Part VII. Miscellaneous topics
Module 3. Coarsening

3 Coarsening

3.1 Motivation

Consider a precipitation hardenable alloy. As a function of aging time, after peak aging the strength reduces. It is found that the decrease in strength continues even though no new phase is formed and the phases and volume fractions of the precipitates do not change. Why?

3.2 Coarsening or Ostwald ripening

Coarsening is a process that is quite similar to grain growth in that the interphase interfacial energy provides the driving force for this process; coarsening is curvature driven; the smaller precipitates grow at the cost of larger precipitates during coarsening. During coarsening, the overall volume of the precipitates remain the same; however, since the precipitate sizes are larger, their separation is also larger which leads to degradation of material properties.

3.3 Gibbs-Thomson effect

The curvature driven increase in the interfacial free energy and hence the overall free energy of the system is known as capillary or Gibbs-Thomson effect.

Consider the β phase particles in an α matrix as shown in Fig. 9; let the interphase interfacial energy be α; much like the excess pressure exerted inside a soap bubble, the excess pressure in such a β particle is given by $2\gamma/r$. The free energy increase associated with this pressure is $2\gamma V_m/r$ where V_m is the molar volume of the β phase.

The increase in interfacial energy with the curvature of the particle, in turn, affects the equilibrium properties; as can be seen clearly from Fig. 10, the composition of the β phase in equilibrium with the α phase changes with the

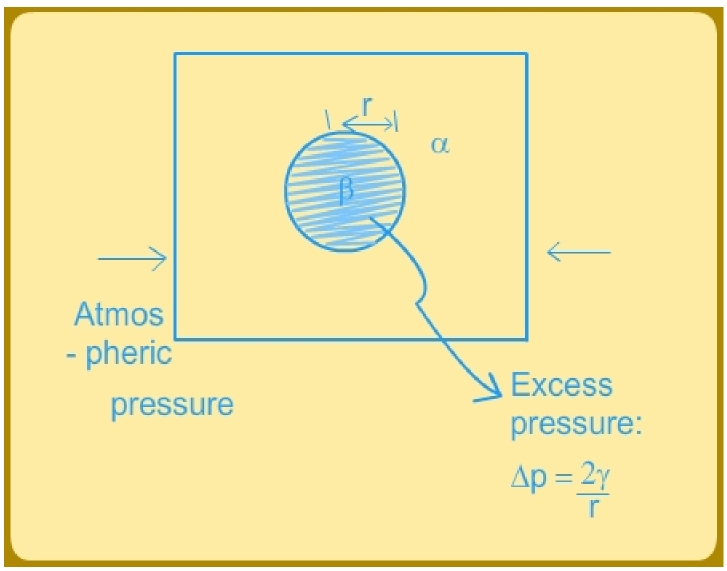

Figure 9: Excess pressure inside a β precipitate of radius r inside an α matrix; the system is at ambient pressure; the precipitate supports an excess pressure which arises from the interfacial energy.

radius of the particle. This shift in equilibrium composition is a manifestation of the Gibbs-Thomson of capillary effect.

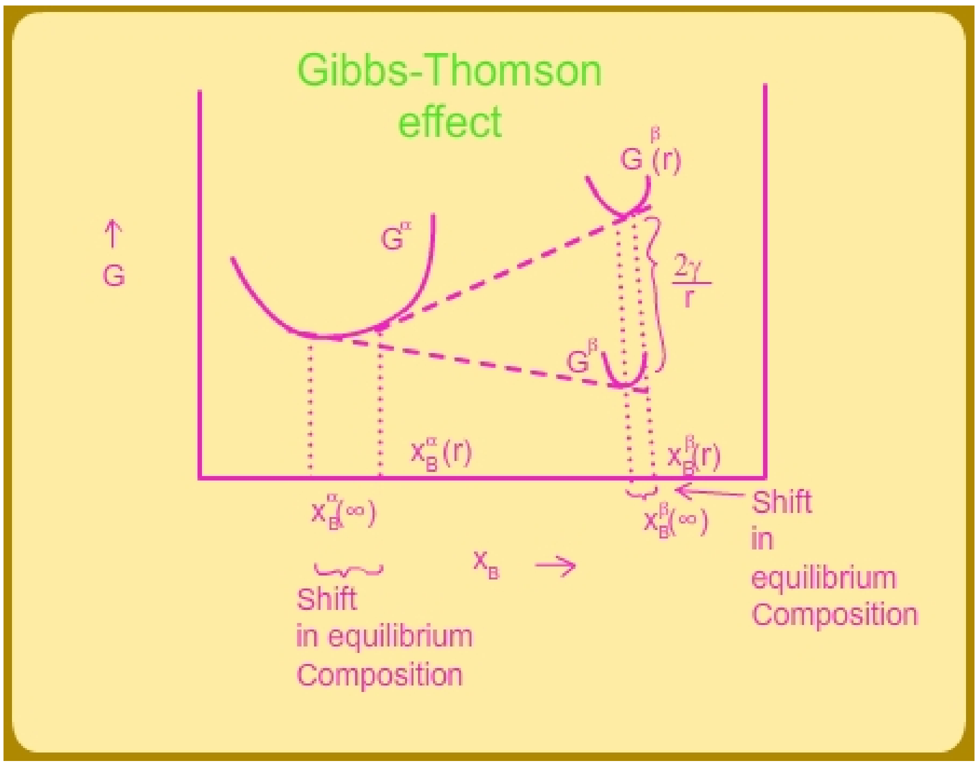

Figure 10: Gibbs-Thomson or capillary effect: the shift in equilibrium composition with the curvature of the β precipitate.

Let us consider two β particles of two different sizes as shown in Fig. 11. As the accompanying free energy versus composition diagram shows, the composition on the α phase across the $\alpha - \beta$ interface for the two particles are such that the B atoms in the α matrix next to the smaller β particle migrate to the regions of α matrix next to the bigger particle; this, in turn makes the smaller β particle shrink; hence, once set in, the process continues till the smaller particle completely disappears with a corresponding increase in the size of the bigger particle. This process is known as coarsening or Ostwald ripening.

3.4 Tutorial problems and questions

1. Using typical values, show that the capillary effects are very important for particle in the range 1-100 nm.

3.5 Solutions to the tutorial

1. As seen in Part III of this course notes, assuming the α phase to be a regular solution and the β phase to be nearly pure B, one can obtain the composition of the α phase in equilibrium with the β phase of radius r as

$$X_r = X_\infty \left(1 + \frac{2\gamma V_m}{rRT}\right) \tag{4}$$

Consider the typical values of 200 mJ/m^2 for γ, and 10^{-5} m^3 for V_m; at 500 K (since R = 8.31 J/mol/K), one obtains

$$\frac{X_r}{X_\infty} = 1 + \frac{1}{r(\text{in nm})} \tag{5}$$

Thus, for radii in the nanometre range, there will be considerable changes in equilibrium compositions which become negligible when the length scales are in the micron range.

3.6 Supplementary information

Under certain (albeit very restrictive) assumptions it is possible to derive a law known as LSW (Lifshitz-Slyozov-Wagner) to describe the kinetics of Ostwald ripening. However, such a derivation it outside the purview of these class notes. The interested reader is referred to [3] for details.

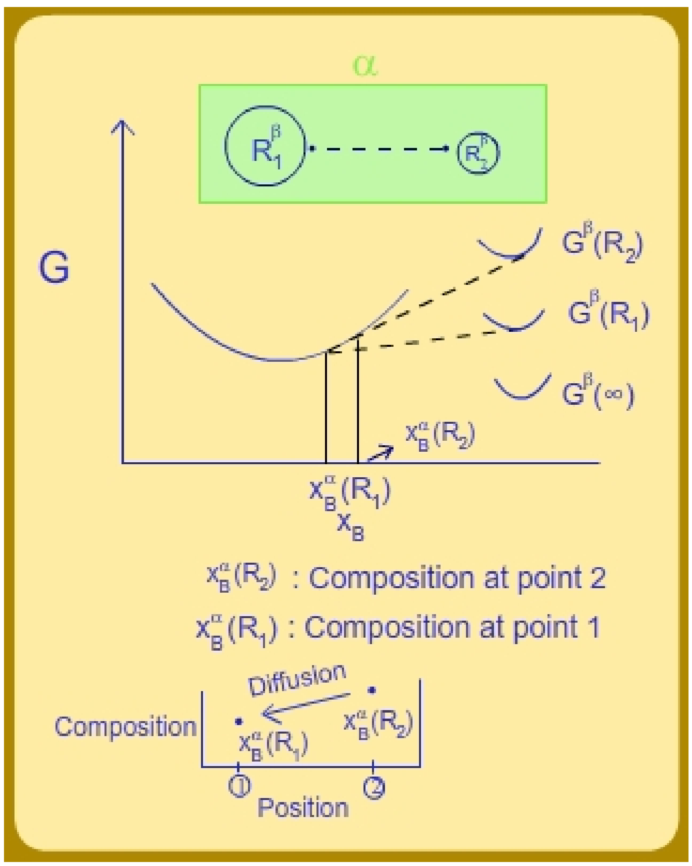

Figure 11: Gibbs-Thomson or capillary effect facilitates the mechanism of Ostwald ripening or coarsening.

References

[1] David A. Porter, Kenneth E. Easterling, and Mohamed Y. Sherif, Phase transformations in metals and alloys, CRC press, Third edition, 2009.

[2] V Raghavan, Solid state phase transformations, Prentice-Hall India Pvt. Ltd., First edition, 1992.

[3] J W Martin, R D Doherty and B Cantor, Stability of microstructure in metallic systems, Cambridge Solid State Science Series, Cambridge University Press, Second edition, 1997.