Tutorial problems and questions

1. Derive an expression for the change of vacancy concentration with temperature.

Answer

Consider a pure material. Let us consider the case wherein some of the lattice sites are left vacant. Production of such sites costs energy because one needs to break atomic bonds to remove an atom from its lattice position. Hence, formation of vacancies always increase the enthalpy. However, introduction of vacancies also increases the configurational entropy. Hence, at any temperature, the optimum vacancy concentration is obtined by minimizing the corresponding free energy.

For simplicity's sake, let us assume that the change in enthalpy $\Delta H = X_v \Delta H_v$ where X_v is the vacancy concentration and ΔH_v is the enthalpy of formation per mole of vacancies; that is, each vacancy increases the enthalpy of the system by $\Delta H_v / N_{Avo}$ where N_{Avo} is the Avogadro number.

There are two contributions to the entropy due to the formation of vacancies: the first is the change in thermal entropy which follows due to the changes in vibrational frequencies of atoms in the vicinity of vacant sites; this contribution (ΔS_v per mole of vacancies) is small. The second is the configurational entropy which can be obtained using random dispersion of vacancies on lattice sites. Hence

$$\Delta S = X_v \Delta S_v - R[X_v \ln X_v + (1 - X_v) \ln (1 - X_v)] \qquad (1)$$

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Thus, the total (molar) free energy of a system containing X_v mole of vacancies is given by

$$G = G_A + \Delta H_v X_v - T \Delta S_v X_v + RT[X_v \ln X_v + (1 - X_v) \ln (1 - X_v)] \qquad (2)$$

where G_A is the molar free energy for the material without vacancies. In Fig. ??, we show these energies (and the equilibrium vacancy concentration).

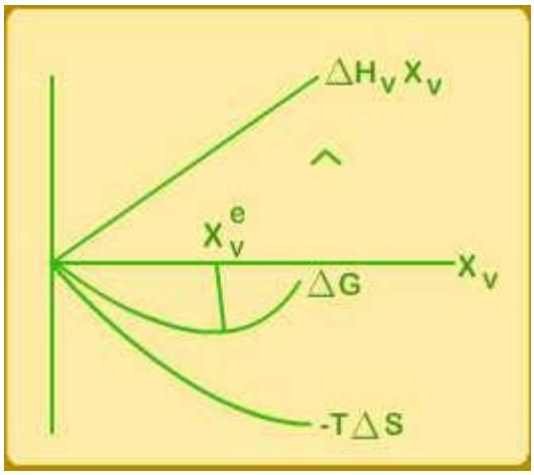

Figure 15: Equilibrium vacancy concentration.

The equilibrium vacancy concentration is then obtained by maximizing the free energy with respect to X_v; that is, by solving the following equation:

$$\left(\frac{dG}{dX_v}\right)_{X_v=X_v^e} = 0 \tag{3}$$

Thus,

$$\Delta H_v - T\Delta S_v + RT\ln X_v^e = 0 \tag{4}$$

where we have further assumed that $X_v << 1$.

In other words,

$$X_v^e = \exp\left(-\frac{\Delta G_v}{RT}\right) \tag{5}$$

That is, with temperature, the vacancy concentration increases exponentially.

2. Consider the formation of GP zones in an Al-Cu alloy aged at room temperature; if GP zones with interzone distance of about 50 nm spacing are found after about a day, estimate the intediffusivity.

Answer

$D = \lambda^2/4t$ where D is the diffusivity and λ is the interzone distance. Hence, for the given data, the estimate of diffusivity is $\approx 1.4 \times 10^{-21}$ m^2/sec. Note that this diffusivity is very high for the temperature considered. Hence, this effective fast diffusion must be a result of availability of excess quenched in vacancies.

3. Explain how PFZ can form due to nucleation at grain boundaries.

Answer

In Fig. ?? we show schematically the formation of grain boundary precipitates. These precipitates will suck in solute from the surrounding matrix. As shown schematically in the figure, this will lead to PFZs on either side of the boundary.

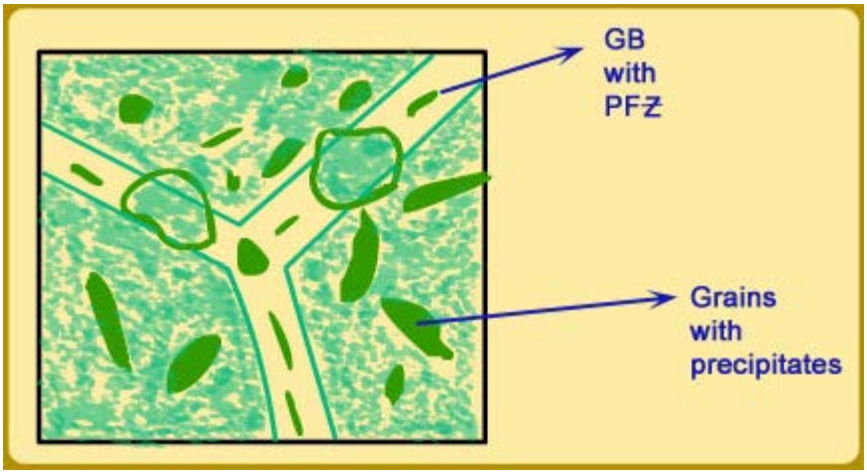

Figure 16: PFZ formation due to grain boundary precipitation.

4. Consider a Ni-base superalloy; the interphase interfacial energy between the matrix and the precipitate phase is 100 mJ/m^2. The misfit is 0.1% and the shear modulus 80 GPa. Calculate the size at which the elastic stress effects will become dominant.

Answer

The interfacial energy is a per unit area quantity while the elastic energy is a per unit area quantity. Hence, as the size of the precipitate increases, the elastic energy becomes dominant. One approximate calcualtion of the size at which elastic energy dominates is obtained by dividing the interfacial energy by the elastic energy. Thus, we obtain a characteristic size of about 1 micron or so.