

Lecture 6: Solid–State Transformations

Grain Size

Most engineering materials are polycrystalline. Grain boundaries are therefore an important feature of the microstructure. They can be manipulated to control the mechanical properties. For example, the strength σ increases as the grain size d is reduced:

$$\sigma = \sigma_0 + kd^{-\frac{1}{2}} \quad \text{Hall–Petch equation}$$

where σ_0 and k are functions of the atomic and microstructure. Grain size refinement is the only mechanism which simultaneously improves the strength and toughness (*i.e.* the ability to absorb energy during fracture).

Grain boundaries are defects, forming easy diffusion paths. Thus, at high temperatures they weaken the material by permitting the easy diffusion of atoms in a way which leads to permanent strain (creep). For elevated temperature applications it is necessary to minimise the amount of grain boundary area per unit volume, and hence turbine blades for severe applications are made as single–crystals.

How can grain size be controlled? We have seen already that this can be done during the solidification stage using inoculants. An alternative method used widely is recrystallisation. But we need to understand the structure and energy of grain boundaries first.

Symmetrical Tilt Boundary

The misorientation θ between grains can be described in terms of dislocations (Fig. 30). Inserting an edge dislocation of Burgers vector \mathbf{b} is like forcing a wedge into the lattice, so that each dislocation is associated with a small change in the orientation of the lattice on either side of the extra half plane. If the spacing of dislocations is d , then

$$\theta \simeq \frac{b}{d}$$

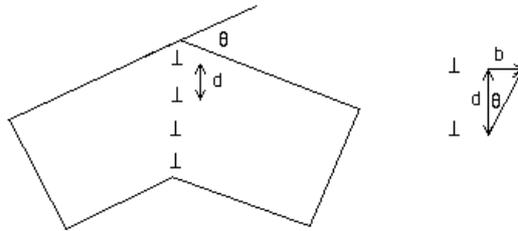


Fig. 30: Structure of a symmetrical tilt boundary

This gives a model for the energy of grain boundaries, based on the density of dislocations in the boundary ($\propto d^{-1}$). The variation in energy as a function of misorientation is illustrated in Fig. 31. The model is not valid for large misorientations where the dislocation spacing becomes comparable with the magnitude of the Burgers vector, since the dislocation cores then begin to overlap.

There are also special orientations where coincidence site lattices occur.

Cold Work

Plastic deformation of a metal (rolling, extrusion *etc.*) may be necessary

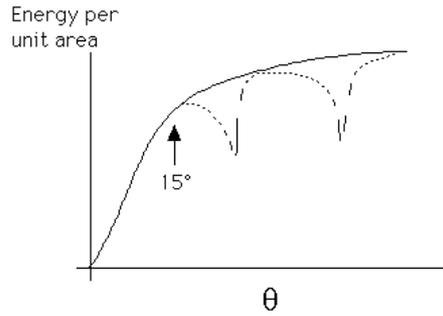


Fig. 31: The interfacial energy as a function of the misorientation for a tilt boundary. The dashed curve represents actual measurements with cusps at coincidence site lattices.

to achieve the required shape. But this may also be useful in optimising the microstructure obtained after solidification.

The effect of deformation is to elongate grains (Fig. 32) with an accompanying increase in the grain surface per unit volume, an increase in dislocation density (ρ) and an increase in the entanglement of dislocations. All of these lead to a higher defect density, an increase in stored energy. The stored energy per unit volume for a plastic strain ϵ due to a stress σ is $\sigma \times \epsilon \times 0.05$ because only about 5% of the work done in deformation actually is stored in the metal. The rest is dissipated as heat.

Annealed metal

$$\rho \simeq 10^{10} \text{ m}^{-2}$$

Cold-worked metal

$$\rho \simeq 10^{15} \text{ m}^{-2}$$

The stored energy per unit volume, due to dislocations is $U \simeq \mu b^2 \Delta\rho$, where μ is the shear modulus.† U is typically $3 \times 10^6 \text{ J m}^{-3}$ or 3 MPa

† This assumes that the energy per unit length of dislocation is μb^2 , but it is in general $\alpha G b^2$ where the factor α is about 0.5.

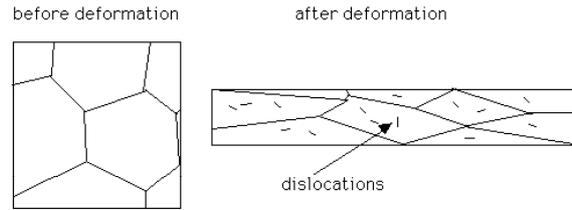


Fig. 32: The effect of cold work on the grain structure and dislocation density

and provides the driving force for transformation. It can be therefore be regarded as the pressure which induces boundaries to move (Fig. 33). The pressure causes the boundary to move so that a dislocation-free grain would grow. This phenomenon is known as *recrystallisation*. How does this difference $\Delta\rho$ arise?

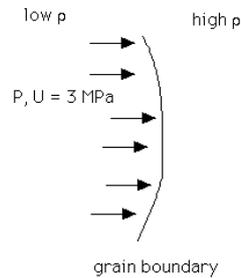


Fig. 33: Driving force for boundary motion

Dislocation Interactions

Dislocations of opposite sign attract and those of opposite sign repel when they lie on the same slip plane (Fig. 34). The former can annihilate by combination. When on parallel slip planes, like dislocations tend to align vertically whereas unlike dislocations form walls at 45° .

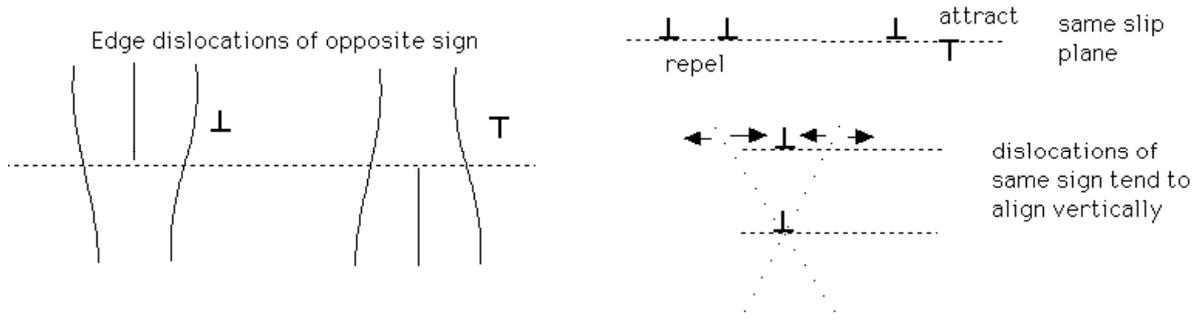


Fig. 33: Dislocation interactions.

The dislocations can also climb by diffusion. The ability to move on to different planes by absorbing or emitting vacancies can only happen at high temperatures. Such movements lead to a phenomenon known as polygonisation (Fig. 35a).

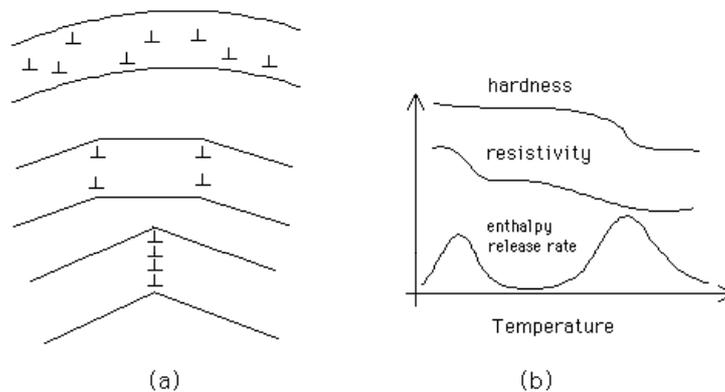


Fig. 35: (a) Polygonisation. (b) Changes during annealing.

Recovery

Let us now examine the changes that occur when a sample is heated from room temperature. At first, recovery occurs in which there is a

change in the stored energy without any obvious change in the optical microstructure. Excess vacancies and interstitials anneal out giving a drop in the electrical resistivity but little change in hardness (Fig. 35b). Dislocations become mobile at a higher temperature, eliminate and rearrange to give polygonisation. Still higher temperatures can lead to recrystallisation.

Anecdote

In nuclear reactors, materials in the close proximity of the core experience a large neutron flux, (*JET* and *NET* projects); the neutrons often knock atoms out of their equilibrium positions to produce a variety of point defects, and a corresponding level of stored energy in the reactor components. This can be quite large and has to be released periodically by low temperature in situ annealing, but the process has to be controlled carefully to avoid overheating due to the sudden release of stored energy. An excessive release of energy led to the most serious nuclear accident in the U.K., at an air-cooled reactor in Windscale during 1957. The energy was stored in graphite as incoming neutrons shifted carbon atoms into higher energy positions. The release of the energy heated the graphite fuel channels, which then reacted with air to produce carbon monoxide that subsequently caught fire.

Lecture 7: Recrystallisation

Nucleation

The dislocation density decreases only a little during recovery and the deformed grain structure is largely unaffected by recovery. It takes the growth of new grains to initiate a much larger change, *i.e.* recrystallisation. The nucleation of new grains happens in regions of high dislocation density (Fig. 36). This can happen when a grain boundary bows (stimulated by $\Delta\rho$) or by particle-stimulated recrystallisation. Large particles are more effective since there is a greater variation in deformation around them.

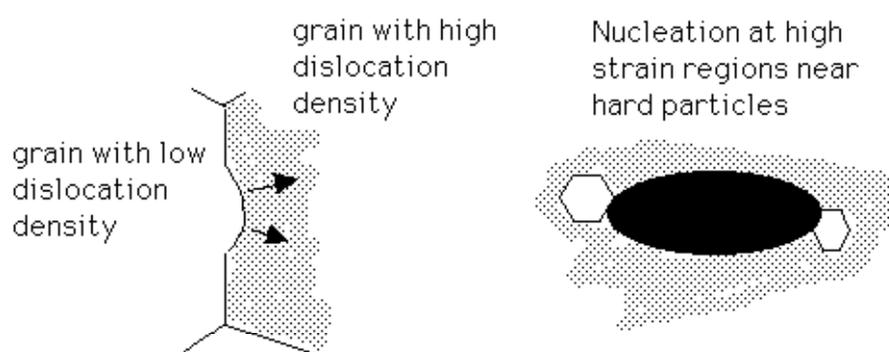


Fig. 36: Nucleation of recrystallisation.

Imagine that nucleation begins in a jumble of dislocations. The recrystallised grain will essentially be free from dislocations. Assume that a new grain is said to form when it has a misorientation of $\theta = 10^\circ \simeq$

0.2 radians with its neighbours and a size D , both arrived at by polygonisation (Fig. 37). We can estimate the critical dislocation density ρ_C required to form this grain:

$$\theta = \frac{b}{d} = 0.2 \text{ radians} \quad \simeq \frac{3 \times 10^{-10} \text{ m}}{d}$$

so that $d = 15 \times 10^{-10} \text{ m}$

Given that D typically $0.1\text{--}1 \mu\text{m}$, $\rho_C = \frac{1}{dD} \simeq 10^{15} \rightarrow 10^{16} \text{ m}^{-2}$

The actual dislocation density required has to be even larger because some will be annihilated during recovery. Such large dislocation densities can only be found in localised regions.

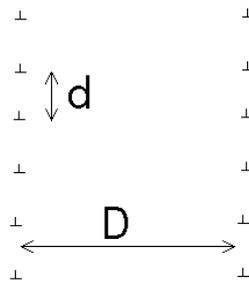


Fig. 37: Critical dislocation density

A greater nucleation rate leads to a finer ultimate grain size (Fig. 38). There is a critical level of deformation below which there will be no recrystallisation at all since recovery removes the effects of deformation before recrystallisation can occur. In fact, a critical strain anneal can lead to a single crystal on recrystallisation.

Boundary Mobility

Solute Drag

Misfitting impurity atoms segregate to grain boundaries where they can

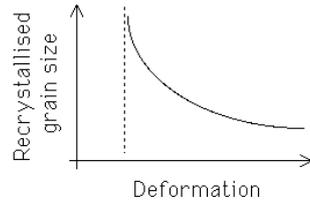


Fig. 38: Recrystallised grain size.

be better accommodated. This leads to a decrease in the energy of the boundary; work therefore has to be done if the boundary has to pull away from the segregated atoms. This can lead to an enormous reduction in the mobility of the grain boundaries. Thus, pure aluminium can recrystallise at ambient temperature whereas commercially pure aluminium has to be heated to very high temperatures.

Zener Drag

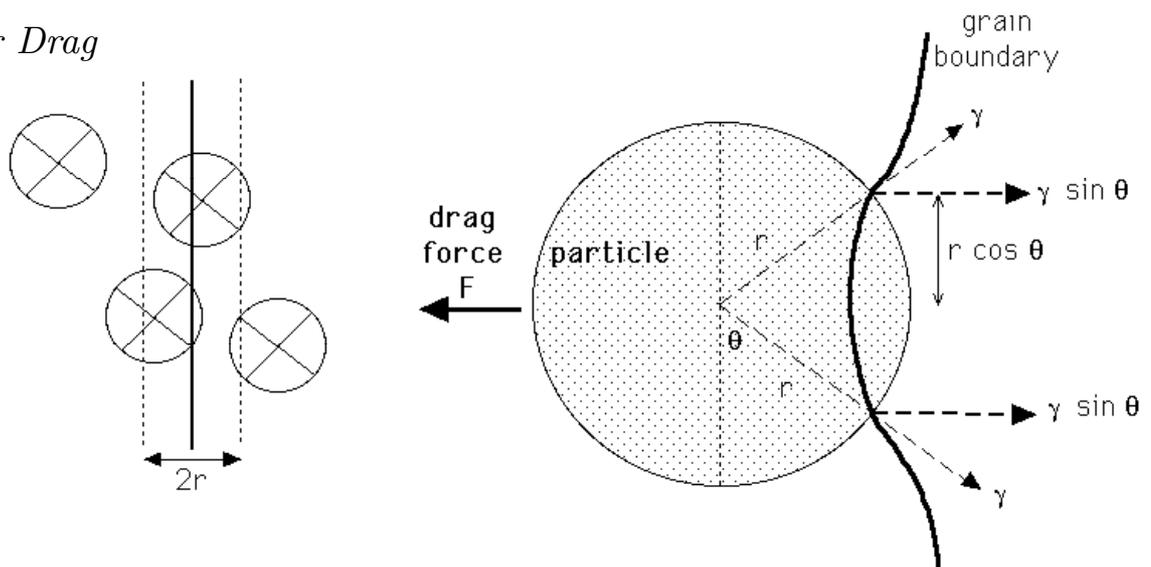


Fig. 39: Zener Drag

Recrystallisation and grain growth involve the movement of grain boundaries. The motion will be inhibited by second phase particles. The drag on the boundary due to an array of insoluble, incoherent spherical par-

ticles is because the grain boundary area decreases when a boundary intersects the particle. Therefore, to move away from the particle requires the creation of new surface. The net drag force on a boundary of energy γ per unit area due to a particle of radius r is given by (Fig. 40)

since $\gamma \sin\{\theta\} = \text{force per unit length}$

$$F = \gamma \sin\{\theta\} \times 2\pi r \cos\{\theta\} \quad \text{so that at } \theta = 45^\circ, \quad F_{max} = \gamma\pi r$$

Suppose now that there is a random array of particles, volume fraction f with N particles per unit volume. Note that

$$N = \frac{f}{\frac{4}{3}\pi r^3}$$

Only those particles within a distance $\pm r$ can intersect a plane. The number of particles intersected by a plane of area 1 m^2 will therefore be

$$n = 2rN = \frac{3f}{2\pi r^2}$$

The drag pressure P is then often expressed as

$$P = F_{max}n = \frac{3\gamma f}{2r}$$

This may be a significant pressure if the particles are fine. Anisotropic particles may have a larger effect if they present a greater surface area for interaction with the boundary.

Grain Growth

A grain of radius r has a volume $\frac{4}{3}\pi r^3$ and surface area $4\pi r^2$. The grain boundary energy associated with this grain is $2\pi r^2\gamma$ where γ is

the boundary energy per unit area and we have taken into account that the grain boundary is shared between two grains. It follows that:

$$\text{energy per unit volume} = \frac{3\gamma}{2r} \equiv \frac{3\gamma}{D} \quad \text{where } D \text{ is the grain diameter}$$

It is this which drives the growth of grains with an equivalent pressure of about 0.1 MPa for typical values of $\gamma = 0.3 \text{ J m}^{-2}$ and $D = 10 \mu\text{m}$. This is not very large so the grains can readily be pinned by particles (Zener drag).

Additional Information

1. Resources on recovery, recrystallisation and grain growth:
www.msm.cam.ac.uk/phase-trans/2005/growth.html

Lecture 8: Precipitation

The precipitation (Fig. 41) of small particles is an important way of controlling microstructure and properties; *e.g.* the particles strengthen by impeding dislocation motion.

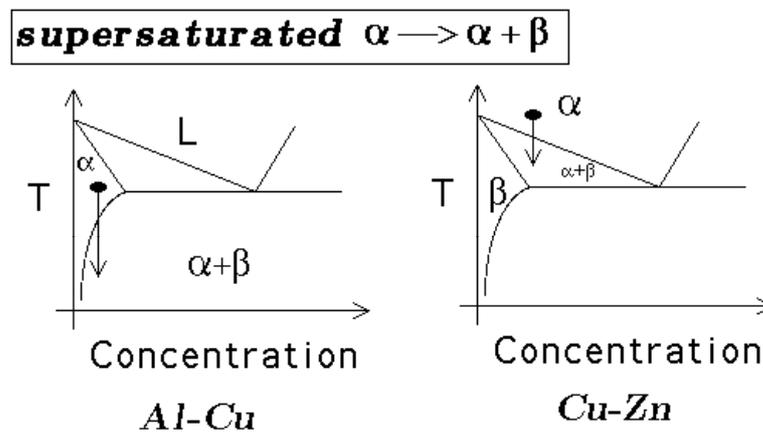


Fig. 41: Typical precipitation reactions

Nucleation of β

Nucleation occurs by random heterophase fluctuation in which a small volume of β is created, surrounded by an α/β interface. For a spherical particle of radius r , the resulting change in free energy is

$$\Delta G = -\frac{4}{3}\pi r^3(\Delta G_V - \psi) + 4\pi r^2\gamma \quad \text{with} \quad G^* \propto \frac{\gamma^3}{(\Delta G_V - \psi)^2}$$

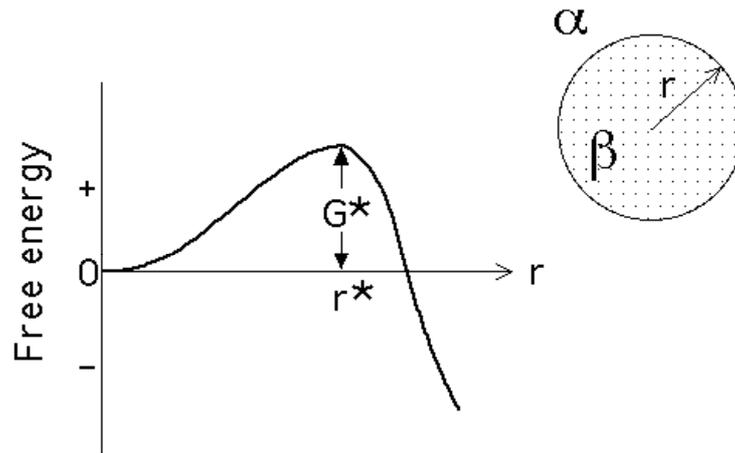


Fig. 42: The barrier to nucleation.

where ΔG_V is the magnitude of the change in free energy per unit volume of β , ψ is the elastic strain energy and as usual, γ is the interfacial energy per unit area (Fig. 42). G^* is the activation energy for nucleation. If the interfacial energy of the equilibrium phase is large then its precipitation may be preceded by a series of metastable phases, *i.e.* those which are less favoured thermodynamically but are easier to nucleate because they have a higher coherency with the matrix. For example, the precipitation sequence typical in Al–Cu (Fig. 43).

Precipitate Growth

Precipitates can have a different chemical composition from the matrix. In solid–state transformations the dissipation of heat is usually a minor effect. The growth of such particles (designated β) is instead controlled by the diffusion of solute which is partitioned into the matrix (designated α).

As each precipitate grows, so does the extent of its diffusion field. This slows down further growth because the solute has to diffuse over ever

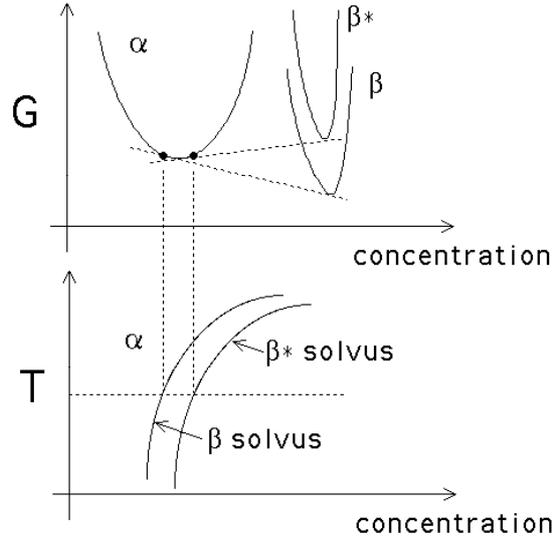


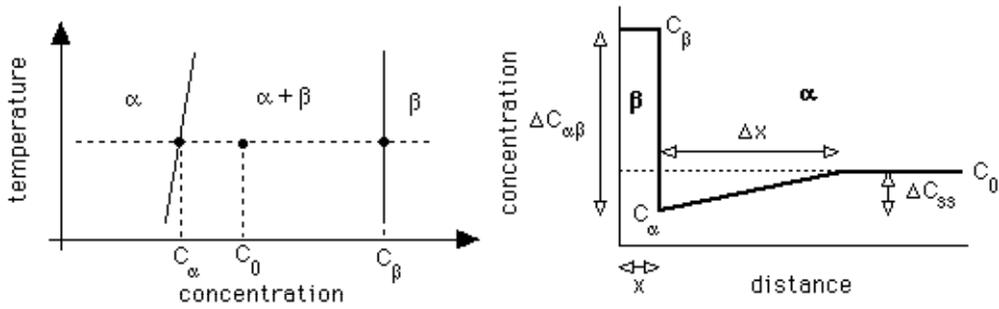
Fig. 43: β is the equilibrium phase

larger distances. As we will prove, the particle size increases with the square root of time, *i.e.* the growth rate slows down as time increases. We will assume in our derivation that the concentration gradient in the matrix is constant, and that the far-field concentration C_0 never changes (*i.e.* the matrix is semi-infinite normal to the advancing interface). This is to simplify the mathematics without losing any of the insight into the problem.

For isothermal transformation, the concentrations at the interface can be obtained from the phase diagram as illustrated below. The diffusion flux of solute towards the interface must equal the rate at which solute is incorporated in the precipitate so that:

$$\underbrace{(C_\beta - C_\alpha) \frac{\partial x}{\partial t}}_{\text{rate solute absorbed}} = \underbrace{D \frac{\partial C}{\partial x}}_{\text{diffusion flux towards interface}} \simeq D \frac{C_0 - C_\alpha}{\Delta x}$$

A second equation can be derived by considering the overall conservation



of mass:

$$(C_\beta - C_0)x = \frac{1}{2}(C_0 - C_\alpha)\Delta x$$

On combining these expressions to eliminate Δx we get:

$$\frac{\partial x}{\partial t} = \frac{D(C_0 - C_\alpha)^2}{2x(C_\beta - C_\alpha)(C_\beta - C_0)}$$

If, as is often the case, $C_\beta \gg C_\alpha$ and $C_\beta \gg C_0$ then

$$2 \int x \partial x = \left(\frac{C_0 - C_\alpha}{C_\beta - C_\alpha} \right)^2 D \int \partial t$$

so that $x \simeq \frac{\Delta C_{ss}}{\Delta C_{\alpha\beta}} \sqrt{Dt}$

and $v \simeq \frac{1}{2} \frac{\Delta C_{ss}}{\Delta C_{\alpha\beta}} \sqrt{\frac{D}{t}}$

where v is the velocity. A more precise treatment which avoids the linear profile approximation would have given:

$$v \simeq \frac{\Delta C_{ss}}{\Delta C_{\alpha\beta}} \sqrt{\frac{D}{t}}$$

The velocity equation contains both a diffusion coefficient (increases with temperature) and a driving force (supersaturation, decreases with

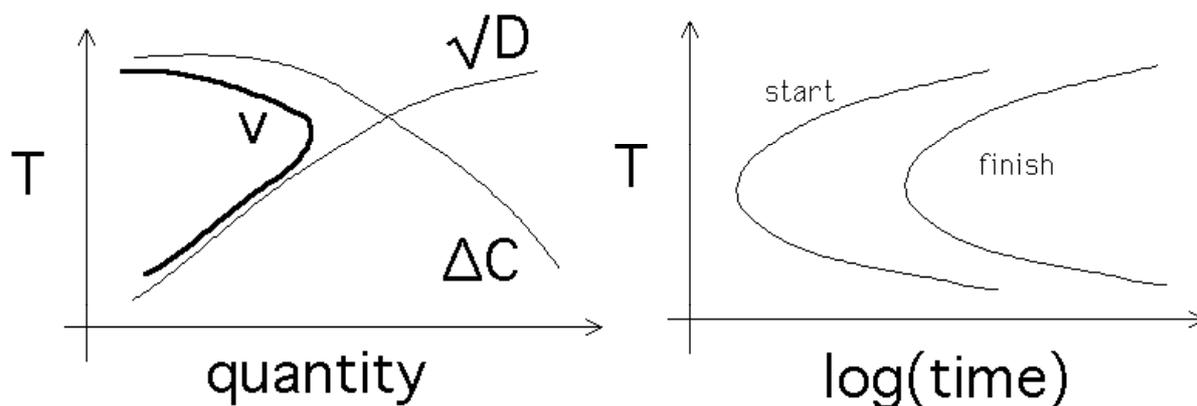


Fig. 44: TTT diagrams

temperature). This means that the velocity has an optimum at an intermediate temperature (Fig. 44).

Nucleation Sites

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. 45. There will, therefore, be a precipitate-free zone (PFZ) adjacent to a grain boundary.

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

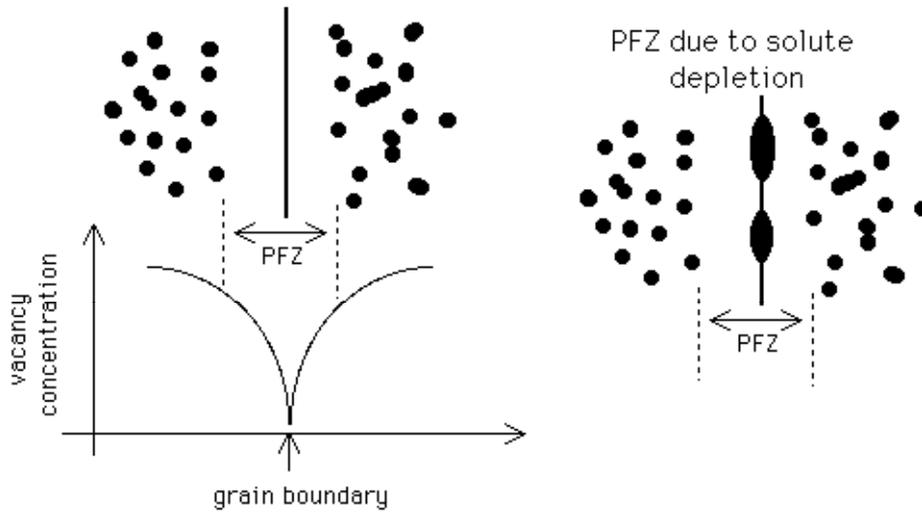


Fig. 45: Precipitate-free zones

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. 46). Thus, for Al-6Zn-3Mg age-hardening alloy, GP zones are used as nuclei for the η (MgZn_2) phase.

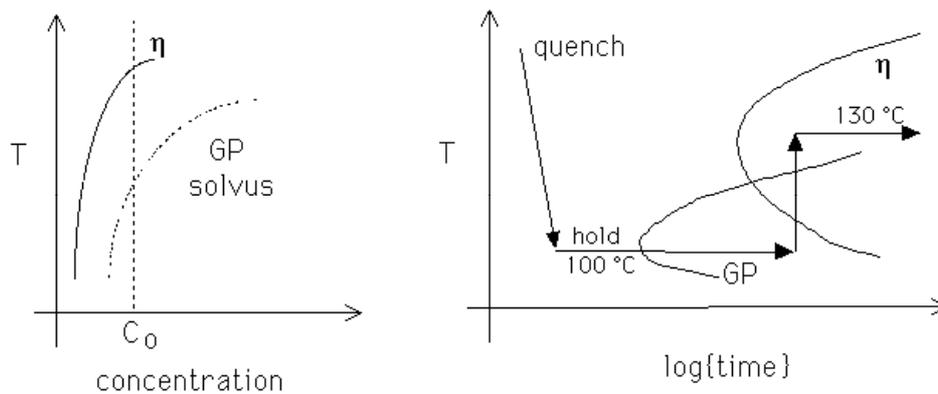


Fig. 46: Two-stage heat treatment

Additional Information

1. Resources on kinetics:

www.msm.cam.ac.uk/phase-trans/kinetics.html

2. Aluminium–copper alloys:

www.msm.cam.ac.uk/phase-trans/abstracts/M24.html

3. Aluminium–silicon alloys:

www.msm.cam.ac.uk/phase-trans/abstracts/M7-8.html