

Worked Examples

The following examples are based on examination questions requiring either 1 hour, half hour or 10 minutes to complete.

1. Question

Give three essential characteristics of a martensitic transformation? Define an experiment by which each of these characteristics could be measured.

Show diagrammatically that it is not possible to transform austenite into body-centered cubic martensite by a deformation which is an invariant plane strain.

In the context of steels, explain clearly the difference between martensite, lower bainite, upper bainite and Widmanstätten ferrite.

Why is martensite hard in steels but not so in iron or in other non-ferrous metals and alloys?

1. Answer

A martensitic transformation is achieved by a deformation of the parent crystal structure; it therefore leads to a shape deformation which can be detected by polishing the parent phase prior to transformation; the shape deformation leads to surface tilts which can be measured using atomic force microscopy, interference optical microscopy or by the deflection of fiducial marks. Martensitic transformations are diffusionless and hence the measured composition of martensite must be the same as that of the parent phase. The interface between martensite and the parent phase must be glissile, *i.e.* it must be able to move without diffusion. The glissile character can be established by electron microscopy in which the Burgers vectors of the interfacial dislocations are measured and shown to lie out of the plane of the interface (although for pure screws they may lie in the interface plane).

Note that it is not correct to state that the transformation must occur at high speeds or at low temperatures, that it requires rapid quenching or that martensite is hard.

Suppose that the austenite is represented as a sphere with its unit cell edges denoted by the vectors \mathbf{a}_i with $i = 1, 2, 3$, as illustrated in Fig. 1a,b. The Bain strain changes the sphere into an ellipsoid of revolution about \mathbf{a}_1 . There are no lines in the $(0\ 0\ 1)_\gamma$ plane which are undistorted. However, it is possible to find lines such as wx and yz are undistorted by the deformation, but are rotated to the new positions $w'x'$ and $y'z'$. Since they are rotated by the Bain deformation they are not invariant-lines. In fact, the Bain strain does not produced an invariant-line strain. It can be converted into an invariant-line strain by adding a rigid body rotation as illustrated in Fig. 1c. The rotation reorients the α' lattice but has no effect on its crystal structure. The effect of the rotation is to make one of the original undistorted lines (in this case yz) invariant so that the total effect \mathbf{BR} of the Bain strain \mathbf{B} and the rotation \mathbf{R} is indeed an invariant-line strain. This is the reason why the observed irrational orientation relationship (KS/NW type) differs from that implied by the Bain strain. The rotation required to generate convert \mathbf{B} to an ILS precisely predicts the observed orientation from the Bain orientation.

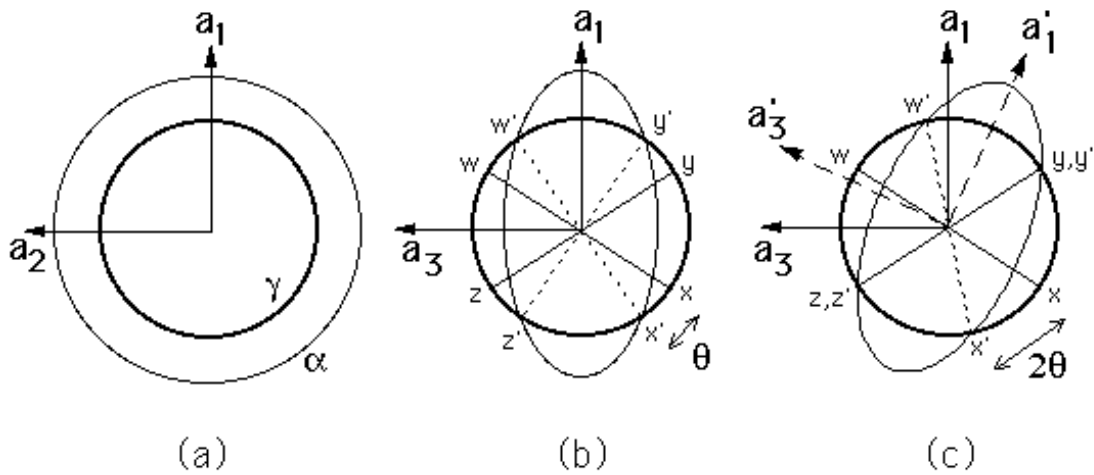


Fig. 1: (a) and (b) show the effect of the Bain strain on austenite, which when undeformed is represented as a sphere of diameter $wx = yz$ in three-dimensions. The strain transforms it to an ellipsoid of revolution. (c) shows the invariant-line strain obtained by combining the Bain strain with a rigid body rotation.

It is also apparent from Fig. 1c that there is no possible rotation which would convert \mathbf{B} into an invariant-plane strain because there is no rotation capable of making two of the non-parallel undistorted lines into invariant-lines. Thus, it is impossible to convert austenite into α' martensite by a strain which is an invariant-plane strain. A corollary to this statement is that the two crystals cannot ever be joined at an interface which is fully coherent and stress-free.

Martensitic transformation is diffusionless. Bainite grows without diffusion but because it forms at relatively high temperatures, the carbon can rapidly (a second or so) escape into the residual austenite. It may then precipitate as cementite, giving an upper bainite microstructure. If the bainite transformation temperature is reduced then the carbon escapes less rapidly so that it is possible for some of it to precipitate inside the ferrite plates, giving a lower bainite microstructure (Fig. 6.12, Honeycombe & Bhadeshia). Widmanstätten ferrite grows by a displacive paraequilibrium mechanism involving the diffusion of carbon. It thus grows at a rate which is controlled by the diffusion of carbon in the austenite ahead of the interface. Furthermore, there is little driving force available at the temperatures at which Widmanstätten ferrite grows so two plates have to grow together in a self-accommodating manner in order to reduce the overall strain energy. This is why it optically appears to be in the form of a thin wedge, since the component plates have slightly different habit planes.

The carbon atom in a b.c.c. lattice causes a tetragonal strain because it resides in an irregular octahedral hole, whose axes are given by the cell edge and two orthogonal face diagonals. A tetragonal strain can interact with both shear and hydrostatic components of stress. Thus, there is a strong interaction with both screw and edge dislocations. By contrast, substitutional solutes (and carbon in austenite) only cause isotropic volume changes which can only interact with the hydrostatic component of stress from edge dislocations, *i.e.* a weak interaction.

2. Question

- (i) What are the mechanisms by which an ordered precipitate, which is coherent with the matrix, may strengthen an alloy?
- (ii) The addition of either aluminium or titanium nickel alloys causes the formation of Ni_3Al or Ni_3Ti ordered precipitates. Why is it usual to use both aluminium and titanium to precipitation harden nickel base superalloys?
- (iii) Explain in terms of the laws of thermodynamics why it is necessary to raise the maximum operating temperature in a jet engine or power station in order to improve efficiency.

2. Answer

Order hardening, because pairs of dislocations have to enter the ordered phase. Also, modulus hardening since the energy per unit length of a dislocation depends on the shear modulus of the crystal. The modulus is likely to be different for the matrix and precipitate phases.

The aluminium to titanium ratio is controlled in order to get an optimum fit between the γ' precipitate and γ matrix. A good fit is necessary to ensure a coherent interface which gives long term microstructural stability.

The first law of thermodynamics states that energy is conserved *i.e.* the most that we can do when we burn fuel is to recover the energy completely. The second law says that complete recovery is only possible when the lowest operating temperature is absolute zero since

$$\text{Thermodynamic efficiency} = \frac{T_h - T_l}{T_h - 0}$$

where T_h and T_l are the highest and lowest temperatures in the cycle. The third law says that absolute zero cannot be reached since in each heat extraction cycle only a fraction of the heat is removed. In any case, reducing the temperature below ambient is impractical so the best way to improve efficiency is to raise T_h . Hence the need for high temperature materials.

3. Question

Explain why:

- (a) precipitation hardened aluminium alloys are frequently clad with thin layers of pure aluminium;
- (b) two-stage heat treatments are used to precipitation harden aluminium alloys;
- (c) the most popular titanium alloy contains both aluminium and vanadium as alloying additions;
- (d) the strength of a nickel aluminide (Ni_3Al) at first increases with temperature.

3. Answer

The difference in electrochemical potential between precipitates and matrix, or precipitate-free zones and other regions, leads to intense localised corrosion. Cladding with pure aluminium isolates these corrosion sites from the environment.

Two stage heat treatments help avoid the formation of precipitate free zones. A low temperature treatment causes a large number of nuclei which are allowed to grow to a size where they will not revert on heating. The second stage is at a higher temperature where the growth rate is reasonable. The supercooling in the first stage is sufficient to ensure nucleation even in the vacancy depleted regions.

Aluminium reduces the density of Ti and stabilizes and strengthens the α phase while vanadium provides a greater amount of more ductile β phase during hot-working.

The ordinary slip system is $\{111\} \langle 110 \rangle$. The strength increases with temperatures because of the tendency for dislocations to cross-slip on to the $\{100\}$ planes where they have a lower anti-phase domain boundary energy, which decreases with temperature. Situations arise where the extended dislocation is then partly on the close-packed plane and partly on the cube plane, forming locks, leading to an increase in strength. Eventually, the strength decreases after a peak at about 600 °C as thermal activation helps overcome the obstacles.

4. Question

A b.c.c. crystal contains two intersecting twin variants, the twinning elements being $[1\ 1\ 1]$ ($1\ 1\ \bar{2}$) and $[1\ 1\ \bar{1}]$ ($1\ 1\ 2$) respectively. Find the direction of the line which remains invariant to both of these deformations.

4. Answer

Combination of two invariant-plane strains \equiv invariant-line strain, with the invariant line at the intersection of the two invariant planes, *i.e.* $[1\ \bar{1}\ 0]$

5. Question

Using the concept of forces and fluxes in the theory of irreversible thermodynamics, deduce the relationship between the velocity V of a grain boundary and the free energy change ΔG accompanying its motion. State any assumptions involved in this derivation.

Prove that the general relation between V and ΔG should in fact be as follows:

$$V \propto \exp\{-Q/kT\}[1 - \exp\{-\Delta G/kT\}]$$

where Q is the activation energy for the transfer of atoms across the grain boundary, k is the Boltzmann constant and T is the absolute temperature.

Is it possible to reconcile this equation with the relationship deduced from irreversible thermodynamics?

5. Answer

In an irreversible process, the product of the force Z and the flux J gives the rate of energy dissipation:

$$T\sigma = JZ$$

where T is the temperature, σ is the rate of entropy production. $T\sigma$ is therefore the rate of energy dissipation. In many cases, it is found experimentally that $J \propto Z$.

In the case of grain boundary motion, the rate of energy dissipation is simply $V\Delta G$ so that we immediately get

$$V \propto \Delta G$$

An alternative is to consider the transfer of atoms across a grain boundary (a barrier of height Q). The probability of forward jumps (*i.e.* jumps which lead to a reduction in free energy) is given by

$$\exp\{-Q/kT\}$$

whereas that of reverse jumps is given by

$$\exp\{-(Q + \Delta G)/kT\} = \exp\{-Q/kT\} \exp\{-\Delta G/kT\}$$

.

The rate at which an interface moves is therefore given by

$$V \propto \exp\{-Q/kT\}[1 - \exp\{-\Delta G/kT\}]$$

Note that this relation is hardly that predicted from irreversible thermodynamics. However, they become identical when ΔG is small, *i.e.* there is not a great deviation from equilibrium. Note that for small x , $\exp\{x\} \simeq 1 + x$. Thus, at small driving forces,

$$V_i \propto \exp\{-Q/kT\}[\Delta G/kT]$$

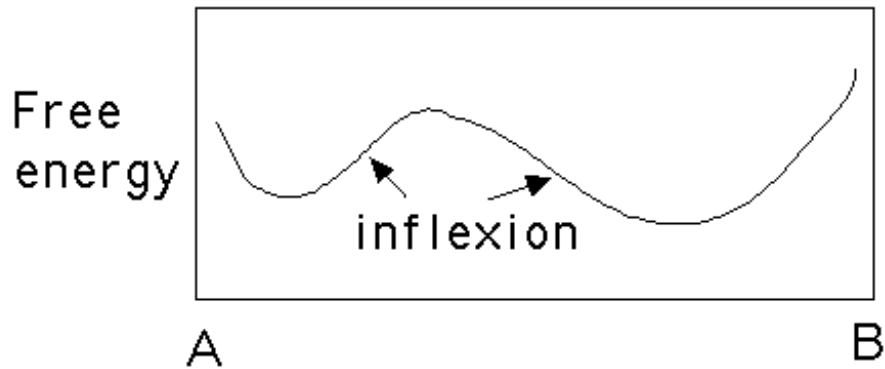
The three parts of the question carry equal marks.

6. Question

In what circumstances does the diffusion coefficient of a solute become zero?

6. Answer

In solutions where clustering is favoured *i.e.* where the solution has a free energy curve of the form illustrated below. At the points of inflexion, the diffusion coefficient is zero, whereas in-between it is negative (spinodal decomposition, uphill diffusion).



Free energy curve of a solution where the enthalpy of mixing is positive

7. Question

Why does ferritic iron change from a ferromagnetic to paramagnetic state as the temperature is raised?

7. Answer

Ferromagnetism involves the alignment of unspinpaired electrons. This is favoured by the accompanying reduction in enthalpy, but there is also an increase in free energy due to a reduction in entropy. As the temperature increases, the free energy increase caused by the reduced entropy of ordering dominates, because it scales with T . Hence, magnetic ordering is destroyed, giving paramagnetic iron.

8. Question

Prove that the distance R between the transmitted beam, and the diffracted beam, as measured on an electron diffraction pattern obtained using a transmission electron microscope is proportional to the reciprocal of the spacing d of planes giving rise to the diffracted beam.

How would you expect R to change if the operating voltage of the electron microscope is increased?

How would you find the Miller indices of the long axis of a rod-shaped crystal, given a bright field image and an electron diffraction pattern taken without moving the crystal?

8. Answer

The diffraction geometry is illustrated below. Since the Bragg angle θ is small, it follows that:

$$\tan(2\theta) \simeq 2\theta = R/L$$

From the Bragg equation,

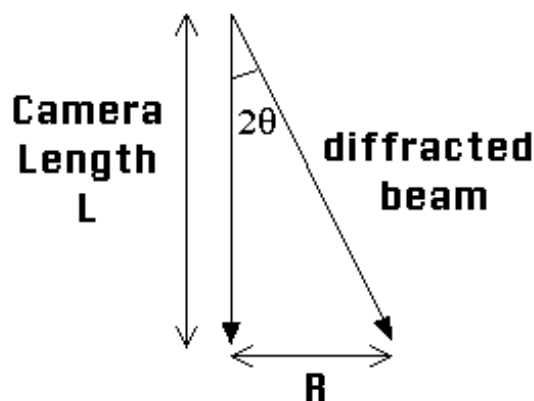
$$2 \sin(\theta) \simeq 2\theta = \lambda/d$$

so that

$$\frac{R}{L} = \frac{\lambda}{d}$$

The wavelength λ decreases as the accelerating voltage increases. Hence, R would decrease.

Electrons follow a spiral path through the column, because electrons spiral in a magnetic field. The pitch of the spiral changes with the strength of the lenses. The lenses are adjusted to project the image plane on to the screen when imaging, and the back focal plane when recording the diffraction pattern. Consequently, the pitch of the spiral is different in the two cases, so that the diffraction pattern is rotated relative to the image. Hence, to obtain the rod-axis it is necessary to correctly orient the diffraction pattern to the image.



Marking scheme; equal marks for each of three components

9. Question

How would you measure the spacing and perfection of a multilayered composite consisting of alternating layers of gold and silver, each of thickness a few nanometres?

9. Answer

The layered structure introduces an additional periodicity (above that of the crystal structure), so that satellite reflections appear in the electron diffraction pattern. Therefore, the spacing can be determined directly. The number of satellite reflections along a row is a measure of the perfection of the layered structure.

10. Question

Explain how a scanning tunnelling microscope works.

10. Answer

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.

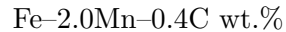
The signal is used to maintain the needle at a constant distance, and hence it is possible to plot out the surface contours on an atomic scale (since the tunnelling distance is of that order). The needle height can be controlled on an atomic scale by using the signal to stimulate a piezoelectric crystal.

11. Question

How would you prove that martensitic transformation is diffusionless?

In steels, the strain needed to change the structure of austenite into that of martensite is an invariant–line strain. However, the shape deformation observed when martensite grows is an invariant–plane strain. Show schematically how these different deformations may be reconciled, and hence explain why martensite frequently contains transformation twins.

Explain the role of the alloying elements in the following high–strength steel which has a quenched and tempered martensitic microstructure:



State a typical heat–treatment for this alloy, and explain how the steel may be improved to achieve even higher strength without sacrificing toughness.

11. Answer

Martensite is diffusionless because: (a) Its composition is identical to that of austenite, a necessary but not sufficient condition; (b) it can grow at 1100 ms^{-1} , a growth velocity which is far in excess of any diffusion velocity; (c) it can grow at temperatures as low as 4 K where diffusion is inconceivable within the time frame of the experiment.

Referring to Fig. 2, the strain illustrated in going from (a) to (c) leaves the line normal to the diagram unchanged (*i.e.* an invariant–line strain). However, the observed change of shape is an invariant–plane strain illustrated in the change from (a) to (b), the invariant plane being the vertical side of (a). The structure of (b) is therefore wrong, but its shape correct. The shape of (c) is wrong but its structure correct.

This can be resolved by adding a further deformation which does not change the structure (*i.e.* slip or twinning), but which gives the correct macroscopic shape corresponding to (b).

The manganese is for hardenability, the carbon for strength. Typical heat–treatment - austenitise at $850 \text{ }^\circ\text{C}$ for an hour, quench in oil, temper at about $400 \text{ }^\circ\text{C}$ for 1 hour. The low austenitisation temperature avoids austenite grain coarsening. The high tempering temperature avoids a toughness minimum at about $350 \text{ }^\circ\text{C}$, caused by coarse cementite. Add about 1 wt.% of silicon to the steel to retard precipitation of cementite, so that the toughness dip is moved to higher tempering temperatures. Thus, the modified steel can be tempered at only $300 \text{ }^\circ\text{C}$ for 1 hour to retain a higher level of strength.

Marking scheme: 20%, 60%, 20%.

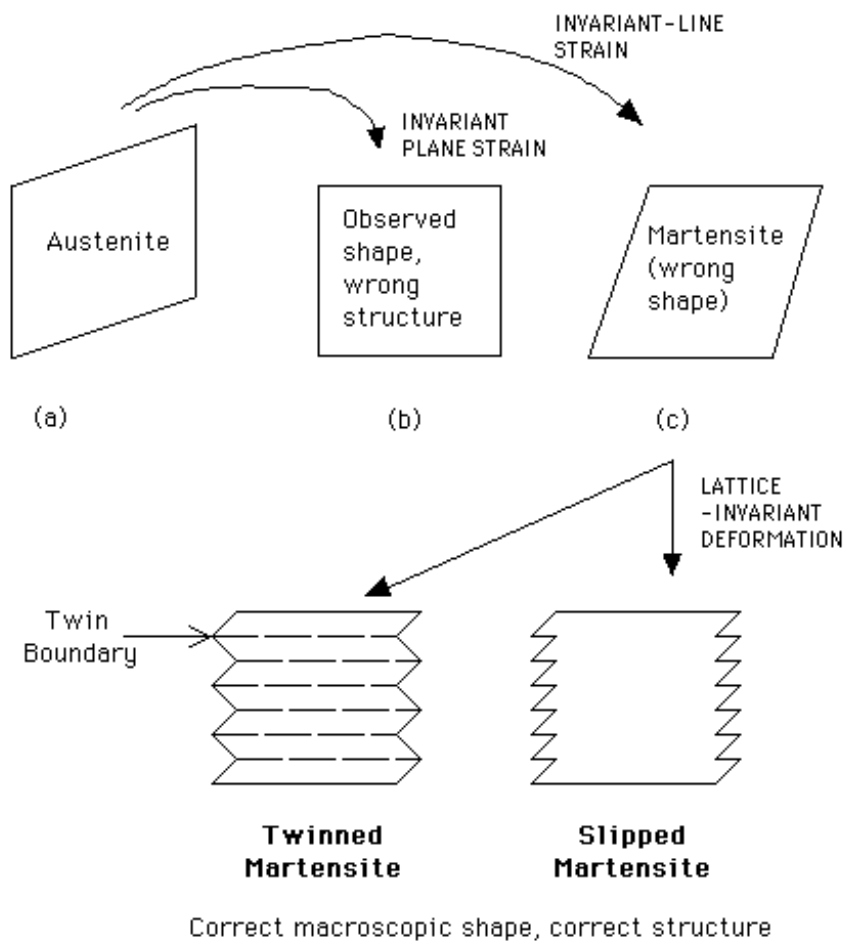


Fig. 2: Crystallographic Theory

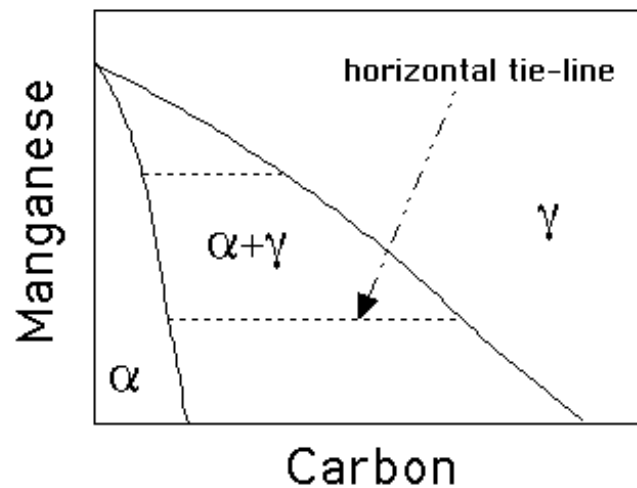
12. Question

Explain what is meant by the term *paraequilibrium*. Illustrate schematically an isothermal section of the paraequilibrium phase diagram for an Fe–Mn–C alloy where austenite and ferrite can coexist. The sketch should include tie-lines.

12. Answer

Paraequilibrium is a constrained equilibrium. It occurs at temperatures where the diffusion of substitutional solutes is not possible within the time scale of the experiment. Nevertheless, interstitials may remain highly mobile. Thus, in a steel, manganese does not partition between the ferrite and austenite, but subject to that constraint, the carbon redistributes until it has the same chemical potential in both phases.

Therefore, the tie-lines in the phase diagram are all virtually parallel to the carbon axis, since Mn does not partition between ferrite and austenite.



13. Question

The Avrami equation gives the fraction ξ of transformation as

$$\xi = 1 - \exp\{-\pi G^3 I t^4/3\}$$

when the product grows in the form of spheres at a constant rate G , with a constant nucleation rate I per unit volume during a time interval t . How would the exponent of time change if (a) growth is diffusion-controlled; (b) growth begins instantaneously from all of a fixed number of nucleation sites.

13. Answer

The Avrami equation comes from the integration of

$$-\ln(1 - \xi) = (4\pi/3) \int_0^t G^3 I (t - \tau)^3 d\tau$$

where τ is the incubation period for each particle.

When the dimension of the particle does not change as $G(t - \tau)$ but instead varies with $t^{1/2}$ (*i.e.* diffusion-controlled growth), the time exponent in the final equation will be reduced to $5/2$. This is because the volume of each particle scales with $t^{3/2}$ and an additional t comes from the nucleation rate.

When there is no nucleation but growth starts instantaneously from a fixed number of sites, the time exponent is obviously reduced to 3.

14. Question

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

14. Answer

A coherent particle has continuity of lattice planes across the matrix/precipitate interface. The displacement caused by its presence is described 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 $\mathbf{g} \cdot \mathbf{R} = 0$. This gives a lobe contrast because it divides the precipitate in effect into two lobes separated by a line of zero contrast.

15. Question

In a room containing twice as many Conservative as Labour politicians, the probability of finding a Conservative politician next to a Labour politician is measured experimentally to be 0.444. Does this imply that a coalition government is a distinct possibility?

Why does an excess specific heat persist in an ordered alloy which is heated to a temperature beyond that necessary to make the long range order parameter zero?

15. Answer

The probability is exactly $2 \times \frac{2}{3} \times \frac{1}{3}$, so that the solution is random. Coalition is not a distinct possibility since they do not appear to have any particular affinity for each other.

The excess specific heat is due to the persistence short range order beyond the temperature where the long range order parameter becomes zero.

16. Question

The surface of a metal M can be oxidised to form a layer of metal oxide MO . The thickness of this layer is controlled by the rate at which oxygen atoms diffuse through the oxide layer. The oxygen atoms then combine with the metal at the M/MO interface.

Show that the thickness of the oxide layer varies with the square root of time at the oxidation temperature.

16. Answer

The rate at which the oxide consumes oxygen is

$$(c^{OM} - c^{MO}) \frac{dz}{dt}$$

where z is the oxide thickness, c^{MO} is the oxygen concentration in the metal at the metal–oxide interface and t is the time. This rate must equal the flux of oxygen arriving at the metal–oxide interface, so that:

$$(c^{OM} - c^{MO}) \frac{dz}{dt} = \frac{D(c^{OA} - c^{OM})}{z}.$$

It follows that

$$z^2 = 2Dt \frac{c^{OA} - c^{OM}}{c^{OM} - c^{MO}}.$$

17. Question

Show that the change in free energy when a solution becomes inhomogeneous (as in spinodal decomposition) depends on the curvature of the free energy versus composition plot – *i.e.*

$$\Delta G = \frac{1}{2} \frac{d^2 G}{dc^2} (\Delta c)^2$$

where ΔG is the change in free energy and $c \pm \Delta c$ represents the composition inhomogeneity.

Hint: represent the free energy curve with a polynomial, an acceptable approximation over a small range of composition:

$$G = G_0 + ac + bc^2$$

where G_0 , a and b are constants.

17. Answer

Assume that the free energy curve as a function of composition can be expressed over a small range $c \pm \Delta c$ as a polynomial

$$G = G_0 + ac + bc^2$$

It follows that

$$G_1 = G_0 + a(c - \Delta c) + b(c - \Delta c)^2$$

and

$$G_2 = G_0 + a(c + \Delta c) + b(c + \Delta c)^2$$

Therefore,

$$\Delta G = \frac{1}{2}(G_1 + G_2) - G$$

is given by

$$\Delta G = b\Delta c^2 = \frac{1}{2} \frac{d^2 G}{dc^2} (\Delta c)^2$$

18. Question

Explain how a scanning tunnelling microscope works.

18. Answer

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.

19. Question

Copper and nickel form an ideal solution. What is the reduction in free energy due to the formation of a solution containing 25 at.% Cu at a temperature of 1000 °C?

Sketch the form of the free energy versus composition curve for a constant temperature. Indicate on it the chemical potentials of Cu and Ni for the 25 at.% solid solution. How does the chemical potential of Cu vary with its concentration?

19. Answer

Since the solution is ideal the enthalpy of mixing is zero. Thus, the free energy change is solely due to the change in configurational entropy,

$$\Delta G = -T\Delta S = 8.3143 \times 1273 \times (0.75 \ln 0.75 + 0.25 \ln 0.25)$$

$$\Delta G = -5952 \text{ J mol}^{-1}.$$

20. Question

The diffusion controlled growth rate of a plate is given by

$$v = \frac{\Omega D}{r} \left(1 - \frac{r_c}{r}\right)$$

where Ω is a representation of the undercooling below the equilibrium transformation temperature, r is the plate tip radius, r_c is the critical plate tip radius at which the growth rate becomes zero and D is the diffusivity in the parent phase.

Sketch the variation in v with r and show that the maximum rate of growth occurs at $r = 2r_c$.

20. Answer

The velocity is zero at $r = r_c$, and then peaks at $r = 2r_c$, as can be demonstrated by differentiating the equation.

21. Question

In an Fe–C alloy, the isothermal growth of ferrite occurs with equilibrium maintained locally at the interface such that

$$(c^{\alpha\gamma} - c^{\gamma\alpha})v = D \frac{\partial c}{\partial z}$$

where $c^{\alpha\gamma}$ is the concentration of carbon in ferrite which is in equilibrium with austenite, $c^{\gamma\alpha}$ is the corresponding concentration in austenite which is in equilibrium with ferrite, D is the diffusivity of carbon in austenite, v is the interface velocity and z is a coordinate defined normal to the interface. The concentration gradient is evaluated at the position of the interface.

Explain separately the meanings of the left and right hand sides of this equation, and hence the origin of the equation.

How would similar conditions be derived for a ternary Fe–Mn–C alloy?

Hence describe two ways in which ferrite can grow in a ternary Fe–Mn–C alloy whilst maintaining local equilibrium at the interface, even though the diffusivities of Mn and C are different by many orders of magnitude.

Explain what is meant by the term *paraequilibrium*. Illustrate schematically an isothermal section of the paraequilibrium phase diagram for an Fe–Mn–C alloy where austenite and ferrite can coexist. The sketch should include a few tie-lines.

21. Answer

The boundary condition defined by the equation relates the interface velocity to the concentration gradient at the interface. The rate at which solute is partitioned as the interface moves (*i.e.* left hand side) must equal that at which it is carried away by diffusion (*i.e.* right hand side) if the compositions at the moving interface are to remain constant.

For a ternary alloy it would be necessary to satisfy two such equations simultaneously, for each of the solutes:

$$\left. \begin{aligned} (c_1^{\gamma\alpha} - c_1^{\alpha\gamma})v &= -D_1 \nabla c_1 \\ (c_2^{\gamma\alpha} - c_2^{\alpha\gamma})v &= -D_2 \nabla c_2 \end{aligned} \right\}$$

where the subscripts refer to the solutes (1 for carbon and 2 for Mn).

Because $D_1 \gg D_2$, these equations cannot in general be simultaneously satisfied for the tie-line passing through the alloy composition \bar{c}_1, \bar{c}_2 . It is, however, possible to choose other tie-lines which satisfy equation 0. If the tie-line is such that $c_1^{\gamma\alpha} = \bar{c}_1$ (*e.g.* line *cd* for alloy A of Fig. 3a), then ∇c_1 will become very small, the driving force for carbon diffusion in effect being reduced, so that the flux of carbon atoms is forced to slow down to a rate consistent with the diffusion of manganese. Ferrite forming by this mechanism is said to grow by a ‘Partitioning, Local Equilibrium’ (or PLE) mechanism, in recognition of the fact that $c_2^{\alpha\gamma}$ can differ significantly from \bar{c}_2 , giving considerable partitioning and long-range diffusion of manganese into the austenite (Coates, 1973c).

An alternative choice of tie-line could allow $c_2^{\alpha\gamma} \rightarrow \bar{c}_2$ (*e.g.* line *cd* for alloy B of Fig. 3b), so that ∇c_2 is drastically increased since only very small amounts of Mn are partitioned into the austenite. The flux of manganese atoms at the interface correspondingly increases and manganese diffusion can then keep pace with that of carbon, satisfying the mass conservation conditions of equation 0. The growth of ferrite in this manner is said to occur by a ‘Negligible

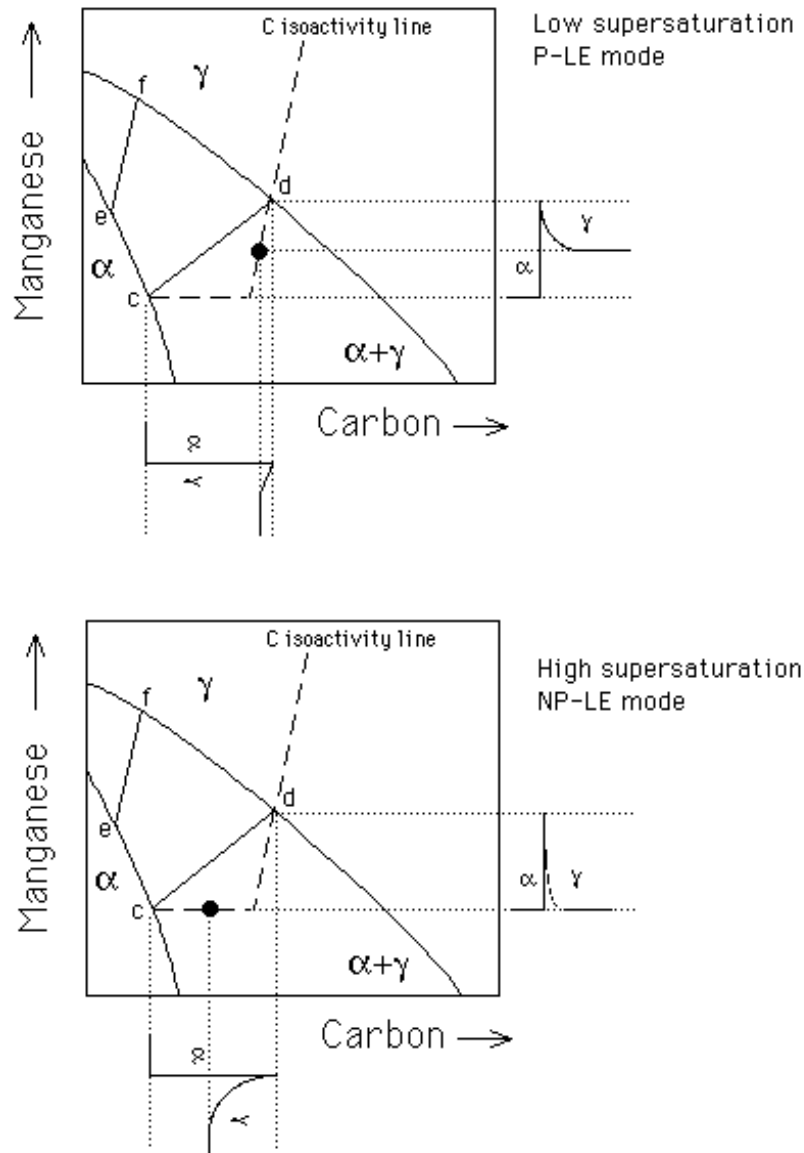


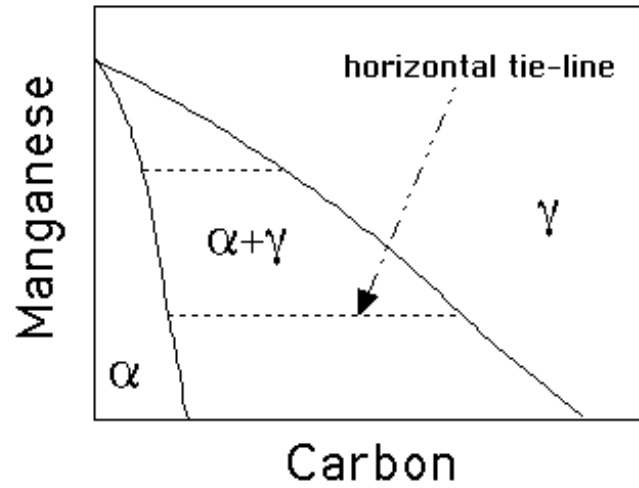
Fig. 3: Schematic isothermal sections of the Fe–Mn–C system, illustrating ferrite growth occurring with local equilibrium at the α/γ interface. (a) Growth at low supersaturations (P–LE) with bulk redistribution of manganese, (b) growth at high supersaturations (NP–LE) with negligible partitioning of manganese during transformation. The bulk alloy compositions are designated by the symbol \bullet in each case.

Partitioning, Local Equilibrium' (or NP-LE) mechanism, in recognition of the fact that the manganese content of the ferrite approximately equals \bar{c}_2 , so that little if any manganese partitions into austenite.

Paraequilibrium is a constrained equilibrium. It occurs at temperatures where the diffusion of substitutional solutes is not possible within the time scale of the experiment. Nevertheless,

interstitials may remain highly mobile. Thus, in a steel, manganese does not partition between the ferrite and austenite, but subject to that constraint, the carbon redistributes until it has the same chemical potential in both phases.

Therefore, the tie-lines in the phase diagram are all virtually parallel to the carbon axis, since Mn does not partition between ferrite and austenite.



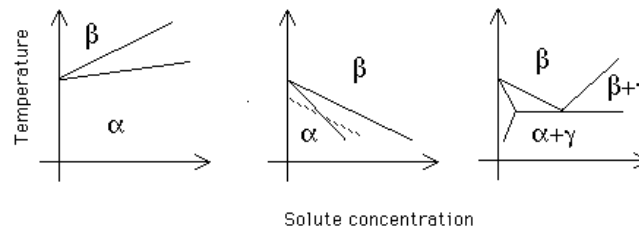
22. Question

- (i) What are the crystal structures of the two main allotropic forms (α and β) of titanium, and which of these two is stable at ambient temperature?
- (ii) Sketch the three main kinds of phase diagrams found for titanium alloys given that some solutes stabilise α , some stabilise β and others are neutral. On the diagram for β stabilising elements, construct and justify a curve defining the locus of the martensite–start temperature as a function of the solute concentration.
- (iii) Why is the eutectoid reaction found in some titanium alloys so sluggish compared with the formation of pearlite in steels?
- (iv) Giving reasons, state typical applications for Ti–Pd and Ti–V–Al alloys.

22. Answer

The high temperature form β is body–centered cubic and the low temperature form α is hexagonal close–packed.

The three types of phase diagrams are illustrated below, for α , β and neutral elements which lead to a eutectoid phase diagram. The locus of M_S temperatures is indicated as a dashed line, with sufficient undercooling to account for strain energy and solute supersaturation.



The eutectoid reaction, for example in the Ti–Cu alloys, involves the solid–state diffusion of substitutional solutes which diffuse at a far smaller rate than interstitial carbon in iron. Consequently, it is frequently possible to avoid the eutectoid reaction by cooling rapidly.

The addition of a small amount ($\simeq 0.2$ wt%) of palladium to titanium makes it much more corrosion resistant in acid. This is because the hydrogen evolution reaction is less polarised (hydrogen evolution is easier), causing the cathodic reaction curve to intersect the cathodic reaction curve in the passive region, leading to a smaller corrosion current.

Ti–6Al–4V is a classic $\alpha + \beta$ alloy with high strength combined with a low density. The α phase is harder and enhances the overall strength, the aluminium helping to stabilise α and lower the density. However, 6Al needs to be balanced by the 4V which is an β stabiliser. The alloy is widely used in sheet and forgings for the aerospace industries.

23. Question

Explain why:

- (a) martensite, Widmanstätten ferrite and bainite all occur in the form of thin plates;
- (b) Widmanstätten ferrite grows at a rate which is much smaller than the speed of sound in the metal;
- (c) an Fe–30Ni wt% martensite is weak compared with martensite in Fe–0.2C wt% alloy;
- (d) alloying elements have a much greater effect on the kinetics of a reconstructive transformation when compared with the corresponding effect on displacive transformations..

23. Answer

All of these transformations are accompanied by a shape deformation which is an invariant–plane strain (IPS). When elastically accommodated, this causes a strain energy per unit volume given by:

$$E = \frac{c}{a} \mu (s^2 + \delta^2)$$

where μ is the shear modulus of the austenite and s and δ are respectively the shear and dilatational components of the IPS. c/a is the thickness to length ratio of the product so that a thin plate shape minimises the strain energy.

Widmanstätten ferrite occurs at temperatures where diffusionless transformation is thermodynamically impossible. Thus, although the change in crystal structure is accomplished by a deformation, the displacements occur at a rate controlled by the diffusion of carbon in the austenite ahead of the interface.

Carbon causes a much greater degree of hardening than any substitutional solute. This is because it leads to a tetragonal distortion of the b.c.c. structure; a tetragonal strain can interact with all components of the stress field of a dislocation. Substitutional solutes cause isotropic strains which can only interact with the small hydrostatic component of stress associated with edge dislocations.

The effect on displacive transformations is thermodynamic alone. On reconstructive transformations the solute may partition between the parent and product phases by a process involving diffusion. This will have a further kinetic effect on reconstructive transformations.

24. Question

A screw dislocation with Burgers vector $[1\ 1\ 0]$ glides on the $(\bar{1}\ 1\ 1)$ plane and intersects another dislocation with Burgers vector $[\bar{1}\ 1\ 0]$. Can the screw dislocation continue gliding on $(\bar{1}\ 1\ 1)$ without hinderance?

24. Answer

As a result of the intersection the screw acquires a jog along $[\bar{1}\ 1\ 0]$, which is the line vector of the jog. The Burgers vector of the jog is still $[1\ 1\ 0]$ so that its glide plane is $(0\ 0\ 1)$ rendering it sessile on $(\bar{1}\ 1\ 1)$.

25. Question

Why does ferritic iron change from a ferromagnetic to paramagnetic state as the temperature is raised?

25. Answer

Ferromagnetism involves the alignment of unspinpaired electrons. This is favoured by the accompanying reduction in enthalpy, but there is also an increase in free energy due to a reduction in entropy. As the temperature increases, the free energy increase caused by the reduced entropy of ordering dominates, because it scales with T . Hence, magnetic ordering is destroyed, giving paramagnetic iron.

26. Question

Give three essential characteristics of a martensitic transformation. Define an experiment by which each of these characteristics could be measured. (12/40)

Given that the Bain strain, which changes the face-centered cubic austenite lattice into that of body-centered cubic martensite is an invariant-line strain, explain why the observed shape deformation accompanying martensitic transformation is an invariant-plane strain. (20/40)

Why is the lattice-invariant deformation unnecessary when austenite transforms by a martensitic mechanism to a hexagonal close-packed lattice? (4/40)

Why is martensite hard in steels but not so in iron or in non-ferrous metals and alloys? (4/40)

26. Answer

A martensitic transformation is achieved by a deformation of the parent crystal structure; it therefore leads to a change in shape which can be detected by polishing the parent phase prior to transformation; the shape deformation leads to surface tilts which can be measured using atomic force microscopy, interference optical microscopy or by the deflection of fiducial marks. Martensitic transformations are diffusionless and hence the measured composition of martensite must be the same as that of the parent phase. The interface between martensite and the parent phase must be glissile, *i.e.* it must be able to move without diffusion. The glissile character can be established by electron microscopy in which the Burgers vectors of the interfacial dislocations are measured and shown to lie out of the plane of the interface (although for pure screws they may lie in the interface plane).

Note that it is not correct to state that the transformation must occur at high speeds or at low temperatures, that it requires rapid quenching or that martensite is hard.

The phenomenological theory of martensite crystallography solves this problem (Fig. 4). The Bain strain converts the structure of the parent phase into that of the product phase. When combined with an appropriate rigid body rotation, the net homogeneous lattice deformation \mathbf{RB} is an invariant-line strain (step *a* to *c* in Fig. 4). However, the observed shape deformation is an invariant-plane strain \mathbf{P}_1 (step *a* to *b* in Fig. 4), but this gives the wrong crystal structure. If a second homogeneous shear \mathbf{P}_2 is combined with \mathbf{P}_1 (step *b* to *c*), then the correct structure is obtained but the wrong shape since

$$\mathbf{P}_1\mathbf{P}_2 = \mathbf{RB}$$

These discrepancies are all resolved if the shape changing effect of \mathbf{P}_2 is cancelled macroscopically by an inhomogeneous lattice-invariant deformation, which may be slip or twinning as illustrated in Fig. 4.

The theory explains all the observed features of the martensite crystallography. The orientation relationship is predicted by deducing the rotation needed to change the Bain strain into an invariant-line strain. The habit plane does not have rational indices because the amount of lattice-invariant deformation needed to recover the correct the macroscopic shape is not usually rational. The theory predicts a substructure in plates of martensite (either twins or slip steps) as is observed experimentally. The transformation goes to all the trouble of ensuring that the shape deformation is macroscopically an invariant-plane strain because this reduces the strain energy when compared with the case where the shape deformation might be an invariant-line strain.

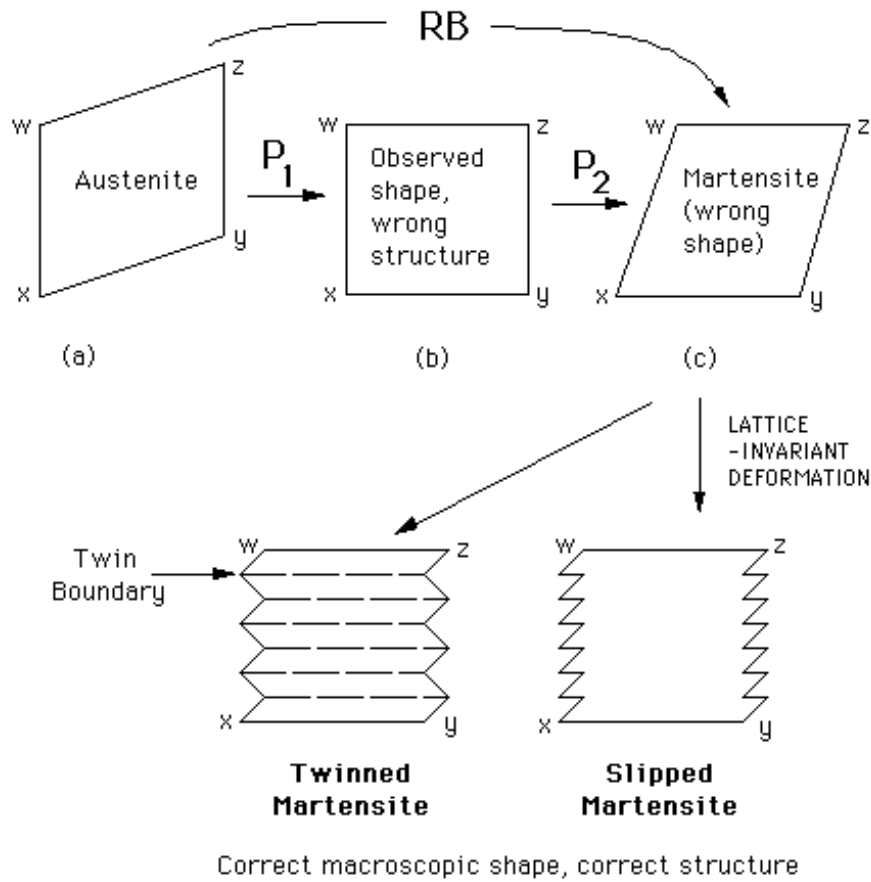


Fig. 4: The phenomenological theory of martensite crystallography

Notice that in the case of the fcc–hcp transformation, the lattice deformation (Bain Strain) itself is an invariant–plane strain, *i.e.* the motion of Shockley partials on the alternate close–packed planes. $\mathbf{B} = \mathbf{P}_1$ so a lattice invariant deformation is not needed. There are no transformation twins or slip steps to be found.

The carbon atom in a b.c.c. lattice causes a tetragonal strain because it resides in an irregular octahedral hole, whose axes are given by the cell edge and two orthogonal face diagonals. A tetragonal strain can interact with both shear and hydrostatic components of stress. Thus, there is a strong interaction with both screw and edge dislocations. By contrast, substitutional solutes (and carbon in austenite) only cause isotropic volume changes which can only interact with the hydrostatic component of stress from edge dislocations, *i.e.* a weak interaction.

27. Question

- (i) What are the mechanisms by which an ordered precipitate, which is coherent with the matrix, may strengthen an alloy? (6/20)
- (ii) Explain the cause of precipitate-free zones and how they might be avoided. (8/20)
- (iii) Why are aluminium-silicon alloys good as casting alloys? How might their microstructures be improved? (6/20)

27. Answer

Order hardening, because pairs of dislocations have to enter the ordered phase. Also, modulus hardening since the energy per unit length of a dislocation depends on the shear modulus of the crystal. The modulus is likely to be different for the matrix and precipitate phases.

It is possible, at large driving forces, for precipitates to nucleate homogeneously. However, it is more common for nucleation to occur heterogeneously because there is a gain in energy as the defect on which the particle forms is partly or wholly eliminated.

Vacancies are a prominent nucleation site for many precipitates, particularly in aluminium alloys where the concentration of vacancies tends to be high. However, there is a vacancy denuded zone next to a grain boundary (which is a sink for vacancies), Fig. 4. There will, therefore, be a precipitate-free zone (PFZ) adjacent to a grain boundary.

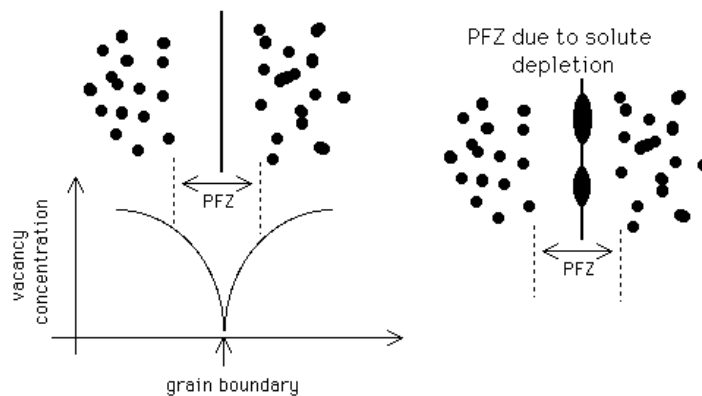


Fig. 4: Precipitate-free zones

An alternative reason for PFZ formation is that nucleation happens first on grain boundaries which are themselves potent nucleation sites. These precipitates drain the adjacent matrix from solute and hence a solute depleted PFZ arises, with coarse particles at the boundaries.

Precipitate-free zones can be eliminated by a two-stage heat treatment where nucleation is induced homogeneously at a low temperature, and the precipitates are then allowed to grow at a higher temperature (Fig. 5). Thus, for Al-6Zn-3Mg age-hardening alloy, GP zones are used as nuclei for the η (MgZn_2) phase.

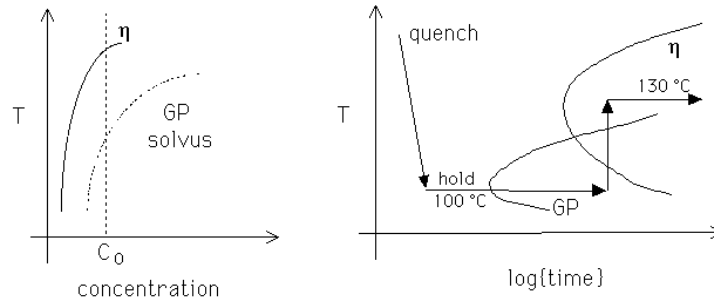


Fig. 5: Two-stage heat treatment

Aluminium casting alloys closely resemble cast irons. Aluminium–12 wt% silicon eutectic compositions are frequently used because this gives the minimum melting temperature. The silicon which has a density of just 2.34 g cm^{-3} , precipitates virtually as pure silicon. The resulting expansion compensates for freezing contractions to give castings with minimal porosity.

The silicon is coarse and brittle. The addition of a minute quantity of sodium (0.02 wt%) greatly refines the Si particles giving a higher toughness. It does so by removing P; AlP is a good nucleant for Si so its removal allows solidification to occur at a higher undercooling, where the nucleation rate can be larger.

28. Question

- (a) Explain why the addition of a small amount of palladium to titanium can improve its corrosion resistance in oxidising solutions. (5/20)
- (b) Explain why the most popular titanium alloy contains both aluminium and vanadium as alloying additions. (5/20)
- (c) Giving one example, explain what is meant by *solute trapping*. (5/20)
- (d) Distinguish between martensite, lower bainite, upper bainite and Widmanstätten ferrite. (5/20)

28. Answer

Pure titanium has excellent resistance to corrosion and is used widely in the chemical industries. There is a passive oxide film which makes it particularly resistant to corrosion in oxidising solution. The corrosion resistance can be further improved by adding palladium (0.15 wt%), which makes hydrogen evolution easier at cathodic sites so that the anodic and cathodic reactions balance in the passive region (Fig. 6).

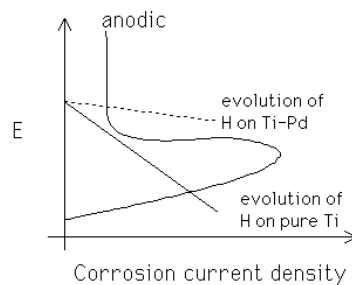


Fig. 6: Corrosion of Ti and Ti-Pd

Aluminium reduces the density of Ti and stabilizes and strengthens the α phase while vanadium provides a greater amount of more ductile β phase during hot-working.

Solute is said to be trapped when its chemical potential increases on transfer across the moving interface. It occurs when the interface velocity becomes comparable to the diffusion velocity (D/λ) where λ is the interatomic jump distance. Examples: rapid solidification, martensitic transformation (C in Fe), paraequilibrium (Mn in ferrite).

Martensitic transformation is diffusionless. Bainite grows without diffusion but because it forms at relatively high temperatures, the carbon can rapidly (a second or so) escape into the residual austenite. It may then precipitate as cementite, giving an upper bainite microstructure. If the bainite transformation temperature is reduced then the carbon escapes less rapidly so that it is possible for some of it to precipitate inside the ferrite plates, giving a lower bainite microstructure (Fig. 6.12, Honeycombe & Bhadeshia). Widmanstätten ferrite grows by a displacive paraequilibrium mechanism involving the diffusion of carbon. It thus grows at a rate which is controlled by the diffusion of carbon in the austenite ahead of the interface. Furthermore, there is little driving force available at the temperatures at which Widmanstätten

ferrite grows so two plates have to grow together in a self-accommodating manner in order to reduce the overall strain energy. This is why it optically appears to be in the form of a thin wedge, since the component plates have slightly different habit planes.

29. Question

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

29. Answer

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

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

30. Question

Upper bainite in conventional steels consists of a mixture of bainitic ferrite and cementite. How can this cementite be eliminated from the microstructure?

When the precipitation of cementite is prevented, the microstructure obtained by isothermal transformation in the bainite temperature range consists of just bainitic ferrite and carbon-enriched retained austenite. State four potential advantages of this microstructure from the point of view of toughness and strength.

One difficulty with the mixed microstructure of bainitic ferrite and retained austenite is that the austenite, when present in large quantities, is unstable and hence forms high-carbon, brittle martensite. Explain three ways in which this problem can be eliminated.

30. Answer

Silicon has an incredibly small solubility in cementite. Therefore, increasing the silicon concentration of a steel to a value greater than about 1.5 wt% ensures the absence of cementite in upper bainite. Aluminium and to a lesser extent chromium, have the same effect. Note that silicon has a similar effect in cast irons. (20%)

The six potential advantages (only four required in the answer) of the microstructure can be listed as follows: (40%)

- (i) Cementite is responsible for initiating fracture in high-strength steels. Its absence is expected to make the microstructure more resistant to cleavage failure and void formation.
- (ii) The bainitic ferrite is almost free of carbon, which intensely strengthens ferrite and hence embrittles it.
- (iii) The microstructure derives its strength from the fine grain size of the ferrite plates, which are less than $1\ \mu\text{m}$ in thickness. It is the thickness of these plates which determines the mean free slip distance, so that the effective grain size is less than a micrometer. This cannot be achieved by any other commercially viable process. Grain refinement is the only method available for simultaneously improving the strength and toughness of steels.
- (iv) The ductile films of austenite which are intimately dispersed between the plates of ferrite have a crack blunting effect. They further add to toughness by increasing the work of fracture as the austenite is induced to transform to martensite under the influence of the stress field of a propagating crack. This is the TRIP, or transformation-induced plasticity effect (Chapter 12).
- (v) The diffusion of hydrogen in austenite is slower than in ferrite. The presence of austenite can therefore improve the stress corrosion resistance of the microstructure.
- (vi) Steels with the bainitic ferrite and austenite microstructure can be obtained without the use of expensive alloying. All that is required is that the silicon concentration should be large enough to suppress cementite.

The problem of unstable retained austenite arises because the amount of bainite that can form is limited by the T_0 curve on the phase diagram. Therefore, the three ways all relate to the T_0

curve, as follows: (40%)

- (i) By reducing the isothermal transformation temperature to increase x_{T_0} . The lower limit is set by either the lower bainite or martensite–start temperature.
- (ii) By reducing the overall carbon concentration of the steel, so that the austenite reaches its limiting composition at a later stage of reaction.
- (iii) By moving the T_0 curves of the phase diagram to larger carbon concentrations. This can be done by adjusting the concentration and type of substitutional solute (Fig. 7a).

31. Question

Explain why martensite grows in the form of thin plates.

31. Answer

The shape deformation accompanying the growth of martensite is an invariant-plane strain with a large shear component (Fig. 8). The shear strain is typically $s = 0.25$, with a dilatational strain of about $\delta = 0.03$ normal to the habit plane. The strain energy per unit volume of martensite is given by (thickness c and length r) is given by:

$$E = \frac{c}{r} \mu (s^2 + \delta^2)$$

where μ is the shear modulus of the parent phase. It follows that this strain energy is minimised by adopting a plate shape. Another way of looking at this is illustrated in the figure below. The absolute magnitude of the displacements gets larger as the product gets thicker in the direction normal to the habit plane (compare displacements at **a** and **b**). Therefore, the thinner the plate, the smaller the absolute displacements that have to be accommodated.

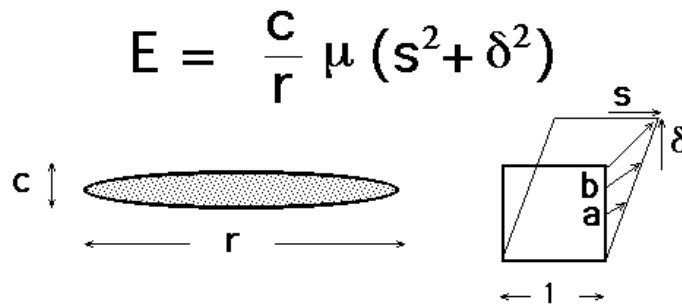


Fig. 8: Strain energy

32. Question

Explain what is meant by the term *paraequilibrium*. Illustrate schematically an isothermal section of the paraequilibrium phase diagram for an Fe–Mn–C alloy where austenite and ferrite can coexist. The sketch should include tie-lines.

Why does the austenite+ferrite phase field converge to a point when the carbon concentration becomes zero?

Define in thermodynamic terms, what is meant when an element is said to be *trapped* during transformation.

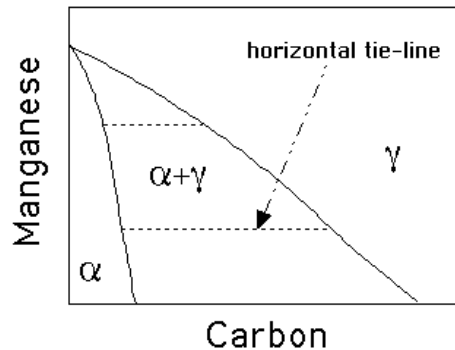
During the paraequilibrium growth of ferrite in an Fe–Mn–C alloy, which of the elements is trapped in the ferrite, and which in austenite?

32. Answer

Paraequilibrium is a constrained equilibrium. It occurs at temperatures where the diffusion of substitutional solutes is not possible within the time scale of the experiment. Nevertheless, interstitials may remain highly mobile. Thus, in a steel, manganese does not partition between the ferrite and austenite, but subject to that constraint, the carbon redistributes until it has the same chemical potential in both phases. (40%)

Therefore, the tie-lines in the phase diagram are all virtually parallel to the carbon axis, since Mn does not partition between ferrite and austenite. (20%)

At zero carbon concentration, the austenite and ferrite have exactly the same chemical composition since Mn does not redistribute during transformation. Therefore, there is a unique concentration at which the two phases have equal free energy, *i.e.* they are in equilibrium. (10%)



An element is said to be trapped when its chemical potential increases on transfer across the moving interface. (10%)

The manganese is trapped in the ferrite since its chemical potential increases on transfer across the interface, the iron is trapped in the austenite for the same reason. Manganese is an austenite stabiliser so its equilibrium concentration in austenite should be greater than that in ferrite. (20%)

33. Question

Describe the characteristics of the $\beta \rightarrow \omega$ transformation in some titanium or zirconium alloys and explain the mechanism of the transformation.

How would the transformation manifest in an electron diffraction pattern?

Describe any other diffusionless transformation possible in titanium alloys and state the observed orientation relationship.

How would you represent the temperature below which diffusionless transformation becomes thermodynamically possible on a phase diagram for a binary titanium alloy?

33. Answer

ω is a metastable phase which forms from β in alloys based on titanium, zirconium and hafnium. It is important because its formation generally leads to a deterioration in the mechanical properties. In Ti–Nb alloys its formation influences superconduction. The transformation to ω is diffusionless, occurs below the T_0 temperature and frequently cannot be suppressed even by quenching at 11000 C s^{-1} . Its presence causes diffuse streaking in the electron diffraction patterns of the β phases. The streaks become more intense and curved as the temperature or the solute concentration increases. There is also an increase in the electrical resistance as ω forms.

The $\beta \rightleftharpoons \omega$ transformation is reversible and diffusionless but is not martensitic in the classical sense since there is no invariant–plane strain shape deformation. However, it does involve the coordinated motion of atoms.

The body–centred cubic (bcc) crystal structure of β can be imagined as the stacking of $\{111\}_\beta$ planes in an $\dots ABCABC\dots$ stacking sequence. Note that these planes are not close–packed in the bcc structure. The $\beta \rightleftharpoons \omega$ transformation occurs by the passage of a longitudinal displacement wave along $\langle 111 \rangle$ which causes the B and C planes to collapse into each other, leaving the A planes unaffected. The stacking sequence thus changes to $\dots AB'AB'AB'\dots$ in which the B' planes have twice the density of atoms as the A planes. The $\dots AB'AB'AB'\dots$ stacking is consistent with a ω a hexagonal crystal structure with a $c/a \simeq 0.6$. The atoms in the B' plane have a trigonal coordination which is similar to that in graphite and the bonding becomes partly covalent. (60%)

This leads to an increase in the electrical resistivity. The longitudinal displacement waves are responsible for the streaking in the electron diffraction patterns. (10%)

Quenching the β phase leads to the formation of h.c.p. α' martensite. The orientation relationship is with the most densely packed planes parallel and the corresponding most densely packed directions parallel (the relationship is actually irrational, so the stated orientation is approximate).

$$(1\ 1\ 0)_\beta \parallel (0\ 0\ 0\ 1)_{\alpha'} \quad [1\ \bar{1}\ 1]_\beta \parallel [1\ 1\ \bar{2}\ 0]_{\alpha'}$$

and the habit plane of the martensite is close to $\{3\ 3\ 4\}_\beta$. (20%)

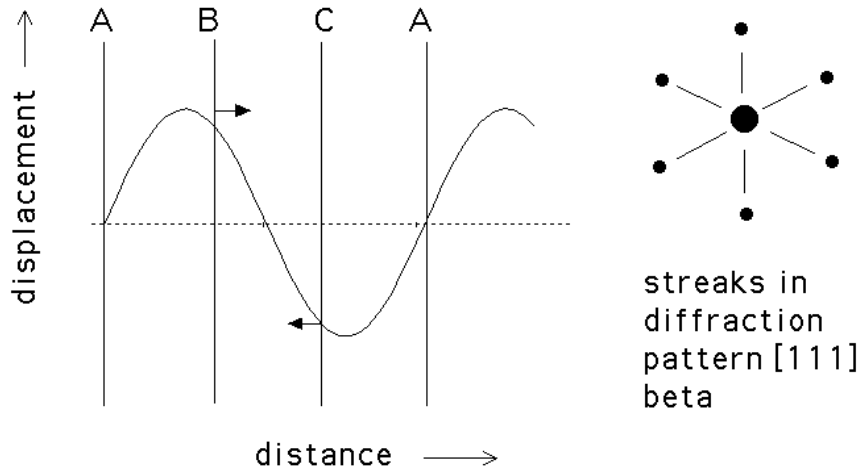


Fig. 8: (a) Displacement wave associated with the β to ω transformation. The A planes are unaffected since they lie at the nodes. (b) Streaks in the electron diffraction pattern during the ω transformation.

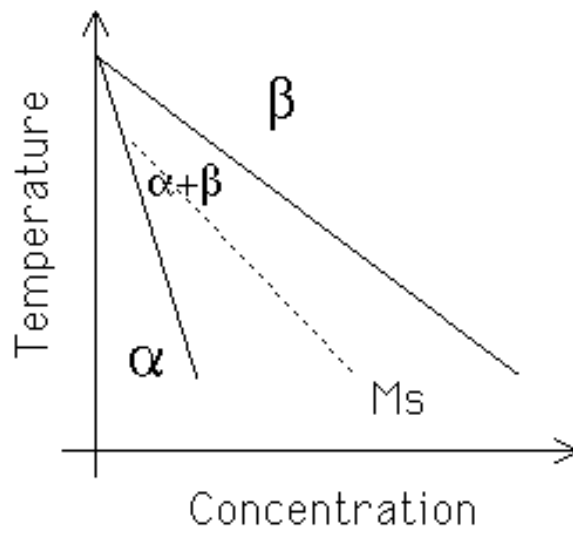


Fig. 9: The M_S temperature.

The temperature is represented by the T_0 curve (Fig. 9):

34. Question

Give three features of martensite that distinguish it from a reconstructive transformation such as allotriomorphic ferrite. Explain how you might characterise each of these features using experiments. [9 marks]

Giving reasons, explain which of the following deformations is an invariant-plane strain [12 marks]:

- (i) simultaneous slip on two independent slip systems;
- (ii) mechanical twinning;
- (iii) elastic elongation of a material with a zero Poisson's ratio;
- (iv) hydrostatic expansion.

Show diagrammatically that it is not possible to transform austenite into body-centred cubic martensite by a deformation which is an invariant plane strain. [12 marks]

Why is martensite hard in steels but not so in iron or in other non-ferrous metals and alloys? [7 marks]

34. Answer

A martensitic transformation is achieved by a deformation of the parent crystal structure; it therefore leads to a shape deformation which has a large shear component, and which can be detected by polishing the parent phase prior to transformation. The shape deformation causes surface tilts which can be measured using atomic force microscopy, interference optical microscopy or by the deflection of fiducial marks. The formation of allotriomorphic ferrite is not accompanied by any shear strain, simply a small volume change which does not deflect any fiducial marks.

Martensitic transformations are diffusionless and hence the measured composition of martensite must always be the same as that of the parent phase. The chemical composition of allotriomorphic ferrite corresponds to its equilibrium composition and hence in general will differ from that of the parent phase. The chemical composition can be measured using energy dispersive X-ray microanalysis, the atom-probe technique and X-ray diffraction.

The interface between martensite and the parent phase must be glissile, *i.e.* it must be able to move without diffusion. The glissile character can be established by electron microscopy in which the Burgers vectors of the interfacial dislocations are measured and shown to lie out of the plane of the interface (although for pure screws they may lie in the interface plane). There are no such requirements for the structure of the interface between allotriomorphic ferrite and austenite (it may be sessile or glissile, and will always require diffusion in order to translate).

Note that it is not correct to state that the transformation must occur at high speeds or at low temperatures, that it requires rapid quenching or that martensite is hard. Martensite can be soft, slow, and can take place at high temperatures.

- (i) slip is an invariant-plane strain (IPS), but the simultaneous operation of slip on two non-parallel planes leaves only the line of intersection undeformed and unrotated. This deformation is therefore an invariant-line strain;

- (ii) mechanical twinning is a shear on a plane which remains invariant (*i.e.* an IPS);
- (iii) elastic elongation of a material with a zero Poisson's ratio is also an IPS since the deformation is only normal to the invariant-plane. Beryllium has virtually a zero Poisson's ratio;
- (iv) hydrostatic expansion distorts all vectors and hence is not an IPS.

Suppose that the austenite is represented as a sphere with its unit cell edges denoted by the vectors \mathbf{a}_i with $i = 1, 2, 3$, as illustrated in Fig. 10a,b. The Bain strain changes the sphere into an ellipsoid of revolution about \mathbf{a}_1 . There are no lines in the $(0\ 0\ 1)_\gamma$ plane which are undistorted. However, it is possible to find lines such as wx and yz are undistorted by the deformation, but are rotated to the new positions $w'x'$ and $y'z'$. Since they are rotated by the Bain deformation they are not invariant-lines. In fact, the Bain strain does not produced an invariant-line strain. It can be converted into an invariant-line strain by adding a rigid body rotation as illustrated in Fig. 10c. The rotation reorients the α' lattice but has no effect on its crystal structure. The effect of the rotation is to make one of the original undistorted lines (in this case yz) invariant so that the total effect \mathbf{BR} of the Bain strain \mathbf{B} and the rotation \mathbf{R} is indeed an invariant-line strain. This is the reason why the observed irrational orientation relationship (KS/NW type) differs from that implied by the Bain strain. The rotation required to generate convert \mathbf{B} to an ILS precisely predicts the observed orientation from the Bain orientation.

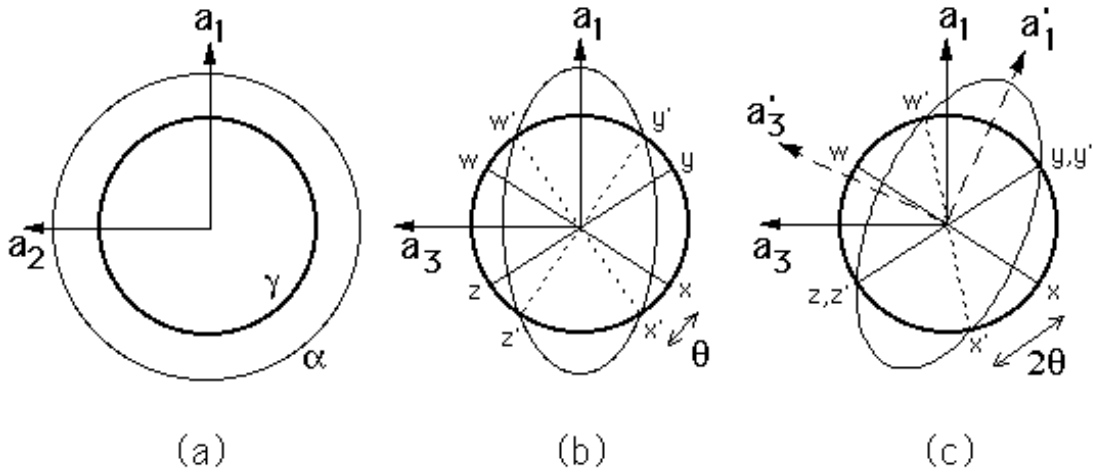


Fig. 10: (a) and (b) show the effect of the Bain strain on austenite, which when undeformed is represented as a sphere of diameter $wx = yz$ in three-dimensions. The strain transforms it to an ellipsoid of revolution. (c) shows the invariant-line strain obtained by combining the Bain strain with a rigid body rotation.

It is also apparent from Fig. 10c that there is no possible rotation which would convert \mathbf{B} into an invariant-plane strain because there is no rotation capable of making two of the non-parallel undistorted lines into invariant-lines. Thus, it is impossible to convert austenite into α'

martensite by a strain which is an invariant-plane strain. A corollary to this statement is that the two crystals cannot ever be joined at an interface which is fully coherent and stress-free.

The carbon atom in a b.c.c. lattice causes a tetragonal strain because it resides in an irregular octahedral hole, whose axes are given by the cell edge and two orthogonal face diagonals. A tetragonal strain can interact with both shear and hydrostatic components of stress. Thus, there is a strong interaction with both screw and edge dislocations. By contrast, substitutional solutes (and carbon in austenite) only cause isotropic volume changes which can only interact with the hydrostatic component of stress from edge dislocations, *i.e.* a weak interaction.

35. Question

Describe the roles of aluminium and vanadium in Ti-6Al-4V alloy. Why should the use of this alloy in an aeroengine be limited to temperatures less than about 400 °C?

35. Answer

Al reduces density, stabilises and strengthens α while vanadium provides a greater amount of the more ductile β phase for hot-working. This alloy is very commonly used because of its strength (1100 MPa), creep resistance at 300 °C, fatigue resistance and castability.

Common titanium alloys have low densities and can be creep resistant. However, titanium fires can occur when titanium components accidentally rub against other metals when the temperature of the environment is greater than about 400 °C.

36. Question

Explain what is meant by the term *paraequilibrium*. Illustrate schematically an isothermal section of the paraequilibrium phase diagram for an Fe–Mn–C alloy where austenite and ferrite can coexist. The sketch should include tie-lines with an explanation of how you construct them. [10 marks]

Explain the mechanism of the Widmanstätten ferrite transformation in steels, including a description of the factors that determine its growth rate and shape. [6 marks]

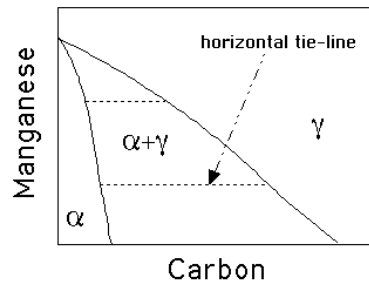
Which solute is said to be trapped in the product phase during transformation of austenite in a Fe–Mn–C alloy, in the following cases [4 marks]:

- (i) the growth of Widmanstätten ferrite;
- (ii) the growth of martensite.

36. Answer

Paraequilibrium is a constrained equilibrium. It occurs at temperatures where the diffusion of substitutional solutes is not possible within the time scale of the experiment. Nevertheless, interstitials may remain highly mobile. Thus, in a steel, manganese does not partition between the ferrite and austenite, but subject to that constraint, the carbon redistributes until it has the same chemical potential in both phases.

Therefore, the tie-lines in the phase diagram are all virtually parallel to the carbon axis, since Mn does not partition between ferrite and austenite.



Widmanstätten ferrite grows by a displacive paraequilibrium mechanism involving the diffusion of carbon. It thus grows at a rate which is controlled by the diffusion of carbon in the austenite ahead of the interface. Furthermore, there is little driving force available at the temperatures at which Widmanstätten ferrite grows so two plates have to grow together in a self-accommodating manner in order to reduce the overall strain energy. This is why it optically appears to be in the form of a thin wedge, since the component plates have slightly different habit planes.

- (i) manganese; carbon partitions during the paraequilibrium growth of Widmanstätten ferrite;
- (ii) both carbon and manganese since martensitic transformations are diffusionless.

37. Question

Prove that the solubility of solute in an aluminium alloy containing copper is greater when the matrix is in equilibrium with a metastable precipitate such as GP1, when compared with the case where it is in equilibrium with the stable precipitate CuAl_2 . [9 marks]

Assuming that the Al–Cu solution can be described by a regular solution thermodynamic model, show that the solubility x of solute in the matrix varies as follows:

$$x = \exp\left\{-\frac{z\omega}{kT}\right\}$$

Note that the molar free energy of mixing is

$$\Delta G_M = N_a z(1-x)x\omega + N_a kT[(1-x)\ln\{1-x\} + x\ln\{x\}]$$

where N_a is Avogadro's number, k is the Boltzmann constant, T is the absolute temperature and ω is positive for the Al–Cu system. [9 marks]

Would you expect the copper atoms to cluster or to order at low temperatures? [2 marks]

37. Answer

The *solubility* of solute in the matrix (α) is therefore of importance. This solubility cannot be defined in isolation – it depends on the phase with which the α is in equilibrium with, *e.g.* Fig. 11. In the Al–Cu system, the stable precipitate is CuAl_2 but because it is difficult to nucleate, metastable GP1 zones form first. Thus, the free energy curve for GP1 zones is located above that for CuAl_2 in Fig. 11b. The common tangent construction shows that this leads to an increase in the solubility of copper in α when it is in equilibrium with GP1 zones. Another interpretation is that a greater undercooling is required before GP1 zones can precipitate.

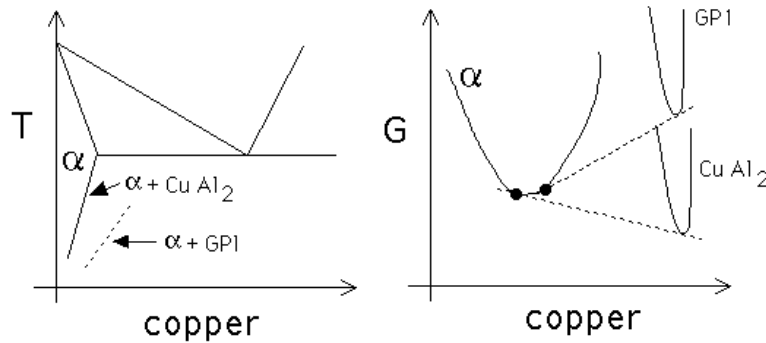


Fig. 11: (a) The solubility of solute in α is larger when it is in equilibrium with GP1 zones compared with when it is in equilibrium with CuAl_2 . (b) This can be justified using free energy diagrams.

Since ω is positive, so is the enthalpy of mixing ΔH_M . The free energy versus composition plot will therefore have two minima at low temperatures. The minimum at lower concentrations gives the solubility in matrix, *i.e.* it is safe to assume $x \ll 1$:

The miscibility gap at any temperature can be determined by the usual common tangent construction on the free energy curve with the two minima. Noting that the regular solution model has symmetry about $x = 0.5$, the compositions corresponding to the common tangent construction can in this special case be obtained by setting

$$\frac{\partial \Delta G_M}{\partial x} = 0$$

that is, $N_a z(1 - 2x)\omega + N_a kT \ln \frac{x}{1 - x} = 0$

which in the limit of small x gives $x = \exp\left\{-\frac{z\omega}{kT}\right\}$

The solubility therefore changes exponentially with the reciprocal of temperature, and increases as ΔH_M tends to zero.

A positive enthalpy of mixing indicates a tendency for clustering.