

Chapter

V

**Role of elastic strain energy and
interface energy**

V-1. Introduction

During the 1st order phase transformation process a heterogeneous state appears, even though the initial and final states are single-phase. After the formation of the center of the new phase, the phase transformation is manifested by the displacement of the interface boundary (between the two phases). The energy level of the interface boundary and its properties are determined by the atomic structure of the boundary (the degree of disorder) and the difference in the chemical composition of the adjacent phases. It is obvious that the greater the difference in the atomic structure of the phases (difference in interatomic distances and coordination) and the nature of the atoms, the greater the interface energy must be.

V-2. Total coherently, semi-coherently and total incoherently

In crystals, different phases can be determined by the crystallographic directions along which coincident interatomic directions. Examples of complete coincidence (in all three directions) in the arrangement of atoms can be the formation of ordered domains or when a phase arises from a solid solution, either isomorphic to the matrix, but differing in composition. In this case, we can speak of a total coherence of the lattice of the new and the old phase (figure V-1-a-).

Differences in specific volumes (atomic radii and interatomic distances) lead to elastic deformation. Lattice mismatch (ϵ) during the growth process of the new phase crystal can lead to the appearance of dislocations which reduce this elastic deformation (figure V-1-b-).

$$\epsilon = \frac{(a_p - a_M)}{a_M} \quad (\text{V-1-})$$

a_p : lattice parameter of the precipitated phase

a_M : lattice parameter of the matrix

The possibility of formation of a coherent interface is determined by energy gain which depends on the level of mismatch of the adjacent lattice (fig. V-1-a-). In most of each phase, each atom has an optimal arrangement of nearest neighbors which produces low energy. However, at the interface there is usually a change in composition such that each atom is related to wrong neighbors across the interface. This increases the energy of the interface atoms and leads to a chemical contribution to the interface energy (γ_{ch}). For a consistent interface, this is the only contribution, i.e.:

$$\gamma_{(\text{coherent})} = \gamma_{\text{ch}} \quad (\text{V-2-})$$

In general, coherent interfacial energies are up to about 200 mJ.m^{-2} . When the distance between the atoms in the interface is not identical, it is still possible to maintain coherence by stressing one or both lattices as shown in Fig. V-1- (a). The resulting lattice distortions are called coherency strains.

The strains associated with a coherent interface increase the total energy of the system, and for a sufficiently large atomic mismatch, or interfacial area, it becomes energetically more favorable to replace the coherent interface with a semi-coherent interface (V-1- (b)).

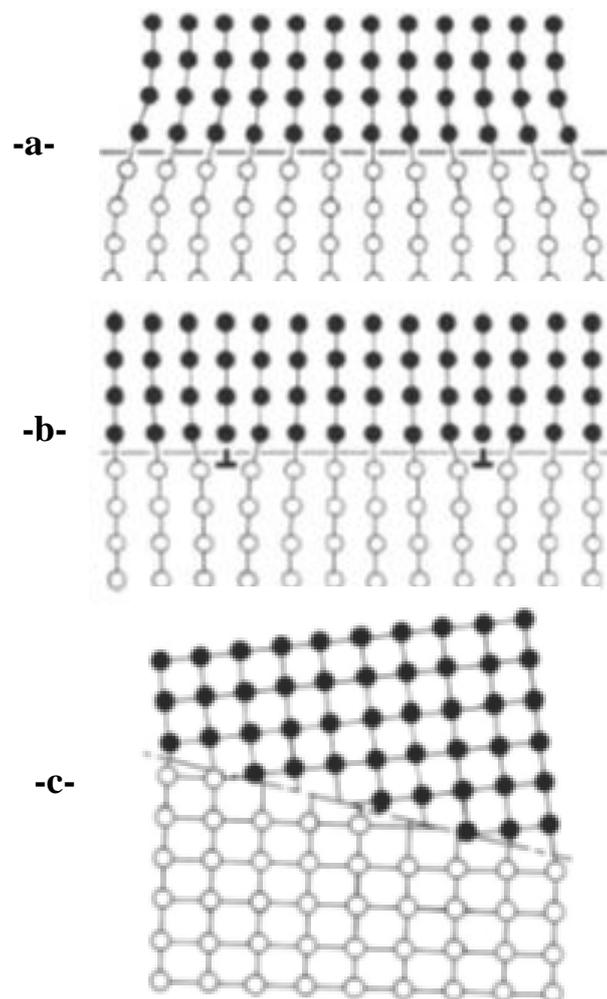


Figure V-1-: Interfaces: (a) coherent (with a slight offset leads to coherence constraints in adjacent lattice), (b) semi-coherent, (c) incoherent

If d_α and d_β are the unconstrained interplanar spacing of the corresponding planes in α and β phases respectively (Fig. V-2-), the misfit between the two lattices is defined by:

$$\delta = \frac{d_\beta - d_\alpha}{d_\alpha} \quad (\text{V-3-})$$

It can be shown that in one dimension, the lattice misfit can be completely compensated without any long range strain field by a set of edge dislocations with a distance D given by:

$$D = \frac{d_\beta}{\delta} \quad (\text{V-4-})$$

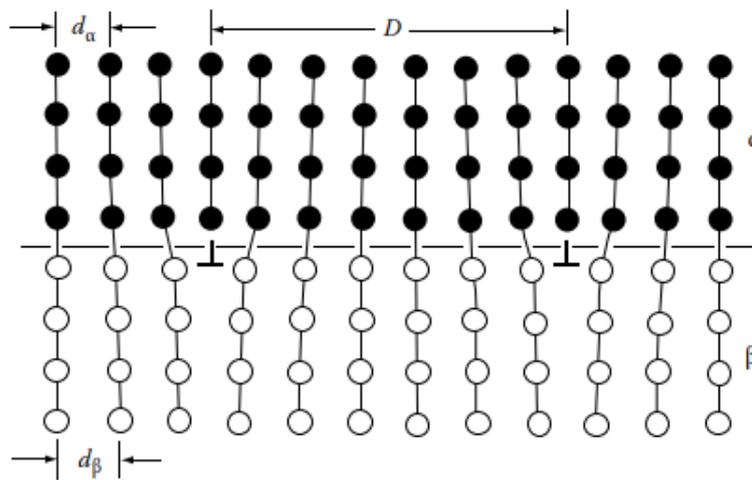


Fig. V-2-: Semi-coherent interface (The misfit parallel to the interface is compensated by a series of edge dislocations).

For small d ,

$$D \cong \frac{b}{\delta} \quad (\text{V-4-})$$

Where b is the dislocation Burgers vector:

$$b = \frac{(d_\alpha + d_\beta)}{2} \quad (\text{V-5-})$$

The interfacial energy of a semi-coherent interface can be viewed approximately as the sum of two parts: (a) a chemical contribution, γ_{ch} , as for a fully coherent interface, and (b) a

structural term γ_{st} , which is additional energy due to structural distortions caused by dislocations, i.e.:

$$\gamma_{\text{(semi-coherent)}} = \gamma_{ch} + \gamma_{st} \quad (\text{V-6-})$$

The equation (V-4-) shows that when the shift δ increases, the spacing of the dislocations decreases. For small values of d , the structural contribution to the interfacial energy is approximately proportional to the density of dislocations in the interface, i.e. for small δ : $\gamma_{st} \propto \delta$

As the spacing of the dislocations decreases, the associated strain fields increasingly overlap and cancel each other. The energies of semi-coherent interfaces are generally between 200 and 500 mJ m⁻².

The introduction of the new dislocation destroys the partial coherence which gives a completely incoherent interface joint (Fig. V-1-c-).

In general, incoherent interfaces occur when two randomly oriented crystals are joined on any interface plane, as shown in Figure V-1-c-. However, they can also exist between crystals with an orientation relationship if the interface has a different structure in the two crystals.

When the particles reach a sufficiently large size, the lattice coherence is destroyed: the level of elastic energy decrease linked to the formation of accommodation dislocations at the grain boundaries.

Complete relaxation of elastic stresses is achieved after formation of a quantity of dislocations such that the distance between them is:

$$l = \frac{b}{\varepsilon} \quad (\text{V-7-})$$

Where b is the Burger vector of the dislocations,

The mechanism of appearance of dislocations can be different from one particle to another:

- Formation of prismatic loops around the particles in the matrix.
- Birth of dislocation loops inside the precipitates by condensation of point defects.

- Generation of accommodation dislocations on the interface joint itself.
- Dislocations previously formed in the matrix are attracted to the interface.

V-3- Characteristics of the phases formed by precipitation

The notions of order, orientation relations and coherence are three essential notions making it possible to describe the characteristics and certain properties of the precipitates present in a matrix.

A phase is ordered if its various constituent atoms are arranged according to the geometric pattern of the crystallographic structure of the compound and if each crystallographic site is assigned a chemical nature of the atom. This is called *long-range order*. If there are fluctuations or a shift from the chemical assignment, the compound is ordered only at *short-range*. In the extreme, if the atoms are randomly arranged on the crystallographic lattice, the phase is disordered.

Ordered precipitates generally consist of defined stoichiometric compounds with a restricted chemical composition range (case of the majority of equilibrium compounds). Metastable precipitates, appearing during maturation or tempering treatments, are often ordered.

Another important characteristic of structural precipitation is the almost systematic existence of preferential crystallographic orientation relations between the matrix and the precipitates formed by homogeneous precipitation or by heterogeneous precipitation on dislocations, sub-grain boundaries, or even on certain grain boundaries or phases present in the matrix. This is reflected in particular by epitaxial relations, i.e. parallelism relations between the crystallographic planes or directions of the matrix and those of the precipitates.

Finally, precipitates are coherent if there is geometric continuity of the crystallographic lattice of the matrix and of the precipitates in all crystallographic directions. Only the atoms disposition on the lattice is modified (figure V-3-a-).

In aluminum alloys, coherent precipitation is the first stage of homogeneous precipitation during or after the formation of GP zones (Guinier-Preston zones). Coherent precipitates are necessarily very small (up to 5 nm) unless the deviation from coherence is very small. For the GP zones, this difference is small (0.1 to 1%).

When the coherence misfit is too high, dislocations are geometrically necessary at the precipitate-matrix interfaces to accommodate the elastic distortions. This mechanism is observed for precipitates with a very high coherence misfit, which is common for heterogeneous precipitation induced by crystallographic defects and can also result from excessive magnification of initially coherent precipitates. In this case the orientation relationships are semi-coherent i.e. the lattice of the matrix and the precipitates are only coherent along a few planes systems or crystallographic directions (figure V-3-b-).

Finally, the precipitates are incoherent if there is no particular crystallographic orientation relationship between the lattice of the matrix and that of the precipitate (figure V-3-c-). This is the final stage of precipitation, most often in the form of equilibrium phases. The θ (CuAl_2) precipitate in Al-Cu alloys is an example of an incoherent precipitate. It is seen that there is an orientation relationship between θ and the aluminum matrix, but this is probably due to the fact that θ forms from the θ' phase and does not imply that θ is semi-coherent with the matrix.

❖ Precipitation on grain boundaries

Quite particular situations arise when a second phase particle is on a grain boundary, because it is necessary to consider the formation of interfaces with two differently oriented grains. Three possibilities then arise (Fig. V-4-): the precipitate can have (1) incoherent interfaces with the two grains, (2) a coherent or semi-coherent interface with one grain and an incoherent interface with the other, or (3) it can have a coherent or semi-coherent interface with the two grains. The first two cases are commonly encountered but the third possibility is unlikely.

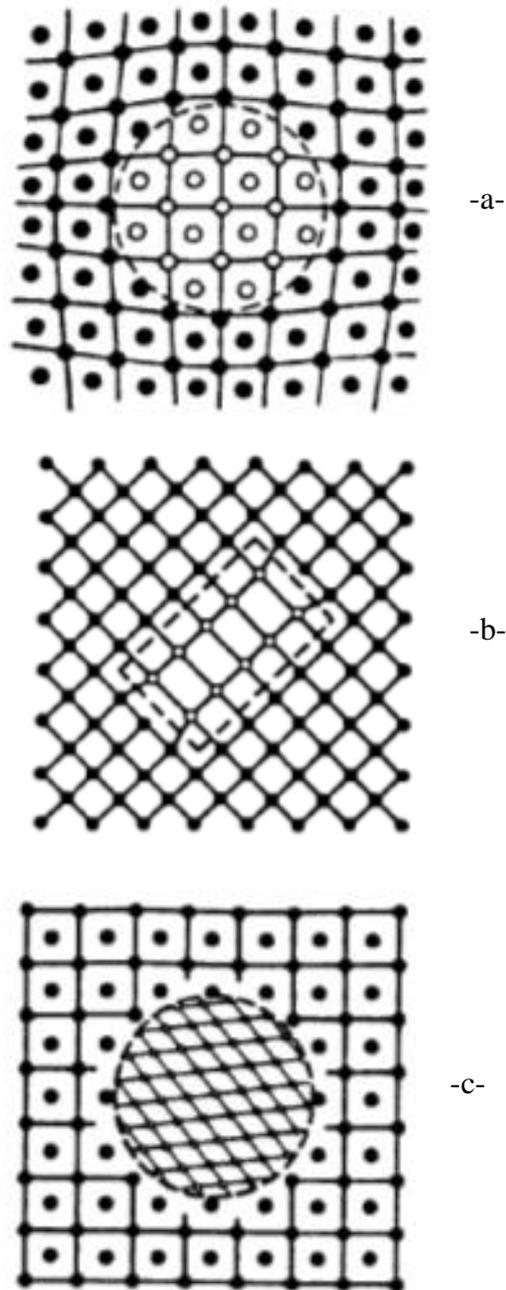


Figure V-3- : (a) Coherent precipitate with lattice distortion due to the volume variation,
(b): Semi-coherent precipitate, (c): Incoherent precipitate.

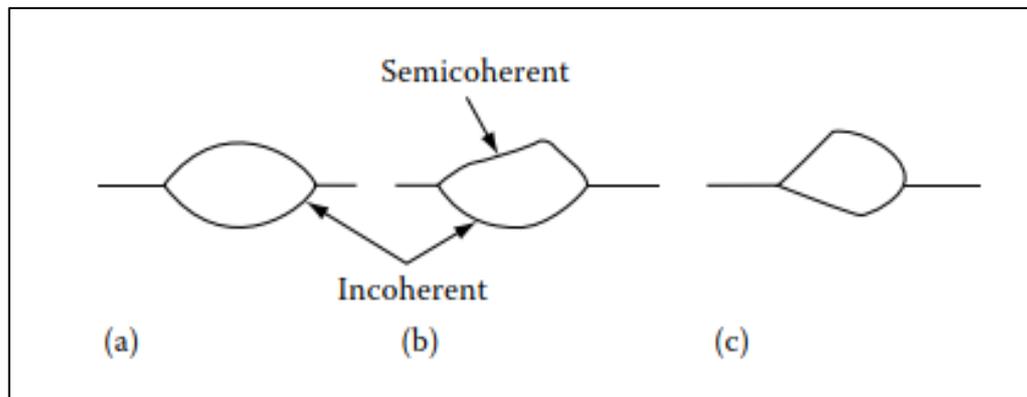


Fig. V-4-: Possible morphologies for grain boundary precipitates. Incoherent interfaces slightly curved. Coherent or semi-coherent interfaces planar.

The minimization of interfacial energy in these cases also leads to semi-coherent or coherent interfaces planar, and slightly curved incoherent interfaces. An example of a grain boundary precipitate is shown in Fig. V-5-.

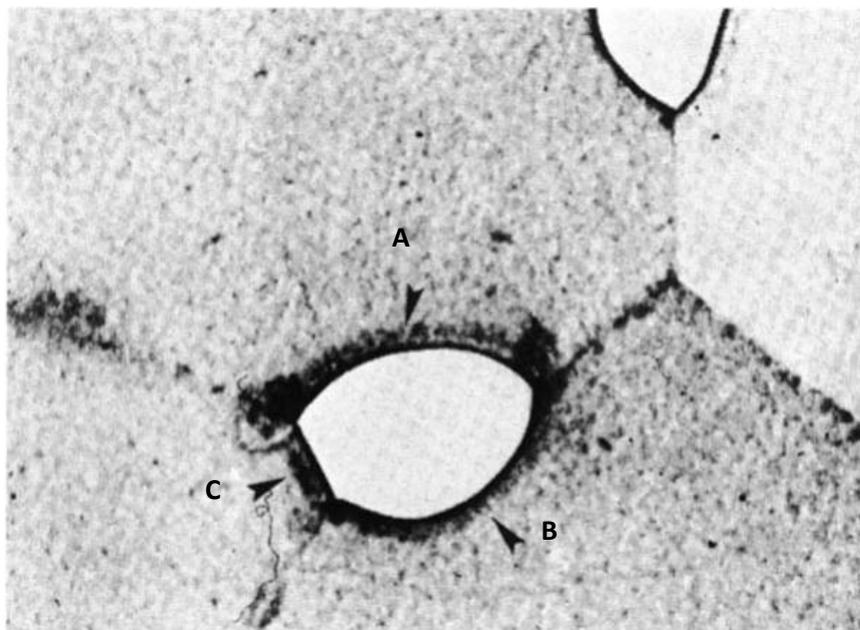


Fig. V-5-: A precipitate at a grain boundaries triple point in an α - β Cu-In alloy. Interfaces A and B are incoherent while C is semi-consistent ($\times 310$) (After G.A. Chadwick, Metallography of Phase Transformations, Butterworths, London, 1972.)

V-4- Misfit Strain effects

When a misfit is present, the formation of coherent interfaces increases the free energy of the system due to the elastic strain fields that occur. If this elastic strain energy is denoted ΔG_s , the equilibrium condition becomes:

$$\sum A_i \gamma_i + \Delta G_s = \text{minimum} \quad (\text{V-8-})$$

The origin of coherence constraints for a misfitting precipitate is demonstrated in Fig. V-6-. If the circled matrix volume in Figure V-6-(a) is sheared and the matrix atoms are replaced by smaller atoms, the sheared volume will undergo a uniform negative expansion strain toward an inclusion with a smaller lattice parameter, Figure V-6-(b). In order to produce a fully coherent precipitate, the matrix and the inclusion must be strained by equal and opposite forces, as shown in Fig. V-6-(c).

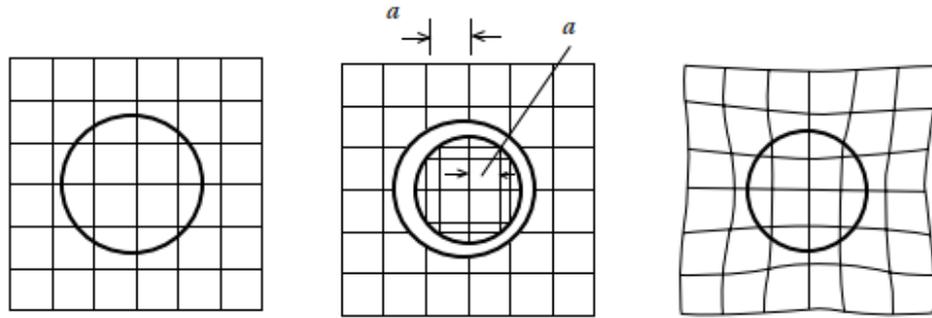


Fig. V-6-: The origin of coherency constraints.

If the lattice parameters of the unconstrained precipitate and the matrix are respectively a_β and a_α , the unconstrained misfit δ is defined by:

$$\delta = \frac{a_\beta - a_\alpha}{a_\alpha} \quad (\text{V-9-})$$

However, the constraints maintaining coherency at the interfaces deform the lattice of the precipitate, and in the case of spherical inclusion the distortion is purely hydrostatic, i.e. it is uniform in all directions, giving a new parameter of $a_{\beta'}$ network. The misfit with constraint ε is defined by:

$$\varepsilon = \frac{a'_{\beta} - a_\alpha}{a_\alpha} \quad (\text{V-10-})$$

If the elastic moduli of the matrix and the inclusion are equal and the Poisson's ratio is 1/3, ϵ and δ are simply related by:

$$\epsilon = \frac{2}{3}\delta \quad (\text{V-11-})$$

In practice, the inclusion has elastic constants different from the matrix, nevertheless ϵ is always generally in the interval $0.5 \delta < \epsilon < \delta$.

When the precipitate is a thin disk, the in situ misfit is no longer equal in all directions, but is rather large perpendicular to the disk and almost zero in the plane of the broad faces, as shown in Figure V-7-.

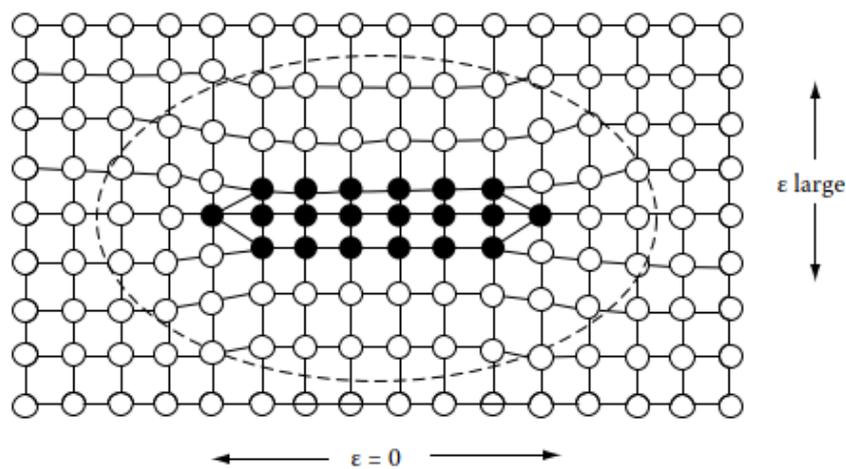


Fig. V-7-: For a coherent thin disk, there is little misfit parallel to the plane of the disk. The maximum misfit is perpendicular to the disc.

In general, the total elastic energy depends on the shape and the elastic properties of the matrix and the inclusion. However, if the matrix is elastically isotropic and the precipitate and matrix have equal elastic moduli, the total elastic strain energy ΔG_s is independent of the shape of the precipitate, and assuming Poisson's ratio (ν) = 1/3, it is given by:

$$\Delta G_s \cong 4\mu\delta^2V \quad (\text{V-12-})$$

Where μ is the shear modulus of the matrix and V is the volume of unstressed precipitate in the matrix. Therefore, the coherence strains produce an elastic strain energy which is proportional to the volume of the precipitate and which increases as the square of the lattice misfit (δ^2).

When the inclusion is incoherent with the matrix, there is no attempt to match the two lattices and the lattice sites are not preserved across the interface. Under these circumstances, there are no consistency constraints. Misfit strains can, however, occur if the inclusion is not the correct size for the hole it is in, Fig. V-8-. In this case, the lattice shift δ has no significance and it is better to consider the volume shift Δ as defined by:

$$\Delta = \frac{\Delta V}{V} \quad (\text{V-13-})$$

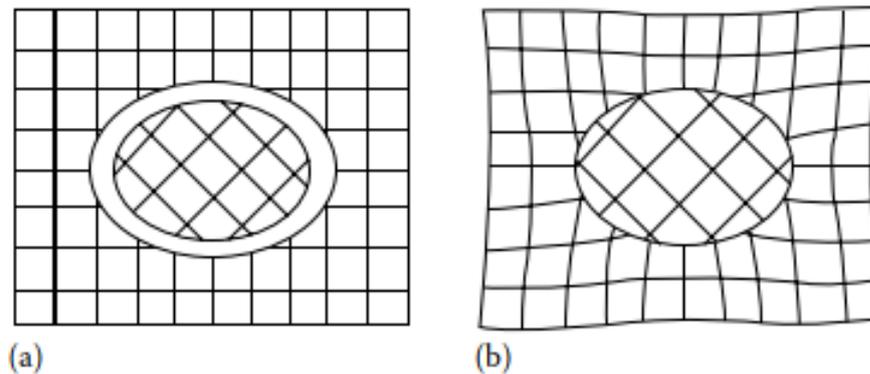


Fig. V-8-: The origin of misfit strain for incoherent inclusion

The researcher Nabarro gives the elastic strain energy for a homogeneous incompressible inclusion in an isotropic matrix as:

$$\Delta G_s = \frac{2}{3} \mu \Delta^2 V f \left(\frac{c}{a} \right) \quad (\text{V-14-})$$

Where μ is the shear modulus of the matrix. Thus, the elastic strain energy is proportional to Δ^2 . The function $f(c/a)$ is a factor which takes shape effects into account and is shown in Fig. V-9-. For a given volume, a sphere ($c/a = 1$) has the highest strain energy while a thin, flattened spheroid ($c/a \rightarrow 0$) has a very low strain energy and a shape of needle ($c/a = \infty$) lies between the two. Therefore, the equilibrium shape of an incoherent inclusion will be an oblate spheroid with a c/a value that balances the opposing effects of interfacial energy and strain energy. When Δ is small, interfacial energy effects should dominate and the inclusion should be roughly spherical.

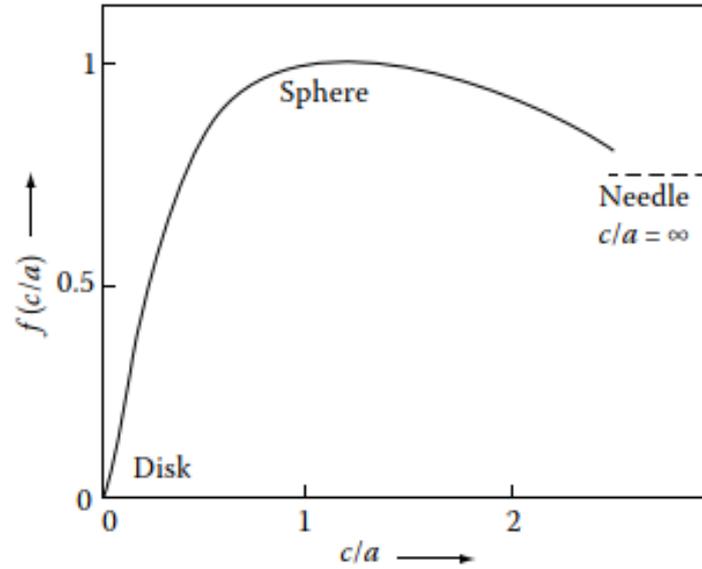


Fig. V-9- : The variation of $f(c/a)$. (After F.R.N. Nabarro, Proceedings of the Royal Society A, 175 (1940) 519.)

V-5- Loss of coherence

Precipitates with coherent interfaces have low interfacial energy, but in the presence of shifting they are associated with coherent strain energy. On the other hand, if the same precipitate has non-coherent interfaces, it will have a higher interfacial energy. Now consider which state produces the lowest total energy for a spherical precipitate with misfit δ and radius r .

The free energy of a crystal containing a fully coherent spherical precipitate has contributions from:

- The coherence strain energy given by the equation below,
- The interfacial chemical energy γ_{ch} .

The sum of these two terms is given by:

$$\Delta G_{coh} = 4\mu\delta^2 \frac{4}{3}\pi r^3 + 4\pi r^2 \gamma_{ch} \quad (V-15-)$$

If the same precipitate has incoherent or semi-coherent interfaces, there will be no mismatch energy, but there will be an additional structural contribution to the interfacial energy γ_{st} . The total energy in this case is given by:

$$\Delta G_{non-coh} = 0 + 4\pi r^2 (\gamma_{ch} + \gamma_{st}) \quad (V-16-)$$

For a given δ , $\Delta G_{(coherent)}$ and $\Delta G_{(non-coherent)}$ vary with r as shown in Fig. V-10-. When small, therefore, the coherent state gives the lowest total energy, while it is more favorable for large precipitates to be semi-coherent or incoherent (depending on the magnitude of δ). At critical radius (r_{crit}); $\Delta G_{(coherent)} = \Delta G_{(non-coherent)}$ giving:

$$r_{crit} = \frac{3\gamma_{st}}{4\pi\delta^2} \quad (V-17-)$$

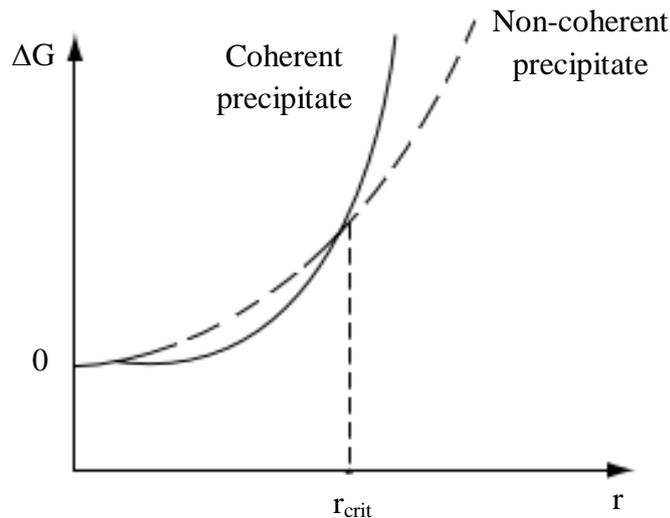


Fig. V-10-: Total energy of the matrix plus precipitate with respect to the radius of the precipitate for the coherent and non-coherent spherical precipitates (semi-coherent or incoherent).

❖ **Characteristics of the phases formed during precipitation and modulated structure:**

These structures are formed, for example, during the demixing of solid solutions. In the binary Ni-Al, Ni-Ti, Ni-Au, and ternary Cu-Ni-Fe, Fe-Ni-Al alloys, two new isomorphic phases with different compositions are formed; the dependence of the lattice parameter on the concentration obeys Vegard's law:

$$a = a_0(1 + q_0C) \quad (V-18-)$$

Where:

a_0 is the lattice parameter of one of the constituents.

q_0 is the expansion coefficient of the lattice.

C is the concentration of the 2nd component.

Differences in composition and therefore in lattice parameters must lead to the appearance of constraints. It can be shown that with respect to the elastic energy, the formation of complexes of alternating lamellae, enriched and depleted in one of the elements, is more advantageous than the formation of discs of the same independent phases.

Practice exercise

Exercise 1:

Mg can dissolve in Al to form a substitutional solid solution. However, Mg atoms are larger than Al atoms and therefore each Mg atom distorts the surrounding Al lattice, i.e. stress field coherence effectively exists around each Mg atom.

- Show the strain energy in kJ mol^{-1} and eV atom^{-1} .
- What hypotheses are implicit in this calculation?

We give: The shear modulus of $\mu_{\text{Al}} = 25\text{GPa}$, $r_{\text{Al}} = 1,43 \text{ \AA}$, $r_{\text{Mg}} = 1,60 \text{ \AA}$.

Exercise 2:

Figure -1- shows the different phases, stable and metastable, present in the Al-4 at.% Cu. They are given on this figure not necessarily in the chronological order of their appearance.

- Characterize the interfaces for each phase and indicate which phases are a priori the easiest to germinate. Deduce the hardening precipitation sequence in Al-Cu alloys.

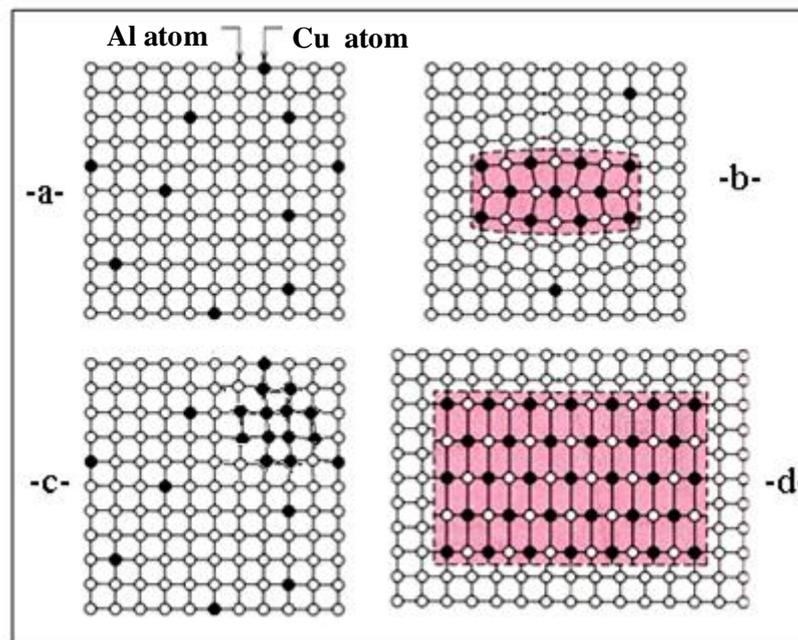


Figure 1

Exercise 3:

- 1- A coherent interface between a precipitate and a matrix is characterized by a chemical energy γ_{ch} .
 - What is the form of precipitate that minimizes this surface contribution?
- 2- In reality, the lattice parameters of the precipitates are not perfectly equal to the lattice parameter of the matrix, so that the interfaces are coherent,
 - What is the free energy associated with the presence of a spherical precipitate?
- 3- If the same precipitate has an inconsistent (or semi-coherent) interface,
 - What is going on?
 - What is the free energy associated with the presence of this precipitate in this case?
- 4- For a given gap δ , schematize the variation of ΔG_{coh} and ΔG_{incoh}
 - What do you notice?