Part II: Worked Examples

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Question 14

Why does the growth rate slow down as a precipitate thickens during diffusion-controlled growth?

The surface of a metal M can be nitrided to form a layer of metal nitride MN. The thickness of this layer is controlled by the rate at which the nitrogen atoms diffuse through the nitride layer. The nitrogen atoms then combine with the metal at the M/MN interface.

Show that the thickness of the nitride layer varies with the square root of time at the nitriding temperature, assuming that the nitrogen concentration in the atmosphere is maintained constant.

How would you expect the thickness to vary with time if the process is interface-controlled?

Answer 14

As the precipitate grow, diffusion has to occur over larger and larger distances, so that the gradient decreases with time. This makes the growth rate slow down as the particle thickens. A good example is the thickening of ice on a pond in winter. As the ice becomes thicker, the heat has to diffuse through larger distances to get to the surface.

The rate at which the nitride consumes nitrogen is

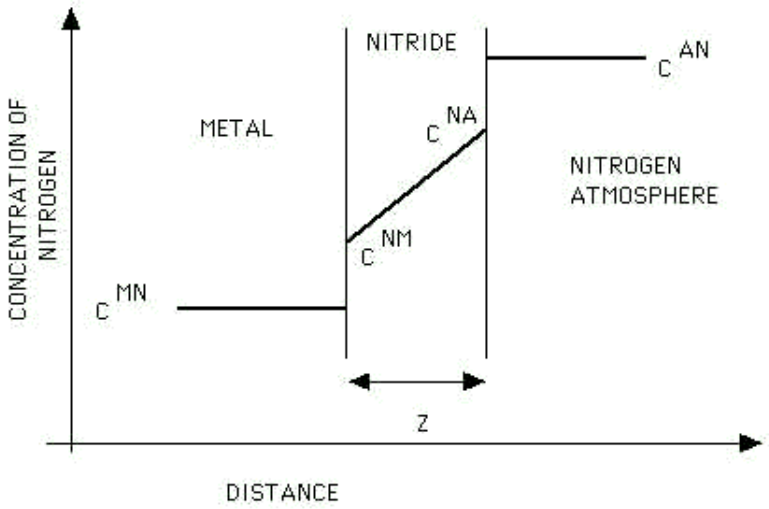
$$(c^{NM} - c^{MN})\frac{dz}{dt}$$

where z is the nitride thickness, c^{MN} is the nitrogen concentration in the metal at the metal-nitride interface and t is the time. This rate must equal the flux of nitrogen arriving at the metal-nitride interface, so that:

$$(c^{NM} - c^{MN})\frac{dz}{dt} = \frac{D(c^{NA} - c^{NM})}{z}.$$

It follows that

$$z^2 = 2Dt\frac{c^{NA} - c^{NM}}{c^{NM} - c^{MN}}.$$



In interface-controlled growth, the rate is determined by the jump of atoms across the interface. The velocity is therefore constant.

Question 15

Show that for small degrees of transformations, the volume fraction of precipitates varies with the fourth power of time, when the growth and nucleation rates are constant.

Why is this not the case at large fractions?

How would you measure the kinetics of transformation?

Answer 15

Consider the nucleation process. Particles do not form the instant a sample reaches the transformation temperature, but there is an incubation period τ. Thus, the volume w of a particle is given by

$$w_\tau = (4\pi/3)G^3(t-\tau)^3 d\tau \qquad (t > \tau)$$

$$w_\tau = 0 \qquad (t < \tau)$$

where G is a growth rate assumed to be constant, t it the time defined to be zero at the instant the sample reaches the isothermal transformation temperature and the growing particle is assumed to be spherical.

Let us first consider the simple case where we ignore impingement. Thus, we will overestimate the amount of β phase, so that we call the calculated volume of β phase to be an *extended volume* with the change in extended volume being given by

$$dV_e^\beta = w_\tau IV d\tau$$

$$V_e^\beta = (4\pi V/3) \int_{\tau=0}^{t} G^3 I (t-\tau)^3 d\tau$$

where V is the total volume. When integrated, this equation gives the fourth power dependence required.

At small volume fractions, the extended volume is about the same as the real volume. The expression should therefore be a good approximation. This is not the case when the chance of impingement between particles nucleated in different locations becomes high. The full Avrami approach must then be used.

Measurement: dialatometry, calorimetry, dynamic observations on a microscope....

Question 16

What is an ideal solution? What is the probability of finding an A atom next to a B atom in an equiatomic ideal solution?

Answer 16

An ideal solution is one where the enthalpy of mixing is zero. This means that A atoms are indifferent to who their neighbours are. The atoms are dispersed at random, so that

$$p_{AB} = 2 \times 0.5 \times 0.5 = 0.5$$

Question 17

The phase angle ϕ between the incident and diffracted beams is given by

$$\phi = 2\pi \mathbf{r}.\mathbf{g}$$

where $\mathbf{r}$ is the vector between scatterring centres and $\mathbf{g}$ is the reciprocal lattice vector.

Using a phase-amplitude diagram explain why when imaging using two-beam conditions in a transmission electron microscope, the intensity of either the transmitted or diffracted beams is expected to oscillate as a function of depth in the thin foil.

Hence explain the contrast associated with thickness fringes.

Answer 17

Question 18

In the context of transmission electron microscopy, distinguish between the following aberrations: spherical, chromatic and astigmatism.

Why is it so difficult to correct for spherical aberrations in transmission electron microscopy but not so in light optical microscopy?

Why is the diffraction pattern rotated with respect to the image, and why does the extent of rotation vary with magnification.

How could you correct for this rotation?

Answer 18

Spherical aberration is a consequence of the variation in lens properties as the beam deviates from the optic axis of the lens. Thus, a beam at an angle to the optic axis is brought to focus at a different position than an axial ray.

Chromatic aberration comes from variations in the power supply causes corresponding variations in the electron wavelength.

Astigmatism is due to lens distortions, giving variations in magnification as a function of orientation in the image. This can usually be corrected electronically.

Spherical aberration is more difficult to correct in TEM because of the magnetic lenses, for which only convex lenses can be made since the focal lenght does not depend on the sign of the magnetic field. For optical microscopes, the aberration can be partly corrected by mixing convex and concave lenses.

Electrons spiral down the column of a TEM, because they are moving through a magnetic field. The pitch of this spiral depends on the strength of the field. To project the diffraction pattern on the lens requires a projection of the back focal plane, whereas the image is a projection of the image plane, different lens settings. Therefore, the two will be relatively rotated.

To measure the rotation, and hence correct by calibration, use needle crytals of molybdenum trioxide (say) whose length is along a particular crystallographic direction. Superpose the image of needle on the appropriate diffraction pattern, to give the rotation.

Question 19

Explain the origins of *lobe contrast* when thin foil samples containing coherent precipitates are observed using transmission electron microscopy.

Answer 19

A coherent particle has continuity of lattice planes across the matrix/precipitate interface. The displacement caused by its presence is decribed by a vector $\mathbf{R}$ which points in all directions. Consequently, whatever the imaging $\mathbf{g}$ vector, there will be a line of zero contrast where $\mathbf{g}.\mathbf{R} = \mathbf{0}$. This gives a lobe contrast because it divides the precipitate in effect into two lobes separated by a line of zero contrast.

Question 20

Explain how a scanning tunnelling microscope works.

Answer 20

A sharp needle approaches a surface, until electron tunnelling gives rise to a tunnelling current between the needle and the sample. This current is a signal, so that the needle position relative to the sample surface can be monitored.

The signal is used to maintain the needle at a constant distance, and hence it is possible to plot out the surface contours on an atomic scale (since the tunnelling distance is of that order). The needle height can be controlled on an atomic scale by using the signal to stimulate a piezoelectric crystal.

Previous set of Worked Examples

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2000-06-09