PHYSICS OF MATERIALS

Physics School Autumn 2025

Series 12 Solution **12 December 2025**

Exercise 1: Precipitation sequence in Al-Cu

In equation 12.1 of the course textbook:

$$\Delta G_{hom} = V\left(\Delta g_v + \Delta g_{el}\right) + S\gamma \qquad (12.1.1)$$

We observe that two terms limit nucleation: the elastic energy and the interface energy. If the precipitate is coherent, the interface energy is low, and the elastic term of the energy is the dominant contribution to the free energy (the chemical force of the transformation Δg_v remains the same).

We find the opposite situation in the case of incoherent precipitates. Indeed, the loss of the coherent interface with the matrix increases the disorder and the interface energy, but it also decreases the "misfit" strains between precipitates and the matrix that generate internal stresses. Considering a penny-shaped precipitate of thickness *t* and radius *r*, we define the aspect ratio $A = \frac{r}{t}$ that we assume is constant. Thus: $r = A \cdot t$

In the case of an incoherent precipitate, we neglect the elastic energy, and the total energy is given by:

$$\Delta G_{hom/nc} = -\pi\left(At\right)^2 t\Delta g_v + \gamma\left[2\pi\left(At\right)^2 + 2\pi\left(At\right)t\right] \qquad (12.1.2)$$

In the case of a coherent precipitate, the volume term dominates :

$$\Delta G_{hom/c} = \pi\left(At\right)^2 t\left(-\Delta g_v + \frac{3}{2}E\eta^2\right) \qquad (12.1.3)$$

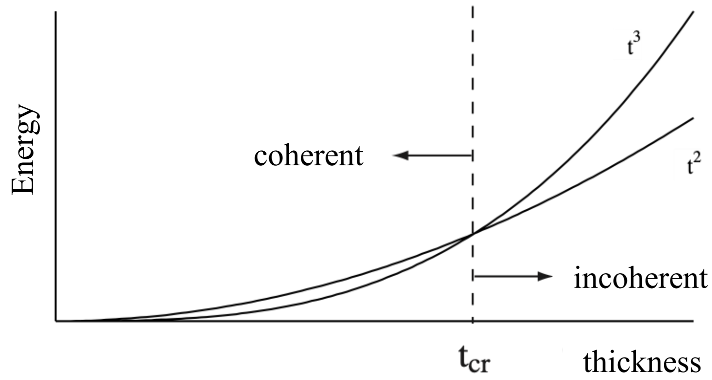


Fig. 12.1 Sum of the elastic and interface energies depending on the coherent and incoherent precipitate thickness.

Thus, the part of energy (positive) that opposes the nucleation varies depending on t^3 in the case of coherent precipitates and on t^2 in incoherent precipitates. As illustrated in Fig. 12.1, small-sized (thickness) precipitates have a coherent interface with the matrix.

The transition occurs for $V\Delta g_{el} = S\gamma$, which gives:

$$t_{cr} = \frac{4}{3}\frac{\gamma}{E\eta^2}\left[1+\frac{1}{A}\right] \tag{12.1.4}$$

Numerical application

From the structure of the precipitates in Cu-4%al, we observe that the volume expansion of the θ'' phase is given by $\eta = \frac{(2.02+1.82)-4.04}{4.04} = -4.95\%$. Using the formula (1.4), we get:

$$t_{cr} = 5.6\ nm$$
$$r_{cr} = A{\cdot}t_{cr} = 28.2\ nm$$

These dimensions agree with the typical dimensions of the GP zones in Cu-4%Al, as shown in TEM figure 12.2. The dark contrast features with plate morphologies are the diffraction contrast from GP zones with 3-7 nm sizes.

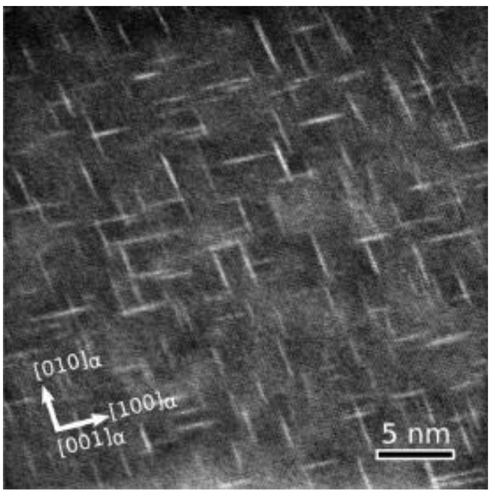


Fig. 12.2 Guinier-Preston zones in Al-Cu

Exercise 2 Localized nucleation

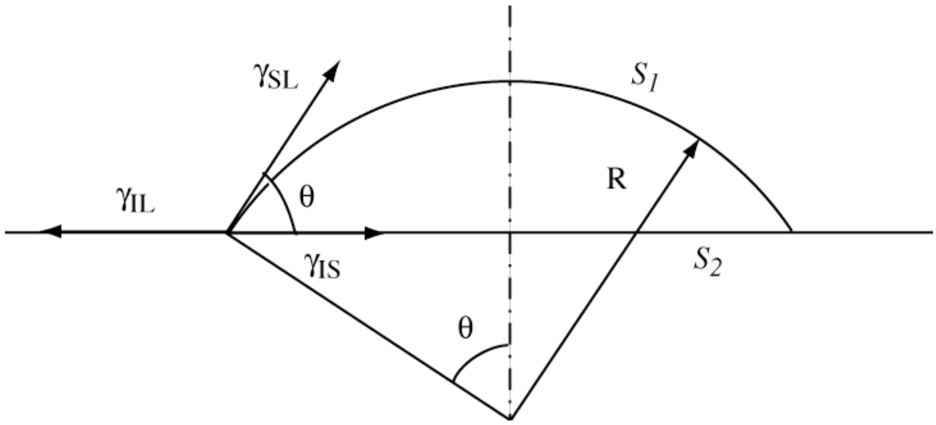


Figure 12.3: Wetting angle geometry for Young's law formalism for heterogeneous nucleation on a surface

Figure 12.3 represents the interface (surface) of the impurity or the mold's wall. Young's law gives the force equilibrium:

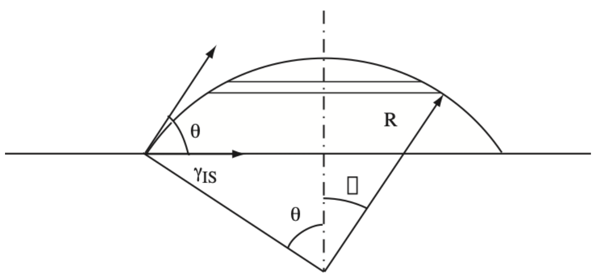
$$\gamma_{IL} = \gamma_{IS} + \gamma_{SL} \ \cos \ \theta \qquad (12.2.1)$$

Variation of the free energy at the creation of a nucleus in the shape of a spherical cap:

$$\Delta G = \Delta g_v \cdot V + \gamma_{SL} \cdot S_1 + \left(\gamma_{IS} - \gamma_{IL}\right) S_2 \qquad (12.2.2)$$

S_1 is the external surface of the spherical cap, whereas S_2 is the surface of the base. The difference between /and /gives the tension acting on the base's surface. The cap extension is favorable (and, consequently, the energy variation is negative) if $\gamma_{IS} < \gamma_{IL}$. This justifies the sign of the factor $\gamma_{IS} - \gamma_{IL}$ in (12.2.2).

Calculation of volume V of the cap:



$$dV = \pi \ R^2 \sin^2 \varphi(-dz)$$

$$z = R \ \cos\varphi \ \rightarrow \ dz = -R \ \sin\varphi \ d\varphi$$

$$V = \int_o^\theta \pi \ R^3 \sin^2 \varphi \cdot \sin\varphi \ d\varphi =$$

$$= \pi \ R^3 \int_o^\theta \left(1 - \cos^2 \varphi\right) \ \sin\varphi \ d\varphi =$$

$$= \pi \ R^3 \left[-\cos\varphi + \frac{\cos^3 \varphi}{3} \right]_o^\theta =$$

$$= \pi \ R^3 \left[-\cos\theta + \frac{\cos^3 \theta}{3} - \left(-1 + \frac{1}{3} \right) \right] =$$

$$= \frac{\pi \ R^3}{3} \left[2 - 3\cos\theta + \cos^3 \theta \right]$$

We consider a small slice of thickness *dz* and radius $R\sin(\phi)$.

Surface IS: $S_2 = \pi R^2 \sin^2\theta$

Surface SL: $S_1 = \int_0^\theta 2\pi R \sin\varphi \cdot R\, d\varphi = 2\pi R^2 (1-\cos\theta)$

$$\Delta G = \Delta g_v \frac{\pi R^3}{3}\left[2 - 3\cos\theta + \cos^3\theta\right] + \gamma_{SL} 2\pi R^2 \left[1-\cos\theta\right] + \left(\gamma_{IS} - \gamma_{IL}\right)\pi R^2 \sin^2\theta$$

But equation (1) gives: $\gamma_{IS} - \gamma_{IL} = -\gamma_{SL}\cos\theta$

$$\Delta G = \Delta g_v \frac{\pi R^3}{3}\left[2 - 3\cos\theta + \cos^3\theta\right] + \gamma_{SL}\pi R^2\left[2 - 2\cos\theta - \cos\theta\sin^2\theta\right]$$

$$= \Delta g_v \frac{\pi R^3}{3}\left[2 - 3\cos\theta + \cos^3\theta\right] + \gamma_{SL}\pi R^2\left[2 - 3\cos\theta - \cos^3\theta\right]$$

$$\Delta \mathrm{G} = \left(\frac{\pi R^3}{3}\Delta g_v + \pi R^2 \gamma_{SL}\right)\left[2 - 3\cos\theta + \cos^3\theta\right] \tag{12.2.3}$$

$\cos\theta = \dfrac{\gamma_{IL} - \gamma_{IS}}{\gamma_{SL}}$ does not depend on *R* and, therefore:

$$\frac{\partial \Delta G}{\partial R} = \left(\pi R^2 \Delta g_v + 2\pi R \gamma_{SL}\right)\left[2 - 3\cos\theta + \cos^3\theta\right] = 0$$

$$\Rightarrow \qquad R^* \Delta g_v + 2\gamma_{SL} = 0$$

Thus: $$R^*_{loc} = -\frac{2\gamma_{SL}}{\Delta g^*_v} \tag{12.2.4}$$

And also: $$\Delta g^*_v = \left(g_S - g_L\right) = -\frac{L}{T_F}\Delta T \Rightarrow R^*_{loc} = \frac{2\gamma_{SL} T_F}{L \cdot \Delta T} \tag{12.2.5}$$

By combining (3) and (5), we get the potential barrier ΔG^*_{loc}:

$$\Delta G^*_{loc} = \left[\frac{\pi}{3}\left(\frac{-8\gamma^3_{SL}}{\Delta g^2_v}\right) + \pi\frac{4\gamma^3_{SL}}{\Delta g^2_v}\right]\left[2 - 3\cos\theta + \cos^3\theta\right] \tag{12.2.6}$$

and therefore:

$$\Delta G^*_{loc} = \frac{4}{3}\pi\frac{\gamma^3_{SL}}{\Delta g^2_v}\left[2 - 3\cos\theta + \cos^3\theta\right] \tag{12.2.7}$$