PRECIPITATE NUCLEATION IN ALLOYS

INTRODUCTION:

This set of notes is written as what the literati call an "Interlinear." My notes fit in between the lines of the corresponding sections in Porter and Easterling, Phase Transformations in Metals and Alloys, Chapters 4, 5. I like Porter and Easterling better than Reed-Hill and Abbaschian, mostly because the former understand the material better than do the latter. There are a number of things in R-H and A that are just plain wrong, and I am a bit tired of correcting them. Also, students don't like to be told the text is wrong: they want it to be the *final* word. Those looking for a more complete treatment of nucleation in solids are referred to my review listed in the References.

There are a number of ways which nucleation in solids may be approached. I remain convinced that the laid out by J.W. Gibbs over 100 years ago is still the best, in that it produces the most usable results. Gibbs ascribed macroscopic properties to microscopic clusters of only tens of atoms, a treatment that has been shown to work better than anyone could expect.

I can hear the groans and see the eyes rolling. Why not use something more modern, like *molecular dynamics* and calculate the nucleation parameters straight away? A quick calculation rules out such a scheme.

Nucleation is a fluctuational process, which means that a horde of small clusters is formed for every critical nucleus. The system must be large enough to encompass a large number of these fluctuational events to ensure the appearance of even one critical nucleus. I would want a system of at least 10^9 atoms, which is a cube 1000 atoms on an edge. We are interested in multi-component alloys at about half the absolute melting point, at which temperature the atomic jump frequency is about $1/s$. We will need to calculate over, say, 10^6 jump times to give the fluctuations ample chances to form and decay. Molecular dynamics requires that the time step be small compared to the atomic vibration period, which is about 10^{-13} sec. If the time step is 10^{-14} s, we need 10^{20} steps times 10^6 atoms, or 10^{26} bits of information, or whatever they are called. Talk to Prof. Gerd Ceder of DMSE or one of his students and you will be told that the biggest computers are nowhere near handling a job of that size.

The *phase field technique* has been used to good effect in describing a number of processes, including grain growth in pure metals (XX). So why is precipitation from solid solution so much tougher? First and foremost grain growth in pure metals involves only atoms on the grain boundary, which for a 0.1 mm grain size

is about one atom in 10^5. Then, at $T_m/2$ boundary atoms jump about 10^8 times faster than lattice atoms. The required "work" of simulation is thus cut by thirteen orders of magnitude and the task is do-able with today's computers.

Maybe someday before today's students are retired some computer technique will give a reasonable representation of precipitation in solid alloys, but that time is not near.

RATE EQUATION:
How does one get from such obviously relevant quantities as driving force, surface energy, and diffusivity to get an equation for the rate at which particles of the new phase appear? The treatment in P&E leading up to Eq. 4.12 is delightfully simple and as good as any. The more complex treatments given in R-H&A gain very little in accuracy and their complexity greatly increases the chance for serious error. Those interested in all the gory details are referred to Ref. (XX).

The assumptions are basically those of so-called "Absolute Rate Theory".
1.   Critical nuclei exist which are in equilibrium with the matrix.
2.   The critical nuclei gain atoms at a rate, f_o to become supercritical.
3.   Supercritical nuclei do not decay to become sub critical.

The nucleation rate N_{HOM} (nuclei/m^3/s) is given as:

$$N_{HOM} = f_o C^*$$

Where C* is the metastable equilibrium concentration of critical nuclei, in nuclei/m^3.

$$C^* = C_o \exp.(-\Delta G^*/kT)$$

where C_o = # nucleation sites/unit volume and ΔG^* = free energy of forming a critical nucleus.   This equation is of general validity for all nucleation conditions. Of course, f_o and C* depend on the kind of nucleation being described.

SOLIDIFICATION:
I start with crystal nucleation in solidification in a pure metal because the physics are simpler than precipitate nucleation from solid solution. The latter involves compositional effects, including solid-state diffusion and complicated thermodynamics. In addition almost all nucleation in solids involves the energy due to straining of the crystalline lattice. Solidification makes a nice, simple starting point.

Section 4.1.1 gives a nice derivation of ΔG* for homogeneous nucleation. ΔG* and r*, the critical nucleus radius are seen to take on very simple forms. The text does not say so, but f_o = (number of liquid atoms contacting the critical nucleus)(frequency of atomic jumps from the liquid to the solid.) To a good approximation, $f_o = D_L/a^2$, where D_L = diffusion coefficient in the liquid and a = lattice parameter. The various geometrical factors do a nice job of canceling out, as you can easily show for yourselves, should you so desire.

The ancillary data needed to calculate N_{HOM} are readily available, save γ_{SL}. Even so, if one makes a reasonable estimate of γ_{SL} it is easy to calculate that solid nucleation should only occur at undercoolings of about $T_m/3$, where T_m = the absolute melting point. In real life ingots start to solidify at a fraction of a degree of under cooling.

The error was in assuming homogeneous nucleation. In fact, 99.99999+ % of nucleation is heterogeneous. The first crystals form on the mold wall or on little pieces of crud in the melt. Carefully controlled experiments on micron-sized droplets may eliminate all heterogeneities. In such experiments the predicted undercoolings of about $T_m/3$ are observed.

Section 4.1.3 gives a nice treatment of heterogeneous nucleation in solidification. The cap-shaped model in Fig. 4.7 will also be useful in nucleation in solids. The catalytic potency of the mould is governed by the contact angle, θ.
A   θ.
The solid-liquid surface energy γ_{SL} is proportional to the enthalpy of melting, L_v, which in turn is proportional to the absolute melting point, T_m. There isn't much you can do to change γ_{SL} except maybe add a surface-active alloying element. The contact angle and ΔG* are minimized for a high γ_{ML} compared to γ_{SM}. That is, the energy of the interface created is a lot smaller than that of the interface replaced. In general a high level of lattice matching and strong chemical interactions between the solid and mould promote a small γ_{SM}.

The critical radius, r* of the curved part of the cap is the same as for homogeneous nucleation. Gibbs showed that ΔG* is proportional to V*: thus, a low θ leads to just a thin spherical segment being formed and a small ΔG*. This point is illustrated in Figs. 4.8 and 4.9(a). Figure 4.9(A) gives me reason to enunciate one of my rules of thumb (ROT). Nucleation becomes appreciable on a human time scale only if ΔG*/kT<60. Nucleaters may quibble as to whether the number should be 50, 60, or 70, but they are all the same to me.

I have modified Fig. 4.9(b) which originally showed that $N_{het} > N_{hom}$ for all undercoolings. Tain't so! Heterogeneous nucleation indeed becomes appreciable at smaller undercoolings, but maxes out due to a limited number of

heterogeneous nucleation sites. The modified figure shows that homogeneous nucleation becomes dominant shortly after becoming appreciable.

Figure 4.10 shows that pits in the mould wall may be extremely effective heterogeneous nucleation sites. I recently had a project involving the nucleation of hydrogen bubbles from a solidifying melt. Calculations by my student, Sridhar Seetharaman (Now a fast-rising Professor at Carnegie-Mellon U) showed that bubble nucleation could only occur in very sharply pointed pits or in sharp cracks in a nonmetallic heterogeneity (such particles are commonly referred to as crud.)   The reason is that ΔG_v for bubble nucleation is so small that an extremely potent heterogeneity is needed to make $\Delta G^*/kT < 60$ and allow nucleation.

HOMOGENEOUS NUCLEATION OF PRECIPITATES:
Figure 5.1 (a-i) shows a phase diagram with conditions conducive for precipitate nucleation. Homogeneous nucleation in solids almost never occurs. I discuss it as a simple starting point. Homogeneous nucleation in solids may ONLY occur if precipitate (β) and matrix (α) have the same crystal structure and have nearly the same lattice constants. Otherwise the surface energy and/or strain energy will be so great as to preclude nucleation.

No driving force (save due to irradiation) is great enough to overcome the energy barrier inherent in a less than coherent interface. Homogeneous nucleation with less than full coherency, as for a BCC or HCP phase in a FCC matrix is out of the question.

Two very important facts simplify calculation of ΔG^*.
   1. $\gamma_{\alpha\beta}$ is very nearly independent of interface orientation.
   2.   The strain energy is INDEPENDENT of nucleus shape.
Accordingly, a sphere may represent the critical nucleus.

Section 5.1 develops the equations for homogeneous nucleation and does so correctly. I will dig further into means of obtaining $\gamma_{\alpha\beta}$, ΔG_v, and ΔG_s later. The text is a bit vague on f. the frequency factor. It is simply the number of solute (B) atoms contacting the critical nucleus times their jump frequency toward the nucleus. The various geometrical factors cancel out, as they did in solidification, and to good approximation $f = X_o D/a^2$, where X_o = atomic fraction of B in the matrix, D = volume diffusion coefficient, and a = lattice spacing. In EQ. 5.11, ΔG_m = free energy of volume diffusion, which is nearly equal to the enthalpy of diffusion, ΔH_m, and ω = lattice vibration frequency, which I always take as $10^{13}/s$.

HETEROGENEOUS NUCLEATION:
The vast majority of nucleation is on heterogeneities. In condensation from the vapor gaseous ions and dust particles are choice nucleation sites. In solids grain

boundaries and inclusion interfaces, free surfaces, and dislocations are choice nucleation sites.

The central result of many years of discussion and argumentation between various other nucleaters and myself is that the interfaces bounding the critical nucleus will be "as coherent as possible." In extreme cases the most perfect coherency would result in a strain energy exceeding ΔG_v, the chemical driving force. Nucleation under such circumstances is impossible. Otherwise the "coherent as possible" rule will apply and provide crucial aid in deducing the orientation and morphology of the critical nucleus in heterogeneous nucleation.

Grain Boundaries:
Many alloy systems have intermediate phases with complex crystal structures. Lattice matching with the matrix is poor and the interfacial energies tend to be high. Nucleation of such phases is only possible in the presence of a potent heterogeneity, most likely a grain boundary. The strain energy associated with such nucleation is fairly small and I will take $\Delta G_s = 0$.

A vast variety of critical nucleus shapes may apply to nucleation at grain boundaries, especially when α and β have different crystal structures. Some proposed shapes resemble the result of a switchblade attack on an apple, with various bits of curved and faceted interface. Calculation of the surface energy of such particles is outright punitive. The results are dreadful polynomials of trig. functions that are unlikely to be written correctly to begin with, let alone remembered.

I will not subject you to it. Just remember that the critical nucleus is in unstable equilibrium with the surrounding material, and that:

$\Delta G^* = -V^* \Delta G_v / 2$

the curvature of the interfaces is given by

$r^* = 2\gamma / \Delta G_v$.
Where γ = energy of the interface in question and V^* = volume of critical nucleus. This result is from Gibbs. So, the smaller the critical nucleus, the easier it is to form. You should be able to tell intuitively from the following constructions just how much help the grain boundary is providing in forming the critical nucleus.

The nucleus will have different orientations with respect to the two adjacent grains, hence different interfacial energies. Let the lower energy interface have an energy of γ_c and the larger energy interface γ_i. The critical nucleus shape is

given by the following construction. Draw spheres of radii of γ_c and γ_i and separate the centers by γ_b, where γ_b = grain boundary energy. (See Figure N-1.) The volume common to the two spheres is geometrically similar to the critical nucleus, which will be bounded by curved surfaces of radii r^*_c and r^*_i. Gibbs is satisfied, as both curved interfaces are in equilibrium with the matrix and the construction ensures that equilibrium is satisfied at the three-grain junction.

As γ_b approaches $\gamma_c + \gamma_i$ the critical nucleus becomes a minute lens and DG*--> 0. Figure 5.6 shows the same construction done with the traditional balance of surface energies.   For the very simple case of $\gamma_b = \gamma_c = \gamma_i$ (Fig. 5.6), the construction gives a simple symmetrical lens with 120° contact angles at the three grain junctions as seen in Fig. 5.6. The nucleus rather resembles a piece of M&M candy. Just eyeballing, I estimate V* and ΔG* at a bit under half that for homogeneous nucleation so the boundary is not a very effective catalyst. The first condition, where the critical nucleus is very flat is rather more likely to occur in practice.

Figure5.10 shows a case where a low energy interface is possible at only particular particle: matrix orientation. Such might occur with a HCP nucleus and FCC matrix. The respective close packed planes (you know what they are, by now) match and give a low energy interface. V* and DG* are thus reduced over those for the non-truncated lens (Figure 5.6).

Fabrication of thin film integrated circuits and magnetic materials involve vapor deposition of a phase (β) on a solid surface (b). The surface remains stationary but may have considerable catalytic effect. In this case the construction is as shown in Figure N-2. Let γ_s = substrate: vapor surface energy, γ_β = particle: vapor surface energy, and γ_β = particle: substrate surface energy. Construct a sphere of r = γ_β with a plane a distance γ_b -γ_{β_b} above the center of the sphere. The critical nucleus is the part of the sphere above the plane. As γ_b -γ_{α_b} approaches γ_s, the critical nucleus becomes very thin and ΔG* approaches zero. Conversely, for γ_b =γ_{α_b} the critical nucleus is a hemisphere and ΔG* is half that for homogeneous nucleation, which is not a whole lot of help.

The difference between the constructions in N-1 and N-2 is easily understood. In the earlier case the area of grain boundary occupied by the nucleus disappeared, hence the entire energy went to catalyzing nucleation. In the latter case the free surface is replaced by a β–s surface. Only the difference in energies goes to catalyzing nucleation.

I leave the calculation of the actual ΔG* for the various cases to the students who may be masochistic enough to want the job. I expect that those of you who need to use heterogeneous nucleation theory will do so to predict conditions that will

or will not give nucleation. I hope that the previous formulation is of some help toward that end.

Dislocations:
Dislocations may catalyze nucleation in a number of different ways. In an early paper Cahn proposed that the precipitate be an incoherent particle that lay along the dislocation core and relieved the core strain energy.   The resulting interface would of necessity be incoherent, and nuclei simply do not form with fully incoherent interfaces. There have been various semi-coherent models proposed whereby part of the nucleus lay on the dislocation core. Some of the geometries resemble the apple attacked by a switchblade knife mentioned earlier.

The most realistic model is that of Larche' and Cahn, who assumed a fully coherent nucleus lying near, but not upon the dislocation core. The stress fields of the dislocation and particle interact, as the dislocation is most assuredly NOT a center of dilatation. The stress field of a screw dislocation has no dilatation and that of the edge is only partly dilatation.

Larche and Cahn performed a brutally difficult elasticity calculation to reach a disarmingly simple result. The interaction of the strain fields is reflected in an *effective* lowering of the coherent particle: matrix interfacial energy γ to give a value $\hat{\gamma} = \gamma - (\dfrac{\mu b (1 + \nu)}{9 \pi (1 - \nu)})$ [e]

Where m = shear modulus, n = Poisson's ratio, and [e]= absolute value of e, the misfit strain. ΔG^* is that for homogeneous nucleation, but with the modified surface energy, $\hat{\gamma}$. C_o in the equation for C^* is ρ_d/a, where is ρ_d = dislocation density in m/m^3 and a = lattice parameter. C_o is thus the number of sites per unit volume lying along dislocation cores

STRAIN ENERGY:

The great French philosopher-mathematician Descartes who showed that at small x the value of a polynomial P (x) is determined by the term with the lowest power of x. The free energy of nucleating a particle with some linear dimension, r, is almost always the sum of a surface energy term proportional to r^2 and a volume free energy term proportional to r^3. Nuclei are almost always very small, so the surface term dominates. The minimum ΔG^* nucleus will almost always be that with the minimum total surface energy, that is a particle which is "as coherent as possible" with the matrix. Suppose the precipitate and matrix phases differ only in lattice parameter, and that the precipitate has the larger value of a. Coherency requires complete matching of planes and rows of atoms across the interface so the precipitate phase will have to be compressed and the neighboring matrix expanded until both have the same lattice parameter. The amount of stretching and compression must be such that the forces across the interface are equal and opposite.

All this stretching and squeezing requires work, which will retard the nucleation rate and must be reflected in ΔG^*. But how can this work (free energy) be calculated? In the simple case of a uniaxial tensile specimen Hooke's law relates stress and strain and the strain energy density is one half the product of stress and strain. The stress state in the misfitting particle is a long way from uniaxial tension.

Various authors have presented solutions for the strain energy associated with a misfitting ellipsoid that is fully coherent with the matrix. I prefer the treatment of Eshelby (See Refs.). His result is especially simple for the case of a linear, isotropic, uniform, continuum. Those may sound like dreadfully restrictive approximations, but they aren't so bad. Linear means small strains so that linear elasticity applies. (Nonlinear elasticity is for hard-core masochists only.) I will deal with cubic materials that are fairly close to isotropic. The continuum assumption works pretty well even though the nuclei are only a few atoms across. The uniform means that the particle and matrix have the same elastic constants. With all that said, the coherency strain energy per unit volume of particle is:

$$\Delta G = Ee^2/(1-\nu)$$

Where E = Young's modulus, e = $\Delta a/a$ = fractional lattice parameter difference, and ν = Poisson's ratio. For small lattice parameter differences, the only kind we can consider, a may be for either phase. ΔG_s is seen to be independent of the sign of e, which of course makes sense.

Here I introduce what I have dubbed the Bitter-Crum theorem after two men who enunciated it separately. It states that <u>centers of dilation do not interact</u>.

The precipitates are of course centers of dilatation. This theorem means not only that ΔG_ε is independent of the shape of the particle but also that two separate particles have the same associated strain energy as a single particle twice the size. Also, the total strain energy is the same whether two particles are formed next to one another or are widely separated. The Bitter-Crum theorem is in the same class as LeChatlier's principle or St. Venant's principle in being useful to the materials scientist. It of course is strictly true only for a linear, isotropic, uniform, continuum, but is still very valuable approximation for most cubic solids.

SPINODAL DECOMPOSITION:
Figure N-3 is a schematic sketch showing the rates of heterogeneous and homogeneous nucleation, much as was done in Fig. 4.9 (b). Heterogeneous nucleation becomes observable at small undercoolings, but is limited by the number of potential nucleation sites. Homogeneous nucleation involves a much larger ΔG^*, but once commenced, quickly outstrips heterogeneous nucleation. The vertical line to the right is for the onset of spinodal decomposition, wherein $\Delta G^* = 0$ and decomposition is spontaneous. To the right of this line there will be neither homogeneous nor heterogeneous nucleation. Spinodal decomposition wipes out **EVERYTHING** else. See P&E for spinodal decomposition.

REFERENCES:

K. C. Russell, "Nucleation in Solids: The Induction and Steady State Effects," Advances in Colloid and Interface Science **13**, 205-318 (1980)

J. D. Eshelby, Proc. Roy. Soc., **A241** 376 (1957)

D.A. Porter and K.E. Easterling, "Phase Transformations in Metals and Alloys," CRC Press, 1992.

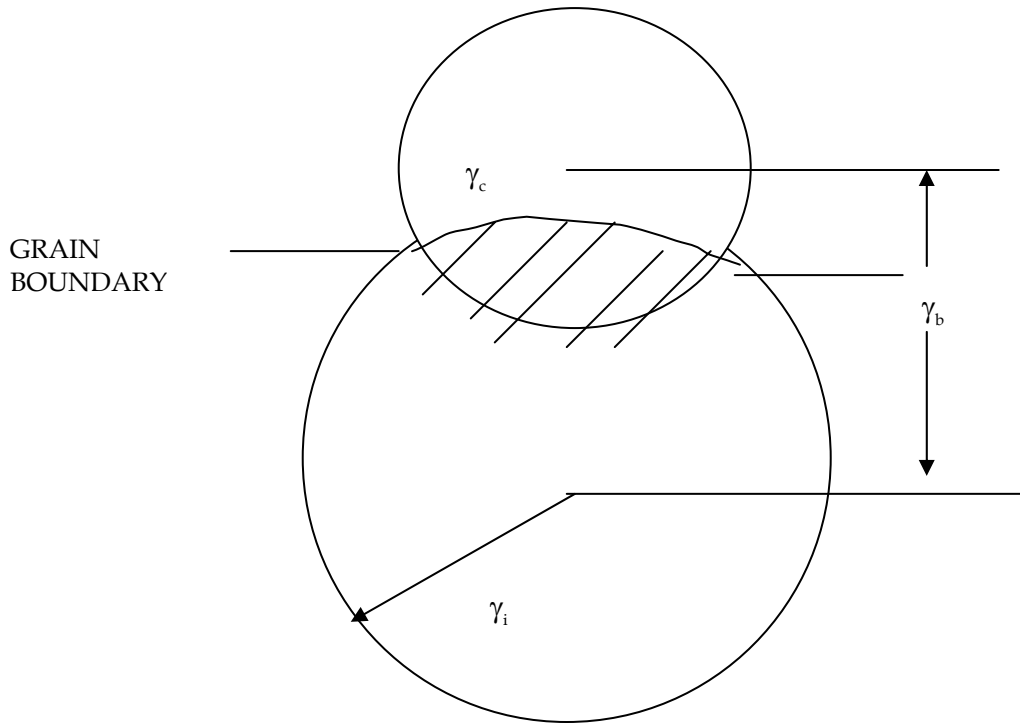Figures to supplement those in Porter and Easterling

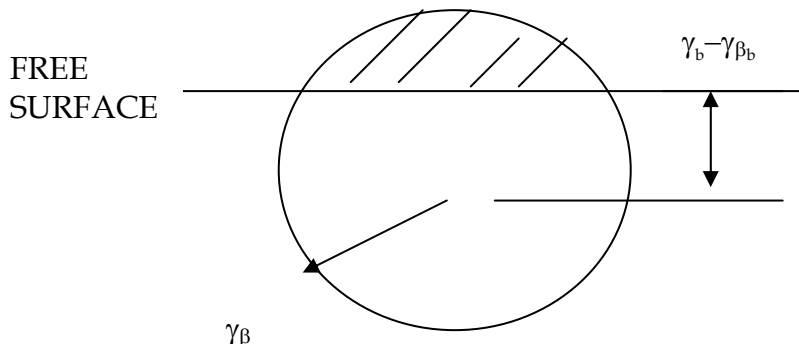Figure N-1. Construction for critical nucleus lying on a grain boundary.

Figure N-2. Construction for critical nucleus lying on a non-reactive surface.
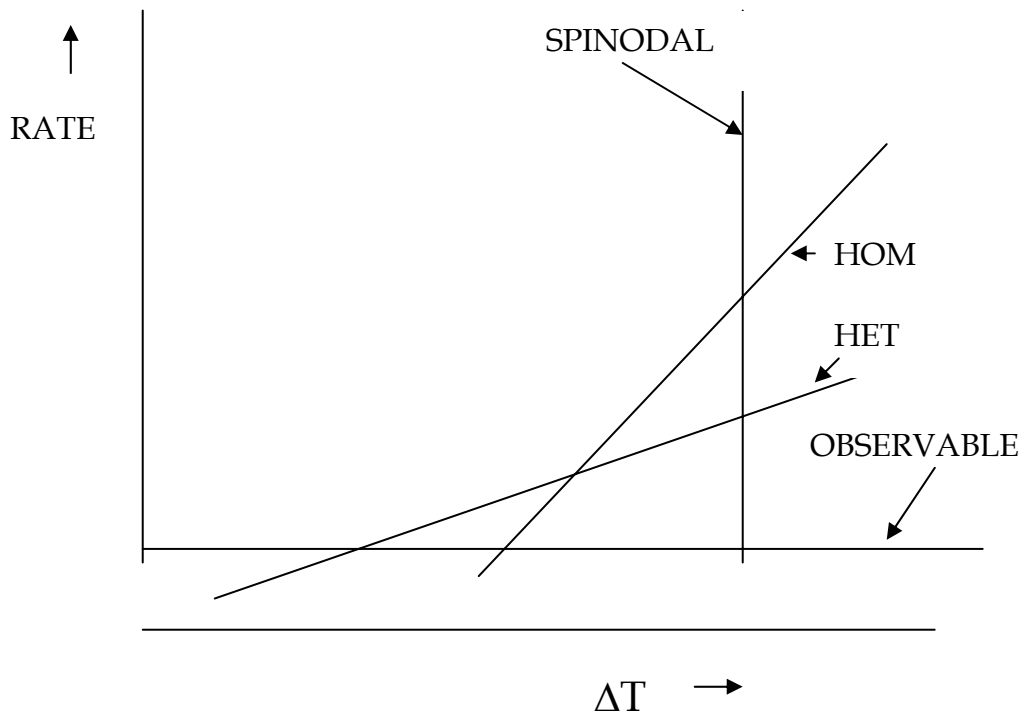
RATE

SPINODAL

HOM

HET

OBSERVABLE

ΔT

Figure N-3. Schematic representation of homogeneous and heterogeneous nucleation rate vs. undercooling below solvus. Hetrogeneous nucleation occurs at smaller undercoolings, followed by homogeneous nucleation and finally spinodal decomposition.

Spacer