0 Z \left[h_{AB} - \frac{1}{2}(h_{AA} + h_{BB}) \right]$, where Ω is the interaction parameter defined as $\Delta H = \Omega X_A X_B$, $N_0 =$ Avogadro's number, $Z =$ coordination number.

Then, $N_V = \frac{N_0}{V_M}$, where $V_M =$ molar volume, then, $N = N_V \cdot a = \frac{N_0 a}{V_M}$,

$$\text{so, } \gamma = \frac{Z'}{2} \frac{N_0 a}{V_M} \left[h_{AB} - \frac{1}{2}(h_{AA} + h_{BB}) \right] (X_A^{(1)} - X_A^{(2)})^2$$

$$\text{i.e., } \gamma = \frac{Z' a}{2ZV_M} \Omega (X_A^{(1)} - X_A^{(2)})^2 = \frac{Z' a^3}{2ZV_M} \Omega \left(\frac{X_A^{(1)} - X_A^{(2)}}{a} \right)^2 \quad (4)$$

considering, $\frac{X_A^{(1)} - X_A^{(2)}}{a} \cong \frac{dX_A}{dx} \longleftrightarrow$ gradient in concentration

$$\text{then we have, } \gamma \approx \frac{Z' a^3}{2ZV_M} \Omega \left(\frac{dX_A}{dx} \right)^2$$

This is Becker's model describing the interfacial energy, i.e., $\gamma \sim \left(\frac{dC}{dx} \right)^2$.

γ is proportional to the square of the concentration gradient across the interface.