

Precipitation Hardening

Second edition

J. W. Martin

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FOR EVERY TITLE THAT WE PUBLISH, BUTTERWORTH-HEINEMANN
WILL PAY FOR EVERY TO PLANT AND CARE FOR A TREE.

Preface to the Second Edition

Producing this new edition has involved virtually re-writing the text, and the casual reader would be hard pressed to recognize the surviving sections of the original book, which consisted of about one half text and one half excerpts of 'selected readings' from the relevant literature.

The text is divided into four chapters, opening with a consideration of the development and characterization of the microstructure of precipitation-hardened alloys, followed by chapters on their strength and fracture behaviour at room temperature. The final chapter is concerned with high temperature properties – which were totally ignored in the first edition. The text is again aimed at the undergraduate level, although perhaps something more advanced than the 'first year' undergraduate knowledge is assumed.

The excerpts now comprise less than twenty per cent of a somewhat expanded text, but they still represent, in my view, important milestones in the development of the study of precipitation hardening. They now appear inserted at the end of the appropriate chapter of text. Wilm and Preston appear at the end of Chapter 1, together with a fascinating recent memoir published by Professor A. Guinier about the birth of GP zones. The classical papers by Jeffries and Archer and by Orowan appear after Chapter 2, and quotations from a rare paper by Constance F. Tipper on the role of particles in ductile fracture are placed after Chapter 3. The most recent paper is that by Davies and Stoloff on the anomalous high temperature yield behaviour: it is a model presentation in clarity and reasoning for the student reader.

The work does not constitute an advanced research monograph, but it hoped that this outline of the principles of age-hardening will also prove of value to practising materials engineers, as well as to the undergraduate reader. Some guidance to more advanced reading is given at the end of each chapter. The final appendix includes not only a number of phase diagrams which should prove useful in interpreting some recommended age-hardening heat-treatments, but there is also a list of sources of alloy property data (including on-line data) to which the materials engineer could usefully turn.

I am particularly grateful to Dr Ian Palmer of the Oxford University Department of Materials for reading much of the original manuscript and for making numerous helpful suggestions for its improvement, and also to Dr M. B. Henderson of Farnborough, for his helpful comments on an early draft of Chapter 4. I nevertheless take full responsibility for all shortcomings in this, the final version. Finally, I wish to thank Professor Brian Cantor F.Eng the Cookson Professor of Materials in the University of Oxford, for granting me a Senior Fellowship in the Department of Materials in the University of Oxford, and for the working facilities provided there which have been of incalculable value.

Finally, I am indebted to my granddaughter Rebecca Beardmore for the cover design.

J. W. Martin
July 1998

Preface to the First Edition

The metallurgical industry is one of the oldest of the arts but one of the youngest of the subjects to be investigated systematically and considered analytically in the tradition of the pure sciences, and I was very conscious of this when I was invited to prepare this series of Selected Readings on the theme of precipitation hardening. The result cannot, by the very nature of the subject, be analogous to similar volumes in the field of physics, for example, and few of the papers selected here are 'classical' to the extent of the really great papers of, for example, quantum physics or relativity.

On the other hand, the topic of precipitation hardening nicely illustrates the transition of metallurgy from an art (exemplified by the contribution of Wilm) to a science. In preparing my commentary, in making the selection of papers and in choosing the extracts, I have tried to keep the text at a simple and introductory level, only 'first year undergraduate' knowledge being assumed. Elementary acquaintance with crystallography and diffraction, phase equilibria and transformations, the principles of metallography, and deformation behaviour (including the simple geometry of dislocations) has been assumed: any of the several standard introductory texts on physical metallurgy will cover the ground. In the commentary some references for more advanced reading will be found.

Both the commentary and the papers are grouped into four sections. The broad basis of age-hardening is outlined in the first section, and this is accompanied by extensive extracts from the remarkable 1921 paper of Jeffries and Archer. The changes in mechanical and physical properties on ageing are examined next, and this is followed by a section on the metallography of aged alloys. The final section outlines some theories of the mechanisms of hardening, but because of the complexity of the subject the scope is rather limited at the given level of discussion, and I can only hope that the reader will be inspired to follow up the more elaborate theories in his later years.

Finally I wish to thank the metallurgy undergraduates of St Catherine's College, Oxford, for so willingly disclosing shortcomings in the early drafts of the book, Mr A.J. Bryant for his comments on the subject of quench sensitivity, and most particularly Professors W. Hume-Rothery and J.W. Christian for their valued advice during the preparation of the text.

J. W. Martin
Oxford

Introduction

HISTORICAL BACKGROUND

There are four important general methods by which the resistance to plastic deformation of a metal crystal may be increased, namely by cold working, by refining the grain size, by solid solution strengthening and by precipitation hardening, and many modern high-strength alloys depend on the use of one or more of these effects. The first of these methods has been known from ancient times, but the latter technique sprang from Alfred Wilm's observations and experiments during the years 1906–1909 in Germany. Wilm was searching for an aluminum alloy which could be hardened by quenching from an elevated temperature in a similar manner to steel. In one alloy, known later as 'duralumin', which contained 4% copper, 0.5% magnesium and a small amount of manganese, it was accidentally discovered that the hardness of the quenched alloy was relatively low, and subsequently increased with time. It has been said that this discovery of 'age-hardening' represents the only new method of hardening alloys since the quenching of steel was discovered in the second millennium BC.

[Wilm's original paper, first published in 1911, appears in English translation in the Appendix to this chapter, where it will be seen that the author compares the hardening behaviour of quenched aluminium alloys (containing magnesium and copper) with that of quenched carbon steels. The effect upon the hardness of cooling-rate after solution heat-treatment, and of subsequent cold-working was also investigated and reported upon.]

The fundamental reasons for the age-hardening of duralumin remained unknown to Wilm, but the epoch-making paper of Merica, Waltenburg and Scott in 1919 demonstrated the decreasing solid solubility of copper in aluminium with decreasing temperature. These workers proposed that age-hardening arises due to this effect; at high temperature the alloy will exist as a homogeneous solid solution. If, after such 'solution heat-treatment', the alloy is then rapidly cooled to room temperature by quenching into water or other fluid, the separation of the θ -phase (of approximate composition CuAl_2) is suppressed, and an unstable supersaturated solid solution is produced. Merica *et al.* suggested that hardening resulted from precipitation of the second phase taking place when the quenched alloy is 'aged' for a sufficient time, and that the precipitate was in the form of a fine 'submicroscopic dispersion'. From that date the search for new age-hardenable alloys became susceptible to a scientific approach.

The main requirements for strengthening were first clearly stated by Jeffries and Archer in their classic paper of 1921, excerpts of which appear in the Appendix to Chapter 2. They considered not only Merica's results with

duralumin, but a wide range of dispersion-hardened structures such as cementite in steel, cuprous oxide in copper, and also their own powder metallurgically produced ThO_2 in tungsten. They laid the foundations of the principles of this type of alloy, and proposed that strengthening is obtained by 'slip interference' within the grains due to the 'keying effect' of the dispersed hard particles, and that the effect increases with the fineness of subdivision of the hard constituent (for a given amount of the phase), further suggesting that the strengthening reaches a maximum at an average particle size denoted by the term 'critical dispersion'. With a given amount of precipitate, larger particles would have less strengthening effect because there would be fewer keys: this would explain why at some ageing temperatures the hardness increased initially and then decreased as the particles coarsened beyond the critical dispersion size.

MORE RECENT DEVELOPMENTS

Since these early years, aluminium-based alloys (and aluminium-copper alloys in particular) have been those most widely studied. Because the structural changes taking place during the early stages of ageing are beyond the resolution of the optical microscope, little progress was made in understanding the processes until sophisticated X-ray diffraction techniques were applied independently by Guinier and by Preston in the late 1930s, and more direct evidence of the changes occurring did not emerge until the application of the electron microscope to the problem in the 1950s.

The early concept of 'slip interference' due to the precipitate particles is today discussed in terms of interactions between moving glide dislocations and precipitates. The size and shape of the precipitate particles, their nature (i.e. whether they are hard or soft), and the nature of the interface between a precipitate and its matrix have a great influence on the mechanical properties of the aged alloy, as these factors often determine whether or not glide dislocations moving in the matrix can pass through the precipitate.

In this text, the first chapter is concerned with the development of the microstructure of alloys that are precipitation-hardened. After reviewing the nature of the various types of dispersed phase encountered in such alloys, the thermodynamics and kinetics of ageing will be considered. The chapter will conclude with a review of the metallography of aged alloys.

1 The microstructure of precipitation-hardened alloys

1.1 THE DISPERSED PHASES PRESENT IN METALS

In most theoretical discussions of strengthening mechanisms in particle-hardened alloys, attention is usually confined to the interaction of glide dislocations with finely dispersed precipitates typically 10 nm in size. In real alloys of this type, however, dispersions of coarser particles also exist, which may play an important role in the deformation behaviour and particularly in the fracture behaviour of the alloy. The dispersed phases that may be present can be conveniently classified into three families, the hardening precipitates themselves, the coarse 'residual' particles, and the so-called 'dispersoids' whose size range is intermediate between that of the other groups.

1.1.1 Hardening precipitates

These may range in size from, say, 1 to 100 nm. Section 1.2 is concerned with the formation of such dispersions and Chapter 2 will consider their effect upon the room temperature mechanical properties of the alloy. In steels and in age-hardening non-ferrous alloys the particles are formed by precipitation from supersaturated solid solution, and this constitutes by far the most commonly used technique for producing a dispersed second phase. Other methods include diffusion reaction techniques, such as nitriding of steel or internal oxidation of, for example, copper alloys, and powder-metallurgical techniques such as 'mechanical alloying', and we will briefly consider at this point the production of *oxide dispersion strengthened* (ODS) materials.

Internal oxidation

In this technique an alloy consisting of a dilute solid solution of a base metal in a more noble metal is heated under oxidizing conditions, when oxygen diffuses into the alloy and a dispersion is produced of the oxide of the base metal in a matrix of the noble metal.

Silver, copper and nickel have commonly been employed as solvent metals, and suitable solutes include silicon, aluminium, magnesium and beryllium. After internal oxidation, dispersions of silica, alumina, magnesia or beryllia are formed

in a matrix of Ag, Cu or Ni, and these oxides are stable at temperatures up to that of their formation, which can be close to the melting point of the alloy.

The time required for the complete internal oxidation of large cross-sections is very long, since the rate of formation of an internal oxide layer follows a parabolic law. Furthermore, the oxide particle size is not uniform, but becomes coarser as the depth from the specimen surface increases.

A limited amount of internally oxidized material with useful engineering properties has been produced industrially by employing a powder-metallurgical approach: if the alloy is in a finely divided form, diffusion times are short for the complete internal oxidation of each powder granule. The oxidized (two-phase) product can then be compacted and densified into a useful product. A much more flexible powder-metallurgical technique for the production of ODS materials is that of *mechanical alloying*.

Mechanically alloyed ODS materials

Conventional powder metallurgy involving the mechanical mixing of metal and oxide powders cannot achieve a sufficiently uniform dispersion of oxide particles in the final product, which is essential for good mechanical properties. In 1970 J.S. Benjamin announced the discovery of mechanical alloying, in which elemental or alloyed powders, together with the oxide are charged into a dry, high-energy, high-speed ball mill, known as a Szegvari attritor grinding mill. The process consists of repeated fracturing and rewelding of powder particles by high energy compressive-impact forces. Eventually the process establishes a uniform fine oxide dispersion (of sizes of the order of tens of nanometres) within relatively coarse (60–100 μm) powder particles. The mechanically alloyed powders are finally consolidated, usually by placing them in a steel can followed by degassing under vacuum, and hot extrusion. Their microstructure consists of finely dispersed oxide particles in a matrix which could be (rarely) a pure metal, or (more usually) a solid solution which may be susceptible to a further precipitation-hardening heat-treatment (see Section 1.2).

The most widely used ODS alloys are nickel-based superalloys, and their properties will be discussed in Chapter 3.

1.1.2 Coarse residual particles

When considering such particles, which are larger than 1 μm in size, it is convenient to discuss separately the occurrence of these coarse inclusions in *steels* and those encountered in *non-ferrous alloys*.

Inclusions in steels

The origin and constitution of non-metallic inclusions in steels have been the subject of intense study over many years, as it has long been recognized that they are a potential source of weakness. For this reason strenuous efforts are now

made in the production of 'clean' steels for many applications. The three main sources of non-metallic inclusions are:

- (i) deoxidation, and the segregation of the products of deoxidation;
- (ii) the presence of sulphur and phosphorous, and the segregation of their compounds;
- (iii) extraneous sources, including the trapping of slag and eroded refractory materials within the molten steel.

Inclusions in non-ferrous alloys

Coarse insoluble particles are formed during casting of non-ferrous alloys, and although these may be broken up and distributed more uniformly through the structure by hot-working of the ingot, they are again recognized as a potential source of weakness in the material. Commercial *aluminium alloys* contain from about 1% to 5% by volume of large iron or silicon-rich inclusions, and may also contain copper-bearing particles arising from non-equilibrium microsegregation during solidification. Iron is, of course, the principal impurity in bauxite, so that its presence is not unexpected in the final product. These particles in commercial aluminium alloys are often referred to as *constituent* particles.

1.1.3 Intermediate-sized dispersoids

These may range in size from, say 0.1 to 1 μm , and we will again take as our example aluminium alloys (in which such particles are commonly found), although they may occur in many materials. Chromium, zirconium, or manganese is added to many commercial wrought aluminium alloys. The element usually remains in solution during casting, but during fabrication these alloys are normally given a so-called 'homogenization' heat-treatment at relatively high temperature. The heat-treatment results in the formation of particles of intermetallic compounds containing chromium, zirconium or manganese, whose size and spacing depend upon the temperature and time of homogenization. An example of a Mn-bearing dispersoid in an Al-Mg-Si alloy is shown in Fig. 1.1.

These dispersions have pronounced retardation effects upon the response of the alloy to recrystallization and grain growth, and are also known in some alloy systems to reduce the tendency for intergranular embrittlement in the fully aged condition. We will return later (Chapter 2) to a consideration of their effect upon deformation and fracture processes in age-hardenable alloys.

It is clear, therefore, that in industrial alloys of practical significance, several families of particles of differing size ranges are likely to be present and to have an effect upon the deformation and/or fracture behaviour of the material. We will next consider the kinetics of the nucleation and growth of hardening precipitates from supersaturated solid solutions, how such precipitates are distributed in the microstructure, and examine ways in which this distribution may be controlled. We will conclude with a consideration of how the distribution of particles in alloys may be quantitatively determined.

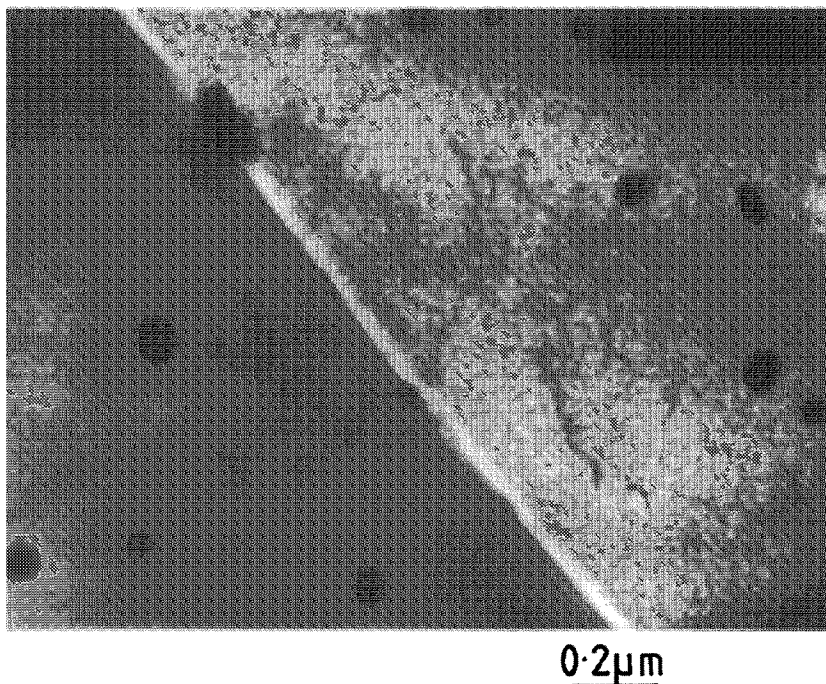


Fig. 1.1 Electron micrograph of an Al–0.6 wt % Mg–1 wt % Si–0.6 wt % Mn alloy aged to peak hardness. The Mg_2Si phase is present as non-coherent particles at the grain boundaries and as the fine, coherent hardening phase within the grains. Note the narrow precipitate-free zone adjacent to the grain boundary. The Mn is present as dispersoids of the $\alpha\text{-Al}_{12}\text{Mn}_3\text{Si}$ phase, typically $0.1\ \mu\text{m}$ in size.

1.2 THE THERMODYNAMICS AND KINETICS OF AGEING

The decomposition of a phase into one or more phases may be divided into three stages: (i) the formation of nuclei of the new phase; (ii) the growth of these nuclei; and (iii) the coarsening of the precipitate without change in its volume fraction. Stage (i) may occur in one of two ways: if small concentration fluctuations lead to a decrease in free energy, the reaction may proceed spontaneously by *spinodal decomposition*, and there is no barrier to nucleation; if all small fluctuations are unstable and tend to decay, there is said to be a *nucleation barrier*.

Precipitation by spinodal decomposition is a situation which leads to a very uniform, homogeneous distribution of coherent second-phase particles. In this type of system, no structural change is involved in the transformation, but compositional changes do occur and Fig. 1.2 shows a free-energy/composition curve for a homogeneous phase which is metastable with respect to phases A and B between compositions C_A and C_B .

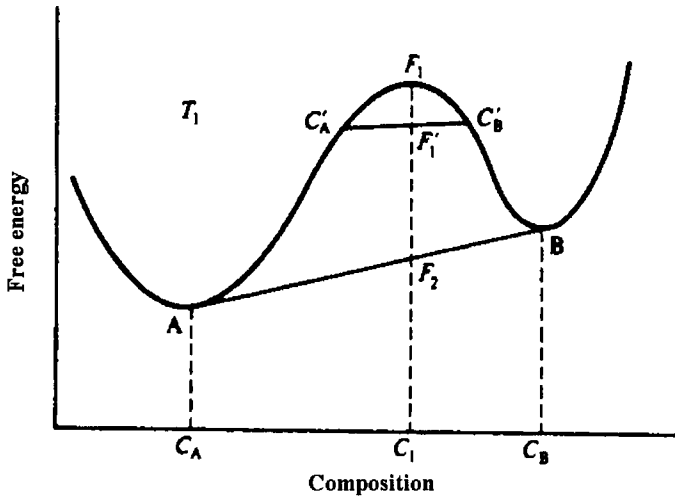


Fig. 1.2 Free-energy/composition relationship corresponding to spinodal decomposition.

An alloy of initial composition C_1 and free energy F_1 decomposes into a mixture of two phases of composition C_A and C_B and average free energy F_2 . At an early stage in the transformation the compositions of the two separating phases may be C'_A and C'_B with an average free energy F'_1 which is always lower than F_1 , so the decomposition proceeds with a *continual* decrease in free energy and there is no thermodynamic barrier to decomposition of the solid solution. Spinodal decomposition thus occurs simultaneously throughout the matrix, although there is no precise stage at which the new phases appear.

Precipitation by nucleation and growth. We will now consider the energy relations which determine the rate at which the nucleation barrier is overcome, and successful nucleation occurs. Nucleation that occurs completely at random throughout a system is said to be *homogeneous*. Usually there are regions where nucleation is observed to take place more readily. These are regions where there is atomic disarray – such as grain boundaries and around dislocations or inclusions, since these regions will have high free energy per atom and so will be the first to become unstable during the transformation. Nucleation occurs preferentially at these places and a state suitable for *heterogeneous nucleation* is said to exist, but we will consider homogeneous nucleation first.

1.2.1 Structural relationship between precipitate and matrix

In describing the structural relationship between the matrix and a precipitate there are two independent factors which must be considered. First, the *orientation relationship* between the crystal lattices of matrix and precipitate must be described. This is normally defined by planes and/or directions in each phase which are parallel, e.g.

$$(h_1 k_1 l_1)_\alpha \parallel (h_2 k_2 l_2)_\beta, [U_1 V_1 W_1]_\alpha \parallel [U_2 V_2 W_2]_\beta$$

Clearly, two sets of parallel planes or two sets of parallel directions in each phase would be equally suitable.

Secondly, in the case of plate-like precipitates, the *habit plane* must be described. This is the plane of the matrix which is parallel to the plane of the precipitate plate. Obviously this parameter does not arise in the case of spherical particles, and in the case of *rod-shaped* precipitates, only the matrix direction parallel to the rod axis need be defined.

1.2.2 Homogeneous nucleation from supersaturated solid solution

Energy relations

The basic ideas of nucleation theory were originally expressed by Gibbs [1878], namely that work is necessary for the formation of the *surface* of a new phase.

Let us assume that, in a metastable α -phase, a β -region forms consisting of n atoms. If σ is the specific surface energy of the $\beta\alpha$ interface and Δg_c the specific chemical free energy of the β phase, the balance of surface energy ($a\sigma n^{2/3}$) and the chemical energy due to the transformation in the new structure ($\Delta g_c n V$) is

$$\Delta G = a\sigma n^{2/3} + \Delta g_c n V$$

where V is the atomic volume, and a depends upon the shape of the β -region, which in the simplest case is a sphere. Transformations in the solid state are also usually associated with a change in specific volume, which leads to distortions during nucleation. An elastic strain energy term (g_e) should thus be included in the energy balance to give

$$\Delta G = a\sigma n^{2/3} + (\Delta g_c + g_e)n V \quad (1.1)$$

The variation in ΔG with n will therefore be of the form shown in Fig. 1.3 and the condition for continued growth of an embryo is that the number of atoms it contains should exceed n^* , where $d\Delta G/dn = 0$, i.e.

$$n^* = \left(\frac{2a\sigma}{-3V(\Delta g_c + g_e)} \right)^3 \quad (1.2)$$

The critical free energy, or activation energy for nucleation, is given by

$$\Delta G^* = (1/3)\sigma n^{*2/3} \quad (1.3)$$

For a spherical nucleus of radius r , the surface area is given by $4\pi r^2 = an^{2/3}$. Since $n = 4\pi r^3/3V$, we may substitute in equations (1.2) and (1.3) to obtain

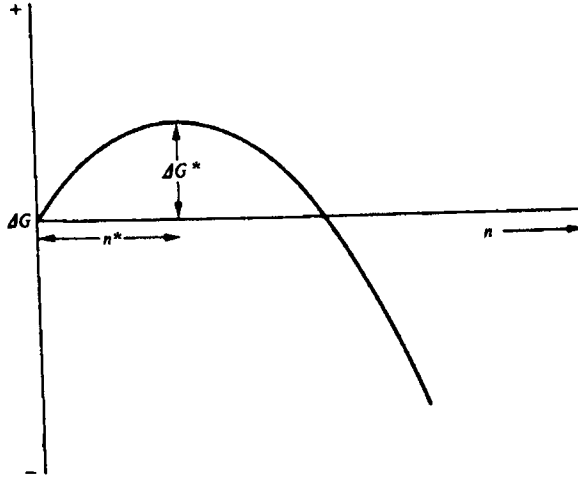


Fig. 1.3 Free energy (ΔG) of a precipitate as a function of the number of atoms it contains (n).

$$r^* = \frac{2\sigma}{-(\Delta g_c + g_e)} \quad (1.4)$$

and

$$\Delta G^* = \frac{16\pi\sigma^3}{3(\Delta g_c + g_e)^2} \quad (1.5)$$

Any nucleus or embryo that may form by chance fluctuations in the matrix will grow only if its radius exceeds r^* . If it is smaller than r^* it can lower the total free energy by re-dissolution. Δg_c (and hence r^*) will vary with temperature. We can write Δg_c as:

$$\begin{aligned} \Delta g_c &= (U_\alpha - TS_\alpha) - (U_\beta - TS_\beta) \\ &= (U_\alpha - U_\beta) - T(S_\alpha - S_\beta) \end{aligned}$$

At the solvus temperature, T_s , $\Delta g_c = 0$ by definition, so

$$(U_\alpha - U_\beta) = T_s(S_\alpha - S_\beta)$$

$(U_\alpha - U_\beta)$ is the heat of transformation, or latent heat, ΔH , so

$$\Delta g_c = \Delta H \Delta T / T_s$$

where ΔT is the amount of supercooling. So below the equilibrium temperature Δg_c becomes negative and increases with increasing undercooling. The values of

σ and g_e are assumed to be independent of temperature. Incidentally, since Δg_c is *negative*, if the value g_e were to be decreased, the magnitude of $(\Delta g_c + g_e)$ is thereby *increased*, so, from equation (1.5), ΔG^* is reduced.

The temperature dependence of r^* and ΔG^* may be assessed in terms of the temperature dependence of Δg_c , so we can write as a first approximation

$$r^* \propto 1/\Delta T, \Delta G^* \propto 1/\Delta T^2 \quad (1.6)$$

Basic kinetic theory

A steady-state nucleation rate, $\dot{N}_v$, may be defined as the number of stable nuclei produced in unit time in unit volume of untransformed solid. The theory assumes that the atomic fluctuations which give rise to the embryos are present in statistical equilibrium, so that if the number of atoms, n , in these fluctuations is much smaller than the total number of atoms, n_0 , it follows from equation (1.1) that

$$n = n_0 \exp(-\Delta G/kT)$$

where k is the Boltzmann constant and T the absolute temperature.

An embryo which contains a larger number of atoms than n^* (Fig. 1.3) can grow with decreasing free energy and is called a nucleus, and it follows that the nucleation rate $\dot{N}_v$ is proportional to $\exp(-\Delta G^*/kT)$. The rate at which individual nuclei grow will also be dependent on the frequency with which atoms adjacent to the nucleus can join it, and this will be proportional to the volume diffusivity, D . One may therefore write a simplified representation of the rate of nucleation of a precipitate

$$\dot{N}_v = K D \exp \frac{-A\sigma^3/(\Delta g_c + g_e)^2}{kT} \quad (1.7)$$

where A is a geometrical constant and K another constant.

Because of the high value of the energy of activation for diffusion (1 to 4 eV for substitutional atoms) the value of D , and thus the rate of nucleation, becomes very low at low temperatures. At temperatures close to equilibrium, $\dot{N}_v$ again becomes low because $\Delta G^* \rightarrow \infty$ (since $\Delta g_c \rightarrow 0$), so the resultant variation of $\dot{N}_v$ with temperature will appear as shown in Fig. 1.4. We have assumed that the nucleation rate is constant, although in practice $\dot{N}_v$ will initially be low, then gradually rise, and finally decrease again as the first nuclei to form start growing and thereby reduce the supersaturation of the remaining matrix.

The form of Fig. 1.4 accounts for the observed minima in the incubation time in temperature–time–transformation (TTT) curves (see later).

In alloys of practical interest, instead of the homogeneous nucleation of an equilibrium phase we have been considering, metastable phases are commonly observed, and furthermore, nucleation sites are very commonly associated with lattice defects in the matrix – in other words one usually encounters *heterogeneous nucleation*.

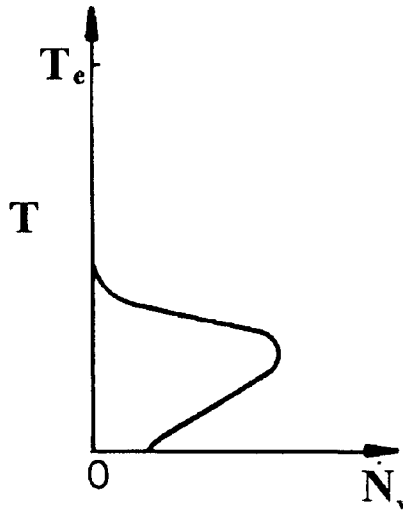


Fig. 1.4 Sketch of nucleation rate versus temperature for homogeneous nucleation of equilibrium precipitate from supersaturated solid solution.

1.2.3 Heterogeneous nucleation

In supersaturated solid solutions the following types of lattice defects can be expected:

- 0-dimensional faults – vacancies and interstitialcies;
- 1-dimensional faults – dislocations;
- 2-dimensional faults – grain and twin boundaries, stacking faults, antiphase domain boundaries, and possibly interphase boundaries.

The rate of heterogeneous nucleation is again proportional to $\exp(-\Delta G^*/kT)$ and the magnitude of ΔG^* is lower for heterogeneous nucleation than for homogeneous nucleation due to the reduction in one or both of σ and g_e caused by the interaction of the defects and the critical nucleus.

The crystal structures of the matrix and the precipitate must also be considered, because quite different structures and hence energies of the interface will arise from this factor. There are three important cases to define.

- (i) *Coherent nucleation*: this will occur if the crystal structures and lattice parameters of both phases are closely similar (Fig. 1.5a). The precipitation of the Ni_3Al -phase (γ') in Ni is of this type, the dispersed particles being in parallel crystallographic orientation with the matrix.
- (ii) *Semicoherent nucleation* arises if the two phases are related in such a way that an interface can be built from well-defined defects, such as interfacial

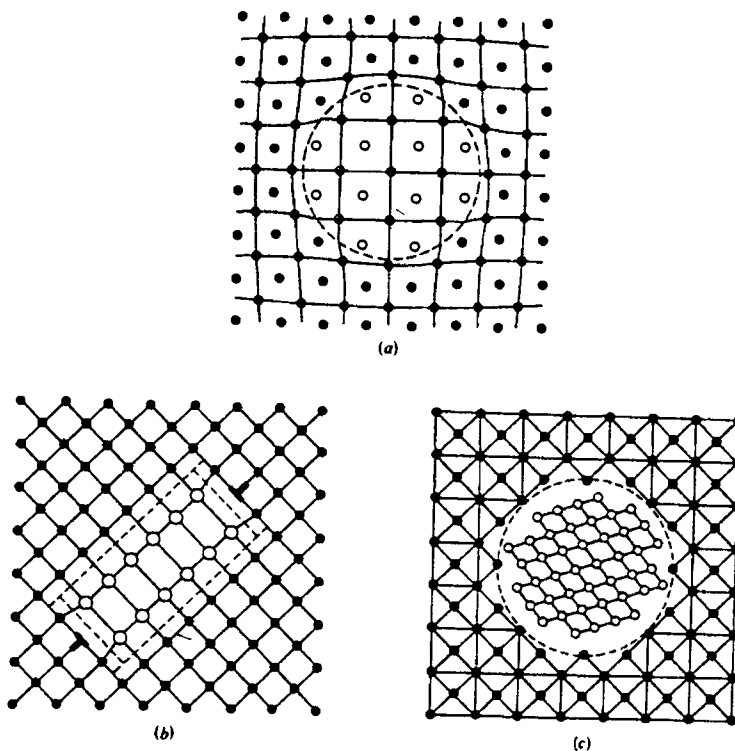


Fig. 1.5 (a) Fully coherent precipitate showing coherency strains in matrix. (b) Partially coherent precipitate showing interface dislocations (c) Non-coherent precipitate.

dislocations (Fig. 1.5b). The θ' -phase in the Al–Cu system is an example of this type.

- (iii) *Non-coherent nucleation* arises if the structures of the two phases are so different that the interface has a structure similar to that of a high-angle grain boundary (fig. 1.5c). The θ -phase in the Al–Cu system is of this type.

There is a limited number of fixed orientations between the two phases which will allow coherent or semicoherent nucleation. In non-coherent nucleation, however, a random orientation between the two phases can be expected.

Heterogeneous nucleation on point defects

Quenched-in vacancies can affect the rate of precipitate nucleation in two ways. First, they can increase the diffusion rate of solute atoms and thereby increase the

growth rate of precipitate embryos. Secondly, vacancies may become an integral part of the nucleus and thereby reduce the nucleation barrier to precipitate formation. It is this latter function we will consider further for the moment. The nucleation of a misfitting precipitate will be facilitated if a number of vacancies accumulate in order to counteract the volume change, thus reducing g_e (see equation (1.5)) For strain-free nucleation (i.e. $g_e = 0$) the nucleus requires ρ_0 vacancies per atom, ρ_0 is given by

$$\rho_0 = (V^\beta - V^\alpha)/V^\alpha$$

where V^β is the atomic volume of the precipitate and V^α that of the matrix. Thus, in the presence of vacancies, the strain-energy may be written as $g'_e = g_e (1 - \rho/\rho_0)$, and the energy barrier to nucleation (equation (1.5)) now becomes

$$\Delta G^* = \frac{16\pi\sigma^3}{3[\Delta g_c + \Delta g_v + g_e (1 - \rho/\rho_0)]^2}$$

where Δg_v is the change in free energy associated with vacancy precipitation.

Excess point defects can of course condense to form small dislocation loops, or stacking-fault tetrahedra (depending on the material), and the possibility cannot be discounted that the nucleating sites in irradiated specimens are in fact vacancy aggregates of this type.

Heterogeneous nucleation on dislocations

The main effect of dislocations is to reduce the contribution of g_e to ΔG^* by reducing the total strain-energy of the embryo (equation (1.5)), although nucleation on dislocations may also be assisted by solute segregation which may locally bring the composition nearer to that of the precipitate. Furthermore, a dislocation may provide a diffusion pipe with a lower value of D , which in a given time will assist an embryo to grow beyond its critical size.

The greatest effectiveness of a dislocation in lowering the strain-energy and therefore the activation energy of nucleation is to be expected if the nucleus can be formed by dissociation of the dislocation into two partial dislocations. In fcc crystals the $a/2\langle 110 \rangle$ unit dislocations can dissociate: $a/2[110] \rightarrow a/6[121] + a/6[21\bar{1}]$ giving a ribbon stacking fault on $(1\bar{1}1)$ separated by two Shockley partials. Since the stacking fault is comprised of four close-packed layers of hcp crystal it can act as a potent nucleation site for an hcp precipitate. This is observed in Al-Ag alloys, where Ag atoms diffuse to the fault and the hexagonal γ' phase is nucleated with the orientation relationship:

$$(0001)_{\gamma'} // (1\bar{1}1)_{\alpha}$$

$$[11\bar{2}0]_{\gamma'} // [110]_{\alpha}$$

which ensures low-energy interfaces due to the good matching.

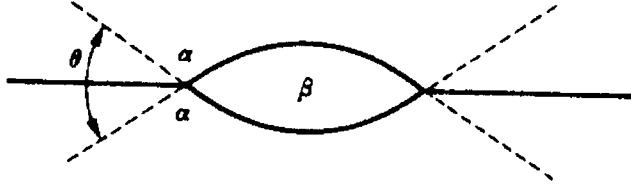


Fig. 1.6 Nucleation of β -phase in an isotropic $\alpha\alpha$ grain boundary.

Heterogeneous nucleation on grain boundaries

Grain boundaries are effective in increasing $\dot{N}$, the rate of nucleation, since, when a precipitate nucleus is formed in a boundary, part of the boundary area is eliminated and this energy is available effectively to reduce the σ -term in equation (1.7). The energy of a phase boundary is composed of two parts: (i) energy arising from the *structure* of the interface; and (ii) the chemical energy due to the difference in composition and order on both sides of the interface. Term (ii) leads to a difference between $\sigma_{\alpha\beta}$ and $\sigma_{\alpha\alpha}$ for an identical structure of grain boundary ($\alpha\alpha$) and phase boundary ($\alpha\beta$). Figure 1.6 illustrates the form of a β -phase nucleus at an α -grain boundary, which for isotropic surface energies is in the form of a doubly spherical lens. The ratio of the specific surface energies is

$$\sigma_{\alpha\alpha}/2\sigma_{\alpha\beta} = \cos \frac{1}{2}\theta$$

The ratio of the critical energy of formation of a boundary nucleus ΔG^*_{het} to that for homogeneous nucleation of a spherical nucleus ΔG^*_{hom} is given by:

$$\Delta G^*_{\text{het}}/\Delta G^*_{\text{hom}} = 2(2 - 3 \cos \theta + \cos^3 \theta) \quad (1.8)$$

The potency of a given boundary as a nucleation site depends therefore on $\cos \theta$, i.e. on the ratio $\sigma_{\alpha\alpha}/2\sigma_{\alpha\beta}$.

ΔG^* can be reduced even further by nucleation on a grain edge or a grain corner. Figure 1.7, from the work of J.W. Cahn [1] shows how $\Delta G^*_{\text{het}}/\Delta G^*_{\text{hom}}$ depends on $\cos \theta$ for the various grain boundary nucleation sites.

If the matrix and the precipitate are sufficiently compatible in their crystal structures to allow the formation of lower energy facets, then ΔG^*_{hom} can be further reduced, as shown in Fig. 1.8. The nucleus will then have an orientation relationship with one of the grains. Such nuclei are commonly encountered in practice, since the most successful nuclei will have the smallest nucleation barrier.

Because there are fewer potential sites available for grain-boundary nucleation than for homogeneous nucleation within the grains, the nucleation rate for a grain size d is changed from the homogeneous rate by a factor

$$\frac{\delta}{d} \exp \left(\frac{\Delta G^*_{\text{hom}} - \Delta G^*_{\text{het}}}{kT} \right)$$

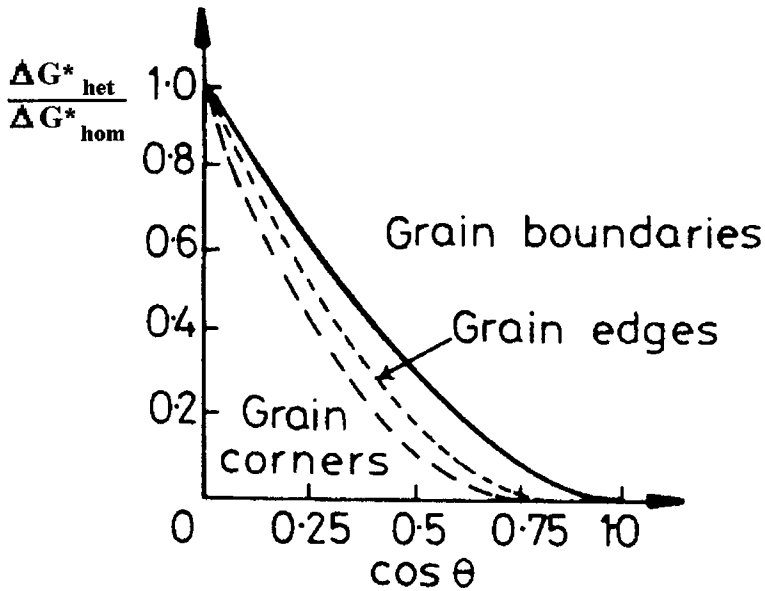


Fig. 1.7 The effect of θ on the activation energy for grain boundary nucleation relative to homogeneous nucleation (after Cahn [1]).

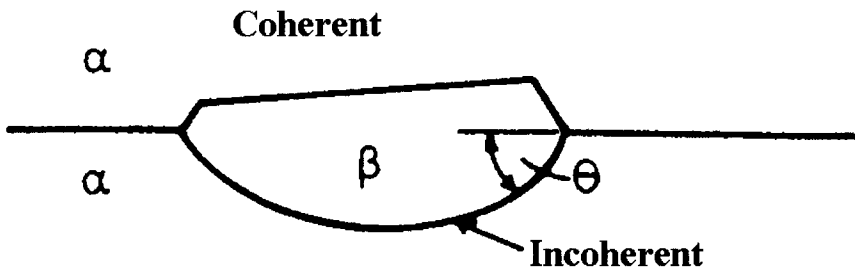


Fig. 1.8 Formation of a low-energy coherent interface between a precipitate particle and one grain.

where δ is the grain-boundary thickness. The order of magnitude of the ratio δ/d is typically 10^{-6} , so one would expect to observe grain-boundary nucleation being faster than homogenous nucleation when $\Delta G^*_{\text{hom}} - \Delta G^*_{\text{het}} \geq 14kT$.

Nucleation on other planar defects

Figure 1.9 provides an example which compares the precipitation kinetics of a particular phase (the carbide $(\text{Cr,Fe})_{23}\text{C}_6$) in association with various interfaces in an austenitic stainless steel. A family of 'C' curves is shown which represent

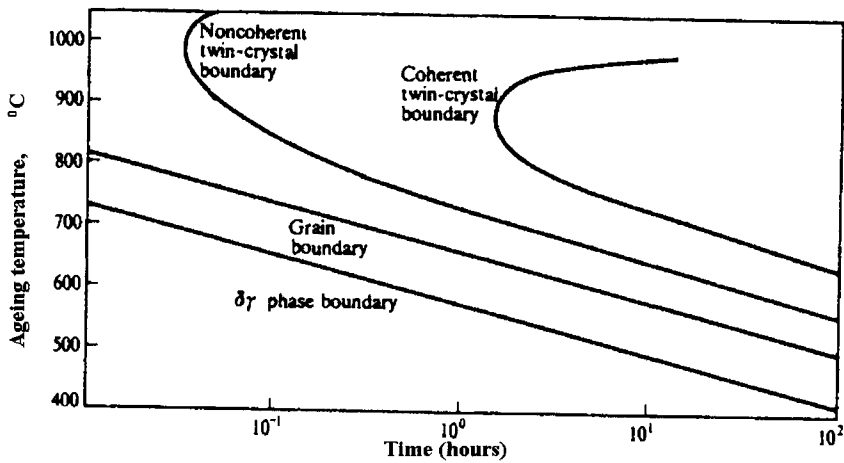


Fig. 1.9 Rate of nucleation of $(\text{Cr, Fe})_{23}\text{C}_6$ at different types of interfaces in an austenitic stainless steel (after Stickler and Vinckier [2]).

the time of first appearance of the carbide at a particular site. In comparison with grain-boundary nucleation, it is seen that *twin boundaries* form nuclei at longer times, because of their lower interfacial energy (equation (1.7)). In accord with this principle, *coherent twin* interfaces are seen to be more difficult to nucleate upon than *incoherent twin* interfaces. On the other hand, it is seen that $\delta\gamma$ -phase boundaries in the matrix are more effective than γ -grain boundaries in promoting carbide nucleation. This is because the energy of $\delta\gamma$ -interfaces is higher than that of $\gamma\gamma$ -boundaries due to a change in composition as well as a change in structure across them.

1.2.4 Strain-energy effects

Lattice misfit between a precipitate nucleus and the matrix can arise from the difference in lattice parameters or the difference in lattice symmetry of the two phases. As illustrated in Figs 1.5a and b, the misfit can be accommodated by elastic distortions or by defects lying in the interface.

If the unit cell sides of the precipitate and matrix are a_β and a_α respectively, then the misfit between the lattices (δ) is defined as

$$\delta = \frac{2(a_\beta - a_\alpha)}{a_\beta + a_\alpha} \approx \frac{a_\beta - a_\alpha}{a_\beta} \quad (1.9)$$

In order to calculate g_e , Nabarro [3] assumed that the nucleus *and* matrix are both strained isotropically, and applied a continuum mechanics approach to obtain the value of g_e , which was *independent* of the shape of the particle

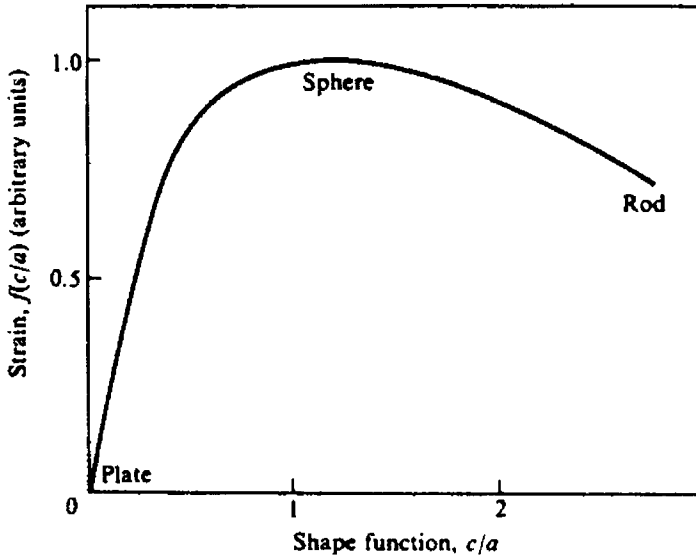


Fig. 1.10 The strain, $f(c/a)$, of an incoherent spheroidal nucleus as a function of its shape: a is the radius and $2c$ the thickness of the spheroid (after Nabarro [3]).

$$g_e = \frac{6G_\beta \delta^2}{1 + 4G_\beta/3K_\alpha} \quad (1.10)$$

where G_β is the shear modulus of the precipitate phase and K_α is the bulk modulus of the matrix. If the value of Poisson's ratio is taken as 0.3 then $K = 2G$, so if the moduli of the matrix and precipitate are similar, then

$$g_e \approx 4G\delta^2$$

For hard particles in a softer matrix, it is more realistic to assume that the nuclei are unstrained, and that only the matrix suffers hydrostatic strain. In this case Nabarro found that g_e becomes a function of the shape of the particle, in that the specific strain-energy decreases in the direction sphere $\rightarrow$ rod $\rightarrow$ plate (Fig. 1.10).

Plate-shaped nuclei are frequently observed in systems of practical importance. There are factors additional to that of maintaining g_e which favour such a particle shape, namely: (i) the anisotropy of the *surface energy*, so that the habit plane of the plate is that of best crystallographic fit; (ii) the anisotropy of the *elastic constants* of the crystal lattice, so that the habit plane of the plate is perpendicular to the direction of minimum Young's modulus; and (iii) the planes in which dislocations dissociate, or upon which vacancy clusters condense, may lead, as already discussed, to the nucleation of plate-like precipitate particles.

When a *semicoherent* nucleus is considered, some of the elastic strain energy associated with the nucleus is replaced by interfacial dislocations (Fig. 1.5b)

which contribute to the interfacial energy, σ . If a nucleus of n unit cells of each lattice is now considered, the misfit m is given by

$$m = n(a_{\beta} - a_{\alpha})$$

By introducing an interfacial dislocation with a component of Burgers vector b_m in the direction of misfit defined above, the effective misfit, m_{eff} , is reduced to

$$m_{\text{eff}} = n(a_{\beta} - a_{\alpha}) - b_m$$

and so

$$\delta = \frac{n(a_{\beta} - a_{\alpha}) - b_m}{na_{\beta}} \quad (1.11)$$

Thus $\delta = 0$ when $n(a_{\beta} - a_{\alpha}) = b_m$, and only the interfacial energy term need be considered in equation (1.7).

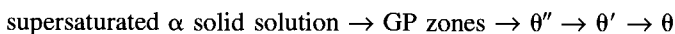
1.2.5 The formation of transition phases

When supersaturated solid solutions decompose, one or more metastable *transition phases* may appear prior to, or in addition to, the equilibrium precipitate. By definition, metastable phases possess a smaller negative Δg_c at a given temperature than the more stable phase, so that if common tangents to free-energy/composition curves are constructed it will be obvious that metastable phases are in metastable equilibrium with a matrix of different (higher) solute concentration than the stable phase. Consequently there will be as many metastable phase diagrams as there are metastable phases.

A schematic molar free energy diagram is shown in Fig. 1.11a for GP zones and the three phases θ'' , θ' and θ which form in Al–Cu solid solutions. The crystallographic features of these phases are given in Fig. 1.11b, and the corresponding phase diagram is shown in Fig. 1.11c. It should perhaps be emphasized that *prediction* of the number of transition phases, their crystal structure and composition has not yet been achieved for any alloy system, even on an empirical basis.

In Fig. 1.11a, the GP zones and the matrix have the same crystal structure so they lie on the same free energy curve. The transition phases θ'' and θ' are less stable than the equilibrium θ phase, and so have higher free energies.

In considering the *nucleation sequence* of transition phases, we will discuss the particular case of the Al–Cu system, although the conclusions are of quite general applicability. In that system, if the supersaturated solid solution is aged at temperatures below all the solvi of Fig. 1.11c, the experimentally observed ageing sequence is



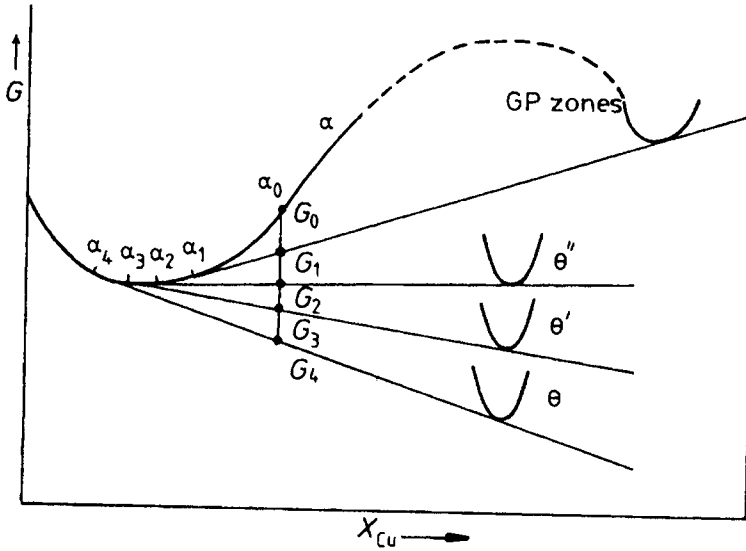


Fig. 1.11 (a) Schematic molar free energy diagram for the Al-Cu system.

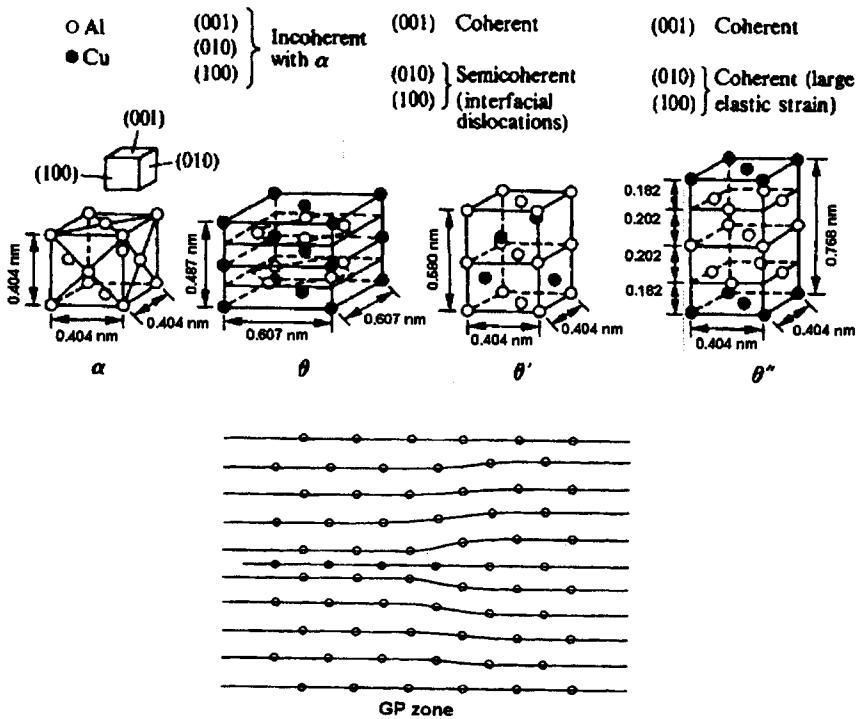


Fig. 1.11 (b) The crystal structures of the equilibrium θ phase and the transition phases (θ' , θ'' and GP zone).

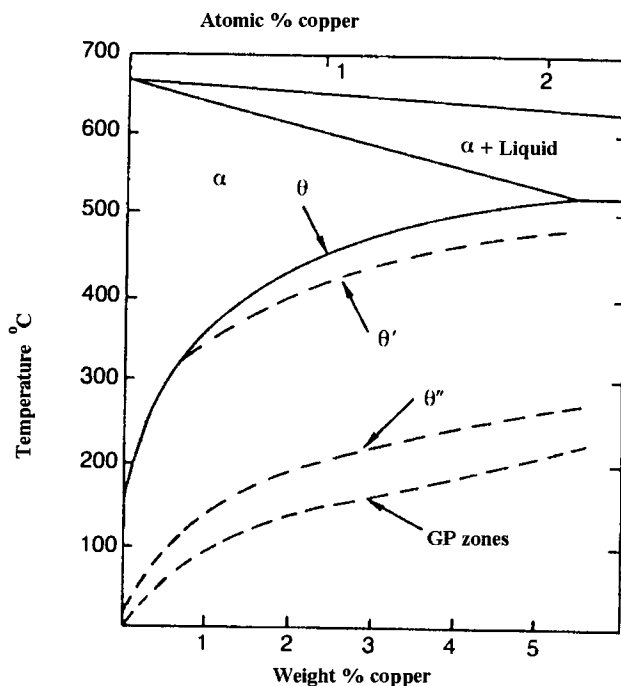


Fig. 1.11 (c) The Al-rich end of the Al-Cu phase diagram showing the metastable GP zone, θ'' and θ' solvi (after G. Lorimer [4]).

Table 1.1 Some precipitation-hardening sequences

<i>Base metal</i>	<i>Alloy</i>	<i>Sequence of precipitates</i>	<i>Equilibrium precipitate</i>
Aluminium	Al-Ag	Zones(spheres) $\rightarrow$ γ' (plates)	$\rightarrow \gamma$ (Ag_2Al)
	Al-Cu	Zones (discs) $\rightarrow$ θ'' (discs) $\rightarrow$ θ' (plates)	$\rightarrow \theta$ (CuAl_2)
	Al-Zn-Mg	Zones (spheres) $\rightarrow$ η' (plates)	$\rightarrow \eta$ (MgZn_2)
	Al-Cu-Mg	Zones (rods) $\rightarrow$ S' (laths)	$\rightarrow S$ (Al_2CuMg)
	Al-Mg-Si	Zones(rods) $\rightarrow$ β' (rods)	$\rightarrow \beta$ (Mg_2Si) (plates)
Copper	Cu-Be	Zones (discs) $\rightarrow \gamma'$	$\rightarrow \gamma$ (CuBe)
	Cu-Co	Zones (spheres)	$\rightarrow \beta$ (Co) (plates)
Iron	Fe-C	ε -carbide (discs)	$\rightarrow \text{Fe}_3\text{C}$ (plates)
	Fe-N	α'' (discs)	$\rightarrow \text{Fe}_4\text{N}$
Nickel	Ni-Cr-Ti-Al	γ' (cubes or spheres)	$\rightarrow \gamma$ ($\text{Ni}_3\text{Ti,Al}$)

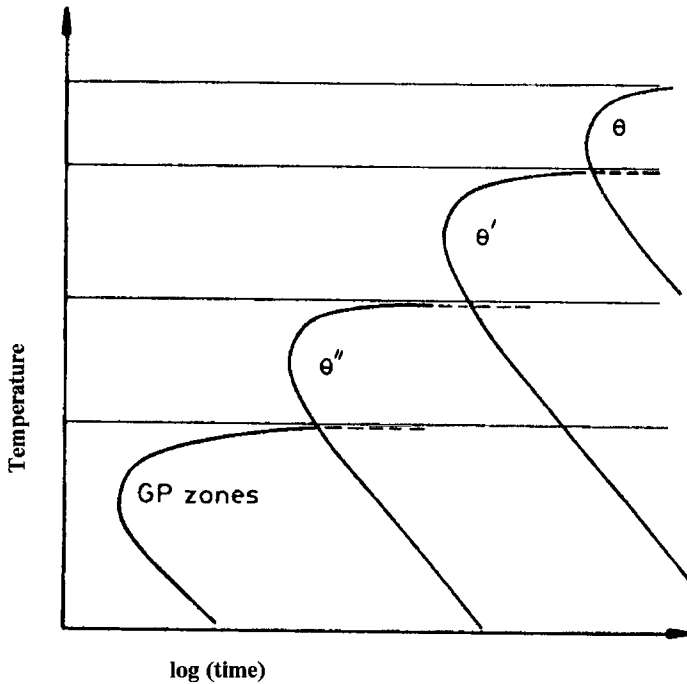


Fig. 1.12 Time for start of precipitation in Al–Cu alloy of composition X for each of the possible precipitates.

GP zones are formed as the first precipitate during low temperature ageing of many technologically important alloys, as indicated in Table 1.1.

The interfacial energy (σ) (equation (1.7)) decreases with progression through the series θ , θ' , θ'' and GP zones. Therefore once Δg_c becomes sufficiently negative for all possible precipitates, the interfacial energy factor is dominant, since ΔG^* in equation (1.5) is proportional to σ^3 , but only to $(\Delta g_c + g_e)^2$, and this accounts for the observed sequence of precipitates. The effect of ageing temperature on the precipitation sequence is shown in Fig. 1.12. The fastest transformation rates are associated with the highest nucleation rates and therefore the finest precipitate distributions. The microstructure thus coarsens as the precipitation sequence progresses.

1.2.6 Reversion, or retrogression

This phenomenon, commonly observed in precipitation-hardening alloys, is the temporary softening which is observed if an alloy hardened by ageing at a low temperature is subsequently heated to a higher ageing temperature: the temporary softening is followed by a further hardening on prolonged heating.

One explanation advanced for the effect considers the relative critical sizes for stable nuclei at the different ageing temperatures; a given alloy aged at the lower

temperature will form many small nuclei at a slow rate (because of the relatively low temperature for solute diffusion). When the temperature is raised, few of the particles will have reached the larger critical nucleus size appropriate to the higher temperature (equation (1.6)), therefore most of them dissolve and the alloy softens rapidly. Eventually new larger nuclei form and grow (at a faster rate at this higher temperature).

This explanation is not generally acceptable, since it has been shown experimentally that a series of specimens aged such that they contain zones of widely differing size will all exhibit the same minimum reversion temperature. The effect may be alternatively accounted for in terms of the metastable phase diagram (such as Fig. 1.11c: reversion of zones and intermediate precipitates at the metastable phase boundary being interpreted as being completely analogous to the dissolution of the equilibrium phase at the solvus line. It has been shown that the reversion temperature for aluminium copper alloys containing zones is the same as the limiting temperature for their formation.

1.2.7 Precipitate growth from supersaturated solid solutions

In the analysis of the *growth* of precipitates subsequent to their nucleation in a supersaturated solid solution, the possible limiting factors considered are the rate at which atoms are brought to or removed from the interface by *diffusion*, and the rate at which they *cross the interface*. The interface reaction is likely to be the rate-limiting step during the early stages of growth since the diffusion distance tends to zero in this situation. At large particle sizes, lattice diffusion is likely to be the slower step, since the continuous removal of solute from solution reduces the concentration gradient (the driving force for diffusion). We shall only refer to diffusion-controlled growth here, since this is the process which has been analysed in greater detail.

The subject has been recently reviewed in detail by Martin, Cantor and Doherty [5], and we will here simply refer to the calculations of Aaron, Fainstein and Kotler [6]. These workers predicted that the growth of spherical precipitates should obey an equation of the form

$$r = \alpha(Dt)^{1/2} \quad (1.12)$$

where r is the particle radius after time t , D (assumed independent of composition) is the volume diffusion coefficient and α is a function of the supersaturation. A similar calculation made for the growth of planar precipitates again predicted a parabolic relationship between thickness and time.

Most of the data available to test the above theories relate to the formation of crystals of pre-eutectoid ferrite forming in austenite grain boundaries in steel (grain-boundary allotriomorphs).

1.2.8 Precipitate growth in saturated solid solutions

When precipitation from supersaturated solid solution is complete, further annealing leads to precipitate coarsening driven by the interfacial free energy

between the precipitate and the matrix – the process known as *Ostwald ripening*. The physical process by which the microstructure coarsens and releases its excess surface energy is due to the higher solubility of small particles, since these have a larger ratio of surface area to volume. The larger particles thus grow at the expense of the smaller ones, and the growth kinetics depend upon the rate-controlling step in the process.

If *lattice diffusion* is the rate-controlling step, then the analyses of Wagner [7] and Lifshitz and Slyozov [8] lead to a coarsening rate given by the expression

$$\bar{r}_t^3 - \bar{r}_0^3 = 8D\sigma V_m C_\alpha(\infty)t/9RT \quad (1.13)$$

where

- $\bar{r}_t$ is the average particle radius at time t ,
- $\bar{r}_0$ is the average particle radius at time $t = 0$,
- D is the volume diffusion coefficient of the diffusing species,
- σ is the specific surface free energy of the particle/matrix interface,
- V_m is the molar volume of the precipitate,
- $C_\alpha(\infty)$ is the equilibrium solute content in the matrix,
- R is the gas constant,
- T is the temperature in K.

When the rate of coarsening is controlled by the rate of atom transfer across the *interface*, Wagner predicts:

$$\bar{r}_t^2 - \bar{r}_0^2 = 64KV_m C_\alpha(\infty)t/81RT \quad (1.14)$$

where K is a proportionality constant that includes the interface mobility.

Finally, if the coarsening precipitates are situated on grain boundaries and the dominant diffusion path is that down the grain boundaries, Kirchner [9] obtains

$$\bar{r}_t^4 - \bar{r}_0^4 = 9\sigma D_B \delta C_\alpha(\infty)_B V_m t / 32ABRT \quad (1.15)$$

where

- δ is the grain-boundary thickness,
- D_B is the grain-boundary diffusion coefficient,
- $C_\alpha(\infty)_B$ is the solute content at a grain boundary in equilibrium with an infinitely large precipitate.

A is the parameter defined by

$$A = \frac{2}{3} - (\sigma_B/2\sigma) + \frac{1}{3}(\sigma_B/2\sigma)$$

B is the parameter defined by

$$B = 2 \ln (1/f)$$

where

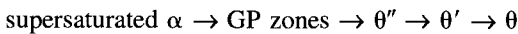
σ_B is the grain-boundary energy,

f is the fraction of the grain boundary covered by precipitates.

Experimentally it is found that in the vast majority of cases the kinetics are diffusion-controlled, that is, the mobility of the interface does not limit the reaction.

1.2.9 Calorimetry of precipitation processes

Calorimetric techniques have been used to study precipitation in age-hardening alloys since the 1930s. In recent years *differential scanning calorimetry* (DSC) has been widely employed for this purpose. Modern microcomputer-based thermal analysis systems are available which are able to perform a programmed experiment, collect, record and analyse data, and display or transmit the results automatically. Essentially the difference in heat input into a test specimen and a reference specimen of equal thermal mass is measured while the specimen and reference material are subjected to a controlled temperature programme. A feedback control system measures the temperatures of the specimen and reference material and ensures that they remain the same. The differential heat flow to the specimen and reference material is monitored, thus readily distinguishing (exothermic) *precipitation* reactions from (endothermic) *dissolution* reactions. For example, Papazian [10] studied the ageing sequence in the aluminium alloy 2219, which is nominally Al with 6.3 wt% Cu and small amounts of several other elements. Its age hardening behaviour is comparable to that of the pure binary Al–Cu system, with the sequence:



Papazian first measured the characteristics in the DSC of the individual precipitate phases, by comparing the DSC and TEM results from samples that had been aged such that only one precipitate phase was present. These ‘signatures’ were then used to identify the phase changes in specimens given different commercial heat-treatments (or ‘tempers’). For example Fig. 1.13 shows a plot of differential heat capacity (ΔC_p) versus temperature (T) for the alloy in the following conditions:

T31: Solution treated and quenched, followed by a small amount (1%) of deformation, then subsequently aged at room temperature.

T42: As T31 but undeformed.

Figure 1.13 shows four characteristic reaction regions which were identified as follows:

- I An endothermic (dissolution of GP zones) reaction between 50 and 200°C.
- II An exothermic (precipitation of θ') reaction between 200 and 300°C.

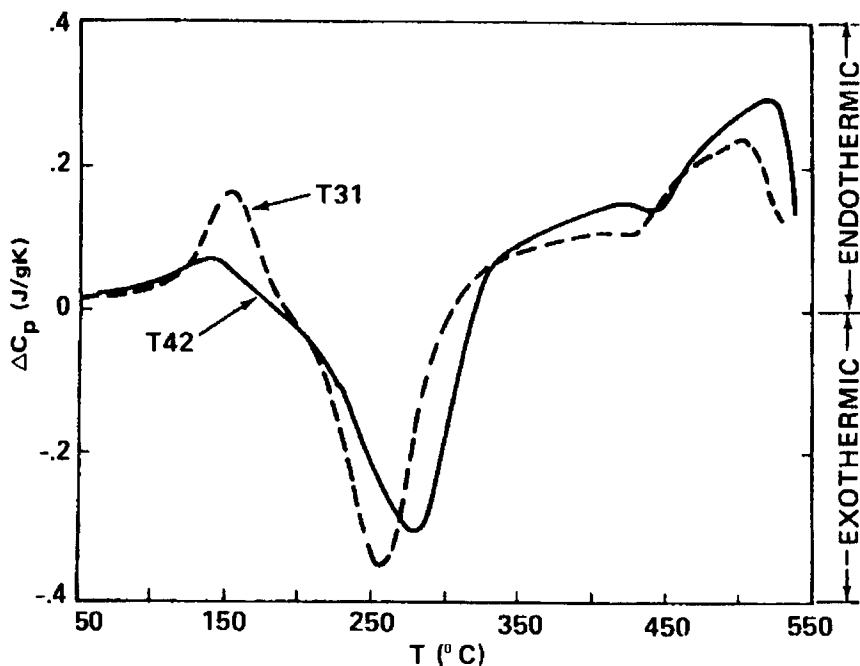


Fig. 1.13 Differential heat capacity of Al alloy 2219-T31 and 2219-T42 (after J.M. Papazian [10]).

- III Multiple endothermic reactions (dissolution of θ' and θ) between 300°C and 550°C.
- IV A superimposed exothermic (precipitation of θ) reaction between 400°C and 475°C.

The difference between the curves for the two specimen conditions arises from the small plastic deformation given to T31. Since GP zones are not thought to nucleate on dislocations, and since the concentration of vacancies produced by 1% deformation is about two orders of magnitude smaller than the quenched-in vacancy concentration, the effect of cold work in this case is the freeing of vacancies from temporary sinks (such as vacancy-solute clusters), which accelerates GP zone formation.

The effect of cold work on subsequent θ' formation is also apparent in Fig. 1.13. The temperature of maximum reaction rate for θ' formation is lowered from 278°C in T42 to 255°C in T31. This is due to the availability of dislocations to act as nucleation sites.

1.2.10 Changes in electrical resistivity

Although electrical resistivity measurements have been used to study ageing processes for many years, the use of this method to study the kinetics of zone

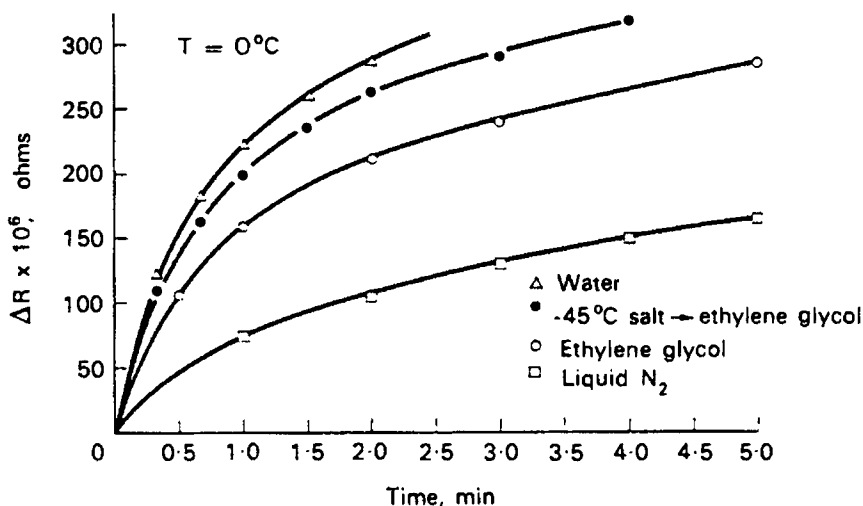


Fig. 1.14 The effect of quenching media on the rate of change of resistance in Al-2% Cu (from W. DeSorbo *et al.* [11]).

formation in the early stages of ageing at low temperatures has been particularly valuable.

If the electrical resistance of a specimen of length l and cross-sectional area A is R , resistivity (ρ) of the material is defined by

$$R = \rho l / A$$

The electrical resistivity of a pure metal is dependent on the number and distribution of point defects and dislocations, and the processes of recovery and recrystallization of deformed metals have been followed by this method. In single-phase alloys the solute concentration is generally several orders of magnitude higher than the vacancy concentration, and larger changes of ρ will arise with any redistribution of solute atoms ($\sim 1 \Omega \text{ cm}$) than, for example, that arising from the annealing out of defects in a cold-worked metal ($10^{-2} \Omega \text{ cm}$), so resistivity measurements are a useful means of following changes in solute distribution.

The detection of enhanced diffusion rates in quenched alloys

The changes observed in quenched aluminium alloys will mainly be discussed below, but the conclusions are broadly applicable to other substitutional alloy systems where there is a tendency for zone formation. In the Al-Cu system at room temperature, quenched alloys show a very rapid initial increase in resistivity, which is interpreted as arising from the clustering of the majority of solute atoms into zones or precipitates. As stated earlier (p. 10), the diffusion

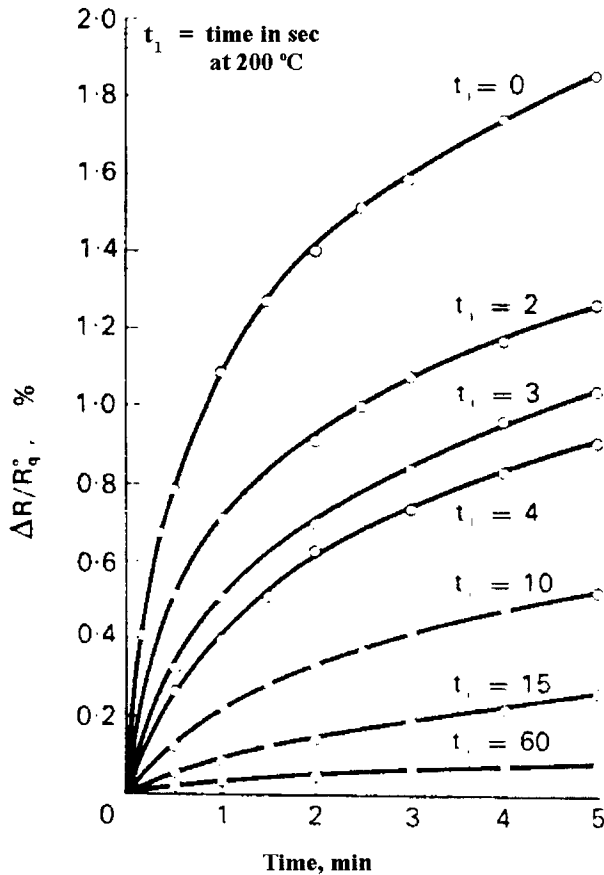


Fig. 1.15 Resistance–time isotherms at 0°C for various intermediate holds at 200°C (Al–2% Cu) (from DeSorbo *et al.* [11]).

coefficient (D_{Cu}) calculated from this rate of clustering is many orders of magnitude greater than that obtained by extrapolation of high temperature measurements. This anomalous value is thought to be due to the large vacancy supersaturation caused by quenching contributing to the transport of solute atoms. Thus the fact that higher solution treatment temperatures and faster quenching rates increase the rate of zone formation even further can be attributed to the resultant increase in the vacancy content of the supersaturated solid solution. The effect of quenching rate on the rate of change of resistance is illustrated in Fig. 1.14: the rates are about in the order of the specimen cooling rates expected for the different media. Conversely, if the quenching is followed by a reversion treatment (for example, a few minutes at 200°C) a remarkable decrease in the rate of zone formation is observed, resulting from the rapid annihilation of vacancies at 'sinks' (such as grain boundaries and dislocations) at that temperature (Fig. 1.15).

1.3 CHARACTERIZATION OF MICROSTRUCTURE OF AGED ALLOYS

1.3.1 Metallographic techniques

The initial microstructural changes occurring during the ageing of quenched alloys are beyond the resolution of the optical microscope (which is of the order $1\text{ }\mu\text{m}$), and only the electron microscope can image these features directly. Historically, however, the early stages of ageing were accurately identified by means of X-ray metallography.

X-ray and electron diffraction

A variety of X-ray techniques has been used by numerous authors investigating precipitation processes. Debye-Scherrer photographs do not reveal any pattern of lines belonging to the precipitate, and no significant changes in lattice parameter are observed until the alloy is overaged. Techniques using single crystals have yielded the most significant results, particularly those concerned with anomalous non-Bragg diffraction.

The use of the reciprocal lattice concept is essential to interpret the effects obtained by the Laue and oscillating single crystal methods, and standard textbooks should be consulted for a full treatment of its use. The essential features are as follows: in the diffraction from a single-phase crystal, each set of parallel diffracting planes in the lattice can be represented by a point in the reciprocal lattice (relpoint). The distribution of the spots on an X-ray or electron diffraction photograph can be more readily related to the relpoints than to the real lattice planes.

In aged crystals, the precipitate particles are commonly in the form of plates or rods, so that the periodic distribution of electron density is destroyed in one or more of the principal directions of the precipitate particle crystal. This leads to increasing indeterminacy of the direction of diffraction of the incident beam. The resulting broadened spots and/or streaks on the pattern obtained may be interpreted if the reciprocal lattice representation of such particles is appropriately modified as illustrated in Fig. 1.16. If the electron density distribution ceases to be strictly periodic in one direction only, the relpoint is replaced by a line or rod ('relrod'). If the periodicity ceases in two directions, the relrod becomes a plane in reciprocal space ('relplane'). Thus atomic arrangements in which periodicity exists in two directions are represented by rods in reciprocal space, while arrangements in which periodicity exists in one direction only are represented by planar areas in reciprocal space.

Laue and oscillating single crystal methods These principles underlie the results obtained independently by Guinier and by Preston in 1938. They found that the single crystal X-ray patterns of a quenched Al-Cu alloy developed streaks extending from an Al lattice reflection along $\langle 100 \rangle$ directions. This was attributed to the formation of copper-rich plate-like zones on $\{100\}$ planes of the Al lattice. These zones are known as Guinier-Preston (or GP) zones, and, being

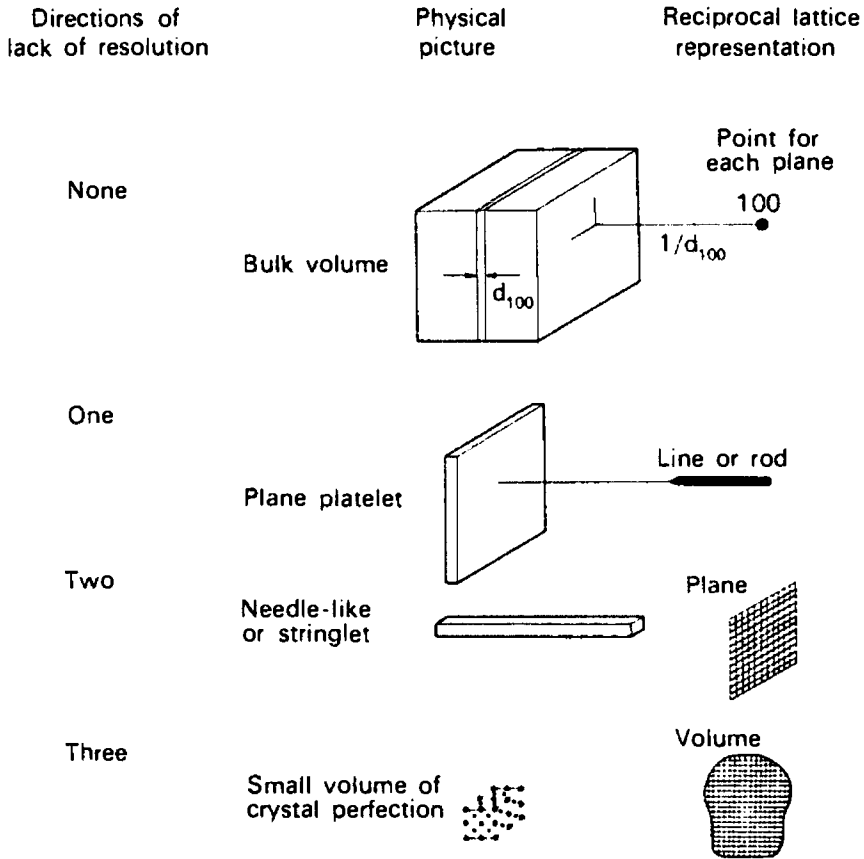


Fig. 1.16 Interpretation of diffraction effects caused by crystal size limitations in terms of the reciprocal lattice (from A. H. Geisler and J. K. Hill [12]).

only a few atomic planes thick, they produce the diffraction effects typical of a two-dimensional lattice discussed above.

An excerpt from Preston's 1938 paper is given in Appendix 2 to Chapter 1.

Small-angle scattering (SAS) This phenomenon is strictly analogous to the case of visible light being scattered by a dispersion of opaque particles, e.g. the formation of a diffuse corona round the moon when its light is diffracted by small droplets of fog. The apparatus shown in Fig. 1.17 provides a sharply defined beam of X-rays of small cross-section, with an absolute minimum of scattering from the slit system and from the air, since the scattering pattern is confined to within a few degrees of the centre spot.

The intensity of scattering in the low-angle region ($2\theta < 10^\circ$) arises from the difference in electron density between inhomogeneities within the crystal (zones or precipitates) and the matrix. The former should have dimensions only 10 to

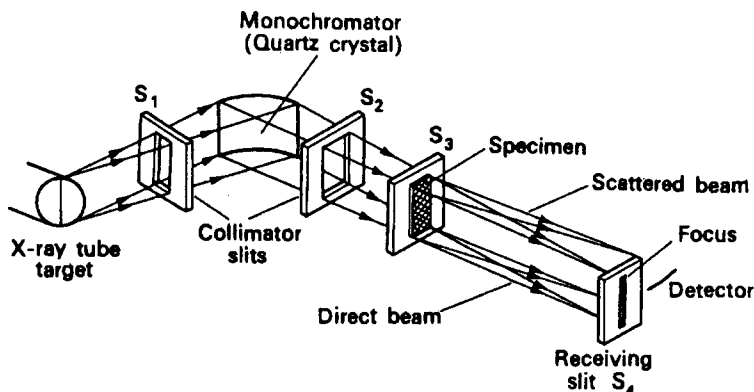


Fig. 1.17 Experimental arrangement for studying the small-angle scattering of X-rays from crystals. The entire apparatus is evacuated to minimize absorption and scattering by the atmosphere.

100 times the wavelength of the incident radiation (λ). If the angle of scatter (2θ) is ε , the intensity I of scatter is given by

$$I = M n^2 I_e \exp(-4\pi^2 \varepsilon^2 R_g^2 / 3\lambda^2) \quad (1.16)$$

where M is the number of scattering aggregates diffracting, n is the difference in number of electrons between the particle and an equal volume of surrounding matrix, R_g is the radius of gyration of the particle (defined as the root mean square of the distances from all the electrons in a particle to its centre of gravity), and I_e the intensity scattered by an electron. If $\log_{10} I$ is plotted as a function of ε^2 , the slope near the origin ($\varepsilon = 0$), known as the 'Guinier Plot', a value of R_g may be obtained.

At this point the reader may refer to the paper entitled 'On the birth of GP zones' by A. Guinier in Appendix 3 to Chapter 1, which contains an illustration of the SAS X-ray pattern from an Al-4% Cu alloy.

Small-angle neutron scattering (SANS)

The availability of intense long wavelength neutron beams at the Institut Laue-Langevin in Grenoble, France, and the development of large area position sensitive neutron detectors has, in recent decades, led to the extensive use of SANS in the investigation of precipitation processes in alloys.

SANS is capable of providing structural information about precipitates ranging in scale from about 10^{-10} m to $0.5 \mu\text{m}$ in bulk specimens. It is a complimentary technique to electron microscopy, which provides very detailed information on precipitates over tiny localized volumes in the specimen. Neutron scattering provides a diffraction pattern of the precipitates averaged over a volume of up to a few cubic centimetres.

The magnitude of the scattering vector Q ($= 4\pi \sin \theta/\lambda$), and in SANS the range of Q is $0 < Q < \pi/d$, where d is the interatomic distance in the material under investigation. If d is of the order 0.3 nm, this means that for neutrons with $\lambda = 1.2$ nm, 2θ is 180° which is hardly a small angle! The terminology is a hang-over from X-ray studies, where the wavelengths used are very much smaller.

A paper by S. Messoloras, B.C. Pike, R.J. Stewart and C.G. Windsor [13] gives details of the technique and the theory of neutron scattering. The intensity of the scattering is measured by the neutron differential scattering cross-section $d\sigma/d\Omega$. For a distribution of precipitate sizes with random orientation in the matrix, the cross-section can be written as:

$$d\sigma/d\Omega = (V_p^2 n_p/N)(c_p - c_m)^2 I(Qd) \langle F^2(Q) \rangle \quad (1.17)$$

where V_p is the average volume of one precipitate, n_p is the number of precipitates per unit volume, N is the number of atoms/unit volume in the sample, c_p and c_m are the mean scattering length in the precipitate and the matrix, respectively, $F(Q)$ is the form factor describing the scattering from one precipitate (the averaging is over all orientations and all precipitate sizes), and $I(Qd)$ describes the interference scattering from the precipitates separated by an average distance d .

The interference term $I(Qd)$ for a random distribution of precipitates in a matrix causes a peak in the scattering cross-section vector Q_m defined by the relation:

$$Q_m = 5.763/d$$

From the position of the maximum of the cross-section Q_m , the interprecipitate distance can be deduced from this relationship. The number of precipitates/unit volume is given by:

$$n_p = 3/(4\pi d^3)$$

As in the case of SAS, the radius of gyration of the precipitates, R_g may be obtained from the slope of a so-called 'Guinier plot', i.e. a plot of the logarithm of the measured cross-section against Q^2 . For spherical precipitates of radius R_s , $R_g = (3/5)^{1/2} R_s$.

The volume fraction f of such precipitates can be obtained from

$$f = n_p V_p = (R_r/d)^3$$

K. Mergia, F. Al-Hazmi, R.J. Stewart and S. Messoloras [14] have studied the growth of the coherent δ' (Al_3Li) phase in Al–Li alloys by *in situ* SANS. Figure 1.18a shows the size of these precipitates against ageing time (t) for three ageing temperatures, and Fig. 1.18b shows the variation in n_p with $1/t$ for the same three temperatures, which illustrates that, as the precipitates increase in size, their number density decreases.

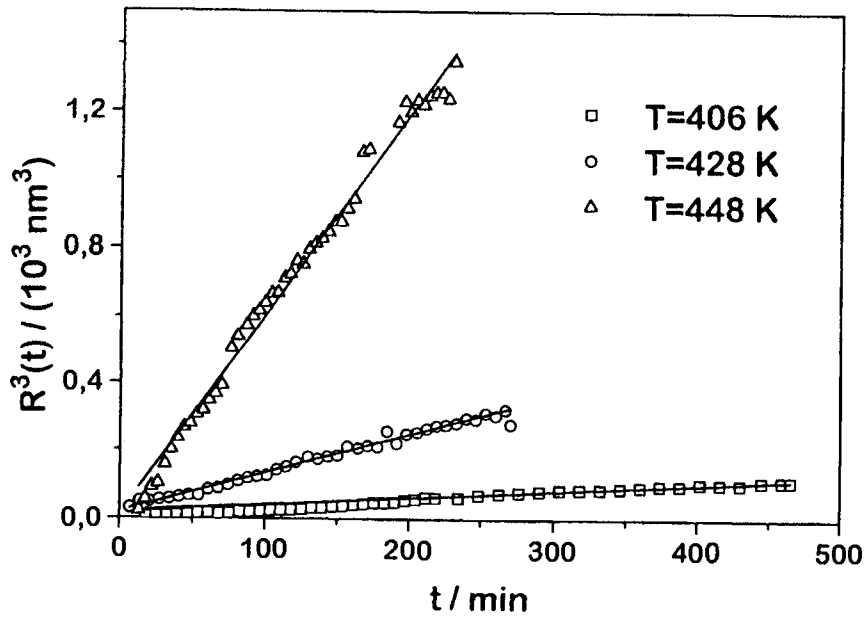


Fig. 1.18 (a) Precipitation of δ' (Al_3Li) in an Al – Li alloy (8090) showing the size of precipitate against ageing time.

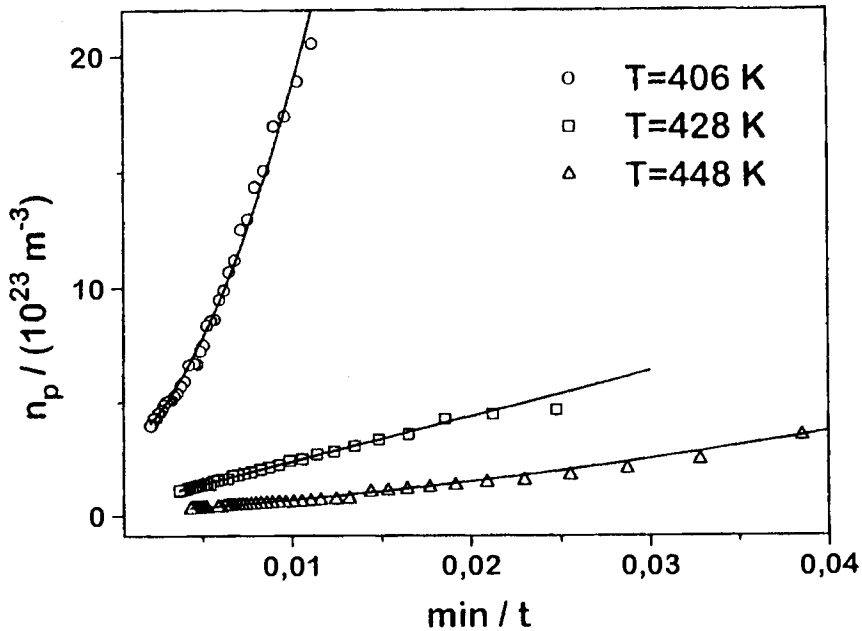


Fig. 1.18 (b) The number density of the precipitates against $1/(\text{ageing time})$ (after K. Mergia *et al.* [14]).

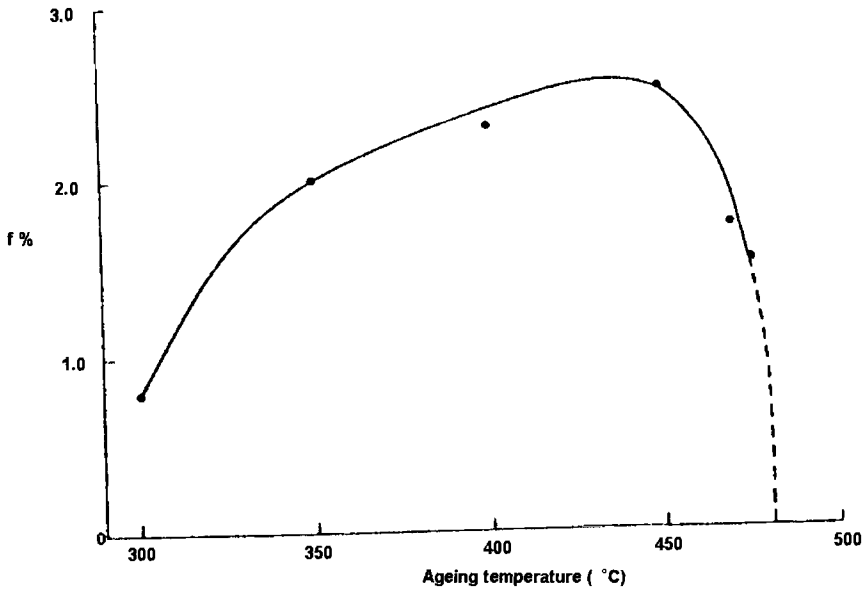


Fig. 1.18 (c) Precipitation of α' phase in a complex iron–chromium–aluminium alloy containing a small amount of yttrium, studied by SANS and showing the change in volume fraction f with ageing temperature (after S. Messoloras *et al.* [13]).

Messoloras *et al.* employed SANS to study precipitation in Fe – Cr – Al alloys of Cr-rich α' precipitates in the Fe-rich α matrix. The mean diameter, number density and volume fraction of the precipitates was again determined as a function of ageing time and temperature: Fig. 1.18c shows the change in volume fraction f with ageing temperature.

Electron microscopy

Electron microscopic techniques have been widely applied to the study of precipitation processes in metals, and the sequence of precipitation has often been established jointly by a combination of the two methods of approach: X-ray diffraction and electron microscopy. It should be borne in mind that the X-ray diffraction information is essentially an average over a large volume of a crystal, whereas electron microscopy provides detailed information of a small localized volume.

Electron microscopes are capable of providing three types of analysis, namely visual analysis of the microstructure at high resolution, structural analysis of the crystals themselves from electron diffraction measurements, and chemical analysis relying on efficient detection and discrimination of X-rays emitted from the specimens when bombarded with high energy electrons in the microscope.

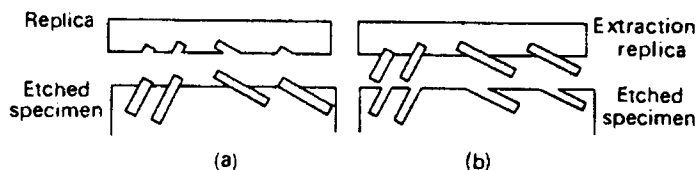


Fig. 1.19 Illustrations of (a) surface replicas and (b) extraction replicas for the study of precipitated microstructures in the TEM.

The reader may obtain fuller details of these techniques in standard textbooks such as *Microstructural Characterisation of Metals and Alloys* by P.E.J. Flewitt and R.K. Wild (The Institute of Materials, London, 1985).

Transmission electron microscopy (TEM) In most microscopes the specimen is viewed in transmission; as a result a great deal of the experimental technique involves methods of producing thin samples (usually by chemical or electrolytic thinning of bulk material), or preparing suitably transparent replicas

Replicas are stripped off the metal surface prior to insertion in the microscope, by immersion in an etchant or by electrolytic attack of the metal. In the case of a specimen containing a dispersed precipitate, it may be possible to adjust the conditions such that the stripped replica retains the actual precipitate particles which originally lay in the surface of the specimen (Fig. 1.19). The latter are known as 'extraction replicas', and thus permit direct examination of dispersed phases in metals and alloys.

Foils. Much wider use is made in the TEM of very thin (< 500 nm) samples, usually produced by electrolytic thinning of the bulk alloy, so that it cannot suffer mechanical damage.

Image contrast Bright and dark field. In the electron microscope, for a parallel incident electron beam, the diffracted beams leaving the sample are focused in the back focal plane of the objective lens, forming a diffraction pattern. Interchangeable objective apertures are used to enhance image contrast: if the objective aperture allows only the direct beam to pass, a bright field image is formed. If a single diffracted beam is selected by the aperture, a dark field image is produced. Bright field imaging is the routine and basic mode used in TEM, and Fig. 1.20 is an example of such a technique. This is a specimen of the Al–Li alloy 8090 aged to form a dispersion of the δ' -phase. Electrons are scattered by the dispersed particles, so that in the image the particles appear darker than the matrix.

As illustrated in Fig. 1.5a, coherency strains may exist in the matrix adjacent to coherent precipitate particles: such a distortion will diffract differently from an equivalent undistorted crystal some distance away. If the crystal is oriented such that the vertical planes in Fig. 1.5a satisfy the Bragg equation, coherency strain contrast may be apparent, as shown in Fig. 1.21.

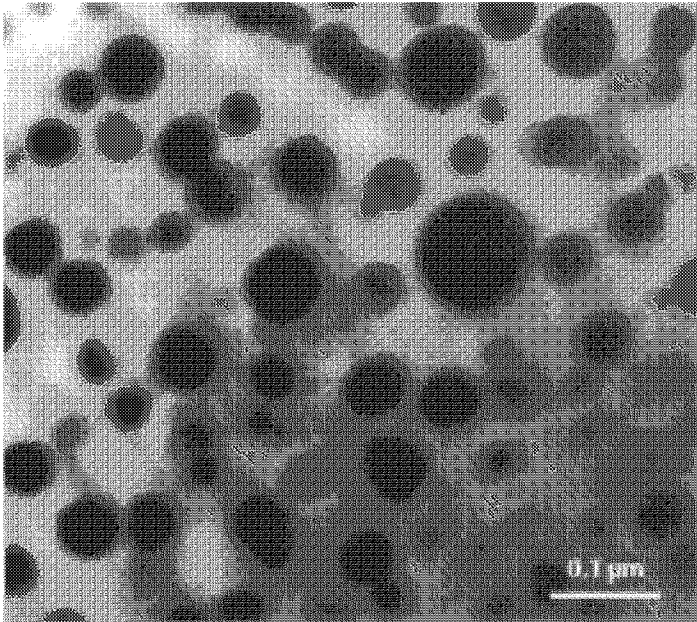


Fig. 1.20 TEM bright field image of δ' particles in an aged Al-Li alloy (8090).

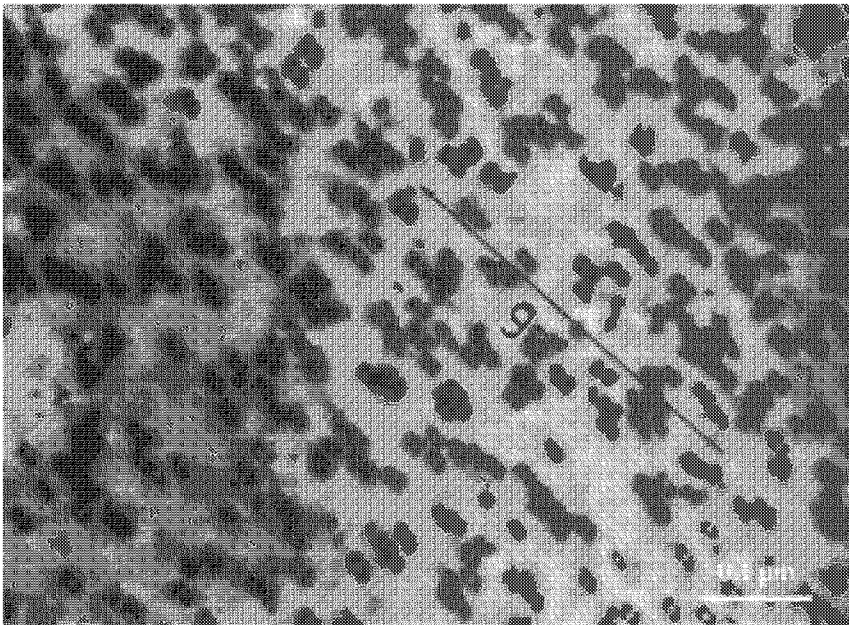


Fig. 1.21 TEM image showing coherency strain contrast.

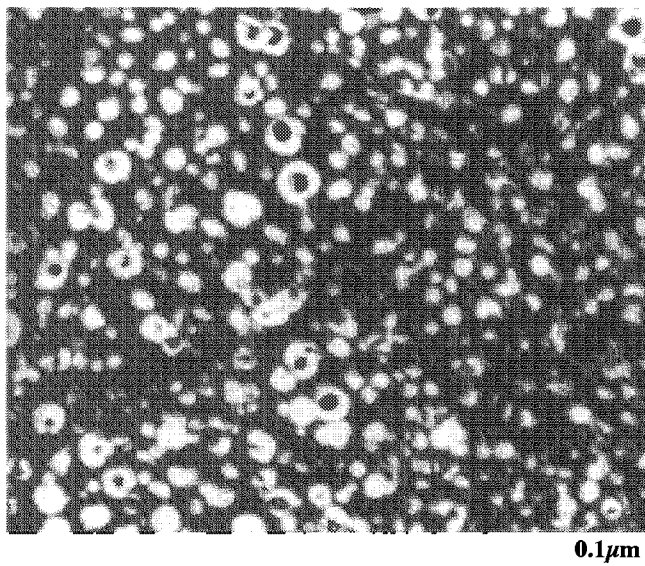


Fig. 1.22 TEM image showing dark field image.

Under these conditions, the misfit vector is equivalent to the operating diffraction vector, and planes through the centre line of these precipitates are undistorted, resulting in a line of no contrast perpendicular to this direction in the image.

If a precipitated microstructure is examined in dark field, an electron beam diffracted by the particulate phase is selected to form the image. In this situation the precipitate particles will appear bright, and the matrix dark, as illustrated in Fig. 1.22, which is a similar alloy to that illustrated in Fig. 1.20.

In Fig. 1.22 it will be noted that certain of the δ' particles appear to contain a central darker area. During ageing, a layer of the δ' phase has in fact been heterogeneously nucleated upon a pre-existing particle of a dispersoid phase, β' (Al_3Zr), which is present to inhibit grain growth in the matrix during solution heat-treatment. A 'duplex' particle has thus been formed by this process.

Direct lattice imaging If the transmitted beam and one diffracted beam from a very thin area of the foil are selected using the objective aperture of a microscope fitted with an objective lens of very high resolving power, under carefully controlled conditions the image may reveal the periodicity of the lattice planes in the specimen. Figure 1.23 is an image formed from a duplex particle in a specimen similar to that shown in Fig. 1.22. The direct lattice imaging reveals that the lattice planes in the inner β' particle are parallel to those in the layer of δ' which has nucleated upon it. The duplex particle is itself coherent with the aluminium solid solution matrix, whose lattice planes are also resolved.

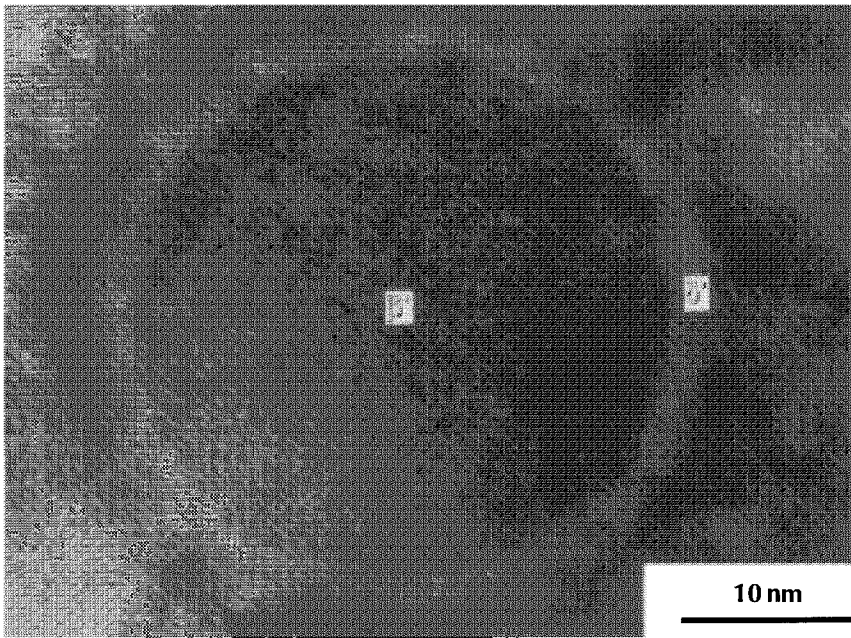


Fig. 1.23 Direct lattice image of a duplex δ'/β' precipitate particle in an Al matrix in an aged Al–Li alloy (8090).

Image analysis Providing the resolving power of the TEM is adequate, particle-counting in the images may be conducted. Corrections may have to be made if some small particles are invisible because their image is overlapped by that of a larger particle, and the thickness of the foil (Z) must also be measured. The most reliable method for the determination of Z is *convergent beam* electron diffraction, which is described in standard textbooks on TEM. If the acceleration voltage of the TEM is 200 keV, the appropriate foil thickness is usually in the range 50–100 nm. The number N_A of particle images per unit area of the thin foil is related to its thickness Z and to the number N_v of particles per unit volume:

$$N_A = N_v Z$$

1.3.2 Characterization of the matrix

Grain size and grain shape

It is well known that a decrease in grain size improves the formability of age-hardening alloys. A cold-worked specimen of a simple binary alloy would, during solution heat-treatment in the single-phase condition, tend to recrystallize and undergo extensive grain growth. The grain size will not change significantly during ageing, so the final product would be coarse-grained. As discussed in

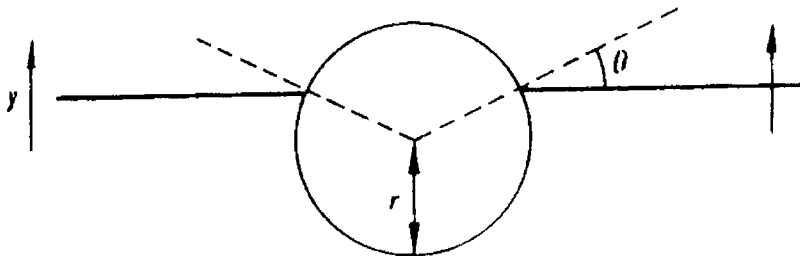


Fig. 1.24 Interaction of a migrating grain boundary with a dispersoid particle.

Section 1.1, a small quantity of a transition element is usually added which, during the initial homogenization anneal, leads to the formation of a distribution of stable dispersoid phases (Fig. 1.1), of the order of $0.1\ \mu\text{m}$ in size, throughout the microstructure.

Solution heat-treatment is carried out at a temperature above the solvus temperature of the age-hardening precipitate. The dispersoid phases remain out of solution at this temperature, however, and their presence has the effect of impeding the migration of grain boundaries. This effect was first pointed out by Zener [15], who derived a relation between the drag per unit area of a boundary and the characteristics of the dispersion.

Fig. 1.24 represents a grain boundary migrating upwards and intersecting a spherical inclusion. The drag exerted by the particle, resolved in the y direction will be given by $\pi r \gamma \sin 2\theta$, where γ is the surface energy of the boundary. The maximum value of this force will be when $\theta = 45^\circ$, when its value will be $\pi r \gamma$.

If there are N dispersoid particles per unit volume, their volume fraction (f) is $(4/3)\pi r^3 N$. Any planar boundary within a unit cube will intersect all particles within a volume $2r$, that is, $2rN$ particles, so the number of particles intersecting unit area of a boundary (n) is given by $3f/2\pi r^2$. Thus the retarding force per unit area of boundary (F_r) is given by

$$F_r = 3f\gamma/2r$$

So if a dispersoid is present with volume fraction 0.06 and diameter $0.1\ \mu\text{m}$, it will exert a retarding force per unit area of about 2 MPa upon the grain boundaries.

During the working of the ingot by hot rolling or extrusion, therefore, the metal will be inhibited from recrystallizing by the presence of the dispersoid, and the grain size and shape in the product (even after a subsequent solution treatment) will reflect this processing history. Figure 1.25 shows a montage of three optical micrographs illustrating in three dimensions the shape of the grains in an aluminium alloy plate. After casting and homogenizing, the ingot was hot-rolled and solution-treated. Due to the inhibition of recrystallization by the

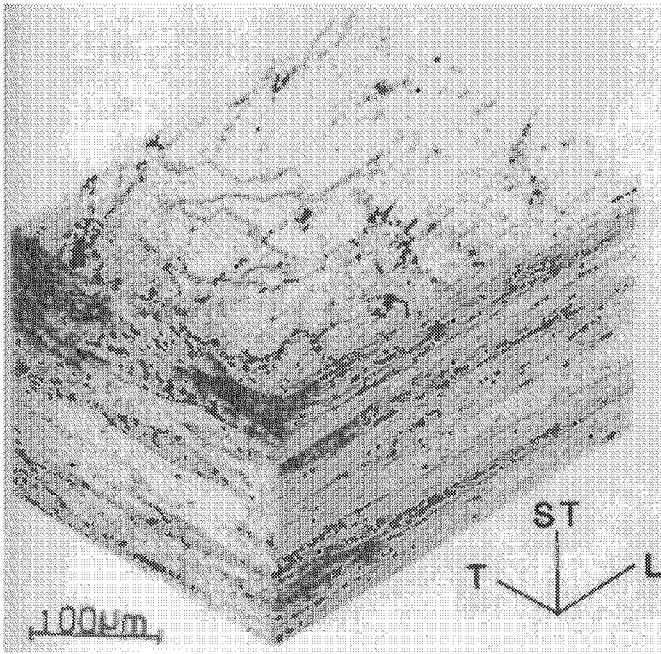


Fig. 1.25 Montage of three optical micrographs showing the size and shape of the grains in a hot-worked plate of Al-Li 8090 alloy.

dispersoid phases, a pancake-shaped grain structure has developed – in this case the grain size is $2.4 \text{ mm} \times 600 \mu\text{m} \times 35 \mu\text{m}$ in the longitudinal (L), long transverse (LT) and short transverse (ST) directions, respectively.

This anisotropy of grain structure is likely to be reflected in anisotropy of mechanical properties in the product.

Subgrain size

During hot deformation, as well as changing the shape of the grains as described above, the grain interiors are subdivided into subgrains. These are approximately equiaxed regions of small misorientation separated by sharp boundaries consisting of arrays of dislocations. They are formed by the motion of dislocations through glide, cross-slip and climb, and the subgrain size depends partly upon the deformation conditions (for example the temperature and strain-rate) and partly upon properties of the material such as composition, stacking-fault energy and second-phase particle distribution.

The subgrain size has a strong influence on the strength of the as-deformed materials and on the subsequent annealing and precipitation-hardening treatments.

Texture

During deformation there is a tendency for certain crystallographic planes and directions to orient themselves parallel to the rolling plane and rolling or extrusion direction. Thus in a rolled sheet or extrusion certain preferred orientations or textures develop. Rolling textures often described by the crystallographic symbols $\{hkl\}\langle UVW \rangle$, where $\{hkl\}$ is the crystallographic plane tending to be parallel to the rolling plane and $\langle UVW \rangle$ the direction tending to be parallel to the rolling direction. Extrusions show a fibre texture $\langle UVW \rangle$ lying parallel to the extrusion direction. Hot rolled aluminium alloys generally exhibit a range of preferred orientations from $\{110\}\langle 112 \rangle$ to $\{112\}\langle 111 \rangle$, together with a large spread in orientations depending on the deformation variables. Aluminium extrusions generally exhibit a strong $\langle 111 \rangle$ and weaker $\langle 100 \rangle$ fibre texture.

Rolled and extruded alloys are, therefore, inherently anisotropic, and it should also be remembered that manufacturing processes can also align intermetallic inclusions and voids, elongate grains (see above), and cause preferential precipitation, all of which can produce differences in properties in different directions.

1.3.3 Precipitate distribution and its control

Homogeneous distribution

As already stated, precipitation by spinodal decomposition is a situation which leads to a very uniform, homogeneous distribution of coherent second-phase particles. The Cu–Ni–Fe system exhibits spinodal decomposition, and the transformed structure consists of regularly spaced quasi-spherical particles at small volume fractions and a lattice of interconnected rods lying along $\langle 100 \rangle$ directions at large volume fractions (Fig. 1.26). It is striking that there is no preferential precipitation on grain boundaries or other lattice defects. Since such nucleation arises (in the absence of spinodal decomposition) because of the reduced activation energy for nucleation at such defects, such an effect would not be expected in spinodal alloys where no nucleation barrier to precipitation exists.

Unfortunately, the stronger spinodal structures are very brittle, failing in an intergranular manner. The real potential of this type of structure remains to be exploited, and most precipitated microstructures of practical importance are developed by nucleation-and-growth processes and hence exhibit a heterogeneity of particle distribution due to the influence of the crystal defects present.

Heterogeneous distribution

We will consider in turn the influence of three types of defect found in metal matrices upon the distribution of precipitates in quenched and aged alloys, namely grain boundaries, dislocations and inclusions. We will finally examine the effects of trace elements upon the precipitation process.

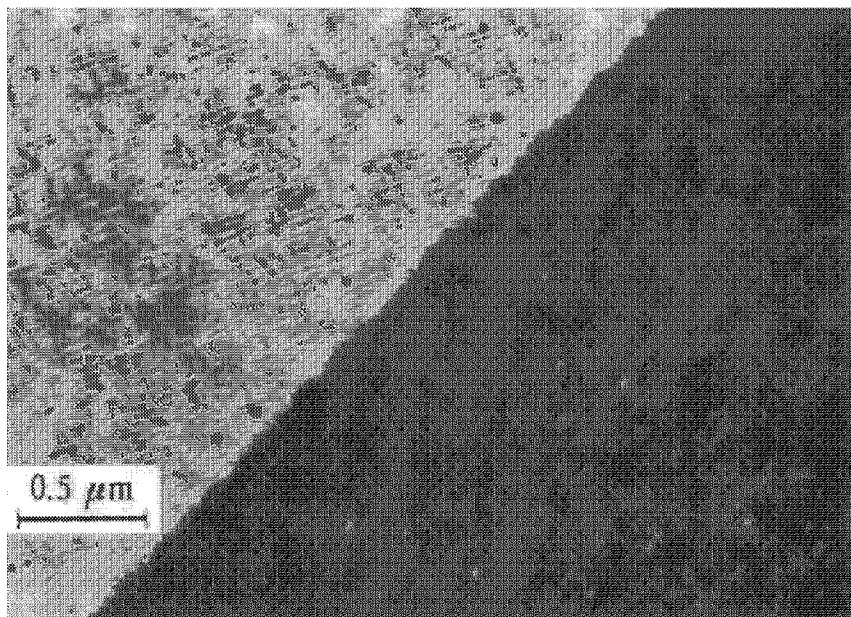


Fig. 1.26 Electron micrograph showing the uniformity of spinodal decomposition in a Cu–Ni–Fe alloy.

Grain boundaries Aged alloys usually exhibit zones denuded of precipitate adjacent to the grain boundaries (Fig. 1.27).

There are two ways in which such precipitate-free zones (PFZ) can arise: either from a local depletion of solute atoms there, or from a depletion of lattice vacancies which, when the alloy is quenched enter the ‘sink’ provided by the grain boundary. We will consider initially the latter factor, taking as an example the formation of PFZs in aluminium alloys aged to precipitate GP zones within the grains.

Jacobs and Pashley [16] define (see Fig. 1.28) a critical temperature at which homogeneous nucleation can occur when no excess vacancies are present at the ageing temperature. Homogeneous nucleation does not occur above this temperature because of inadequate solute supersaturation. This temperature, T_c , decreases as the solute concentration decreases (Fig. 1.28), in a similar manner to the GP zone solvus line (Fig. 1.11c). Jacobs and Pashley further postulate that nucleation is possible with a given critical excess-vacancy concentration $(C_v)_c$ up to a maximum temperature T'_c (Fig. 1.28). An excess of vacancies will arise when the specimen is quenched from the temperature of solution heat-treatment. The higher number of vacancies in equilibrium with the lattice at the upper temperature will tend to be retained in supersaturation at the lower temperature. There are two ways in which these excess vacancies may influence homogeneous precipitation above temperature T_c : either by their contribution to the diffusivity of solute which accelerates the formation of clusters during the quench, and

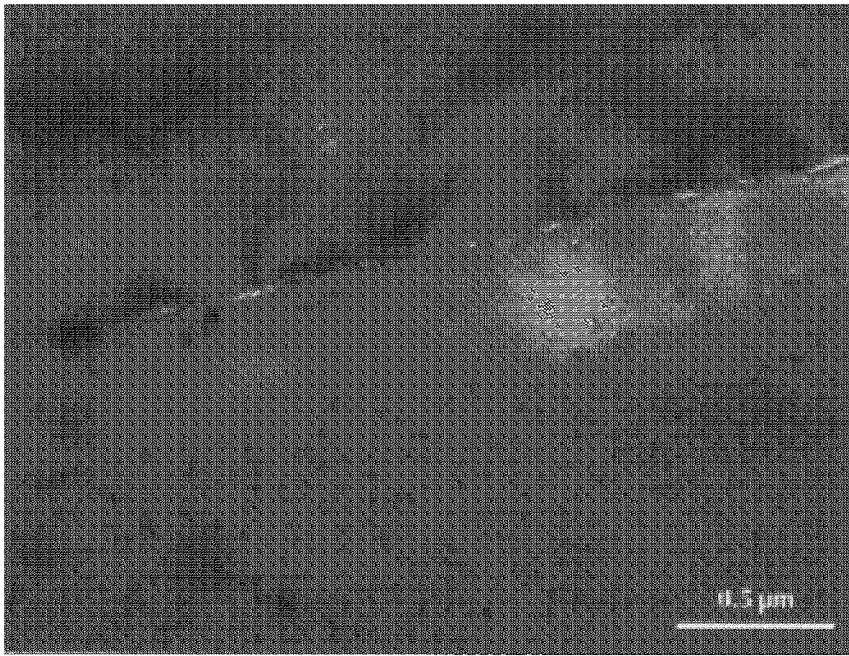


Fig. 1.27 Electron micrograph showing the precipitate-free zone adjacent to a grain boundary in Al-4 wt% Zn-3 wt% Mg aged for 1 day at 150°C (courtesy of I. J. Polmear).

which then give rise to the intermediate precipitate, or by providing vacancy aggregates which nucleate a new phase.

During, and for a short period after a quench from the solution-treating temperature to the ageing temperature (T_A), an excess-vacancy profile will be established in the vicinity of each grain boundary (Fig. 1.29). This is because grain boundaries are sinks for vacancies, and the shape of the excess-vacancy profile will depend on the solution-treatment temperature, since the equilibrium concentration of vacancies increases with temperature and also with the quenching rate. Slower rates will allow diffusion over larger distances and hence result in a decreased slope in the profile. Figure 1.29 shows the profiles for a specimen quenched from a high, a medium and a low solution-treatment temperature. If the ageing temperature, T_A , is above T_c , nucleation of solute clusters can occur in regions of the specimen where the excess-vacancy concentration is greater than the critical value, $(C_v)_c$. In Fig. 1.29, AB thus defines the vacancy-depleted PFZ in the sample quenched from the highest solution-treatment temperature. Since, in this example, the vacancy profile established on quenching from the lowest solution-treatment temperature is shown as lying below $(C_v)_c$ homogeneous nucleation is not possible in this case, and only heterogeneously nucleated precipitates can occur.

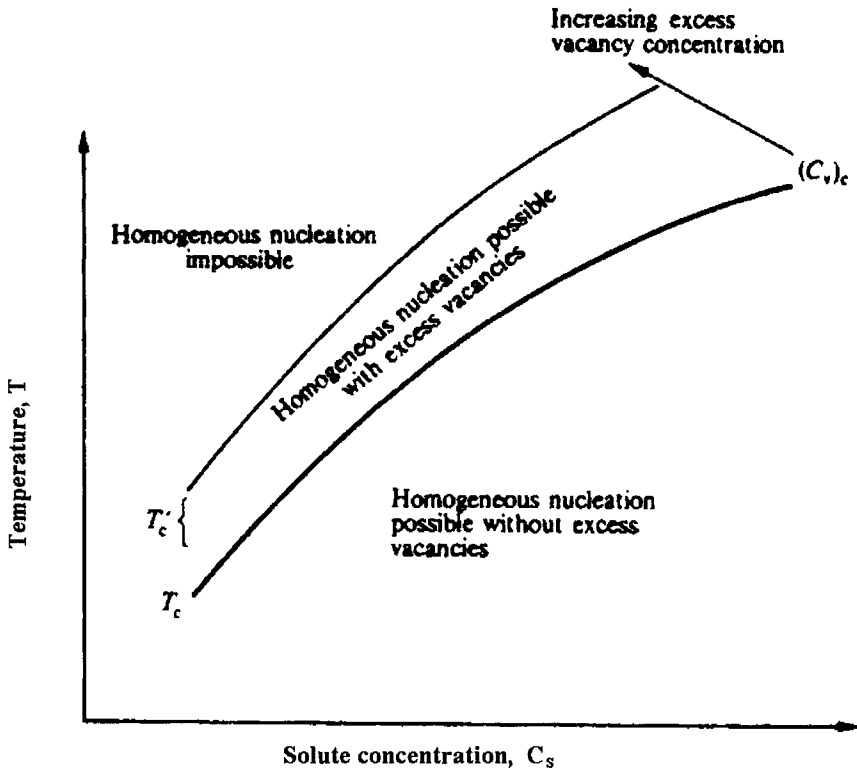


Fig. 1.28 Schematic diagram showing the variation of T and T_c with solute concentration (after Jacobs and Pashley [16]).

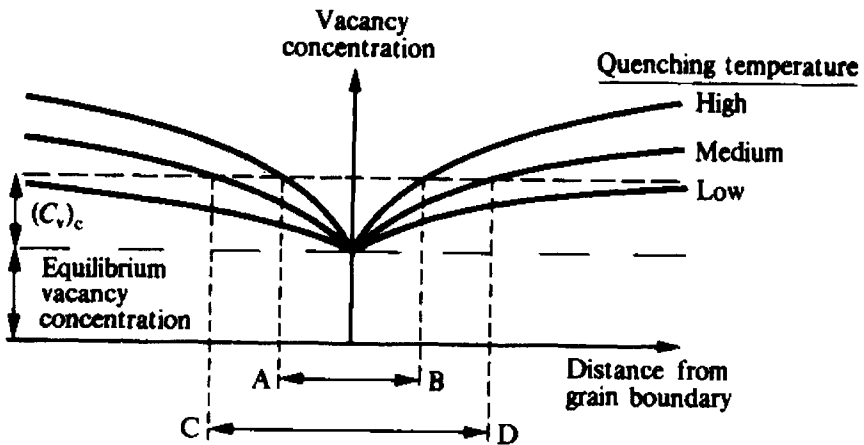


Fig. 1.29 Excess vacancy profiles near to a grain boundary (after Jacobs and Pashley [16]).

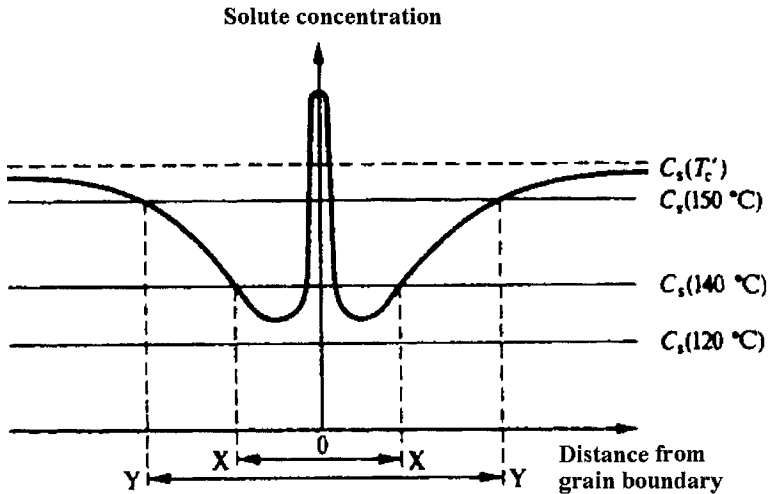


Fig. 1.30 Schematic diagram of the solute-concentration profile after quenching (after Jacobs and Pashley [16]).

The width of the PFZ also decreases as the ageing temperature is decreased. Under these circumstances the greater solute supersaturation allows a smaller critical nucleus size, thereby reducing the critical vacancy concentration required for nucleation.

Solute-depleted PFZs will arise when solute is lost from the vicinity of the boundary during the quench, either because precipitates are nucleated heterogeneously on the boundary during cooling to T_A , or because preferential segregation of solute occurs at the boundary during cooling to the ageing temperature. In either case a solute-concentration profile will be set up as indicated in Fig. 1.30, whose form will depend upon the structure and misorientation of the boundary itself, owing to the influence of these parameters on the nucleation of grain-boundary precipitates. Reference to Fig. 1.30 indicates that with a certain excess-vacancy concentration at the ageing temperature there is a critical solute concentration C_s required for nucleation to occur. Figure 1.30 illustrates the values of C_s for various temperatures as horizontal lines, and the intersection of these lines with the solute-concentration profile gives the width of the solute-depleted PFZ, which is seen to decrease from YY to XX as the ageing temperature is decreased from 150°C to 140°C. Only solute-depleted PFZs are possible when ageing below T_c , and above this temperature a vacancy-concentration profile must be superimposed on the solute-concentration profile. The PFZs which form above T_c may have widths of up to 1 μm or more, whereas solute-depleted PFZs formed below this temperature are usually narrower than 0.2 μm .

Discontinuous precipitation. A fairly common way for precipitation to occur in a terminal solid solution which is undercooled several hundred degrees below the temperature of maximum solubility is discontinuous precipitation. In this case,

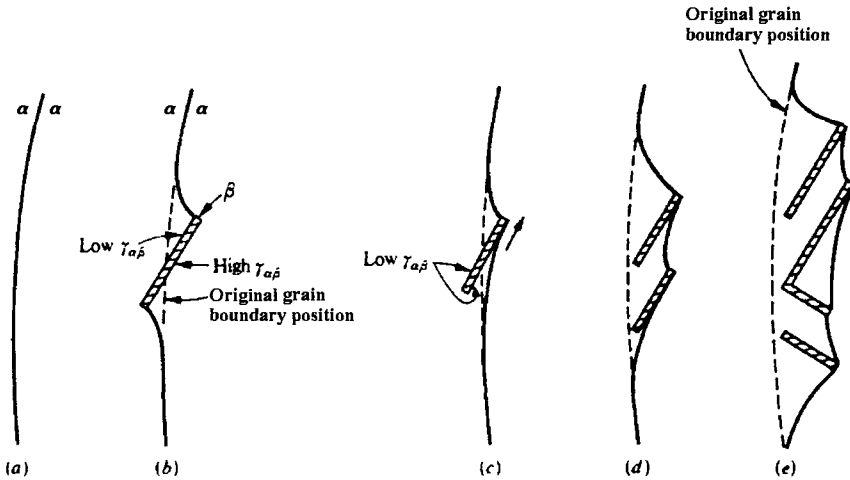


Fig. 1.31 Successive stages in the start of precipitation of β and α by discontinuous precipitation (after Tu and Turnbull [17]).

nodules of a lamellar structure form at the grain boundaries and grow into the grains. The lamellae consist of plates or laths of precipitate embedded in the matrix, and the structure can form when the temperature is so low that nucleation and growth of individual precipitate particles within the matrix occurs at a negligible rate. The precipitate forms only at the advancing interface, so that in a given region, precipitation occurs discontinuously with time instead of by the nucleation and continuous growth of particles.

The barrier to nucleation of the new phase is reduced because of its formation at a grain boundary. The required diffusion of solute takes place along the grain boundary and thus, since it involves a lower activation energy, will tend to be the dominant diffusion mechanism at relatively low temperatures. The energy barrier to nucleation will be further reduced if the new phase has a special orientation so that the energy of the $\alpha\beta$ interface is low between one of the grains forming the grain boundary and the precipitate. Figure 1.31 illustrates successive stages in the start of discontinuous precipitation, which illustrates how the grain boundary moves as the nodule, or 'cell' of precipitate grows.

Because of the low nucleation rate, this process is unlikely to lead to finely dispersed precipitate particles. Somewhat coarse, heterogeneous distributions of plates or laths are normally observed, therefore this method of decomposition is not one which is to be desired if strong microstructures are required.

Dislocations In the case of coherent precipitates (Fig. 1.5a) the lattice of the precipitate matches that of the matrix, so that there is little reason for such precipitates to form in the strain field of a dislocation. However, semicoherent precipitates (Fig. 1.5b) nucleate much more easily on dislocations because some of the faces of semicoherent precipitates must contain dislocations.

Transgranular soft zones, through precipitate denudation, are commonly observed in aged alloys. The effect arises from the presence of matrix dislocations. For example, Al–Cu alloys may, on ageing, develop arrays of θ' -precipitates in association with the matrix dislocations, whereas the bulk of the matrix contains a fine dispersion of the coherent θ'' -phase. The larger plates of the θ' -phase give rise to a local depletion of the θ'' precipitate density.

The dislocations giving rise to heterogeneous precipitate distribution can be formed by quenching stresses during quenching from the solution heat-treatment temperature. Such stresses can arise from differential thermal contraction in the alloy when specimens of appreciable cross-sectional area are quenched, such that steep temperature gradients are formed in the piece. The resulting dislocation arrays are known as quench bands.

Stretching. Precipitation of uniform distributions of semicoherent precipitates can be encouraged by introducing a uniform distribution of dislocations into the alloy prior to ageing. These extra dislocations are introduced by plastically straining the solution-treated alloy by a small amount before ageing. Industrially this would typically be between 1.5 and 8%. Rolling cannot be used, because such small reductions do not provide a uniform distribution of dislocations through the thickness of the material. Instead, tensile deformation is employed in an operation called stretching. Note that stretching prior to solution-treatment will not be effective, because the dislocations introduced are removed at the solution-treatment temperature.

Figure 1.32a,b illustrates the dramatic effect of stretching upon the distribution of the semicoherent S' -phase (Al_2CuMg) in an 8090 Al–Li–Cu–Mg alloy. The alloy was solution treated at 530°C. Figure 1.32a shows the distribution of S' -phase after ageing the as-solution-treated material for 60 h at 190°C: S' has nucleated upon stray dislocations to form sheet-like arrays. The specimen in Fig. 1.32b was stretched 1.5% prior to ageing at 190°C (for 10 h): this dark field TEM image shows the homogeneously distributed S' particles in light contrast.

There are further advantages to be gained from stretching. The differential thermal contraction associated with quenching from the solution-treatment temperature usually introduces residual stresses into aluminium alloys. These can be very detrimental to the fatigue and corrosion resistance of the component, but stretching after solution-treatment can relieve or redistribute the residual stresses and eliminate many of the associated problems.

Other mechanical-thermal treatments (MTT). When a combination of mechanical and thermal treatment is given to supersaturated alloys, advantageous changes in the distribution of precipitates may be brought about.

If an Al alloy is aged under conditions leading to the formation of pronounced PFZs due to vacancy depletion, when there is a large difference in yield stress between the PFZ and the precipitation-hardened grain interior, preferred deformation will occur within these weak zones, which can lead to a low macroscopic ductility in the alloy. If, after ageing, only limited deformation is applied and the alloy is re-aged, further precipitation occurs upon the dislocations

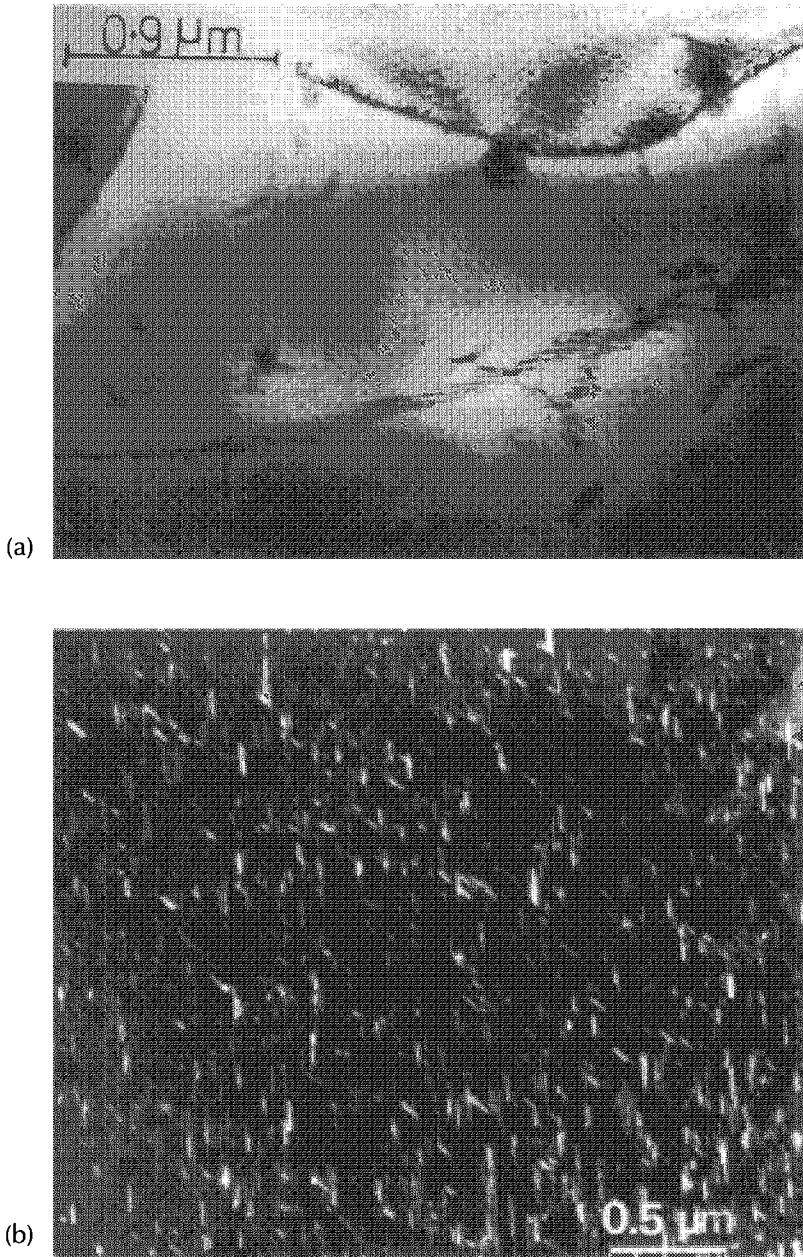


Fig. 1.32 TEM micrographs of an 8090 Al–Li–Cu–Mg alloy showing the effect of stretching after solution-treatment but before ageing. (a) Aged 20 h at 190°C. In the absence of stretching, the S' precipitates (seen in dark contrast in this bright field image) have nucleated heterogeneously upon the stray dislocations present. (b) Stretched 1.5% and then aged 20 h at 190°C, showing the uniformly distributed S' particles in light contrast (dark field image).

introduced into the PFZ by the localized strain. Since the PFZ arose through vacancy depletion and not through solute depletion, the introduction of heterogeneous nucleation sites in the form of an array of dislocations leads to rapid precipitation.

More generally, the effect of mechanical-thermal treatment can either be to influence precipitation by working, or to combine work-hardening and age-hardening. Multiple mechanical-thermal treatment (MMTT) involves the repeated application of cycles of deformation and annealing or ageing, and has been applied to a number of materials, both ferrous and non-ferrous. We will defer a more detailed consideration of this subject until we have considered the deformation behaviour of crystals containing precipitates, confining our discussion here to a consideration of ageing processes in deformed metals.

When a supersaturated alloy is deformed and then aged, it is with the object of increasing the precipitate density by the introduction of prolific heterogeneous nucleation sites. The excess point defects introduced by the deformation may also accelerate the ageing process. In order for the operation to be successful it is obvious that the rate of precipitation must exceed the rate of recovery of the dislocation substructure. If the metal recrystallizes before precipitation commences, the deformation stage is of no value. The order of occurrence of precipitation and recrystallization in this situation has been considered by Köster [18], who considered the temperature dependence of the start of both reactions in the following way.

The time for the start of precipitation (considering the formation of one phase only), t_p , may be written from equation (1.7) as

$$t_p = K_p \exp (\Delta G^* + U_D)/kT \quad (1.18)$$

where K_p is a factor containing the driving force, an entropy term and geometric factors. The time for the start of recrystallization, t_r , may be written as

$$t_r = K_r \exp (\Delta G_r/kT) \quad (1.19)$$

where K_r is a factor containing the driving force for the reaction, an entropy term and geometric factors, and ΔG_r is the activation energy for the formation of a recrystallization front. ΔG_r has the order of magnitude of the activation energy for self-diffusion, but decreases as the dislocation density increases, and increases as a result of segregation of solute atoms at dislocations.

Curves of t_p and t_r as a function of temperature and increasing annealing time are shown in Fig. 1.33. Three temperature ranges in the recrystallization behaviour can be distinguished on the basis of this diagram.

- (i) When the temperature is above T_1 (the solvus temperature) no precipitation occurs, and recrystallization is influenced only by segregation.
- (ii) When the temperature is between T_1 and T_2 precipitation proceeds in the recrystallized structure after completion of recrystallization. Again, recrystallization is influenced only by segregation of solute.

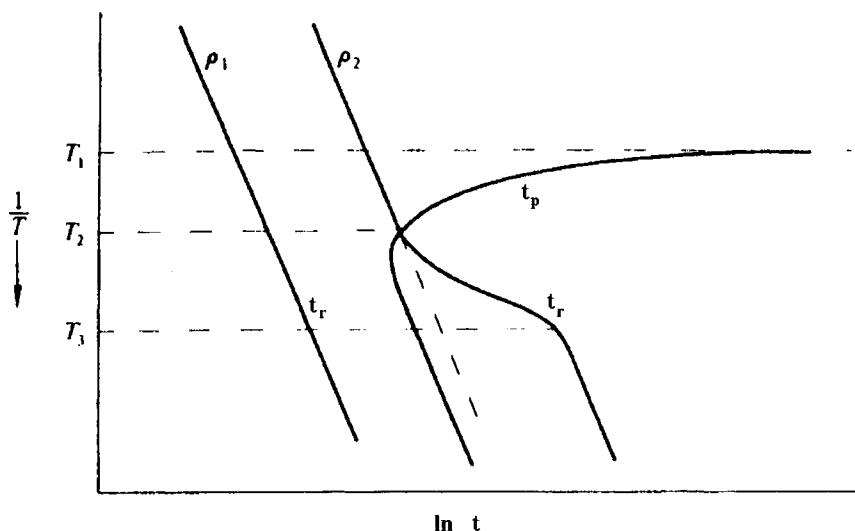


Fig. 1.33 Temperature dependence of the incubation time for precipitation, t_p and for recrystallization, t_r as a function of dislocation density ρ . It is assumed here that the dislocations have little influence on the start of precipitation. With dislocation density ρ_1 , recrystallization is always complete before precipitation. For dislocation density ρ_2 ($\rho_2 < \rho_1$): with $T > T_1$, the single phase is stable; for $T_2 > T > T_3$ discontinuous recrystallization occurs, but is slowed by the pinning effect of the precipitates; and for $T_3 > T$ continuous recrystallization only occurs (schematic diagram after Koster [18]).

- (iii) At temperature below T_2 , precipitation proceeds in the deformed structure, which is the situation sought in MTT. Recrystallization itself will be influenced by the presence of the particles formed, and this is indicated in Fig. 1.33 by a deviation of the curve t_r from linearity towards longer recrystallization times. In this temperature range the precipitating particles influence both the rearrangement of dislocations to form recrystallization fronts and their migration.

For successful MTT therefore, it is important that temperature T_2 should be as high as possible. This implies that the curve of t_p is as far as possible to the left, and that t_r is as far as possible to the right in Fig. 1.33. For the first requirement, U_D and ΔG^* should be minimized, so that systems involving a sluggish diffusion of substitutional solute atoms are unlikely to lend themselves to MTT, whereas systems involving interstitial elements such as carbon in steel, are more likely to respond.

Inclusions Second-phase particles present in a supersaturated solid solution can act in two ways to perturb the uniform precipitation of an ageing precipitate.

First, they may generate matrix dislocations because of quenching stresses arising from differential thermal contraction effects. These dislocations will in turn act as heterogeneous nucleation sites for the ageing precipitate. Secondly, the interface between the inclusion and the matrix may itself act as a preferential precipitation site during ageing.

The presence of heterogeneities forming substrates for phase nucleation can lead to the nucleation of undesired phases during the actual quenching process itself. This obviously reduces the supersaturation of the matrix to a certain extent, hence reducing the subsequent ageing response of the alloy. The tendency for an age-hardening alloy to behave in this manner is known as quench sensitivity.

Quench sensitivity. Quench sensitivity is probably due to a combination of two factors. First, precipitation during the cooling process arises if the cooling rate during the quench is sluggish. This rate depends to a certain extent upon the nature of the quenching medium, but also of course upon the size and shape of the product being heat-treated, the rate of cooling being a function of the ratio of surface area to volume. The argument for a maximum quenching rate is not entirely one-sided, because both the degree of warpage or distortion that occurs during quenching and the magnitude of the residual stresses that develop in the products tend to increase with the rate of quenching.

The second important factor is the concentration of quenched-in vacancies, i.e. the degree of retention at the low temperature of the concentration of vacancies which existed in thermal equilibrium at the solution heat-treatment temperature. Zone formation in aluminium alloys at low ageing temperatures occurs at a rate of seven or eight orders of magnitude greater than that expected from the extrapolation of high-temperature diffusion data, because of the presence of these quenched-in vacancies. A slow quench will sharply reduce the concentration of these vacancies, and hence influence the subsequent rate of ageing. Therefore massive specimens would be expected to show a much lower hardening rate than small specimens, because of their inability to retain excess vacancies.

The range of temperature over which the quenching rate has its most critical influence on the mechanical properties of the aged material was first explored by Fink and Willey [19]) in the case of a high-strength Al–Zn–Mg alloy. Specimens were solution-treated and then held at various intermediate temperatures for various times before finally quenching to room temperature. The hardness of these specimens after subsequent ageing was then expressed in hardness contours on a graph whose axes were intermediate holding temperature and holding time, producing a series of ‘C’ curves (Fig. 1.34) showing the tensile and yield strengths of the alloy expressed as percentages of strengths obtained by quenching without interruption.

Cooling rates represented by time–temperature curves lying to the left of the ‘C’ curves of Fig. 1.34 permit development of virtually the maximum strengths of which the alloy is capable, whereas cooling rates that cut through the ‘C’ curves are not sufficiently rapid to allow development of full strengths during subsequent ageing. Quench sensitivity is found to be dependent upon the constitution of the alloy, and this can at least be qualitatively understood. Thus the presence of second-phase particles may nucleate precipitation during the

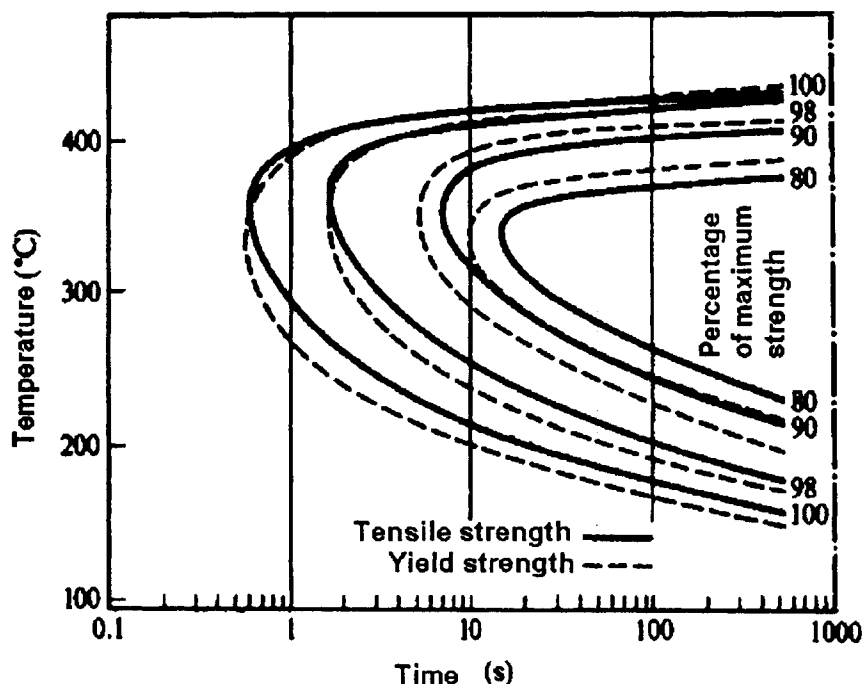


Fig. 1.34 Effect of time at constant temperature in the quenching range on tensile properties of an Al-Zn-Mg alloy (after Fink and Willey [19]).

quench. It is known, for example, that the presence of manganese or chromium enhances the quench sensitivity in aluminium-based alloys to which these elements are added to control grain growth by the formation of incoherent dispersoid particles. Coherent dispersoid particles, as formed in Al-alloys containing Zr (see Fig. 1.23) are much less likely to act as nucleants in this way. For this reason, for example, Cr has been replaced by Zr as the dispersoid forming element in high strength Al-Zn-Mg alloys (especially for applications in thick sections). Again, a binding energy between vacancies and solute atoms would lead to a higher retained vacancy concentration, but the present lack of adequate experimental data preclude the drawing of firm conclusions on this point.

The effect of trace elements on precipitate distribution There appear to be at least four independent ways in which the addition of small quantities of solute to a given age-hardening alloy may have an influence upon the precipitation process.

Vacancy interactions. There has been much recent work on trace element additions to aluminium-based alloys, and some of these additions have been shown to greatly affect the nature of the PFZ. For example, Polmear [20] has

shown that in the Al–Zn–Mg system, trace additions of silver stimulate the nucleation of the η' -phase, resulting in a finer, more uniformly distributed precipitate. On ageing above T_c , silver causes a marked reduction in the width of the PFZs, which implies that there is an interaction between the silver atoms and vacancies, so that the latter are retained within the matrix rather than migrating to the grain-boundary sink. Vacancy–solute interactions have also been observed in Al–Cu alloys, where trace additions of Cd, In or Sn have the effect of changing the kinetics of zone formation, and also have an influence upon the width of the PFZs.

Interfacial energy effects. By segregation to the interface between precipitate and matrix, an added trace element could change the interfacial energy and hence the precipitate morphology. Stewart and Martin [21] have demonstrated this effect in the case of Al–Si alloys to which an addition of Cu was made. A simple binary alloy of Al and 0.5 wt% Si, after solution-treatment and water quenching, on ageing at, say, 230°C precipitates Si as a mixture of submicron-sized plates and equiaxed particles. As the ageing temperature is increased over a small range, there is a marked increase in the particle size of the precipitate, so that coarse Si plates, several microns in diameter, are formed on ageing at 275°C. The additions of 0.45 wt% Cu to the alloy influences the morphology and growth kinetics of the Si precipitated: equiaxed, rather than plate-like Si particles are formed, and their rate of growth upon increase in ageing time or temperature is markedly inhibited.

The effect of Cu appears to be principally on the growth rather than nucleation rate of the Si precipitate particles. This could be attributable to segregation of Cu either to the Si-particle/Al-matrix interface, or within the Al matrix adjacent to the particles, hence lowering the total interfacial energy.

Segregation to grain boundaries. There is evidence that certain solutes may segregate to the grain boundaries of a supersaturated solid solution and hence change the subsequent precipitation process during ageing. For example, when binary Cu–Be alloys are aged, after the initial formation of coherent zones of CuBe, the precipitation process proceeds by a discontinuous mechanism, in that cellular grain-boundary precipitates grow at the expense of the zones with associated grain-boundary migration. This combined precipitation and recrystallization process, which leads to the formation of a relatively coarse dispersion of an intermetallic phase, is associated with a dramatic fall in hardness. However, commercial beryllium bronzes contain 0.2 wt% of Ni or Co in addition to 2.0 wt% Be. The former elements evidently segregate preferentially to the grain boundaries of the Cu for, upon ageing a ternary alloy, it is found that discontinuous precipitation is inhibited and a higher peak hardness may be obtained (Fig. 1.35).

Change in free energy of precipitating phases. An added trace element may also be capable of bringing about a change in the free energy in such a way that a different phase is formed upon ageing. For example, when the ternary Al–2.5 wt% Cu–1.5 wt% Mg is aged, the first stage of ageing involves the formation

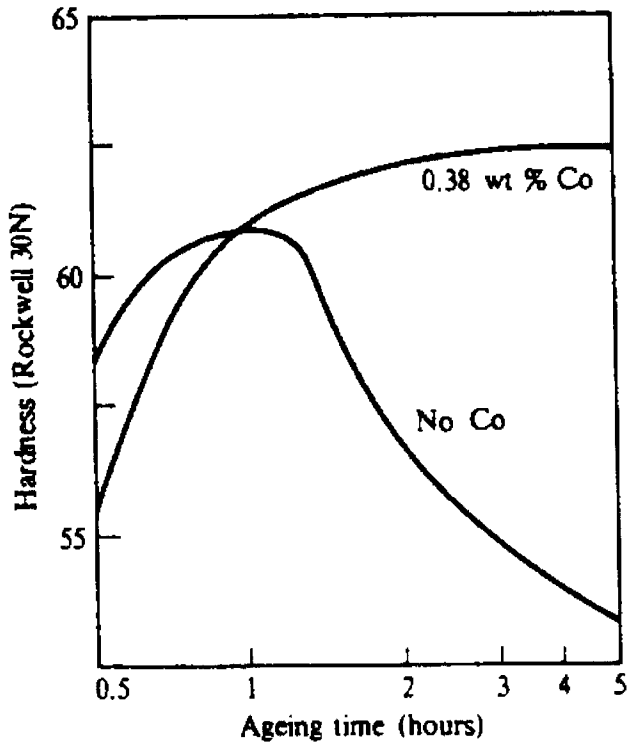


Fig. 1.35 The retardation of softening by the addition of 0.38 wt% Co to an alloy Cu-2 wt% Be when aged at 316°C.

of GP zones comprising ordered clusters of Cu and Mg atoms. These zones persist during the second stage of ageing in which precipitation of laths of the S'-precipitate occurs on dislocation lines generated in the quenching operation, or by cold working prior to ageing. (S' is a distorted form of Al₂CuMg phase.) The addition of 0.5 wt% Ag to the alloy greatly modifies the mechanism of ageing, in that homogeneous nucleation of the ternary T-phase takes place which predominates up to peak hardness, after which it is replaced by the S'-or S-phase. This type of effect could not arise through an interaction between Ag atoms and vacancies alone. It is considered that there is also an interaction between Ag atoms and Mg atoms, which modifies the nucleation processes of the particular precipitates involved.

1.4 QUANTITATIVE METALLOGRAPHY

In order to consider in a quantitative way the relationship between the mechanical properties and the microstructure of a dispersed-phase alloy, the distribution of the precipitate must be considered.

1.4.1 Volume fraction analysis

The volume fraction, f , of the dispersed phase is defined as the ratio of the volume occupied by the particles to the total volume. In a perfectly randomly dispersed microstructure of particles in a matrix, f is also equal to the fractional area occupied by the particles observed on a random polished cross-section, and is also equal to the fractional length occupied by the particles on a random straight line taken through the structure.

In equilibrium phase diagrams, the lever rule allows f to be determined if accurate quantitative data are available regarding the alloy composition and the position of the phase boundaries. f may also be obtained experimentally from small-angle scattering experiments (see Fig. 1.18c). Image analysis of metallographic samples is widely employed to determine f by counting with point and line grids, measurements along straight lines, or area measurements. These may be carried out either manually, or by semi-automatic or fully automatic instrumentation. Such instrumentation has developed dramatically in recent decades, and the reader is recommended to read recent reviews for further information.

1.4.2 Particle size and shape

This is a formidable problem in view of the wide variations in size and shape distribution which are found in precipitated systems. We will, therefore, initially consider a simplified idealized situation.

A dispersion of uniform spherical particles of radius r

If N_v is the number of spherical particles per unit volume, then the definition of f yields:

$$f = (4/3)\pi r^3 N_v \quad (1.20)$$

N_v is not, however, a parameter which is readily measured by metallographic means. A polished cross-section of the structure will reveal the particles as a series of circular areas of radius between 0 and r . Then N_s , the number of particles per unit surface area may easily be obtained. Let us consider the relationship between N_v and N_s .

Consider a unit cube of the structure, and take a section parallel to one of the cube faces. Then the number of intersections with particles (N_s) will be given by

$$N_s = N_v p$$

where p is the probability that the plane will intersect a single particle placed randomly within the cube. Since, of the various positions of the cross-sectional plane, only those positions existing over the length $2r$ lead to the plane

intersecting the single sphere, the probability of intersection is equal to $2r$, thus

$$N_s = 2N_v r \quad (1.21)$$

Applying the equality of area and volume fractions,

$$\begin{aligned} f &= (4/3)\pi r^3 N_v \\ &= N_s \bar{a} \end{aligned}$$

where $\bar{a}$ is the average area of particle intersected by a random plane of cross-section, i.e.

$$f = 2N_v r \bar{a}$$

or

$$\bar{a} = (2/3)\pi r^2 \quad (1.22)$$

Although this provides a means of measuring the true particle size in an opaque sample studied in a random planar section, the analysis of the data is tedious, and further simplification may be obtained.

Lineal analysis. When random lines are passed through the sample parallel to a cube edge, the number of spheres intersected by the line (N_L) is given by

$$N_L = N_v p'$$

where p' is the probability of the line hitting a single randomly placed sphere within the cube. Since possible positions of the line occupy unit area, and the possible positions for which it will pass through the sphere occupy an area of πr^2 , $p' = \pi r^2$. Therefore

$$N_L = \pi r^2 N_v$$

From equation (1.20)

$$f = (4/3)\pi r^3 N_v = N_L \bar{l}$$

and therefore

$$\bar{l} = 4/3.r \quad (1.23)$$

where $\bar{l}$ is the mean lineal traverse length of the random line over the particles. Combining equations (1.21) and (1.23), the particle radius is obtained

$$r = 2N_L/\pi N_s \quad (1.24)$$

so that one may obtain a value for r simply by counting intercepts: lengths or area need not be measured.

Again, from equations (1.21) and (1.24), eliminating r , we have

$$N_v = \left(\frac{1}{4}\right) \pi N_s^2 / N_L \quad (1.25)$$

so that, by substitution of equations (1.24) and (1.25) into the equation for f we obtain

$$f = 8 N_L^2 / \pi N_s \quad (1.26)$$

Equations (1.24) and (1.26) also yield

$$f = (4/3) r N_L \quad (1.27)$$

which provide a means of measuring the volume fraction of a phase dispersed as uniform spheres. In practice these relationships may be used to give approximate measurements of the dispersion parameters provided that the range of particle sizes actually present is small.

The size distribution of spherical particles

Microstructures in real dispersed-phase alloys do not contain dispersions of spheres of uniform size, and metallographic analysis will reveal a distribution of sizes in each of the several phases that may be present (see section 1.1).

The most convenient graphical representation is to plot a histogram (Fig. 1.36) illustrating the relative frequency of occurrence of the classes of particle size observed in a given phase. From the histogram a cumulative frequency distribution curve can be plotted (Fig. 1.36) over the upper limits of each class. The continuous cumulative frequency distribution curve runs from $x_{\min}$ to $x_{\max}$ (where x is the size parameter measured).

For comparing size distributions of similar shape and for the presentation of results it is desirable to know the mathematical function of the size distribution. Two such functions are widely used, namely a log-normal distribution function, and the Wagner, Lifshitz and Slyozov (WLS) distribution function.

The log-normal distribution is a Gaussian distribution with a logarithmic abscissa, and it is used for describing size distributions of grains and particles. If N is the frequency of observation of particle size d and the total number of observations is ΣN , then the arithmetic mean particle size is given by

$$M_a = \Sigma Nd / \Sigma N \quad (1.28)$$

The standard deviation (σ_a) is a measure of the dispersion of the observations and is given by

$$\sigma_a = (\Sigma [N(d - M_a)^2] / \Sigma N)^{1/2} \quad (1.29)$$

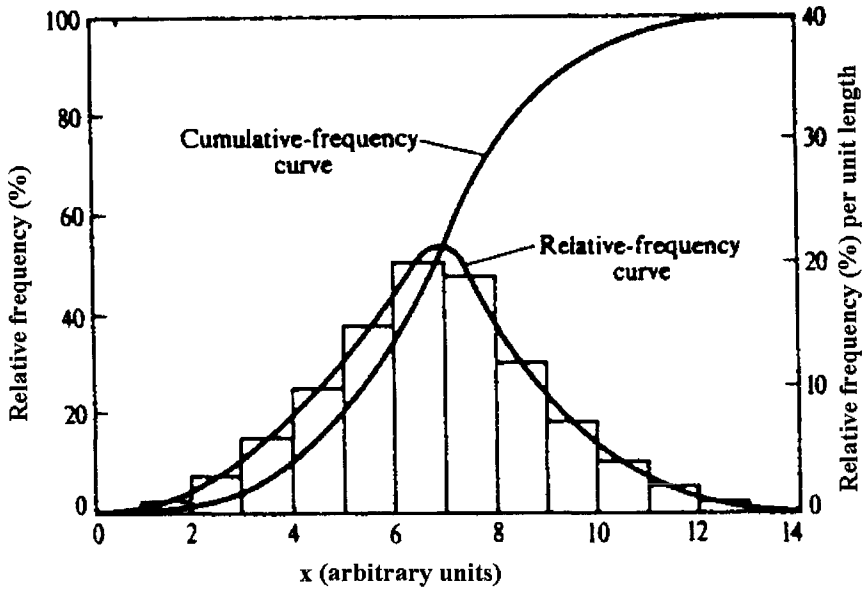


Fig. 1.36 Relative frequency and cumulative frequency curves.

In the case of log-normal distribution, it is usual to calculate the geometric mean, given by

$$\log M_g = \Sigma(N \log d) / \Sigma N \quad (1.30)$$

The standard geometric deviation is given by

$$\log \sigma_g = (\Sigma[\log d - \log M_g]^2 / \Sigma N)^{1/2} \quad (1.31)$$

The equation to the curve describing the log-normal size distribution (Fig. 1.36) is then

$$N = [\Sigma N / (2\pi)^{1/2} \log \sigma_g] \exp [-(\log d - \log M_g)^2 / 2(\log \sigma_g)^2] \quad (1.32)$$

Calculation of M and σ can be laborious, but it is simplified through the use of a graphical solution using logarithmic probability paper. When the cumulative frequency curve is plotted in this way a linear relationship is obtained. Figure 1.37 illustrates a range of experimental data plotted in this way, which demonstrates the log-normal distribution of particle sizes in a number of precipitated alloy systems as well as the log-normal distribution of grain sizes observed in a specimen of α -brass and also the grains in Ni-Zn.

M_g is given by the size corresponding to 50% frequency value on such a plot, and σ_g may be obtained from the ratio

$$\sigma_g = 84.13\% \text{ value} / 50\% \text{ value} = 50\% \text{ value} / 15.87\% \text{ value}$$

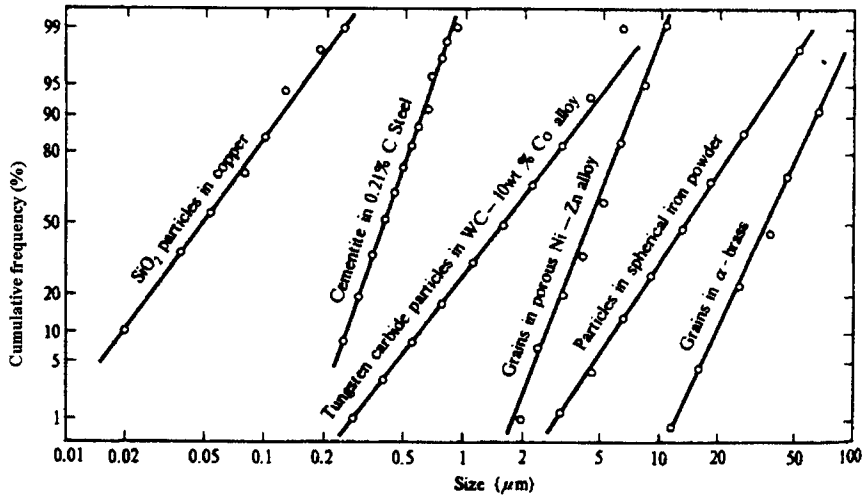


Fig. 1.37 Size distribution of grains and particles of various alloys in the log-normal probability graph (after Exner *et al.* [22]).

Exner [22] concludes that, in spite of the fact that no satisfactory theoretical explanation has been advanced for its occurrence in microstructures, the log-normal distribution should be applied whenever it expresses the experimental results within the limits of experimental error.

The WLS distribution function is employed to describe particle-size distributions during precipitate coarsening. If dispersed-phase alloys are held at elevated temperatures after precipitation is complete, the precipitate particles progressively coarsen, the larger particles growing at the expense of the smaller ones. The average interparticle spacing thus increases with time. The driving force for this process, known as Ostwald ripening, is the tendency to reduce the total area of internal interfaces, and is greater the higher the interfacial energy.

Wagner has shown that the 'steady-state' distribution of particle sizes, $f(r, t)$ to which any initial distribution evolves is dependent upon which process is rate-controlling. In the case of diffusion control

$$f(r, t) = f'(t) \rho^2 h(\rho)$$

where $\rho = r/\bar{r}$ and $h(\rho)$ is given by

$$h(\rho) = \left(\frac{3}{3 + \rho} \right)^{7/3} \left(\frac{3/2}{3/2 - \rho} \right)^{11/3} \exp \left(\frac{-\rho}{3/2 - \rho} \right) \quad \text{for } \rho < 3/2$$

$$h(\rho) = 0 \quad \text{for } \rho \geq 3/2$$

$\bar{r}$ is the arithmetic mean value of particle radius (r), and $f'(t)$ is a function of time only. The function $\rho^2 h(\rho)$ has the following characteristic features:

- (i) a sharp cut-off at $\rho = 3/2$;
- (ii) a maximum at $\rho = 2$;
- (iii) $\int_0^\infty \rho^2 h(\rho) d\rho = 9/4$

In the case of control by the solution reaction at the particle/matrix interface,

$$f(r,t) = f'(t) \rho h'(\rho) \quad (1.34)$$

where $h'(\rho)$ is given by

$$h'(\rho) = \left(\frac{2}{2-\rho} \right)^5 \exp \left(\frac{3\rho}{\rho-2} \right) \quad \text{for } \rho < 2$$

$$h'(\rho) = 0 \quad \text{for } \rho \geq 2$$

1.4.3 Particle spacing parameters

The basic characteristics of a dispersed-phase structure can be described in terms of f and r (the mean radius of spherical particles). The interparticle spacing is a function of these parameters, and it is calculated by their substitution into one of several possible formulae.

The mean free path (MFP)

The MFP is defined as the average distance between the surfaces of particles along any straight line in the structure. In alloys with random particle distributions the value of the MFP is independent of the direction of the chosen line, and is given by

$$MFP = (1-f)/N_L \quad (1.35)$$

Combining equations (1.27) and (1.35), we can write

$$MFP = (4/3) r (1-f)/f \quad (1.36)$$

Mean planar separation of particles

In later chapters we shall attempt to establish the relationship between the microstructure and the mechanical properties of dispersed-phase alloys. Many different spacings can be calculated. The appropriate spacing and method of averaging for a particular problem depends on the nature of the problem. It is usual to assume that the particles form square arrays in parallel planes, in which case the average centre-to-centre spacing, λ , between a particle and its nearest neighbour intersected by a random plane through the array is given by

$$\lambda_s = N_s^{-1/2} \quad (1.37)$$

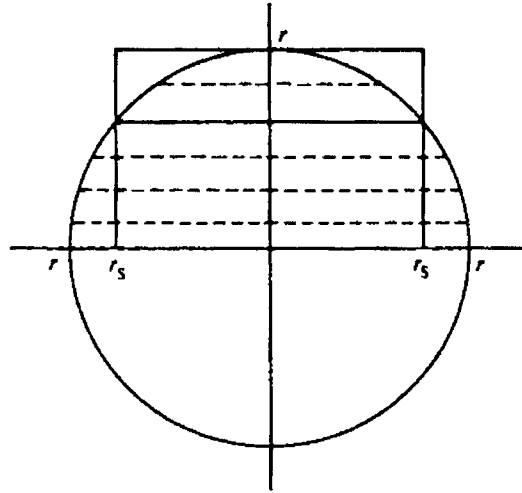


Fig. 1.38 Definition of mean planar particle radius r_s of cross-section of particle of radius r .

This nearest-neighbour spacing is not, however, always appropriate. Thus, in calculating the interaction between a gliding dislocation and a random array of obstacles in its slip plane, the average distance from a particle to its nearest two, three or four neighbours (instead of to its one nearest neighbour) is the correct estimate. Foreman and Makin [23] have considered this problem, and in general the more nearest neighbours that are taken into account the longer will be the resulting evaluated separation (λ_s^*). They obtain

$$\lambda_s^* = 1.23 (N_s)^{-1/2} \approx 1.23 r (2\pi/3f)^{1/2} \quad (1.38)$$

If the size of the particles is negligible in comparison with their centre-to-centre separation, i.e. if $\lambda \gg r$, then equation (1.38) is an appropriate description of the microstructure. If this is not the case, then one must consider the surface-to-surface mean planar separation of the particles, λ_s^{**} , which reduces λ_s^* by an amount $2r_s$, where r_s is the mean radius of intersection of a random plane with a spherical particle of radius r .

The value of r_s can be obtained by considering a particle of radius r intersected by a series of parallel planes (Fig. 1.38). The mean radius of intersection, r_s , is obtained by equating the volume of the hemisphere of radius r to the volume of the cylinder radius r_s and height r :

$$\left(\frac{2}{3}\right)\pi r^3 = \pi r_s^2 r$$

i.e.

$$r_s = \sqrt{\left(\frac{2}{3}\right)} r \quad (1.39)$$

The mean planar surface-to-surface separation thus becomes

$$\lambda_s^{**} = \lambda_s^* - 2 \sqrt{\left(\frac{2}{3}\right)} r \quad (1.40)$$

Spacing of particles with varying size

Once the particle-size distribution has been characterized, it is possible to obtain a value for the 'average particle spacing'. If equation (1.38) is written in terms of particle diameter, $d = 2r$, it becomes:

$$\lambda_s^* = 1.2d (\pi/6f)^{1/2} \quad (1.41)$$

and the average planar spacing, when a distribution of particle sizes is present, may be written

$$\lambda_s^* = 1.2 [(\pi/6f) (1 + \sigma_a^2/\bar{d}_a^2)]^{1/2} \bar{d}_a \quad (1.42)$$

Spacing of plate- or rod-like particles

Many age-hardened alloys contain plate- or rod-shaped precipitates. For example high-strength aluminium alloys commonly contain plates which form in parallel array on $\{100\}_\alpha$ and $\{111\}_\alpha$ planes of the matrix, and rods which form in $\langle 100 \rangle_\alpha$ directions. Nie, Muddle and Polmear [24] have developed expressions for the mean planar end-to-end distance (i.e. effective planar interparticle spacing), λ , for plates and the mean planar centre-to-centre distance between precipitate rods.

Plates For $\{100\}_\alpha$ precipitate plates of uniform diameter D and thickness T , where $D \gg T$, the dihedral angle between the $\{100\}_\alpha$ habit planes and the $\{111\}_\alpha$ slip planes is 54.74°

If N_v is the number of precipitate plates per unit volume, and P the probability that a $\{100\}_\alpha$ precipitate plate is intersected by a $\{111\}_\alpha$ plane, then:

$$N_A = N_v P = N_v D \sin 54.74^\circ$$

$$f = N_A S_p = N_v D S_p \sin 54.74^\circ$$

and

$$f = N_v V = N_v \pi D^2 T/4$$

where V is the volume of a single precipitate plate, and S_p is the mean planar cross-sectional area of a precipitate plate intersected by a $\{111\}_\alpha$ plane. The cross-sectional area of the precipitate in the slip plane is approximately rectangular in shape with mean planar width $T_p = T/\sin 54.74^\circ = 1.225T$ and mean planar length $D_p = \pi D/4$. Therefore, $S_p = \pi D T_p/4 \sin 54.74^\circ = 0.306 \pi D T$.

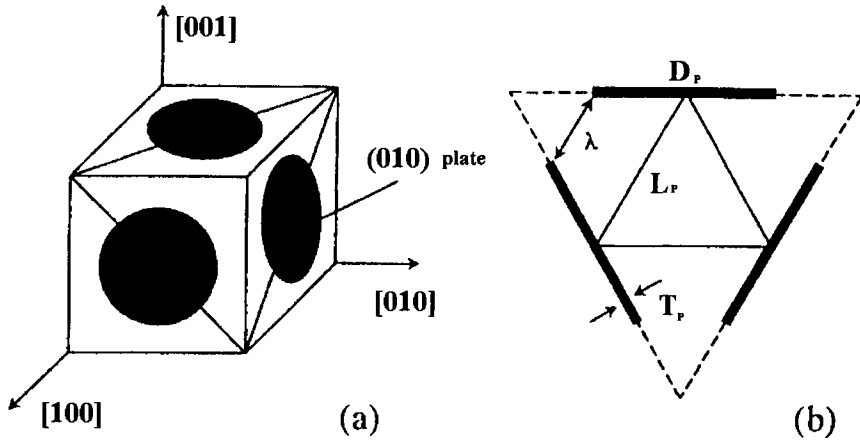


Fig. 1.39 Projection of intersected $\{100\}_\alpha$ precipitate plates on a $\{111\}_\alpha$ plane of the matrix.

Assuming that the $\{100\}_\alpha$ precipitate plates are circular discs distributed at the centre of each surface of a cubic volume in the matrix, then the $\{100\}_\alpha$ precipitate plates will have a triangular distribution on the $\{111\}_\alpha$ slip plane as indicated in Fig. 1.39(b). The effective planar interparticle spacing, λ , between the plates is given by:

$$\begin{aligned}
 \lambda &= L_P - D_P/2 - \sqrt{3} T_P/2 \\
 &= (\sqrt{3}/2)^{1/2} (N_A)^{-1/2} - D_P/2 - \sqrt{3} T_P/2 \\
 &= 0.931 (0.306 \pi D T/f)^{1/2} - \pi(D/8) - 1.061 T
 \end{aligned} \tag{1.43}$$

Rods For $\langle 100 \rangle_\alpha$ precipitate rods of uniform diameter D and length l , where $l \gg D$, the angle between the rod axis and the normal to the $\{111\}_\alpha$ slip plane is 54.74° . So:

$$N_A = N_V P = N_V l \cos 54.74^\circ$$

and

$$f = N_A S_P = N_V V = N_V \pi D^2 l/4$$

This gives $S_P = 0.433 \pi D^2$.

The cross-section of the precipitate rod in the slip planes has an ellipsoidal shape, with major axis of $D/\cos 54.74^\circ = 1.732D$. Approximating this ellipsoidal area to a circle of diameter D_P , then $D_P = \sqrt{1.732} D$.

Assuming that the $\langle 100 \rangle_\alpha$ precipitate rods have a distribution that defines a cubic volume within the matrix phase, then the $\langle 100 \rangle_\alpha$ precipitate rods intersected

on a slip plane of the matrix phase have a triangular distribution. The mean planar centre-to-centre distance between $\langle 100 \rangle_\alpha$ precipitate rods is given by:

$$L_P = (\sqrt{3} N_A/2)^{-1/2} = 1.075 D (0.433 \pi/f)^{1/2}$$

giving

$$\lambda = L_P - D_P = 1.075D (0.433 \pi/f)^{1/2} - \sqrt{1.732D} \quad (1.44)$$

Having discussed the structure of precipitation-hardened alloys, we are now in a position to consider its relationship with mechanical properties. In the following chapters we will therefore examine the mechanical properties of particle-hardened structures.

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APPENDIX 1 TO CHAPTER 1

[Wilms' original paper, first published in 1911, appears in English translation below, where it will be seen that the author compares the hardening behaviour of quenched aluminium alloys (containing magnesium and copper) with that of quenched carbon steels. The effect upon the hardness of cooling-rate after solution heat-treatment, and also of subsequent cold working was also investigated and reported upon.]

PHYSICAL-METALLURGICAL EXPERIMENTS ON ALUMINIUM ALLOYS CONTAINING MAGNESIUM

ALFRED WILM

(Metallurgie, Zeitschrift für die gesamte Hüttenkunde:
Aufbereitung-Eisen-und Metallhüttenkunde- Metallographie, Vol.8
(22 Apr. 1911), edited by Dr W. Borchers and Dr F. Wüst)

Micrographic examination of steels containing carbon reveals graphically the transformations resulting from tempering of the steel. Just as the carbon in iron gives it the characteristic of hardening after heating and quenching, so this characteristic is inherent in aluminium, but its capacity for hardening is not conditional on the presence of carbon, but on another light metal, namely magnesium.

The experiments I have performed on aluminium alloys since 1903 at the Neubabelsberg Scientific and Technical Analysis Centre have shown that even a small quantity of magnesium will make it possible to harden the aluminium by heat treatment. Micrographic examinations have not determined whether such tempering causes any structure changes. Others may have succeeded in illustrating crystallographically the peculiar phenomena shown by aluminium magnesium alloys. Since too the very substantial changes in properties are not accompanied by any appreciable form changes, I can only deal here with the effect of tempering on aluminium alloys containing magnesium without elaborating on the nature of the matter.*

Tempering of alloys with aluminium is approached quite differently from tempering of steels containing carbon. If, for the purpose of hardening, the latter are raised to an appropriate temperature and then quenched, immediately after this quenching they possess their characteristic hardness. On the other hand aluminium alloys containing magnesium are soft directly after quenching and it is only after a few hours that hardness begins to show an increase, considerably in the first hours and subsequently less rapidly. Fig. App. 1.1 illustrates this process. Even adding as little as one-half percent to the aluminium produces the effect described above. Yet the hardness achieved in this way is still very slight when compared with other bronzes. If copper is present at the same time the

* Exact measurements on cylinders show that, immediately after tempering of a piece of 30 mm, the length had increased by 0.006 mm, but that this increase disappeared after a few days.

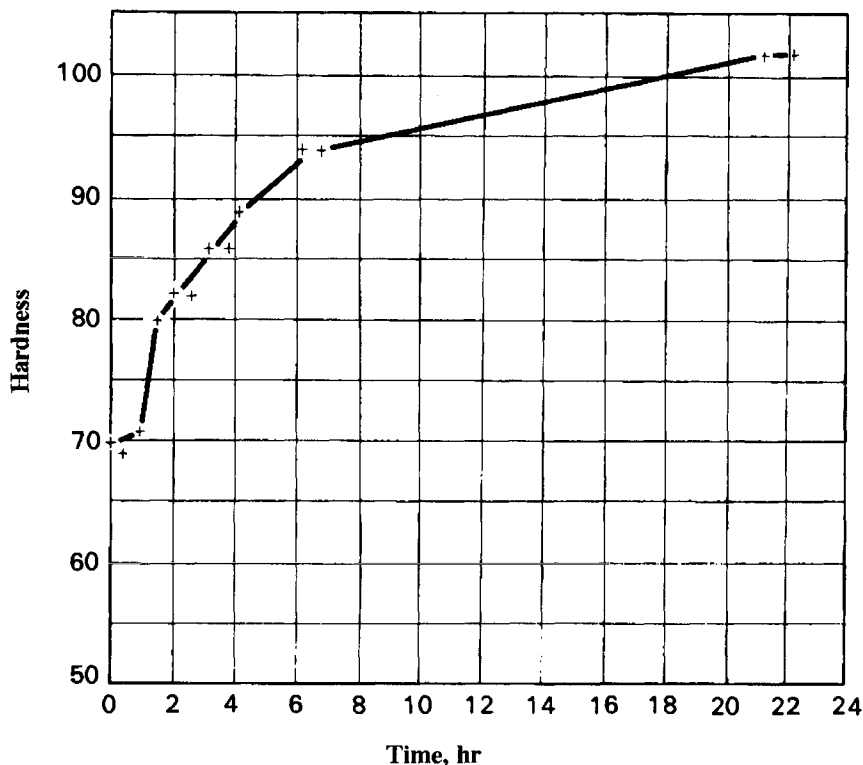


Fig. App. 1.1 The first age-hardening curve published by Alfred Wilm in 1911, and referring to an aluminium-based alloy. J.W.M.

effect both on hardness and other mechanical properties is significantly greater. By examining under the microscope immediately after casting a copper-aluminium alloy containing magnesium, repeated dark veinings may be seen. If the alloy is then heated to about 500°C and quenched in water, the picture reveals a more homogeneous composition. Immediately after this process the picture is the same as after several days, despite the fact that in this time the properties of the material have changed substantially.

The tempering of steels containing carbon has this in common with aluminium alloys containing magnesium, that neither hot working nor cold working can give to the material the mechanical properties which tempering bestows.

The temperature commonly used in hot working of aluminium and its alloys is around 400°C . Aluminium at this temperature can be readily shaped as required either by forging, pressing, or rolling, etc. If after preparation in any of these ways the material needs to be further treated by cold working with the aim of getting as high a yield point as possible, it may then be reheated to 400°C to render it more malleable. Whether cold working follows heating immediately or only after several days, the properties of the material remain unchanged by

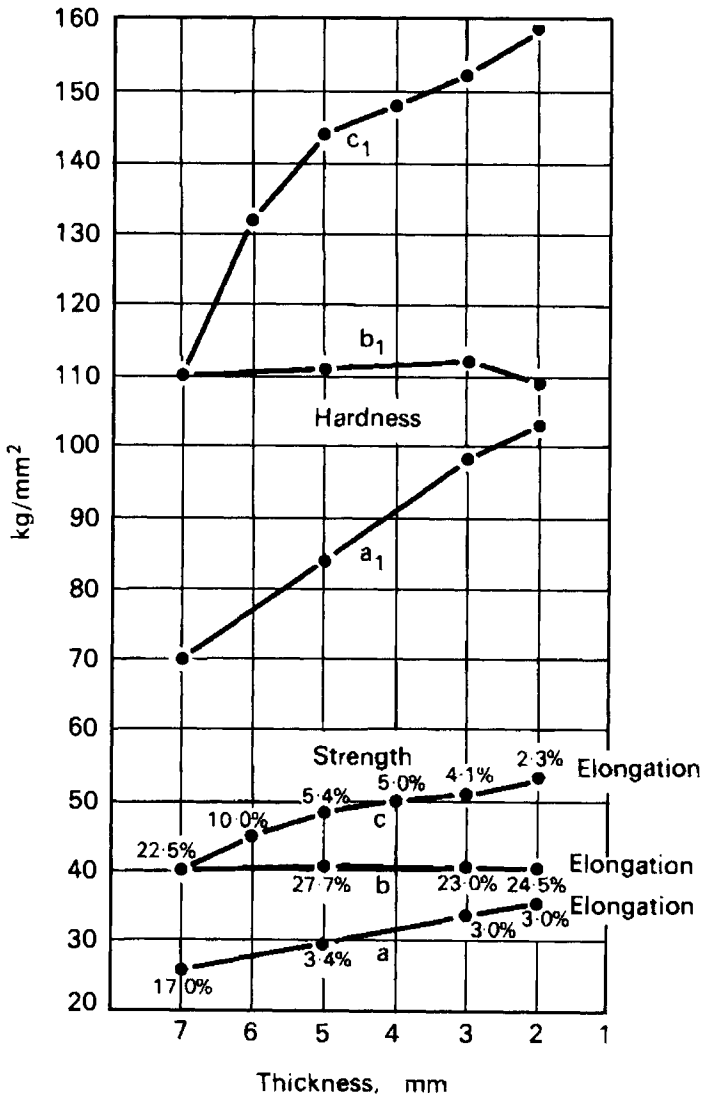


Fig. App. 1.2

heating at this temperature and storing. Cold working results in the mechanical properties represented by Curve a of Fig. App. 1.2. For our experiment we took a plate 7 mm thick, containing 3.5% copper, 0.5% magnesium and the rest aluminium, which was rolled out in stages to 2 mm, and samples of the plate were taken at intervals. Cold working naturally reduced the elongation figure but increased both the strength and the hardness. For the sake of simplicity the elongation figures have been written along the curve. If the plates of all thicknesses are heated at 500° quenched in water and stored for about four days,

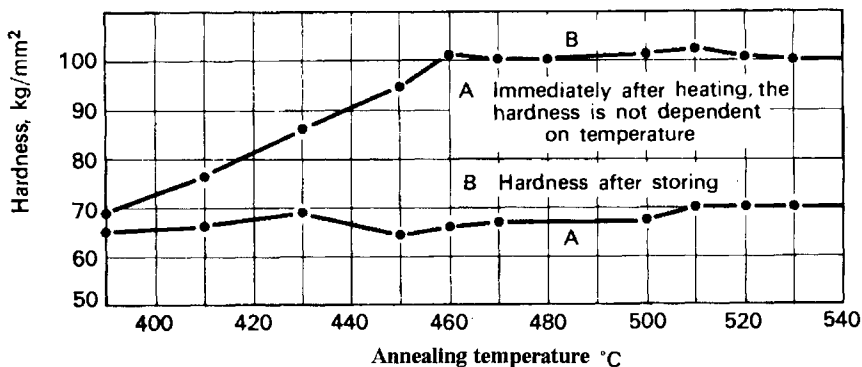


Fig. App. 1.3

they will all take on the mechanical properties represented by Curve b on Fig. App. 1.2. Here again the elongation figures are shown along the curve. It is evident from this that the tempering of aluminium alloys containing magnesium is markedly different from that of steel. Whilst steel through tempering loses its previous elongation, the aluminium alloy, in addition to gaining in hardness and strength, also increases its elongation value. Thus aluminium alloys containing magnesium, by contrast to steel, are capable of being reworked cold after tempering. Curve c shows the result of this process.

It follows from the above that as with the steel the temperature at which tempering is carried out has a direct bearing on the temper attained. Fig. App. 1.3 gives some idea of the measure of increased hardness at given temperatures which results from heating, quenching and subsequent storing. It is safe to suppose that even below 400° there is a slight increase in hardness after storing, but this is so minimal as to be of no practical significance. Indeed for the purposes of working the material it is essential during the process to avoid any increase in hardness by annealing, for even though after temper hardening the elongation figures are quite high, it is still easier to work the material in cold form if it has been annealed at lower temperatures for this purpose, as for example in drawing wire. Thus in practice temper hardening is only introduced when the treatment is already complete, or where specific mechanical properties are required such as high yield point and degree of hardness as against lower elongation of the finished product. In this case after the temper hardening and storing some further cold working is necessary.

Nowadays the demands made on the mechanical properties of light metals are so great that it is essential to produce the maximum attainable strength of which the material is capable. The process of improving the mechanical properties can easily be speeded up by not quenching the material after heating it to a temperature of 500°C, but allowing it to cool slowly. Immediately after such slow cooling the mechanical properties are substantially better than after quenching from the tempering heat. However storing results in only a slight change in the mechanical properties of the slowly cooled material, whilst the quenched material shows greatly superior mechanical properties. Fig. App. 1.4 (I, II, III)

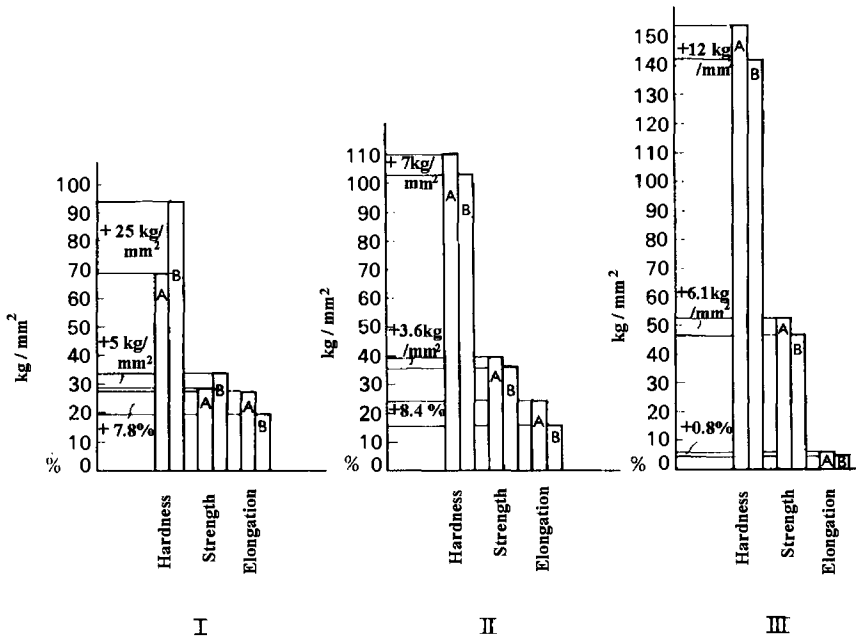


Fig. App. 1.4 I. Tested directly after tempering: A – quenched in water; B – slowly cooled. II. Tested at the end of the ageing period. A – quenched in water; B – slowly cooled. III. Tested after treatment and subsequent cold working.

illustrates this process. Naturally the strength is maintained if the material is subsequently worked. The higher the strength values after temper hardening, the higher they are after subsequent cold working. The material should not therefore be subject to any form of working immediately after tempering, since the mechanical properties right after heating to temper heat are, as Fig. App. 1.4 shows, very poor. As the mechanical properties produced through cold working depend on the properties of the original material, strength curves all run parallel, so that working right after heating would result in extremely poor mechanical properties. By cold working the material and not storing it for a period of time it loses its capacity to develop of itself (see Fig. App. 1.5).

Conditions are similar to those of slow cooling after temper hardening if the material after being raised to tempering heat and then quenched is next reheated in boiling water. The strength shows a sharp rise, just as if the material had been slowly cooled after heating to 500°C. After subsequent storing the mechanical properties decline as is the case with the slowly cooled material. On the other hand, if after the regular tempering cold worked material is annealed in boiling water, hardness and strength fall only slightly, whilst proportionately elongation is significantly increased (see Fig. App. 1.6).

For special purposes a later annealing even at a higher temperature is advisable; it has for example proved useful where coarse threads are cut into the

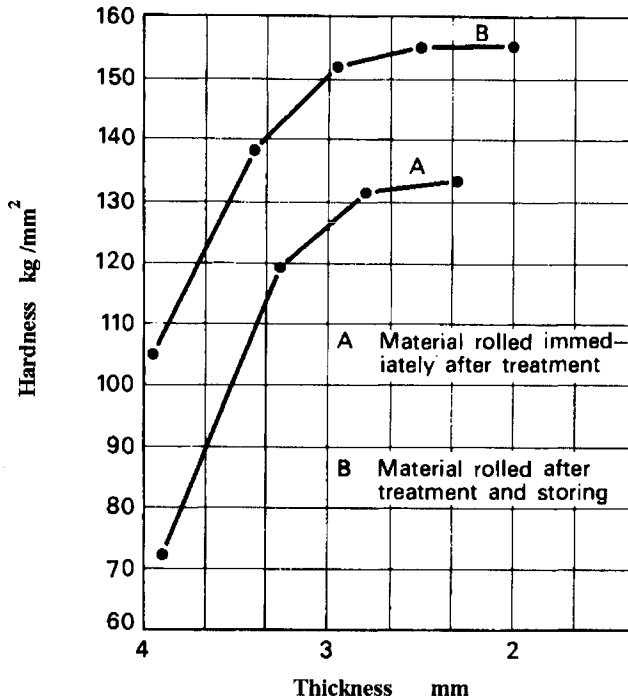


Fig. App. 1.5

material. It may be well to anneal the material in oil at a temperature of 200°, but naturally only those areas which after the cutting process have a tendency to fracture. In general, as with other materials in which high elasticity, hardness and strength are desirable, it is best to avoid excessive heating of the finished product.

During heating the mechanical properties decline as the temperature rises. In calculating them it is necessary to take into account whether the material in the workpiece was exposed to higher temperatures. In the case of aluminium alloys containing magnesium heating up to 150° is not appreciably detrimental to the mechanical properties. At the Neubabelsberg Scientific and Technical Analysis Centre exhaustive tensile tests of heated material have yielded evidence on this point. However, the mechanical properties become noticeably poor at temperatures above 200°. The properties of the material are effected in a specific way by other alloy components, as for instance manganese, nickel, and so on. Thus manganese increases the hardness, whilst nickel produces greater ductility. Generally speaking great care must be taken when working with metal alloys of aluminium, since certain alloy components, even when added in comparatively small amounts, tend to segregate and it is unlikely that a uniform product will result. Addition of manganese, if kept within moderate bounds, has a peculiar effect on the aluminium alloy. Thus for instance metallic quicksilver does not

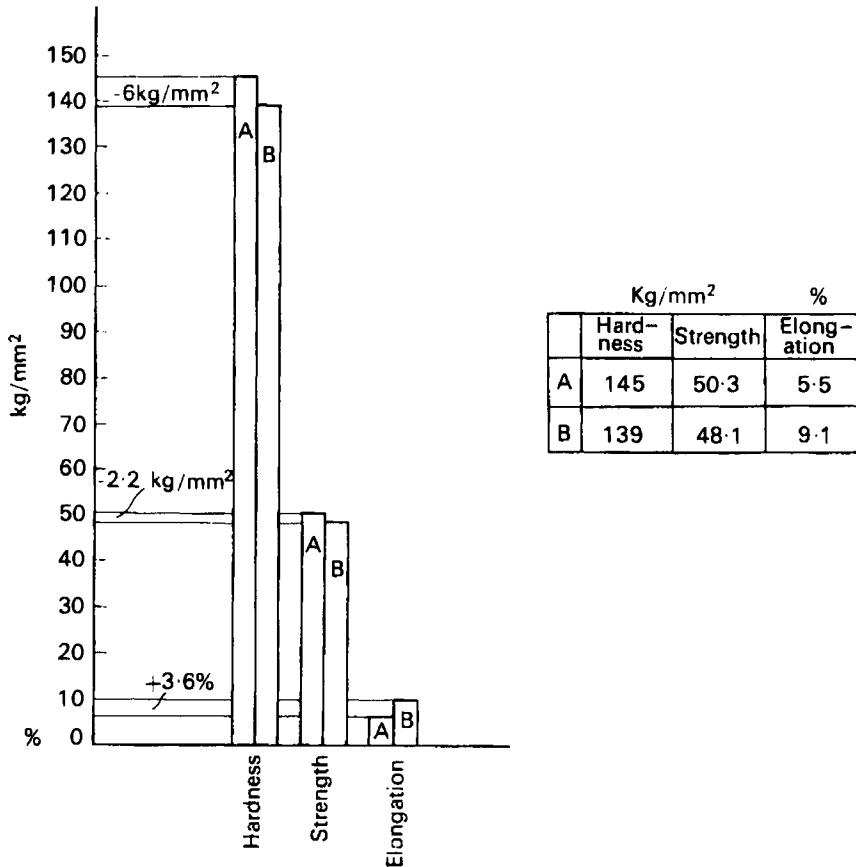


Fig. App. 1.6

even moisten the metal, where pure aluminium as is well known is destroyed after a few hours because of the formation of an amalgam.

In view of the superior mechanical properties which can be conferred on aluminium alloys containing magnesium by this method of treatment, it has in practice a large number of applications, specially for military equipment and in airship construction. The material now in commercial use under the name of 'Duralumin' is produced on a large scale by the Durener Metallwerke A.G. in Germany, Vickers Sons & Maxim in England and Messingwerk C. Kulmiz, Kramscach-Achenrain (Tirol), in Austria-Hungary and in view of the widespread interest in this metal, it would appear that its prospects for the future are excellent.*

* I acknowledge with gratitude my colleagues of many years—Ing. Fritz Jablonski for his conscientious work in examining the materials and Heinrich Rochlitz, head foundryman, for his untiring enthusiasm for work combined with great manual skill.

APPENDIX 2 TO CHAPTER 1

[There follows some extracts from Preston's 1938 paper where this author reports for the first time the presence of the diffraction streaks in aged alloys due to the existence of the zones which later bore his name and that of Guinier.]

THE DIFFRACTION OF X-RAYS BY AGE-HARDENING ALUMINIUM COPPER ALLOYS

G. D. PRESTON

(*Proc. Roy. Soc. A* **167** (1938), 526)

The object of this paper is to draw attention to certain peculiarities in the X-ray diffraction spectra obtained from single crystals of an alloy of aluminium with 4% by weight of copper. The experiments described below were carried out during an investigation into the property of age-hardening exhibited by these alloys, in the hope that some light would be thrown on the processes preceding precipitation of the compound CuAl_2 , which are generally regarded as being the cause of the hardening in alloys of the Duralumin class, of which the simple 4% copper alloy is the prototype.

The material used in the investigation was prepared from aluminium of high purity and after casting the ingots were forged and then drawn into wires of 1 mm diameter. Pieces of the wire after annealing at 500°C , contained crystals of sufficient size (2–5 mm in length) for X-ray examination by the oscillating crystal and Laue methods.

Oscillating crystal photographs of the alloy taken as soon after quenching as possible do not present any striking difference from those of pure aluminium, except in showing a small change of parameter which is measurable only in the high order reflexions.

After ageing at 150°C for 26 days or 200°C for 10 h the intense diffraction spots of the solid solution on the oscillation diagrams are accompanied by two or three rather weak but fairly sharp satellites. These appear before the alloy is in its state of maximum hardness and persist after that maximum has been passed. At the same time, observation of high order reflexions (511) and (333) shows that some material of spacing $4.04 \text{ \AA}$ is making its appearance in the matrix of alloy in which the spacing is $4.033 \text{ \AA}$. The reflexions of the $4.04 \text{ \AA}$ spacing are weak and diffuse. In the oscillation photographs of the alloy aged at room temperature for 6 or 8 months the diffraction spots due to the solid solution are accompanied by lines which pass through the positions occupied by the satellites observed in the spectra of the alloy aged at higher temperatures.

[Excerpts from later sections of the paper appear below.]

Oscillating Crystal Method

A series of photographs has been taken of specimens aged for 6 months at room temperature and after different periods at 150 and 200°C . The orientation of the

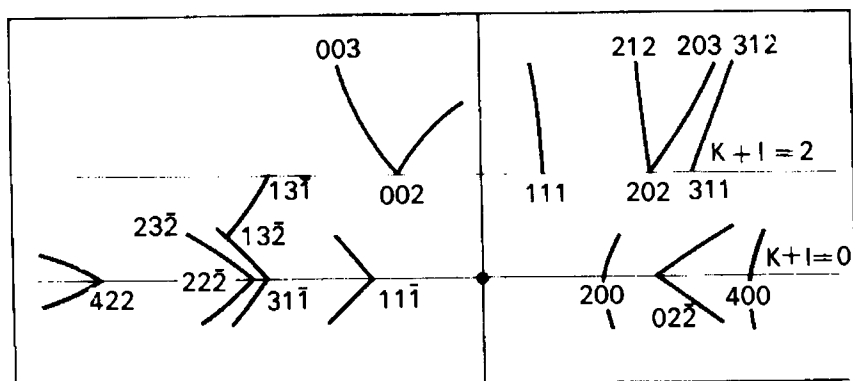


Fig. App. 1.7 Diagram of lines on an oscillating crystal photograph. (Crown Copyright.)

crystals selected for examination was determined by Laue photographs, and the specimens were adjusted so that a $[110]$ or $[100]$ direction was parallel to the axis of oscillation. The general nature of the results obtained by this method of investigation can be illustrated by a description of photographs of the alloy aged at room temperature for 6 months and at 150°C for 26 days.

In the alloy aged at room temperature the reflexions due to the face-centred cubic structure are accompanied by a pair of lines diverging from each spot in the direction of increasing θ . These lines, in the alloy aged at 150°C , are resolved into two or three fairly sharp spots. Actually each reflexion is accompanied by three lines, one of which is masked in the central layer line by the 'white' radiation, but can be seen in the first layer line.

Some idea of the nature of the observed effect may be obtained from Fig. App. 1.7, where a number of diffraction spots with their accompanying lines are shown diagrammatically.

Measurement of the films showed that the lines associated for instance with a (111) spot each proceeded towards the position where (211) , (121) or (112) would occur, if it appeared in the X-ray spectrum. In terms of reciprocal space this means that the point (111) is accompanied by three mutually perpendicular lines parallel to the cube axes of the reciprocal lattice as illustrated in Fig. App. 1.8.

The Laue method

In Fig. App. 1.9 the crystal aged at room temperature is oriented with a $[110]$ direction parallel to the incident beam. The Laue diffraction spots are accompanied by quite intense streaks running round the principal zones and starting quite near the central spot.

These streaks are not completely absent from photographs of the alloy taken immediately after quenching; they are, however, at first much fainter and broader.

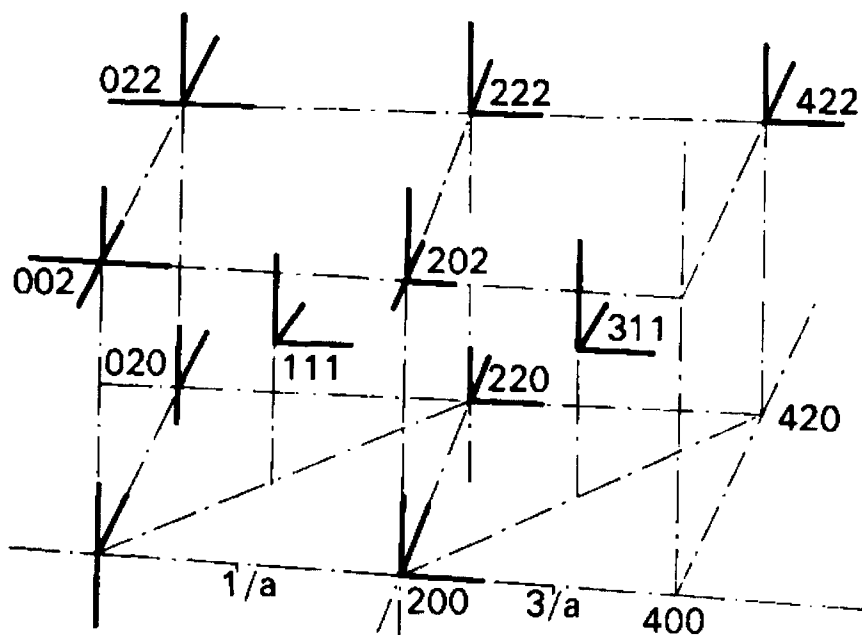


Fig. App. 1.8 Reciprocal lattice showing short lines which give rise to V-shaped streaks in oscillation photographs. (Crown Copyright.)

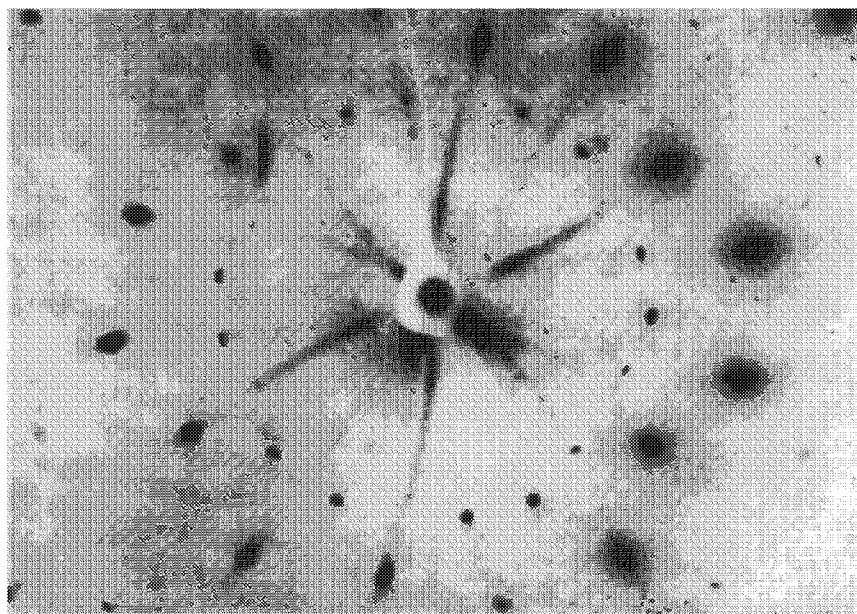


Fig. App. 1.9 Laue photograph of Al-Cu crystal aged 6 months at room temperature.

Conclusion

The results described in the preceding sections must be regarded as preliminary. A fuller interpretation must depend on measurements of the intensity of the diffraction effects, when it should be possible to determine the size of the regions rich in copper and the number of copper atoms involved in each of them. It seems justifiable at the moment to conclude that the process of age hardening in this alloy is associated with the segregation of copper atoms on the (100) planes of the crystal as suggested by C. H. Desch in *The Chemistry of Solids*, 1934.

APPENDIX 3 TO CHAPTER 1

[This memoir by Professor A. Guinier is reprinted by permission of the publishers from *Materials Science Forum* Vols. 217–222 (1996) pp. 3–6.]

ON THE BIRTH OF GP ZONES

A. GUINIER

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At the beginning of the century, the manufacturing process of Aluminium by electrolysis (Heroult) made aluminium an industrial material. Many empirical studies were then carried out in order to find Al-based alloys with advantageous properties.

From all these trial and error experiments, a major discovery emerged. In 1906, Alfred Wilm observed that an AlCuMgMn alloy, soft after quenching from 450°C, became hard by ageing at room temperature: it was called 'Duralumin'. The metallurgists immediately realised that this phenomenon was practically very interesting. Everybody would like to have at his disposal a light metal with a high mechanical resistance. For instance, this kind of metal was used to build the 'Zeppelin'.

At that time, neither Wilm nor other metallurgists knew why Al alloys harden. Duralumin had been found by chance; one had no fundamental ideas to guide research towards other, and better, hardening alloys.

A decisive progress is due to an American metallurgist, Paul Merica (1919). Merica showed that in the equilibrium state, the solubility of the alloyed elements increases with temperature. Thus, Al 4% Cu is single-phase at 450°C, but supersaturated at room temperature. Nevertheless, after quenching, during ageing, no second phase was visible either with the microscope or with X-rays.

Merica proposed the following model: the copper atoms segregate, forming clusters embedded in the aluminium crystal, or they gather into precipitates more or less coherent with the matrix: their boundaries are not well defined. All these possible heterogeneities were not detectable, simply because they were too small.

Today, the Merica model can still be considered roughly valid. But in the twenties, the model had no experimental support: nothing had been precisely described. Thus the model had not the success it deserved, and between both World wars, the problem of age-hardening was not understood. Meanwhile, on the other hand, empirical studies were continued: new age-hardening alloys were prepared with better qualities.

In Paris, around 1937, two chemists (or metallurgists), J. Calvet and P. Jacquet, decided to work again on age-hardening: they had a good reason to do so. Jacquet had just invented electrolytic polishing: he had shown that micrographs were improved, because the surface of the sample was not perturbed as after a



Fig. App. 1.10 First X-ray diagram (1938) of an Al–4% Cu aged alloy: CuK α , several crystals with different orientations.

mechanical polishing. They hoped to detect the clusters of Merica, which nobody had seen before.

At that time, I visited Calvet and Jacquet, because they had the best aluminium foils I needed to make the windows of my X-ray tube. They told me what they were doing and explained the age-hardening problem, of which I was completely ignorant. In turn, I told them that I was working on X-ray small angle scattering: this new technique allowed one to detect submicroscopic particles and to measure their size. It looked as if I could give an answer to their problem. Why not try an X-ray experiment with the age-hardened alloy?

The very first pattern I got was a complete surprise (Fig. App. 1.10). Many diffuse streaks issued from the center. In fact the diagram was complicated because there were a few crystals in the sample. If one single crystal is isolated and conveniently oriented, the diffuse scattering pattern may be easily interpreted. X-rays are reflected by platelets of copper atoms gathered on isolated (100) reticular planes. From the extent of the diffuse streaks, the size of the copper platelets can be evaluated (~ 5 to 10 nm).

I published rapidly these results in the *Compte-Rendus*. Three weeks later, a paper by G.D. Preston appeared in the *Journal of Metals*. Preston had studied the

same AlCu alloy; he had observed the same diffuse scattering and his interpretation was the same as mine.

The two papers should have been discussed at the general meeting of the Institute of Metals in September 1939. But the war had begun . . . During the war and after, Preston abandoned the researches on metals. It happened that I have never had the opportunity of discussing with him.

After 1945, I knew that our papers on AlCu have had some diffusion in the United States and I learned that Robert Mehl and Charles Barrett coined the name G P Zone.

During the war I worked in precarious conditions at the 'Conservatoire des Arts et Métiers', and, after 1954, still there and also in ONERA. We studied in detail the various structures of the AlCu alloy, with time and annealing temperature. The evolution of the alloy is much more complicated than was thought at the beginning. We found examples of coherent precipitates as predicted by Merica. We also investigated AlAg and AlZn alloys. The zones are spherical: the difference with the copper alloy comes from the fact that the atomic radii of Ag or Zn are about the same as the radius of Al. Thus the substitution of an Al atom by a Zn or Ag one distorts very slightly the lattice.

With Jacquet, I studied the CuBe system. The formation of zones produces considerable deformations. Coherent precipitates are complex. But this is not an appropriate place to enter into the details of the structure of the zones in various alloys. I would rather prefer to point out some general remarks.

For the metallurgists in the period 1920–1930, any alloy is made by the juxtaposition of crystals of different nature in polyphased systems. The major advance was the characterisation of the crystalline structures by X-ray diffraction.

The next step is the introduction of the notion that the model of regular crystals is not sufficient. Imperfections, localised defects of periodicity have a considerable influence upon the physical properties of the metal, even if the relative proportion of the perturbed atoms is small. The more obvious example is that of dislocations. Age-hardened alloys are also an important case. The hardening was explained by the interactions of dislocations and local defects. That is why the experimental studies of the zones or coherent precipitates have been important.

Crystalline imperfections produce diffuse scattering. But conversely, the knowledge of this scattering, even if it is complete and precise, does not give an image of the imperfect structure (there are no 'direct methods' as for crystalline structures). Sometimes the interpretation of the diagrams is easy: that was the case, to a first approximation, for AlCu zones. But in spite of numerous studies during decades, a total agreement for the detailed structure of the zones has not yet been reached.

Zones in AlAg (or Zn) give a typical example. The small angle scattering pattern is a ring: when the scattering angle diminishes, the intensity increases, passes through a maximum and decreases towards the 0 angle. Two models are possible (i) the spherical zones of uniform radii are arranged like the molecules in a liquid, or (ii) the zone is complex, made of a central sphere enriched in Ag, surrounded by a depleted shell. The choice between the two models is ambiguous.



Fig. App. 1.11 Electron micrograph of an oxide replica of the needles of precipitate in an AlMgSi alloy.

A priori, the electron microscope seems to offer more advantages than X-rays because it gives direct images, with sufficient resolving power. In fact, the preparation of the sample is so delicate that X-rays are often more easy to use, at least for getting an approximate model. The AlMgSi alloy is peculiar; there appear to be rows of atoms directed along the $\langle 100 \rangle$ axes. It is then likely that the precipitates are also needles along the cubic axes. To test this idea, I asked R. Castaing to make an electron micrograph. At that time (~ 1950), one used the replica method to prepare the samples. The result was very striking [Fig. App. 1.11]. I told this story because the replicas are now obsolete; I wonder whether there are still laboratories equipped to get images as beautiful as those of Castaing. The remark is general: don't forget the old-fashioned techniques which may still give good results.

The development of age-hardened alloys is a good example of the complicated connexions between technical advances and scientific progress.

The starting point was the discovery by Wilm. The phenomenon was observed by pure chance and it was not understood. Nevertheless, empirical studies were continued and some of them led to interesting alloys.

The work and the hypothesis of Merica opened a second stage. After him, the experimentalist was guided by a theoretical idea; he can *a priori* judge which alloys are more promising and he understands what he does. The activity in this domain was thus accelerated.

Finally the problem of age-hardening has been solved, at least partly. The atomic structure of the metal was elucidated, and, on the other hand, the theory of plasticity explained the change of mechanical resistance. From the point of view of pure science the situation became much more satisfactory. But the work of the metallurgist was little changed. Empirical trials are still necessary, since the theoretician is not able to give recipes to make a metal with given properties. More and more experiments are carried out: thus inevitably, significant progress becomes less frequent.

L. Bragg used to give to his students a 'golden rule': 'never be afraid to carry out an experiment declared stupid by theoreticians'. Of course, L. Bragg was exaggerating. It is a fact that some discoveries have been unexpected. But, generally speaking, the experimentalist is well advised to follow the advice of the theoreticians, who conversely always need new experimental data.

2 The strength of aged alloys

2.1 ALLOY DESIGNATION

Although precipitation hardening is encountered in a wide range of both ferrous and non-ferrous alloys, it is the large family of *wrought aluminium-based alloys* which has been most widely studied in this context. An International Alloy Designation System (IADS) is employed for these materials, and an outline of this system is given in the Appendix, and references to particular aluminium alloy systems in the text which follows will use this designation.

A wide range of physical and mechanical tests has been used by various workers to detect the strengthening effects which take place on ageing a quenched alloy. The mechanical tests, notably tensile and hardness tests, are described in most standard textbooks on physical metallurgy, and reference should be made to these for details of methods of carrying out the tests and for discussion of the data they provide.

2.2 HARDNESS

Hardness measurements have been frequently used for following the precipitation sequence in alloys, although the results are not convenient for making quantitative tests of theories for explaining the change of strength. Although the magnitude of the hardness number is related both to the yield stress of an alloy as well as to its work-hardening characteristics, the relative change in hardness is a quick and easy method of following the progress of ageing.

2.2.1 The form of age-hardening curves

A single hardening peak would be expected if precipitation took place by simple nucleation and growth of the equilibrium phase from the solid solution. Such changes are found only at low supersaturations and high ageing temperatures. Figure 2.1 is an example of a family of single ageing peaks, taken from the work of Davenport and Bain [1] on the iron-carbon system. At higher supersaturations and lower ageing temperatures the alloy may show two or more age-hardening peaks. An example of a multi-stage process is shown in Fig. 2.2 for an aluminium – 4% copper alloy at a series of temperatures, which is taken from the work of Gayler and Parkhouse [2]. By careful optical metallography these workers also attempted to correlate the changes in hardness with changes in microstructure. Since the initial changes are beyond the resolution of the optical microscope, this work is of limited value.

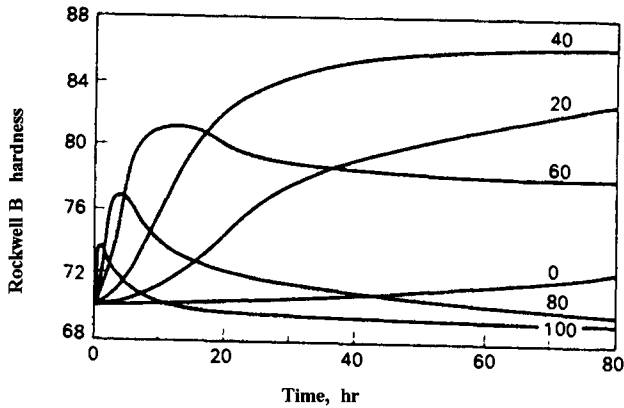


Fig. 2.1 Rate curves for the ageing of an Fe-0.06% C alloy at a series of temperatures (in °C) (from E.S. Davenport and E.C. Bain [1]).

In Fig. 2.1 it is clear that the rate of ageing increases markedly with increasing temperature, whereas the peak hardness achieved is progressively reduced as the ageing temperature rises. This behaviour is in accordance with that expected on thermodynamic grounds: the increasing ageing rate arising from the enhanced rate of diffusion of solute atoms through the matrix as the temperature is raised, and the lowered peak hardness being due (i) to the precipitate forming as larger particles at higher ageing temperatures (equation (1.6)), so that, for a given alloy composition, the particles will be more widely spaced and thus less effective in inhibiting slip, and (ii) to the decrease in volume fraction of the precipitate resulting from the increase in solid solubility with increase in temperature.

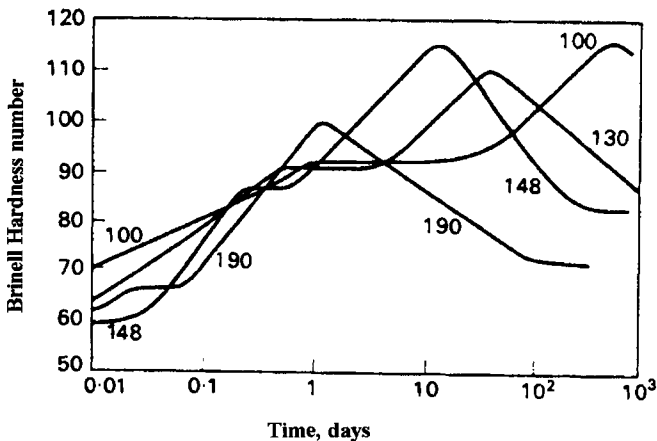


Fig. 2.2 Ageing curves for Al-4% Cu alloy at a series of temperatures (in °C) (from M.L.V. Gayler and R. Parkhouse [2]).

2.2.2. Overageing

At long ageing times the precipitate particles progressively coarsen: the larger particles grow at the expense of the smaller ones, as discussed in Section 1.2.8. The average interparticle spacing thus increases with time and the hardness falls, since the particles will be less effective in holding up dislocations. As previously mentioned, the driving force for this process, known as *overageing*, is the tendency to reduce the total area of internal interfaces, and it will be greater the higher the particle/matrix interfacial energy, σ .

In Chapter 3 we will consider the use of precipitation hardened alloys in elevated temperature applications. Under these conditions, loss of mechanical properties through overageing in service is minimized by selecting alloys with low values of σ .

2.2.3 Use of hardness curves

The hardness test provides a rapid and inexpensive way of establishing the ageing kinetics of a given alloy as a function of ageing temperature. For engineering applications, however, it is important to have information about the strength and ductility of the material which only tensile testing can supply. It is therefore common practice, once the temperature and time of ageing to the 'peak hardness' value has been established, to prepare tensile specimens and to heat-treat them in a similar manner to those used in the hardness tests. These are then tested in tension in order to obtain the required design data.

It is also the tensile data which are most readily interpreted by dislocation models, and it is this aspect that we shall emphasize in the following sections.

2.3 THE TENSILE YIELD STRESS

Fundamental studies of precipitation hardening are normally conducted on single crystal specimens. In these experiments the *critical resolved shear stress* (CRSS) is determined, which represents the resolved shear stress necessary to make dislocation move over macroscopic distances through an array of precipitates. When polycrystalline material is studied, the stress required to initiate plastic flow is often taken as the 0.1% or 0.2% *proof stress* (PS) in an engineering tensile test. The CRSS for single crystals and the PS for polycrystals can be related by the 'Taylor factor' (M), whose value depends on the crystal structure of the matrix materials, and upon the degree of texture present:

$$PS = M \cdot CRSS$$

For the case of random texture, in fcc materials, $M \approx 3.1$ and in bcc materials $M \approx 2.75$. A value of M would have to be computed if a particular material had a specific texture, however.

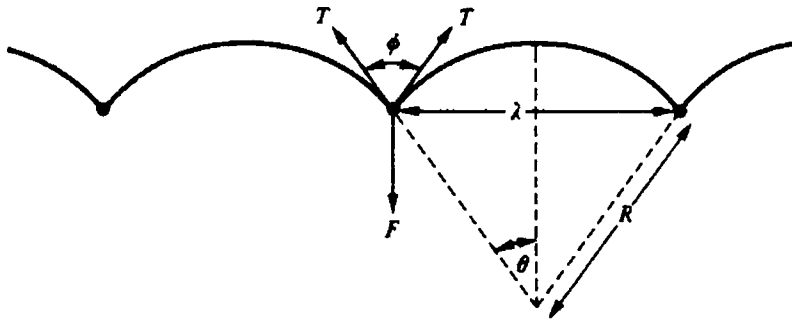


Fig. 2.3 Dislocation held up at array of point obstacles. The bowing angle ϕ is defined as shown.

In the following section we will examine the theoretical derivation of the CRSS in a precipitation-hardened crystal, using the symbol τ for shear stress and τ_c for the CRSS, based on the model illustrated in Fig. 2.3. In the first instance we will treat the precipitates as point obstacles of identical strength lying in the slip plane, and the diagram shows a dislocation interacting with them. For many alloys of practical interest (e.g. aluminum alloys) the concentration of precipitate particles is sufficiently small to enable this 'point obstacle' model to be used.

The glide dislocation bows out between the particles as shown in Fig. 2.3 and, when the included angle ϕ between the two arms of the dislocation reaches a certain critical value, the dislocation breaks away from the obstacle. We shall refer to this value of ϕ as the *breaking angle*, and at this critical point the obstacle strength, F , is related to the dislocation line tension, T , by

$$F = 2T \cos \frac{1}{2}\phi \quad (2.1)$$

When the breaking angle $\phi = 0$, the particle behaves as an impenetrable obstacle, while for values of $\phi > 0$, the particle can be sheared by the glide dislocation, with the required shearing force equal to F . We will consider these two types of interaction separately.

2.3.1 Particle shearing

The shear stress needed to cause the dislocation to break away from the obstacle may be related to the obstacle strength F as follows. The applied shear stress, τ , causes the dislocation of Burgers vector b to bow into an arc of radius of curvature R , where

$$\tau b = T/R \quad (2.2)$$

From Fig. 2.3 it can be seen that

$$2R \sin \theta = \lambda$$

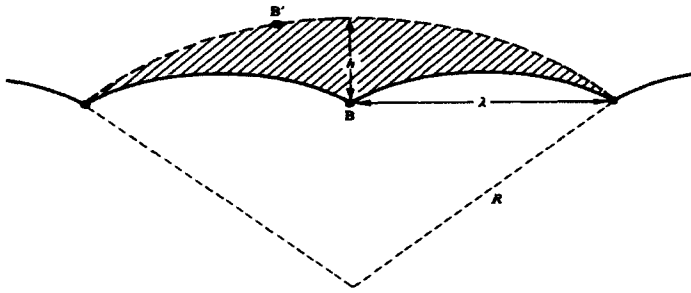


Fig. 2.4 The Friedel process for dislocations interacting with point obstacles.

so

$$\tau b = (2 T \sin \theta) / \lambda$$

But it can also be seen that $\theta = 90^\circ - \frac{1}{2}\phi$, hence from equation (2.1) we have

$$\tau b = F / \lambda$$

i.e.

$$\tau b \lambda = F \quad (2.3)$$

The Friedel relationship In the case of particles that can be sheared by the glide dislocation, it is important to determine how λ , the effective obstacle spacing along the dislocation, depends upon the applied stress. Friedel approaches this by assuming that during the yielding process the dislocation takes up a *steady-state* configuration, namely that each time a dislocation breaks through one obstacle (B, in Fig. 2.4) it meets one, and only one, other obstacle (B' in Fig. 2.4) as it bows out to the configuration compatible with the stress applied (equation (2.2)).

Each time an obstacle is sheared, an area A of the slip plane (shown shaded in Fig. 2.4) is swept out by the dislocation. On average, the value of A is thus inversely proportional to the number of particles per unit area of slip plane (N_s). The so-called 'square lattice spacing' (L) between the obstacles is given by

$$L = N_s^{-1/2}$$

and

$$A = L^2$$

In Fig. 2.4 the area swept out per particle sheared will be given approximately by $h\lambda$, so

$$L^2 = h\lambda \quad (2.4)$$

From the property of a circle (Fig. 2.4),

$$\lambda^2 = 2 h R \quad \text{for } h \ll R \quad (2.5)$$

Eliminating h from equations (2.4) and (2.5), we obtain

$$\lambda^3 = 2 L^2 R = L^2 \lambda / \cos \frac{1}{2}\phi$$

$$\text{i.e. } (\lambda/L)^2 = \sec \frac{1}{2}\phi = 2 T/F \quad (2.6)$$

The effective spacing of the obstacles (λ) thus depends upon the value of the breaking angle, ϕ , and hence upon F . Because the dislocation has some flexibility, the number of obstacles it touches per unit length increases as the particles grow and become stronger, hence the smaller the value of λ . This decrease in λ more than offsets the increase in the 'square lattice' spacing of the particles.

Substituting for λ in equation (2.3) we obtain a value for the yield stress,

$$\tau_c = F^{3/2} / b L (2T)^{1/2} \quad (2.7)$$

Alternatively, this may be expressed in terms of the breaking angle through equation (2.1) as

$$\tau_c = 2 T (\cos \frac{1}{2}\phi)^{3/2} / bL$$

Substitution may be made in equation (2.7) for T and for L . T is often taken as $(\frac{1}{2})\mu b^2$, where μ is the shear modulus, and $L = N_s^{-1/2}$. Furthermore, equations (1.20) and (1.21) give $N_s^{-1/2} = (N_v/2r)^{-1/2} = (3f/2\pi r^2)^{-1/2}$, where f is the volume fraction of particles of radius r , so that

$$L = (3f/2\pi r^2) \quad (2.8)$$

Substitution allows τ_c to be expressed in terms of F , b , μ , f and r .

Effect of random obstacles Equation (2.7) has been derived assuming large breaking angles and a regular square array of particles. Computer calculations by Foreman and Makin for a random array of obstacles showed that this equation is a good approximation, except for strong obstacles where $\phi \rightarrow 0$. These workers therefore suggested the following empirical equation, which applies over the whole range of obstacle strengths,

$$\tau_c = 2 T (0.8 + (1/5) \phi / \pi) (\cos \frac{1}{2}\phi)^{3/2} / bL \quad (2.9)$$

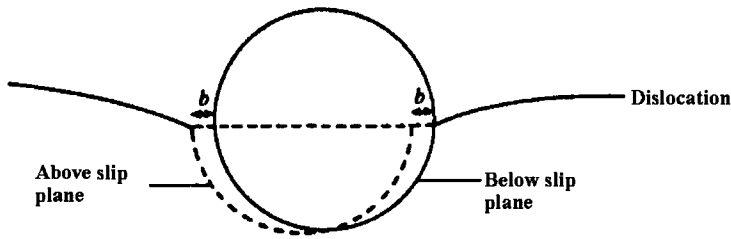


Fig. 2.5 Diagram showing a section of a particle in the slip plane of a screw dislocation. The slipped particle (above the slip plane) is shown as a dotted line.

Precipitate particles can impede the motion of dislocations through a variety of interaction mechanisms. Those for which theories for the value of F (or ϕ) have been developed include:

- (i) *chemical strengthening*, which arises from the energy required to create an additional particle/matrix interface when the particle is sheared by the dislocation;
- (ii) *stacking-fault strengthening*, which occurs when there is a difference between the stacking-fault energy of the particle and that of the matrix when these are either both fcc or hcp in structure;
- (iii) *modulus hardening*, which arises from differences between the elastic moduli of the matrix and particle;
- (iv) *coherency strengthening*, which arises from the elastic coherency strains surrounding a particle that does not fit the matrix exactly;
- (v) *order strengthening*, which is due the additional work required to create an antiphase boundary in the case of dislocations passing through precipitates which have an ordered lattice.

We will consider these mechanisms in turn, and examine the evidence from experiments on real materials which support the theoretical predictions.

Precipitation hardening mechanisms

There is no reason why two or more of the above mechanisms should not operate simultaneously, and this is likely to occur in many real alloy systems. We will consider this situation later, but since in many alloys only **one** of the mechanisms dominate the interaction, we will initially consider the mechanisms individually.

Chemical strengthening A precipitate is sheared when a dislocation passes through it, and a step is produced at the interface. The force on a screw dislocation can be estimated by considering the dislocation of Burgers vector b being inside the particle as shown in Fig. 2.5.

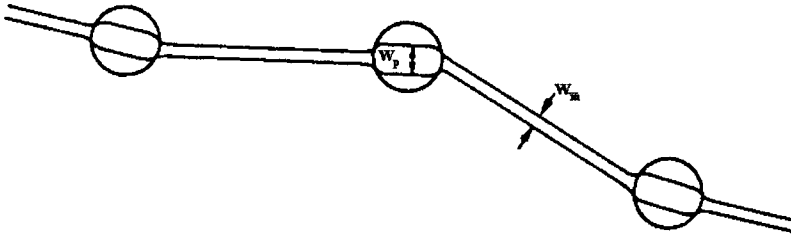


Fig. 2.6 Configuration of a dislocation dissociated into partials of equilibrium ribbon width w_m in the matrix and width w_p within the particles.

When the dislocation advances by δx , the surface area increases by $2 b \delta x$; if the particle exerts a force F on the dislocation, then by applying the principle of virtual work:

$$F = \gamma_s 2 b$$

where γ_s is the specific energy of the precipitate–matrix interface.

Substitution in equation (2.7), if T is taken as $\frac{1}{2} \mu b^2$, and $L = (3 f / 2 \pi r^2)$ (equation (2.8)), gives

$$\tau_c = 2 (3/\pi)^{1/2} \mu (\gamma/\mu b)^{3/2} (b/r) f^{1/2} \quad (2.10)$$

The theory therefore predicts that for a fixed volume fraction, f , the CRSS decreases as the particle size increases, contrary to what is normally observed in age-hardening. It therefore appears that chemical strengthening is not an important mechanism, except perhaps for precipitates of very small size. It is probably safe to conclude that this mechanism does not contribute significantly to the strength of aged alloys.

Stacking-fault strengthening In close-packed lattices it is energetically favourable for a dislocation to dissociate into two partial dislocations. The area between the two partials has a different structure (either hcp or twinned fcc) and is called a stacking fault. The separation between the two partials is governed by the stacking fault energy (sfe) of the material: a material with a low sfe has widely spaced partial dislocations and one with a high sfe has partials close together.

The energy of an extended dislocation is decreased if the energy of the stacking-fault formed between its component partial dislocations is reduced. Hirsch and Kelly were the first to suggest that there should be strong interaction between dislocations and particles in which the stacking-fault energy γ_{sfp} is much lower than that of the matrix, γ_{sfm} .

When a long straight dislocation dissociates into partials with an equilibrium ribbon width w_m , moves into a large particle of lower stacking-fault energy and splits further into a ribbon of width $w_p > w_m$ (Fig. 2.6), the reduction in energy per unit length is

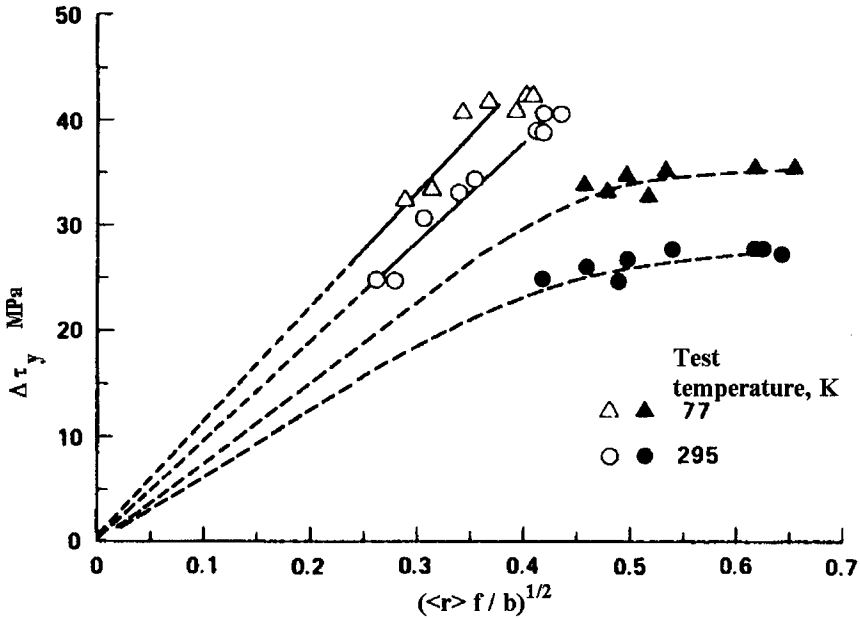


Fig. 2.7 The experimental data of V. Gerold and K. Hartmann [3] on age hardened Al-1.8% Ag single crystals. The open and filled symbols represent data on samples aged at 140 and 225°C, respectively. The dashed curves illustrate expected behaviour.

$$\Delta E = K(\theta) \ln(w_p/w_m)$$

where $K(\theta)$ is a factor dependent upon the angle θ between the dislocation line and the Burgers vector in such a way that it is greater for a screw than an edge.

The maximum force exerted by the split dislocation is given by

$$F = \Delta \gamma \cdot l$$

where $\Delta \gamma = |\gamma_{sfm} - \gamma_{sfp}|$ and l is the length of the chord inside the particle at the critical breaking condition. l will be a function of the average particle radius, $\langle r \rangle$.

By substitution in equation (2.7), this model leads to a variation of τ_c with $\Delta\gamma^{3/2}$ and $(\langle r \rangle f/b)^{1/2}$. In systems such as Al-Ag, the dislocations may be attracted to the GP zones (Fig. 2.6) because the stacking-fault energy of Ag (approximately 20 mJ m⁻²) is less than that for Al (approximately 200 mJ m⁻²). Figure 2.7 shows some experimental data of Gerold and Hartmann [3] on Al-Ag single crystals aged at 140°C (open symbols) and 225°C (filled symbols). The crystals were tested at 77 K and 295 K, and the increase in CRSS due to the presence of the GP zones is shown as a function of $(\langle r \rangle f/b)^{1/2}$. The dashed curves

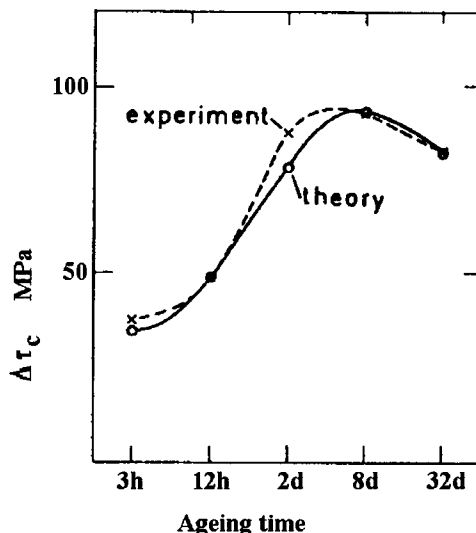


Fig. 2.8 Increase of CRSS due to modulus hardening by GP zones in an AlZnMg alloy as a function of ageing time at 120°C (after A. Melander and P.A. Persson [4]).

schematically illustrate the theoretical behaviour, and good agreement between theory and experiment is apparent.

Modulus hardening Since the energy of a dislocation is a function of the shear modulus of the lattice in which the strain field of the dislocation exists, a change in energy, and hence a force, will be associated with a dislocation interacting with a particle whose shear modulus (μ_{particle}) differs from that of the matrix (μ_{matrix}). There are two interaction regimes, depending on whether the dislocation is inside or outside the particle. The force is proportional to $\Delta\mu$ ($= |\mu_{\text{particle}} - \mu_{\text{matrix}}|$), and is greatest when the dislocation has entered the precipitate, so only this case is relevant for estimating the maximum increment in CRSS due to modulus hardening.

This is a difficult mechanism to deal with theoretically: one attempt has been made by Melander and Persson [4], who derived the following expression for the increment in CRSS arising from this effect:

$$\tau_c = 0.9(\langle r \rangle f)^{1/2} (T/b) (\Delta\mu / \mu_{\text{matrix}})^{3/2} [2b \ln(2\langle r \rangle / f^{1/2} b)]^{-3/2}$$

They tested their theory with experimental data from an Al–2% Zn – 1.4% Mg alloy aged to contain GP zones of various sizes. A major difficulty is that μ_{particle} cannot be measured in the case of these metastable particles, so the authors treated it as an adjustable parameter. A value of μ_{particle} was obtained by fitting the theoretical CRSS to the experimental value obtained for a 12 h ageing time (shown in Fig. 2.8). A value of 4.3×10^{10} Pa was obtained. The value of μ_{matrix}

was assumed to be 2.6×10^{10} Pa, and Fig. 2.8 shows reasonable agreement between theory and experiment.

Coherency strengthening A simplified approach to estimate F arising from coherency strains associated with precipitates may be made as follows.

For a completely spherical inclusion of radius r containing material of atomic volume $(1 + \delta)^3$, where the atomic volume of the matrix is unity, the stress in the precipitate is a uniform pressure

$$p = 3 K (\delta - \varepsilon)$$

where

$$\varepsilon = \frac{3 K \delta}{3K + 2 E/(1 + \nu)}$$

K is the bulk modulus of the precipitate, and E and ν are Young's modulus and Poisson's ratio of the matrix. The strain in the matrix is a shear without a dilation. The shear strain at a distance R from the precipitate is given by $\varepsilon r^3/R^3$. The maximum strain and stress occur at the particle interface, i.e. at $R = r$, and for edge dislocations the appropriate stress is approximately $\mu\varepsilon$. Thus, as a dislocation approaches a particle it will experience a force per unit length of $\mu\varepsilon b$. This force acts effectively over a length of dislocation equal to the particle diameter, hence

$$F \approx 2 \mu \varepsilon r b$$

or

$$F = k \mu \varepsilon r b \quad (2.11)$$

where k is a numerical constant which a more accurate treatment gives as between 3 and 4. Substituting equations (2.11) and (2.8) into (2.7), and putting $T = (\frac{1}{2}) \mu b^2$, we find

$$\tau_c = k^{3/2} \mu \varepsilon^{3/2} (r/b)^{1/2} (3/2\pi)^{1/2} f^{1/2} \quad (2.12)$$

The increment of CRSS due to the presence of the particles is once more predicted to be proportional to $f^{1/2}$ and also to $r^{1/2}$.

Ardell [5] has evaluated the experimental data for a number of Cu alloys in which coherency strengthening is purported to be the predominant strengthening mechanism, and the data are presented in Fig. 2.9 in the form of a graph of values of $\tau_c/\varepsilon^{3/2}$ against $(\langle r \rangle/b)^{1/2}$ in accordance with equation (2.12). The bold line represents the behaviour which is theoretically predicted by more sophisticated theory than that presented above, and the results demonstrate that the theory of coherency hardening is quite inadequate and is incapable of providing us even with reasonable estimates of the strengthening to be expected from this mechanism.

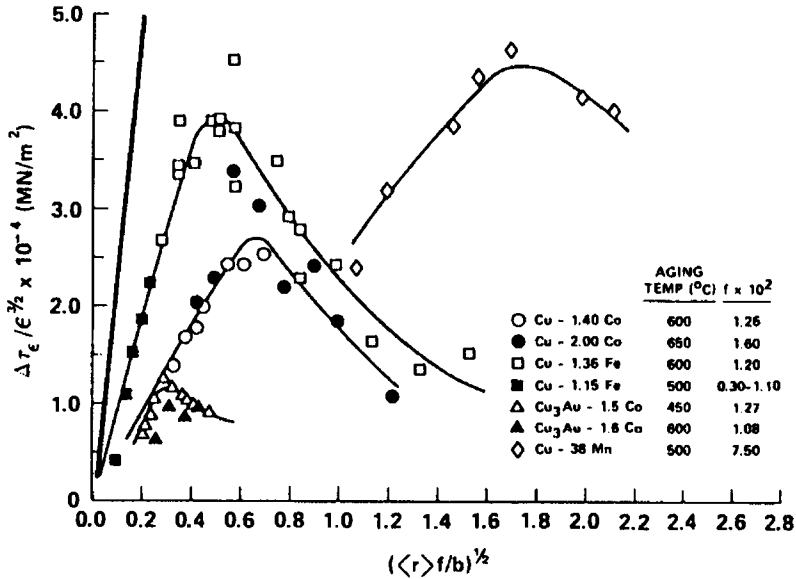


Fig. 2.9 A compilation of precipitation hardening data on a variety of Cu-based alloys. The bold line represents the behaviour theoretically predicted (after A.J. Ardell [5]).

Order strengthening In ordered alloys, the passage of a dislocation creates an antiphase boundary (apb), a region where the order is disrupted. The energy contained in the apb (γ_{apb}) results in an increased resistance to dislocation motion. An estimate of the maximum force exerted by a spherical particle of an ordered phase may be obtained by assuming the dislocation lies along a diameter, in which case

$$F = 2 r \gamma_{\text{apb}} \quad (2.13)$$

From equations (2.7), (2.8) and (2.13) we have

$$\tau_c = \frac{\gamma_{\text{apb}}}{b} \left[\frac{6\gamma_{\text{apb}} f r}{\pi T} \right]^{1/2} \quad (2.14)$$

Equation (2.14) explains the increase of τ_c on ageing in terms of the increase in r for a given volume fraction, and indicates why order hardening is thought to be a very important hardening mechanism in nickel alloys in which large volume fractions of the ordered γ' -phase (Ni_3Al , Ni_3Ti , or $\text{Ni}_3\text{Al,Ti}$) may be present.

A complication which commonly arises in alloys containing ordered precipitates is that the dislocations travel in pairs, as illustrated in Fig. 2.10. The first dislocation creates an antiphase boundary and the second restores the order; these dislocations have the same Burgers vector and so repel each other. The balance of forces between the two dislocations results in

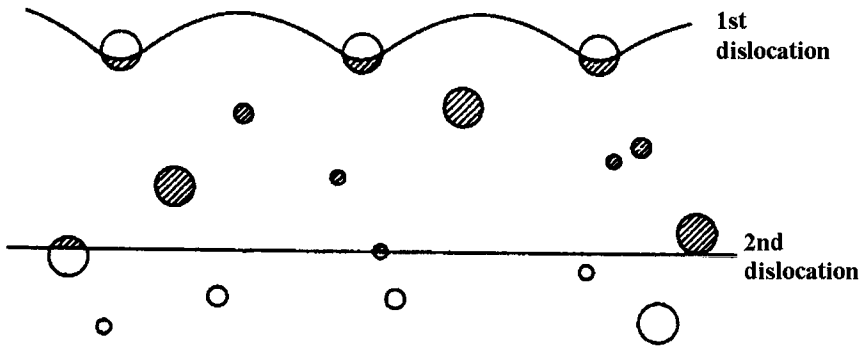


Fig. 2.10 Movement of paired dislocations through a crystal containing precipitates of an ordered phase: shaded areas show the existence of antiphase boundaries within the particles.

$$2\tau_c = \frac{\gamma_{apb}}{b} \left(\frac{d_I}{L_I} - \frac{d_{II}}{L_{II}} \right) \quad (2.15)$$

where d represents the width of the precipitate intersected by the dislocation and L is the spacing between precipitates along the dislocation. I refers to the first dislocation and II to the second dislocation.

The value of d_I corresponds to the diameter of a precipitate at the critical stress, and L_I will be given by the Friedel statistics. If the trailing dislocation is straight, d_{II}/L_{II} will be equal to f , the volume fraction of precipitate particles, giving

$$\tau_c = \frac{\gamma_{apb}}{2b} \left[\left(\frac{3\pi^2 \gamma_{apb} f r}{32 T} \right)^{1/2} - f \right] \quad (2.16)$$

The approximation in the Friedel statistics that the volume fraction of precipitates is small is not applicable to many nickel-based superalloys, where the volume fraction of γ' can exceed 0.7 in some turbine blade alloys. The strengthening behaviour of cubic γ' precipitates in such alloys is not modelled well by the above or similar equations, where there is evidence that the yield stress of nickel-based superalloys *decreases* with increasing precipitate sizes.

Summary The CRSS of alloys strengthened by shearable precipitates has been considered as arising from a number of possible interaction mechanisms, namely chemical hardening, modulus mismatch, stacking-fault energy mismatch, lattice mismatch and order strengthening. If we describe the particular interaction term by Δ , then from Friedel's equations the result is seen to be often of the form

$$\tau_c = A \Delta^{3/2} \left(\frac{rf}{2 T} \right)^{1/2} \quad (2.17)$$

where A is a constant.

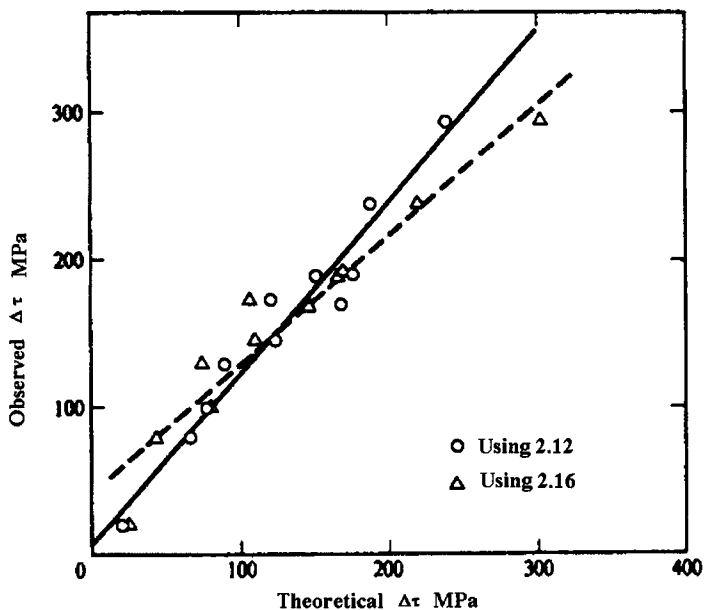


Fig. 2.11 Plots of observed versus theoretical values of $\Delta\tau_c$ during the early stages of ageing of a Co–Ni–Cr superalloy (after M. C. Chaturvedi, D.J. Lloyd and D.W. Chung [6]).

The most difficult problem is to determine the relevant interaction mechanism between particles and dislocations, i.e. to determine the appropriate value of Δ to insert in equation (2.17). For example, Chaturvedi, Lloyd and Chung [6] studied the yielding behaviour of γ' -phase strengthened Co–Ni–Cr superalloys containing various volume fractions of the ordered Ni_3Ti -phase. When these γ' -particles were smaller than 2.8 nm in diameter they were sheared by the glide dislocations. It has been observed that the contribution of modulus strengthening by the γ' -phase in Ni-based alloys is very small, and can be ignored, as is also the case with chemical hardening. Similarly, stacking-fault strengthening is not expected to contribute significantly to the total strength of the alloy, so only coherency and order-hardening mechanisms were considered in the interpretation of their experimental results.

Figure 2.11 shows plots of the observed values and calculated values of the shear-stress increment arising from coherency hardening (equation (2.12)) and from order hardening (equation (2.16)). It can be seen that the experimental data is in reasonable agreement with *each* model. In order to decide which mechanism was operative in controlling the strength, plots were made of $\Delta\tau_c$ versus $r^{1/2}$. If coherency hardening were operative, then equation (2.12) predicts that the graph should be linear and pass through the origin, whereas according to equation (2.16) the straight line should not pass through the origin. In fact the data, when so plotted, did not pass through the origin (figure 2.12), and it was concluded that when, in this alloy system, the precipitate

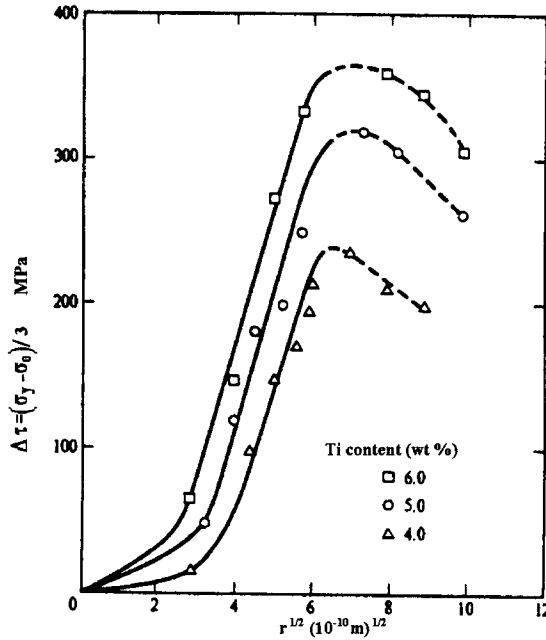


Fig. 2.12 Variation in $\Delta\tau_c$ with $r^{1/2}$ in Co–Ni–Cr superalloy, after Chaturvedi, Lloyd and Chung [6].

particles are sheared by the glide dislocations, the yield stress is governed by the order strengthening mechanism.

In all situations where the models apply to the shearing of precipitates by glide dislocations, we thus observe a parabolic increase in the CRSS with increase in particle size (Fig. 2.13).

We will now consider the alternative interaction.

2.3.2 Impenetrable particles – Orowan looping

As a precipitate grows, it becomes increasingly difficult for it to be sheared by the passage of a dislocation, because of the increase in F with r . However, equation (2.1) indicates that as F increases, the breaking angle ϕ decreases, and eventually becomes *zero*. For larger values of F the dislocation by-passes the particle rather than passing through it (Fig. 2.14), so the force exerted by the particle is balanced by the line tension of the two arms of the dislocation on each side of the particle. The by-passing stress is thus obtained by substituting $F = 2T$ in equation (2.3) giving

$$\tau_c = 2T/b\lambda \quad (2.18)$$

which is the basis of the well-known *Orowan equation*. Appendix 2 to Chapter 2 presents Orowan's first exposition of his theory, published in 1948.

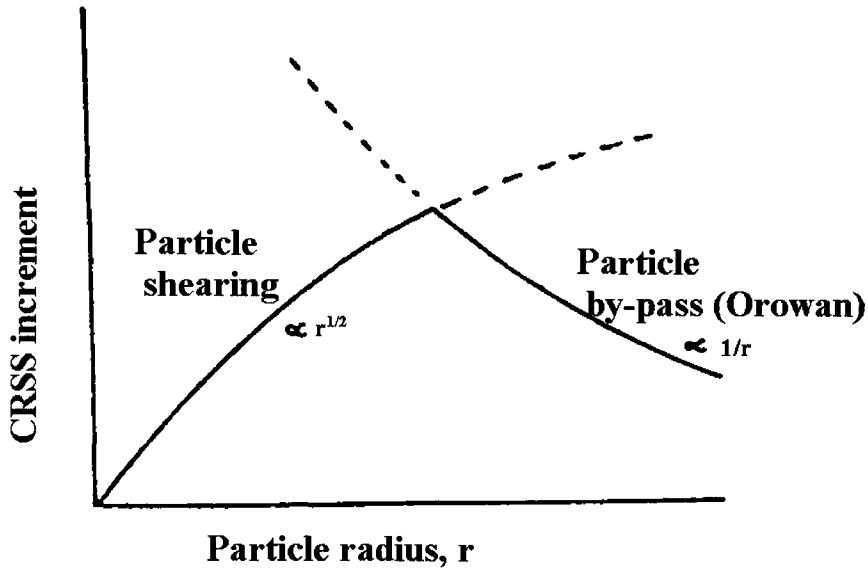


Fig. 2.13 CRSS increment versus particle size for (a) particle shearing and (b) particle by-pass by glide dislocations.

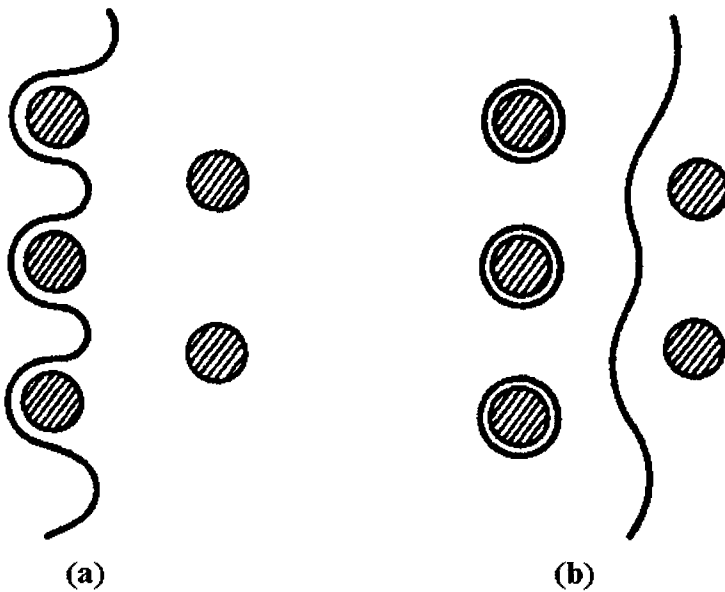


Fig. 2.14 The Orowan process of dislocations: (a) bowing between particles, then (b) by-passing the particles by leaving a dislocation loop surrounding each one.

The Orowan equation may be expressed in its simplest form by putting $T = (1/2)\mu b^2$, giving

$$\tau_c = \mu b/\lambda \quad (2.19)$$

which is often adequate for rough, order-of-magnitude calculations of yield stress increment due to the presence of impenetrable particles of known average spacing. Putting $\lambda = N_s^{-1/2}$, and substituting equations (1.20) and (1.21), the Orowan equation can be expressed as:

$$\tau_c = \left(\frac{3}{2\pi} \right)^{1/2} \cdot \frac{\mu b}{r} \cdot f^{1/2} \quad (2.20)$$

That is, for a given volume fraction of precipitate, the increment of CRSS is inversely proportional to the particle size. This relationship is illustrated in Fig. 2.13. The form of a typical ageing curve, such as Fig. 2.1, in which the hardness initially rises with ageing time, reaches a maximum, and then falls is readily understood in terms of Fig. 2.13: as the particle size increases with time of ageing, the CRSS first rises because the particles become more difficult to shear. Eventually it is easier for the dislocations to loop between the particles rather than to shear them, and this (the Orowan process) becomes easier the larger (and hence further apart) the particles are.

For the purpose of identifying the yield mechanism of a particular alloy as an Orowan process, however, a more exact version of the equation may be derived by taking into account three refinements as follows:

The mean planar interparticle spacing As discussed in Chapter 1, when calculating the interaction between a gliding dislocation and an array of obstacles in its slip plane, the 'mean planar separation' (λ_s) of the particle should be considered.

For a *random* array of obstacles, the effective spacing is taken (equation (1.38)) as $1.23 r (2\pi/3f)^{1/2}$, so the critical flow stress is reduced by a factor of $1/1.23$ (i.e. 0.81) due to this statistical factor. Again, if the size of the particles is not negligible in comparison with their separation, then one must consider the surface-to-surface mean planar separation of the particles, which reduces λ_s by $2r_s$, as shown in equation (1.40).

Dislocation dipole effect There will be an interaction between the two arms of the bulging dislocation on opposite sides of the particle (Fig. 2.14). These dislocation arms have opposite signs and consequently there is an attractive force between them which will reduce the by-pass stress. The arms of the bulging dislocation form a *dislocation dipole* with a width equal to $(2r_s)$, and Ashby calculated that the by-passing stress would be reduced by a factor obtained by writing the logarithmic term in the dislocation line tension equation as $\ln(2r_s/r_0)$, where r_0 is the dislocation inner cut-off ('core') radius, sometimes taken as equal in magnitude to the Burgers vector of the dislocation, b .

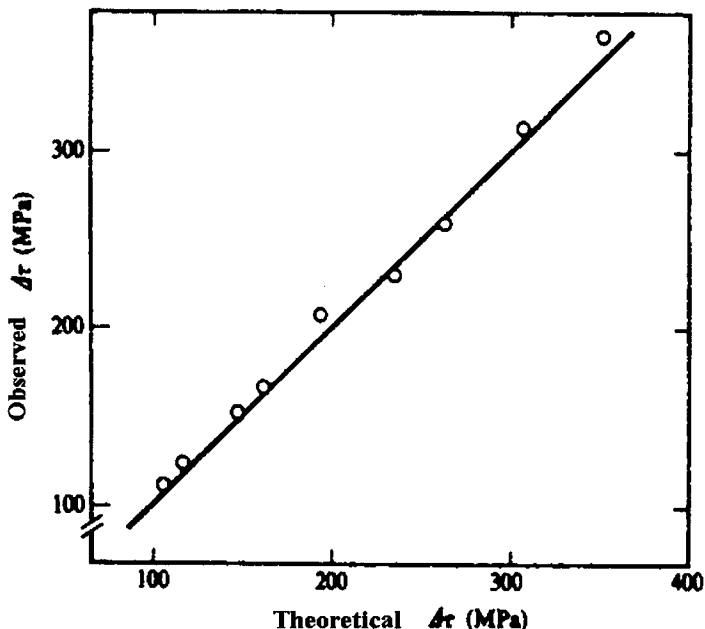


Fig. 2.15 Plot of the observed versus theoretical (calculated using equation (2.20)) values of $\Delta\tau$ during the Orowan process in a Co–Ni–Cr superalloy (after Chaturvedi, Lloyd and Chung [6]).

The line tension of the dislocation The appropriate value of T to be substituted in equation (2.18) is the geometric mean value of T for edges and screws.

The above three refinements may thus be incorporated in equation (2.18) to provide a more exact theoretical estimate of the Orowan stress:

$$\tau_c = \frac{0.81 \mu b}{2\pi (1 - \nu)^{1/2}} \frac{\ln (2r_s/r_0)}{(\lambda_s - 2r_s)} \quad (2.21)$$

The validity of the Orowan equation has been demonstrated in the γ' -strengthened Co–Ni–Cr system referred to earlier, when the alloy is aged so that the particle diameter is greater than 5.6 nm. The 0.2% proof stress (PS) was measured, and the increase in CRSS due to the presence of the particles was obtained by dividing the values of $(PS - PS_0)$ for the polycrystalline specimens by the appropriate Taylor factor (PS_0 is the 0.2% PS in a precipitate-free alloy).

Figure 2.15 shows the plot of the observed flow stress increment due to the presence of the particles compared with that calculated according to equation (2.21). As can be seen, it is a straight line with a slope of 1.004 ± 0.018 , and so it may be concluded that the yield stress can well be accounted for on the basis of the Orowan model.

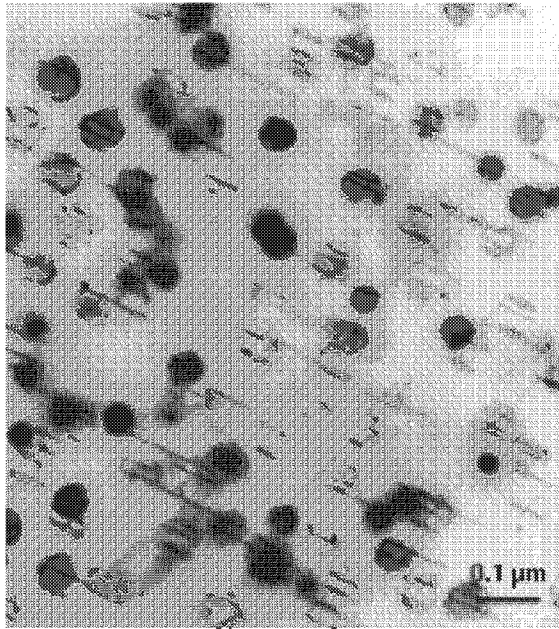


Fig. 2.16 TEM image of Orowan loops surrounding γ' particles in a precipitation-hardened austenitic steel deformed 1% at 650°C.

Direct TEM evidence of the Orowan process is shown in Fig. 2.16, which is a thin foil of an age-hardened austenitic steel containing γ' (ordered Ni_3Ti) precipitates. After 1% plastic deformation at 650°C, loops are seen surrounding the γ' particles with their planes lying in $\{111\}$. The plane of the foil is (110) , and the $(\bar{1}\bar{1}1)$ plane which contains most of the dislocation loops lies nearly parallel to the electron beam, so that the loops appear as lines in the image. On certain precipitates dislocations are lying on two or more slip planes: the loops on different planes appear to interact with each other.

A simplified version of equation (2.21) may be used to estimate the increment of tensile yield stress ($\Delta\sigma$) provided by a dispersion of impenetrable particles of mean spacing λ in a matrix of shear modulus μ and Burgers vector b :

$$\Delta\sigma = 0.8 \mu b M / \lambda$$

where M is the Taylor factor for the structure. Figure 2.17 illustrates the change in $\Delta\sigma$ as a function of λ for the case of a nickel matrix ($M = 3$) where it may be seen that an interparticle spacing of 100 nm produces a strength increase of several hundred MPa at room temperature. However, a relatively small increase in λ will result in a relatively large drop in the magnitude of $\Delta\sigma$, emphasizing the importance of *fine interparticle spacing* for such strengthening phases.

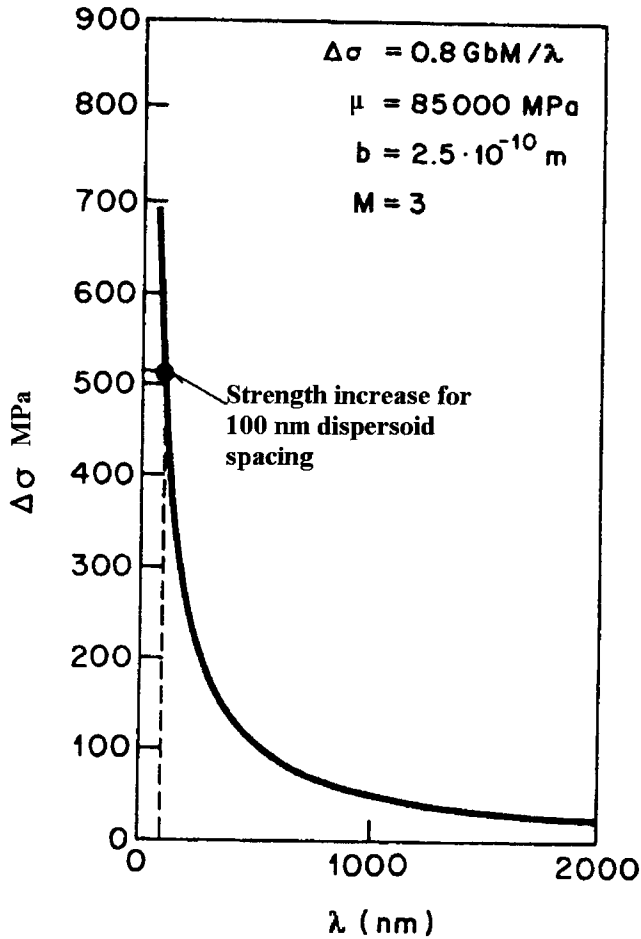


Fig. 2.17 The Orowan stress as a function of the interparticle spacing for a nickel matrix.

2.3.3 Additive strengthening effects

Single precipitate populations

The CRSS (τ_c) of an alloy that is strengthened by the presence of precipitates ($\Delta\tau$) has a component (τ_M) that is due to the intrinsic lattice resistance of the matrix phase and to the strengthening effect of atoms in solid solution. There is ample experimental evidence to justify the linear summation of the two strengths, and this is usually employed:

$$\tau_c = \tau_M + \Delta\tau \quad (2.22)$$

Linear superposition appears to be valid in the case of a structure consisting of a few strong obstacles among a large number of weak obstacles. It follows from

equation (2.3) if the balance of forces is considered. If the forces exerted on the dislocations by the two populations of obstacles are F_1 and F_2 , respectively, then equation (2.3) may be written

$$\tau b \lambda = F_1 + nF_2$$

where n is the ratio of the two obstacle spacings (i.e. the number of population 2 obstacles between population 1 obstacles). Equation (2.22) follows directly from this.

Multiple precipitate populations

Many alloys are strengthened by the presence of more than one type of precipitate population: the alloy may have two distinct phases present (e.g. Fig. 1.32), or the heat-treatment of the alloy may result in the precipitates having two distinct sizes.

There have been several methods of summing the effects of such multiple populations: the most important are (a) linear superposition

$$\Delta\tau = \Delta\tau_1 + \Delta\tau_2 \quad (2.23)$$

and (b) Pythagorean addition. This is derived by considering that the increment in the CRSS is inversely proportional to the average spacing, λ , between obstacles:

$$\Delta\tau \propto 1/\lambda$$

Taking λ to be inversely proportional to the square root of the number of obstacles per unit area, N_s ,

$$\lambda \propto N_s^{-1/2}$$

In the case of two independent populations of obstacles, the average obstacle spacing would be given by

$$\lambda \propto (N_{s1} + N_{s2})^{-1/2}$$

When the increment in the yield stress is considered in terms of the individual incremental increases in the yield stress the result is

$$\Delta\tau^2 = \Delta\tau_1^2 + \Delta\tau_2^2 \quad (2.24)$$

Computer simulations suggest that linear superposition equation (2.23) is valid in the case of a few strong precipitates in the midst of a large number of weak precipitates, and that in other cases Pythagorean superposition (equation (2.24)) gives a good fit.

The effect of grain boundary strengthening

In a pure metal or solid solution, the effect of grain boundaries upon the tensile yield stress ($\Delta\sigma$) may be expressed by the Hall–Petch equation:

$$\Delta\sigma = k_y d^{-1/2} \quad (2.25a)$$

where d is the grain size and k_y the slope of the Petch plot of yield stress versus $d^{-1/2}$.

The grain-size dependence of yield, up to a few per cent of plastic deformation, can be explained by the fact that for a given amount of plastic deformation, ε , the dislocation density generated by the grain boundaries, ρ_b , decreases with increase in grain size. The relationship between dislocation density and yield stress can be derived by means of a simple dimensional analysis.

The yield stress, τ , must depend on an elastic constant, μ , and the magnitude of the Burgers vector in the material, b . The dimensionless combination of these terms may be written

$$\tau/\mu = \alpha (b^2 \rho)^m \quad (2.26)$$

where both sides are pure numbers, and α and m are constants. The applied stress exerts a force τb per unit length of the gliding dislocation; its motion is opposed by the nearest dislocations. The force of interaction between any two dislocations is proportional to b^2 , thus τ is proportional to b , which implies that $m = \frac{1}{2}$ in equation (2.26). In general a frictional stress and a long-range internal stress will also oppose the motion of a glide dislocation, and if these are represented by a term τ_0 , equation (2.26) becomes

$$\tau = \tau_0 + \alpha \mu b \rho^{1/2} \quad (2.27)$$

which is known as the ‘forest hardening’ equation. A detailed calculation provides a numerical value for the dimensionless constant α of between 0.15 and 0.5.

The Hall–Petch equation can now be derived by considering the average distance of travel of each dislocation at the strain at yield (ε). If the average distance of travel, x , is proportional (or equal) to the grain size, d , we can write

$$\varepsilon = b p_b x = C b p_b d$$

where C is a proportionality constant. Thus

$$p_b = \varepsilon / C b d$$

By substitution in the ‘forest equation’ (2.27) we obtain

$$\tau = \tau_0 + \alpha \mu (\varepsilon b / C)^{1/2} d^{-1/2}$$

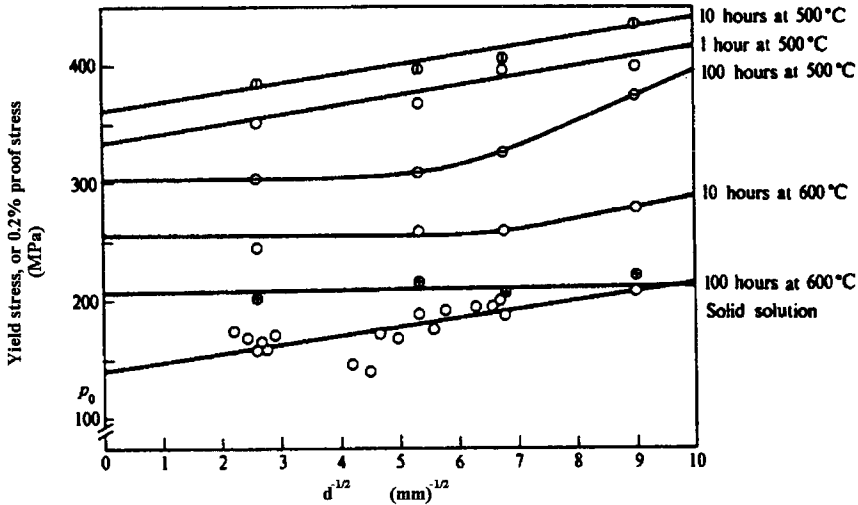


Fig. 2.18 Grain-size dependence of the yield stress of an Fe-1 wt% Cu alloy in different precipitation conditions (after E. Hornbogen and G. Staniek [7]).

which corresponds to the Hall-Petch relation with $k_y = \alpha\mu(\epsilon b/C)^{1/2}$, i.e.

$$\tau = \tau_0 + k_y d^{-1/2} \quad (2.25b)$$

Equation (2.25b) applies to alloys in which only grain boundaries act as dislocation sources at yield, and where the motion of dislocations is not impeded between the grain boundaries. When second-phase particles are present, a precipitate may, in some circumstances, act as a source of matrix dislocations at the same stress level as that at which dislocations are produced by grain boundaries. Finely dispersed coherent particles are unlikely to act in this way, but coarser, incoherent particles may generate such dislocations (e.g. as Orowan loops) whose density ρ_p depends upon the volume fraction of such particles present. Furthermore, if non-coherent particles are able to produce dislocations, the path of travel of the dislocations in the interior of the grain, x , is increasingly impeded by dislocations which have originated in the same way from other neighbouring particles.

Hornbogen and Staniek [7] examined the superposition of precipitation and grain-boundary hardening in an α -Fe - Cu alloy heat-treated to produce a range of grain sizes and with different dispersions of fcc Cu particles. Their data are shown in Fig. 2.18, where it can be seen that the single-phase solid solution obeys a Hall-Petch equation. In the early stages of ageing, when small coherent particles are present (ageing up to 10 hours at 500°C), the data again obey equation (2.25b), indicating that the grain-boundary and particle strengthening processes are additive. However, on ageing for longer times or at higher temperatures, the yield stress becomes independent of grain size (although some

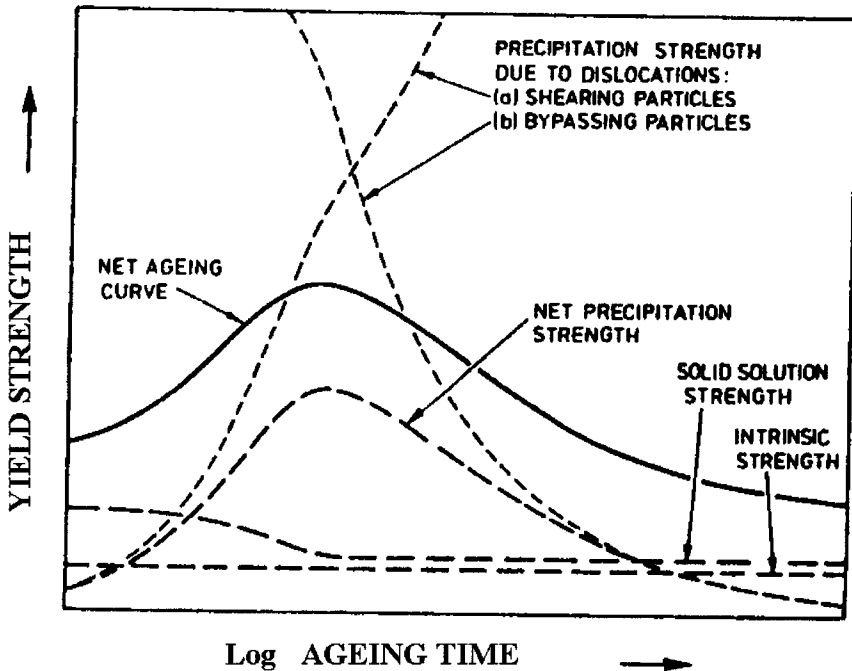


Fig. 2.19 Schematic diagram of the relative contributions to the ageing curve of the intrinsic strength, solid solution strengthening and precipitation hardening due to shearable and non-shearable precipitates, after Shercliff and Ashby [8].

dependence is apparent when the grain size is fine, after intermediate ageing treatments). Although there is only a limited number of experimental points on each graph, Hornbogen and Staniek suggest that the data of Fig. 2.18 illustrates that the Hall–Petch relationship is valid in the range of grain sizes in which the average free path of travel, x , is not smaller than the smallest grain size. As x becomes smaller, however, an independence of yield stress from the grain size is observed for all grain sizes larger than x .

2.4 PROCESS MODELLING OF AGE-HARDENING

We have seen in Chapter 1 that the thermodynamics and kinetics of solution heat-treatment, precipitation, coarsening and reversion are understood, and in this chapter we have discussed the interactions between dislocations and precipitates. H.R. Shercliff and M.F. Ashby [8] have made a first attempt to develop an overall *process model* for age-hardening for aluminium alloys which is general in nature and thus, in principle, adaptable to any age-hardening system.

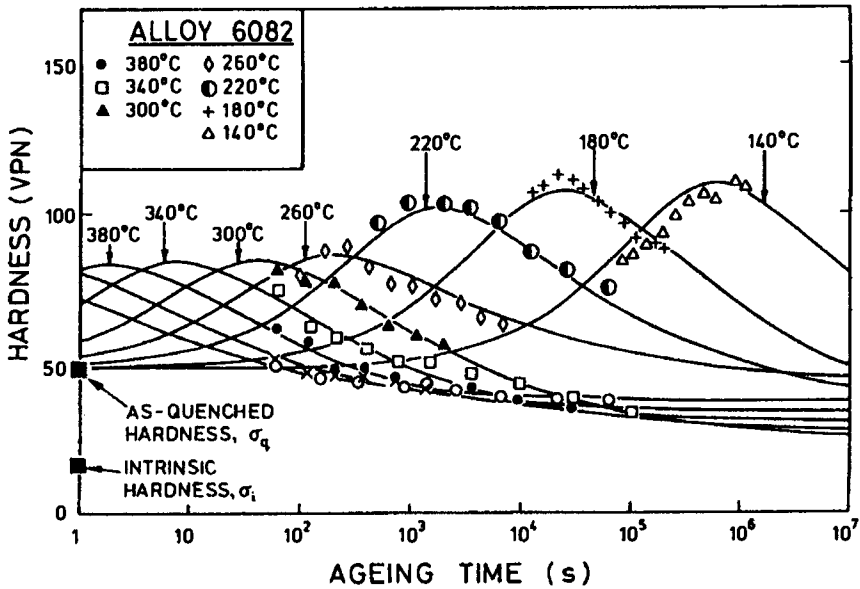


Fig. 2.20 Data for alloy 6082 compared with the model for seven ageing temperatures (after Shercliff and Ashby [8]).

A process model is a mathematical relation between the process variables (alloy composition, and the heat-treatment temperature and time) and the alloy strength or hardness, based on physical principles. A successful model allows optimization of both process and properties and better quality control in manufacturing.

Shercliff and Ashby [8] selected the Al – Mg – Si alloy 6082, which is of nominal composition (weight %): Al – 0.9 Mg – 1.0 Si, with 0.7 Mn which forms dispersoids to control grain growth. The alloy exhibits a single ageing peak, and Fig. 2.19 illustrates how the observed ageing curve may be regarded as the combination of the intrinsic strength of the matrix material σ_i , solid solution hardening $\Delta\sigma_{ss}$ (which will decrease as precipitation occurs) and the effective precipitation strengthening due to shearable and non-shearable particles $\Delta\sigma_{ppt}$ (which is that requiring the least shear stress, with a smooth transition between the two). The yield stress as a function of time ($\sigma(t)$) was given by the sum:

$$\sigma(t) = \sigma_i + \Delta\sigma_{ss} + \Delta\sigma_{ppt}$$

Their components of the physical model included:

- (i) the growth in volume fraction of precipitate and decrease in solute concentration with time during the initial stages of precipitation;
- (ii) the dependence of the equilibrium volume fraction of precipitate on ageing temperature;

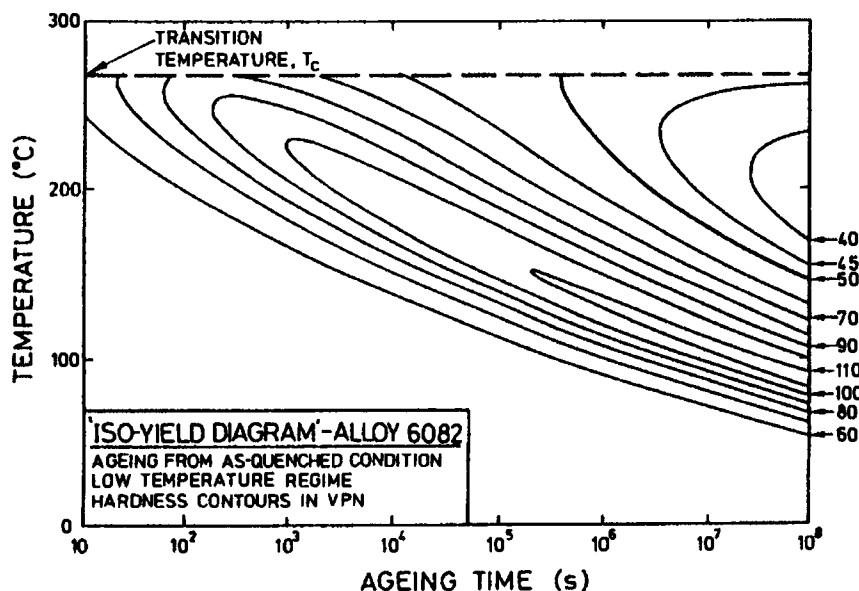


Fig. 2.21 The 'iso-yield diagram' for ageing from the as-quenched condition: temperature against $\log_{10}$ ageing time, with contours of constant hardness for alloy 6082. T_c is the metastable solvus for the low temperature precipitate (after Shercliff and Ashby [8]).

- (iii) precipitate coarsening by competitive growth;
- (iv) the contribution of solid solution to the strength;
- (v) the contribution of shearable precipitates to the strength;
- (vi) the contribution of non-shearable precipitates to the strength.

Many of the constants required in the model cannot be predicted with precision from first principles, and so the model was calibrated by using data from actual ageing curves. Figure 2.20 shows the theoretical curves (continuous lines) and the data (symbols) for alloy 6082 which are available in the literature. The model fits the experimental data to within 10%.

Conventional ageing curves are not always the best way to present information about age-hardening. The process model, being a set of mathematical relationships between the process variables, allows other presentations to be explored, and Fig. 2.21 illustrates one such possibility. The axes are ageing temperature and time; the contours are lines of constant hardness (although the yield stress could be used equally well). This $T - t - H$ (temperature - time - hardness) diagram is the equivalent, for age-hardening alloys, of the $T - T - T$ curves for transformation of steels, but with the 'degree of transformation' expressed by hardness.

Such curves have value in selecting process variables and in assessing the trade-off between temperature and time to achieve a given hardness. The process

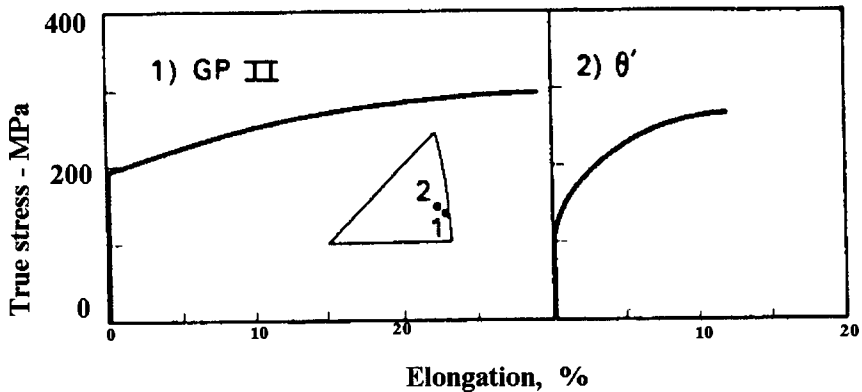


Fig. 2.22 Tensile stress-strain curves of Al – 3.7 wt% Cu crystals aged to contain (i) GP II zones and (ii) precipitates of θ' -phase. The orientations of the tensile axes are shown in the stereographic triangles (after R.J. Price and A. Kelly [9]).

model thus appears to be viable, and to be capable of development for a number of industrial applications, for example to predict the structure and strength of weld heat-affected zones.

2.5 WORK-HARDENING BEHAVIOUR OF PRECIPITATION-HARDENED ALLOYS

As in the case of the yield stress, it is convenient to classify the work-hardening behaviour of precipitation-hardened alloys into

- (i) that involving shear of the particles by the glide dislocations, and
- (ii) that involving dislocations looping between the particles.

In the first case the tensile stress-strain curves of single crystals will have essentially the same shape and characteristics as the curves of crystals of pure metals and solid solution alloys, although of course the level of the flow stress will be raised by the dislocation/particle interactions we have discussed earlier. Most alloys containing zones of coherent precipitates belong to this category, and their work-hardening behaviour can thus be treated theoretically as identical to that of single-phase crystals.

Alloys containing *incoherent* particles belong to the second category, and these alloys will have single crystal stress-strain curves quite different from those of pure single crystals or of single-phase solutions, as shown in Fig. 2.22 from the work of Price and Kelly [9]. This difference arises because the incoherent particles are not plastically deformed when the matrix is sheared, so that dislocations have to be stored (e.g. as Orowan loops) to compensate for the deformation gradient in the material.

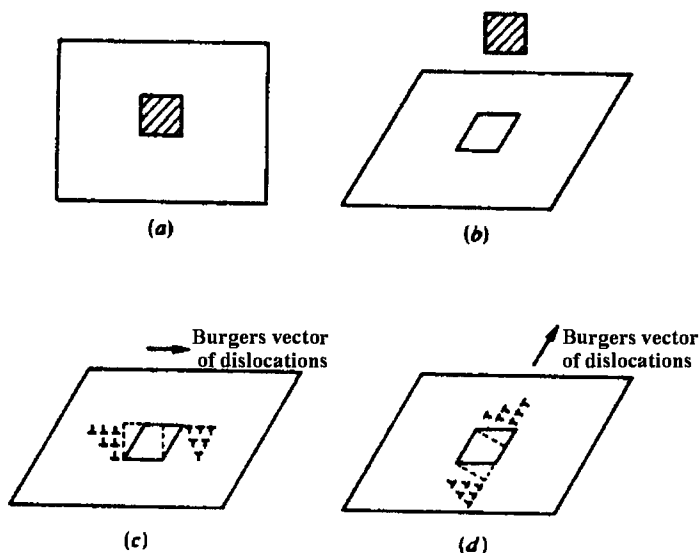


Fig. 2.23 (a) An element of crystal containing a hard inclusion of a second phase, prior to deformation; (b) the inclusion has been removed and the crystal sheared uniformly; (c) and (d) show the hole restored to its original shape by the emission of shear dislocation loops and prismatic dislocation loops, respectively.

As seen in Fig. 2.22, the alloy containing only GP zones has a high yield stress, but its subsequent deformation is similar to that of unaged specimens: the rate of work-hardening is low. The alloy containing θ' has a lower yield stress but a very high initial rate of work-hardening which is due to the high density of dislocation loops (ρ_g) left at precipitate particles. ρ_g are referred to as the '*geometrically necessary*' dislocations, whose density is much greater than the '*statistically stored*' dislocations (ρ_s) which accumulate during the plastic deformation of single-phase materials and also in those containing particles and zones which are sheared by dislocations.

2.5.1 The density of geometrically necessary dislocations (ρ_g)

The order of magnitude of ρ_g in a precipitation-hardened crystal as a function of the applied shear strain (γ) may be estimated as follows.

Figure 2.23a illustrates a cube-shaped cell of matrix containing a single cube-shaped precipitate particle of edge length $2r$. In order to estimate the density of geometrically necessary dislocations we deform the cell by a shear strain γ (Fig. 2.23b) after removing the particle. In order to replace the particle, the hole must be deformed back into its original shape and Figs 2.23c and d illustrate two simple ways of effecting this by the introduction of dislocations.

On the left-hand side of the particle in Fig. 2.23, the amount of material which must be removed by dislocation glide is

$$\Delta V = (1/2) V_p \gamma \quad (2.28)$$

where V_p is the volume of the particle. This volume has to be injected into the matrix, for example as 'interstitial' prismatic loops (Fig. 2.23d) whose Burgers vector is the same as that of the original applied strain. On the right-hand side of the particle, an equal volume has to be *supplied* from the matrix, which is equivalent to generating 'vacancy'-type prismatic loops (Fig. 2.23d). An array of Orowan glide loops (Fig. 2.23c) would have the same geometrical effect. If there are n loops per particle, and their average area is, say, $4r^2$, then

$$\Delta V = n b 4r^2 \quad (2.29)$$

Substituting in equation (2.28), putting $V_p = 8r^3$ we obtain

$$n = r \gamma / b \quad (2.30)$$

The length of dislocation per particle is of the order $8rn$, i.e. $8 r^2 \gamma / b$. So if in the alloy there is a volume fraction f of particles, then the number of particles per unit volume will be $f/8r^3$, so the length per unit volume of geometrically necessary dislocations (ρ_g) will be given by

$$\rho_g = \frac{\gamma f}{b r} \quad (2.31)$$

Substitution in equation (2.27) will give an expression for the flow stress as a function of ρ_g :

$$\tau = \tau_0 + \alpha \mu (fb \gamma / r)^{1/2} \quad (2.32)$$

This equation may also be written in terms of the true stress σ and true strain ϵ , as

$$\sigma = \sigma_0 + \alpha' \mu (fb \epsilon / d)^{1/2} \quad (2.33)$$

where α' is another constant and d is the average particle diameter.

The work-hardening rate may simply be obtained by differentiation of equation (2.33) with respect to strain, giving

$$\frac{d\sigma}{d\epsilon} = \alpha'' \frac{\mu b^{1/2}}{\epsilon^{1/2}} \left(\frac{f}{d} \right)^{1/2} \quad (2.34)$$

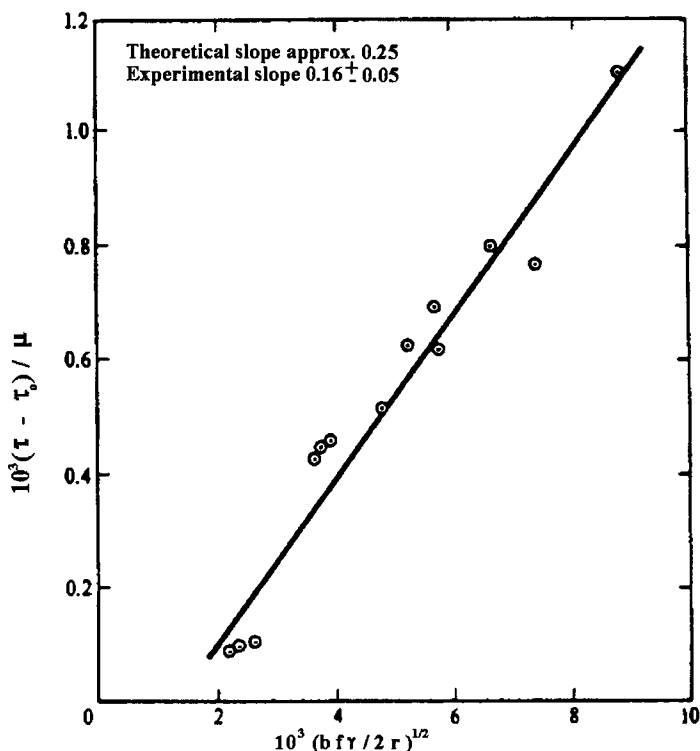


Fig. 2.24 The increment of flow stress after 10% shear strain in Cu + BeO crystals deformed at 77 K, plotted according to equation (2.32) (after M.F. Ashby [10]).

2.5.2 Analysis of work-hardening data

In order to test equation (2.32), analysis of stress–strain curves obtained from single crystals containing non-deforming particles has been carried out. For example, Fig. 2.24 illustrates the work hardening observed in copper crystals containing dispersions of BeO deformed at 77 K, with the data plotted to test the above model. (The Cu – BeO alloys were produced by internal oxidation, see Section 1.1.1.) The data refer to flow stresses corresponding to a strain of 10%, and reasonable linearity is obtained in the plot. The discrepancy between the experimental slope and the theoretical slope arises from the neglect of the other contributions to the flow stress from internal long-range stresses.

An appropriate practical system to which the above model might be applied is that of quenched and tempered steels containing spheroidized carbide particles in a ferrite matrix. Anand and Gurland [11] have examined the strain-hardening behaviour of two high-carbon steels heat-treated to produce microstructures in the form of relatively uniform dispersions of spheroidal cementite particles lying within the ferrite grains, the grain size being greater than the interparticle spacing.

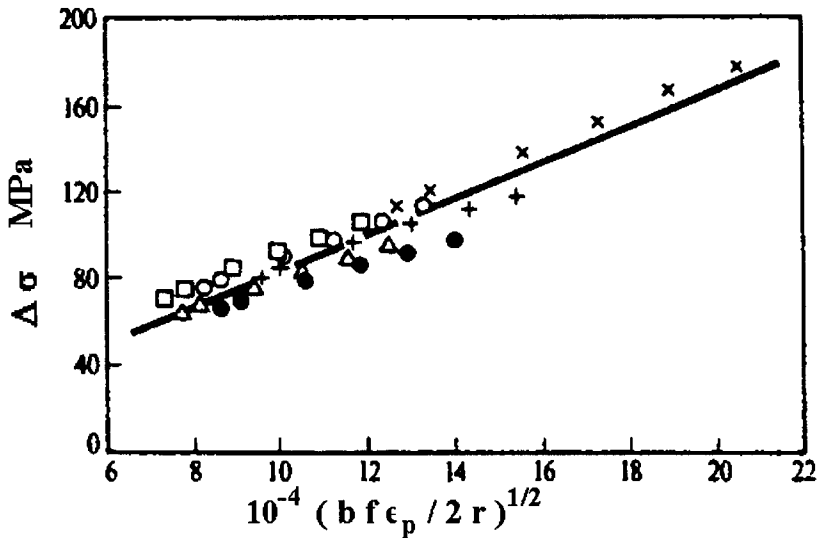


Fig. 2.25 The tensile flow stress increment ($\Delta\sigma$) versus the parameter $(bf\epsilon_p/2r)^{1/2}$ for a number of spheroidized steels at plastic strains of up to 3.5% (after L. Anand and J. Gurland [11]).

Figure 2.25 shows their data plotted according to equation (2.33) showing the tensile flow stress increment ($\Delta\sigma$) for tensile strains (ϵ) of up to 3.5%. The hardening behaviour is broadly consistent with the model, although at plastic strains above 3.5%, $\Delta\sigma$ does not continue to increase parabolically with strain: interactions between the dislocations do not permit a continued increase in the density of geometrically necessary dislocations. *Dynamic recovery* takes place, leading to a deviation from the strain hardening predicted by the model – which overestimates the degree of strain hardening.

2.6 THE ACHIEVEMENT OF STRONG PRECIPITATION-HARDENED ALLOYS

Having surveyed the theories of precipitation hardening, and considered the extent to which the strength of particle-hardened alloys may be accounted for on the basis of these theories, we will conclude this chapter by reviewing how, in the light of our understanding, precipitation-hardened materials of high strength may be developed.

As we have seen, if the precipitates are deformed when the alloy yields, the intrinsic properties of the precipitate are important. For non-deformable precipitates, the alloy strength is independent of the properties of the precipitate phase itself, but is strongly dependent upon its size and spacing. In both cases, the larger the volume fraction of precipitate, the higher the strength.

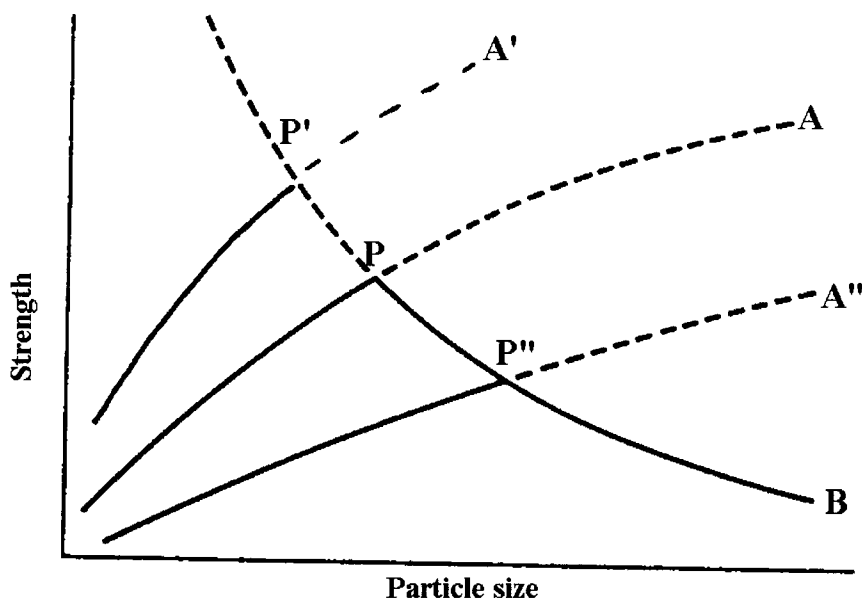


Fig. 2.26 Strength versus particle size in precipitation-hardened material. P represents peak strength, where the curve for deformable particles (A) intersects that for undeformable particles (B), the volume fraction being the same for A and B. Increasing the strength of the precipitate phase to A' increases the peak strength to P', which occurs at a smaller particle size. If inadequate nucleation decreases the volume fraction (giving curve A''), the peak strength is lowered (to P'') and occurs at a larger particle size.

In Fig. 2.26, curve A is for deformable precipitates, and shows the strength varying with particle size. Curve B shows the variation in strength with particle size for non-deforming particles with the same volume fraction as before. The transition from one type of behaviour to the other occurs at P, and this gives the maximum strength (P) developed in the system.

An increase in volume fraction of precipitate raises both curves A and B to give a high peak strength, so this is clearly one desirable objective. Unfortunately, there is a fundamental difficulty in achieving high volume fractions of a precipitate of high binding energy in alloys where the precipitation is a consequence of the temperature dependence of the solute solubility. This is because a high binding energy implies a small solubility, simply from the application of Hume–Rothery's rules. This effect may be overcome by the use of ternary alloys (e.g. the 6000 series Al alloys in which the two solutes, Mg and Si form the Mg_2Si phase of high binding energy, rather than by combining with the matrix element), or, in steels, through the allotropic transformation in the matrix which can be used as an alternative means of producing a high solute supersaturation in the low-temperature (ferrite) phase (see *maraging steels*, below). Other approaches to achieving high volume fractions of precipitate

include rapid solidification processing (RSP) such as spray-forming, which can achieve high supersaturations, and powder metallurgical techniques such as mechanical alloying (MA), which produces alloys whose constitution is essentially independent of any phase diagram.

An increase in the intrinsic strength of the precipitate will raise only curve A (to A'), and hence will increase the peak strength of the alloy to P', but this will occur at a smaller particle size. To exploit this effect, therefore, it is necessary to have sufficiently prolific nucleation of the particles under these circumstances to ensure that the full volume fraction is precipitated by the time the average particle size reaches the critical value for peak strength. If the nucleation rate is inadequate, curve A will be lowered to, say, A'', which leads to a reduction in peak strength to P'', and the displacement of the peak to larger particle sizes.

2.6.1 Thermomechanical treatment (TMT)

A combination of ageing and deformation treatments may be applied in order to introduce a high density of lattice defects into the matrix which in their turn will act as heterogeneous nucleation sites. This will encourage a high nucleation rate during the precipitation heat treatment, and thus lead to the development of microstructures giving enhanced properties.

2.6.2 Combined strengthening processes

The most dramatic increases in strength in precipitation hardened alloys usually owe their properties to a combination of several hardening mechanisms. Thus the matrix may itself be hardened by residual solutes in solid solution, it may possess a very fine grain size, which will contribute to Hall–Petch hardening, and a high dislocation density may also be present. Precipitation-hardened steels provide excellent examples of these approaches:

Marageing steels

Marageing steels are a special class of low-carbon ultrahigh-strength steels which derive their strength not from carbon but from precipitation of intermetallic compounds. The commonly available marageing steels contain less than 0.03 wt% C, with 17–19 wt% Ni, 8–12 wt% Co, 3–5 wt% Mo and Ti varying between 0.2 and 1.5 wt%, which produces an increasing volume fraction of intermetallic phase and hence higher strength after ageing.

Initial studies of this process were carried out with Fe – 18 wt% Ni alloys of very low carbon content. The solid solution was found to be martensitic on air-cooling from 860°C, having a lath-like structure with a very fine grain size and a high density of mobile dislocations, which provides high ductility. A feature of this martensite is the wide thermal hysteresis between the austenite/martensite transformation on cooling and heating. The Fe – 18 wt% Ni alloy has an M_s on cooling of around 280°C, but on heating, the temperature of re-transformation to austenite is about 600°C, which allows high temperature (~ 480°C) ageing of the martensitic matrix to be carried out without reconversion to austenite.

The conventional heat treatment cycle is simple, consisting of solution treatment at 820°C followed by air cooling to room temperature. The martensitic transformation occurs throughout thick sections on air-cooling, and is usually carried out on rough-machined forged stock. The component can at this point be machined to its finished dimensions, since it is relatively soft, and only extremely small dimensional changes occur during the final age-hardening treatment at 480–500°C. Strengthening during ageing results from a very fine precipitation of non-coherent Ni_3Mo and Ni_3Ti , or $\text{Ni}_3(\text{Mo}, \text{Ti})$, which nucleate preferentially at dislocations and at lath boundaries left by martensitic transformation. The high density of dislocations prior to ageing produced by the lattice-invariant shear of the martensitic transformation thus ensures prolific nucleation sites for the dispersed phase.

Thermomechanical treatment (TMT) of steels

In the case of steels, deformation may be introduced either before, during, or after the phase transformation. An example of the first type is High Temperature TMT such as *controlled rolling* which may be applied to structural steels. *Isoforming* is deformation applied *during* the transformation of austenite, and *warm working* is an example of deformation *after* the transformation is complete. We will take controlled rolling as an example of TMT.

The major strengthening mechanisms in controlled rolling of, for example, high strength, low alloy (HSLA) steels are grain refinement, precipitation hardening by the lattice-defect enhanced precipitation of the microalloyed carbides, solid solution strengthening from Mn, Si and uncombined N, and the dislocation substructure.

The relative contribution of any individual mechanism will vary with the change in steel composition and rolling practice.

Finally, it must be emphasized that, in any material, the enhancement of strength which precipitation may bring about is of no value if other engineering properties are not acceptable. In particular the material must possess adequate resistance to fracture for its envisaged application, and it must also be capable of being fabricated into the desired form. In the next chapter we will consider the fracture behaviour of precipitation-hardened alloys.

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APPENDIX 1 TO CHAPTER 2

[An extended excerpt from Jeffries' and Archer's classical paper is given. The authors first consider the concept of hardening in pure metals, and in solid solutions, which has been omitted here, as has also their final section on the hardening of steel. A number of optical micrographs present in the original paper have also been omitted as their quality for reproduction was poor and as they were not essential for following the arguments presented.]

THE SLIP INTERFERENCE THEORY OF THE HARDENING OF METALS

ZAY JEFFRIES AND R.S. ARCHER

(*Chemical and Metallurgical Engineering* **24** (1921), 1057)

Aging of Duralumin

A very important incident in the development of the theory of hardening by hard substances highly dispersed is the study of the light aluminum alloys of the 'duralumin' type, by Merica, Waltenberg and Scott.* The following is typical of the composition of these alloys: Copper, 4.0 per cent; Magnesium, 0.5; manganese, 0.5; aluminum (commercially pure), remainder.

These alloys in the rolled or forged condition can be very materially hardened by a heat-treatment consisting of quenching from about 500 deg. C., followed by aging for several days at ordinary temperatures. The hardness and strength immediately after quenching are about the same as in the 'annealed' condition, but on aging increase spontaneously about 40 per cent.

Merica, Waltenberg and Scott base their explanation of this hardening on the variation of the solubility of the compound CuAl_2 in aluminum with temperature. In Fig. App 2.1 is reproduced a portion of the equilibrium diagram of the aluminium-copper system, showing the solubility curve of CuAl_2 in aluminum. It will be noted that the solubility of the compound decreases from about 4 per cent (copper) at 500 deg. C. to probably less than 1 per cent at room temperature. A piece of duralumin examined microscopically immediately after quenching shows a 'solid solution' structure – that is, a structure free from visible particles of CuAl_2 . After the alloy has aged so that the hardness and strength have greatly increased, the structure is apparently unchanged. There is reason to believe, however, that there has occurred during aging a precipitation of CuAl_2 in the form of particles of submicroscopic size, to correspond to the diminished solubility of the compound at the lower temperatures. Quoting from the paper referred to:

'Upon heating a specimen of duralumin that has been quenched from 500 deg. C., but not aged, an evolution of heat occurs at from 250 to 275 deg. C. . .

'No thermal change takes place upon cooling the same specimen, provided it has not been heated beyond 520 deg. C. Upon reheating the same slowly cooled

* 'Heat-Treatment of Duralumin', P.D. Merica, R.G. Waltenberg and H. Scott, *Bull. A.I.M.E* June 1919, p. 913 (*Chem. & Met. Eng.*, vol. 21, p. 551 *et seq.*

specimen, no evolution of heat is found corresponding to that upon the first heating. Without doubt, therefore, a chemical reaction takes place at 250 to 275 deg. C. upon heating the quenched sample with evolution of heat – i.e., indicating the formation of stable from unstable phases, not a transformation of stable to other stable phases, the two systems being in equilibrium during the transformation. Such a transformation must take place with heat absorption upon raising the temperature.

‘A specimen that has been quenched and aged at from 100 deg. to 150 deg. C. to secure maximum hardness shows little or no evolution of heat upon heating. Whatever may be the chemical reaction that is indicated on the first heating curve of a quenched specimen, it has taken place during the aging of the specimen, during which the hardening also occurs; stable phases have formed and the subsequent heating curve shows no arrest corresponding to that of the quenched specimen.

‘This chemical reaction can hardly be other than the precipitation of CuAl_2 from its supersaturated solution in aluminum although direct visual evidence bearing on this question is also lacking . . .

‘Although it cannot be directly proved that the thermal arrest at about 250 deg. C. noticed upon heating a quenched unaged specimen of duralumin is due to the precipitation of CuAl_2 , no evidence directly contradicts this assumption, which is in entire accord with our knowledge of the equilibrium within the alloy, and this arrest cannot be assigned to any other phase change.

‘It has been shown by many previous investigations and confirmed by the authors that aluminum undergoes no transformation in the solid state between ordinary temperatures and its melting point. No other phase changes could occur in the main mass of duralumin, the grains of solid solution, therefore, except those of solution or precipitation of FeAl_3 , of the X compound, of CuAl_2 , of Mg_4Al_3 , or of Mg_2Si , within the grains. Aluminum, which contains the same amounts of FeAl_3 and of the X compound as does duralumin, is not altered by heat-treatment as is duralumin, nor does it show a reverse heat effect upon heating as does the latter. This heat effect must, therefore, be due to the precipitation either of CuAl_2 , Mg_4Al_3 or Mg_2Si . But the alloys containing only magnesium in amounts up to 3 per cent also do not harden upon aging. There remains only the precipitation of CuAl_2 with which to explain this heat effect.

‘The theory outlined above of the mechanism of the hardening of duralumin during aging most readily explains the interesting fact discovered by Mr. Blough and confirmed by the authors that the amount of hardening during aging increases as the temperature of quenching increases. At higher quenching temperatures more and more CuAl_2 is dissolved in solid solution. After quenching, the CuAl_2 is in excess of its solubility; the higher the quenching temperature the greater is the excess, and this is precipitated during aging. The hardening is in proportion to the amount of the highly dispersed CuAl_2 formed.

‘If this theory is accepted for the moment, it is interesting to consider the effect of degree of dispersion upon hardness in the case of a solid solution, in this case of CuAl_2 in aluminum. Duralumin immediately after quenching is generally

softer than it is in the annealed condition. Thus alloy C-11, in the form of sheet, gave the following values of hardness:

	<i>Annealed at 300°C</i>	<i>Quenched, but not aged</i>	<i>Quenched, and aged 8 days</i>
Scleroscope hardness, magnifying hammer	17	16	35

'This is probably due to the fact that a specimen, as ordinarily cooled after annealing, still contains some dissolved CuAl_2 in excess of its solubility; the material hardens slightly during cooling. Specimens cooled extremely slowly give a scleroscope hardness of from 7 to 10, much lower than that of the quenched, unaged ones.

'Upon aging a quenched specimen at 200 deg. C., for example, the hardness first increases to a maximum and afterwards decreases. During that aging there has been first a formation of fine nuclei of CuAl_2 , followed by coalescence of these particles into ones of larger size. There is, therefore, a certain average size of particle of CuAl_2 for which the hardness of the material is a maximum; atomic dispersion of the solute, CuAl_2 , is not the dispersion that produces the maximum hardness, but some intermediate one between it and that at which the particles become visible by ordinary means.'

An important point in this theory of the hardening of duralumin is the conclusion that there is a certain average size of particle which produces maximum hardness, any size either larger or smaller causing less hardness. This is opposed to the generally held idea that a given amount of a substance added to a metal produces the greatest possible hardening effect when it is in solution – that is, when it is in the highest possible state of dispersion. The degree of dispersion conducive to maximum hardness may conveniently be designated by the term 'critical dispersion'. Dispersions finer than this may be called 'sub-critical', and those coarser 'super-critical'.

It is also important to note the magnitude of the hardening effect in duralumin. It is possible to increase the hardness of pure aluminum approximately tenfold by producing within grains of an aluminum-copper solid solution a critical dispersion of hard particles. This hardening cannot be referred to any of the mystic causes sometimes assigned in the case of steel. The only conceivable explanation is that it is due to the presence of a vast number of very small, hard particles dispersed throughout the grains of aluminum (which probably retain a little copper in true solid solution). These conclusions regarding the hardening of duralumin naturally suggest seeking analogies in other alloy systems. Merica and his co-authors called attention to the case of steel, pointing out a similarity to duralumin in that the decomposition of a solid solution into particles of sub-microscopic size (ferrite and cementite) is involved and also in that some steels (very high-carbon steels and high-speed steels) shown on tempering an increase in hardness, followed by the usual decrease. The theory advanced for the

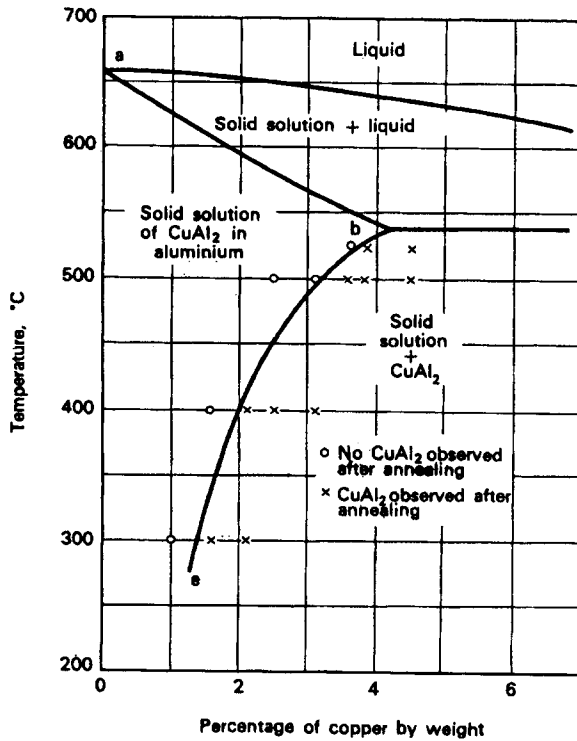


Fig. App. 2.1 Portion of the equilibrium diagram of the Cu–Al series showing the solubility curve of CuAl_2 in aluminium, according to Merica, Waltenberg and Scott.

hardening of duralumin did not include any explanation of the mechanism by which the particles of CuAl_2 cause hardness. Some conception of this mechanism is necessary to any extension of the theory.

The present authors have attempted to analyze the mechanism of this hardening effect, so that the necessary conditions could be defined for all cases. Such analysis involves the explanation, first, of how one constituent dispersed within another produces such great hardness, and second, of why there is a critical dispersion or size of particle which produces maximum hardness.

Easy slip in magnetized plates

In duralumin we are dealing with an aggregate composed of a ductile, relatively weak matrix—aluminum—greatly strengthened by the presence of small hard disconnected particles of CuAl_2 . The strength attained in the duralumin must be derived from the inherent cohesion of the continuous aluminum matrix. There is no conceivable way in which a few per cent by volume of a strong constituent in disconnected particles could impart a new element of cohesion of the magnitude actually obtained. Their action must consist in rendering more effective the

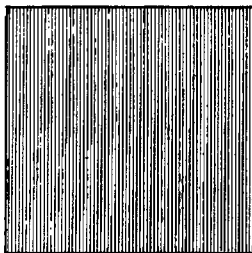


Fig. App. 2.2 Set of planes of easy slip in a crystal having no internal slip interference.

cohesion latent in the aluminum. The logical inference is that this is accomplished by the elimination of extended planes of weakness—that is, by slip interference.

In Fig. App 2.2 is represented a section through a crystal, the fine parallel lines representing a set of planes of easy slip. It may assist in obtaining a concrete conception of the mechanical conditions to consider a stack of iron plates placed in a strong magnetic field at right angles to their surfaces. It would be very difficult to pull these plates apart by a straight tensile effort, but comparatively easy to separate them by sliding them over each other. This stack of plates presents a rather close analogy to the conditions obtaining in a ductile crystal, especially in that the forces which hold the atoms of a crystal together are probably electromagnetic in character.

In separating the magnetized plates by a straight pull it is necessary to overcome the entire magnetic attraction at once, whereas in sliding the plates the magnetic force is overcome only at the edges and then gradually by small increments. The principal resistance due to sliding is the frictional resistance of the plates due to the pressure. In order completely to separate the portions of a crystal on opposite sides of a plane of slip by a direct tensile pull it would be necessary to break simultaneously all the atomic bonds on the plane. This would require a force equal to the absolute cohesion of the metal. The two portions can move with respect to each other on the slip plane without permanent rupture of any considerable proportion of the atomic bonds. Of course, extended slip separates the atoms from their old neighbors, but cohesion bonds are established with their new neighbors. The separation of the magnetized plates by a direct pull results in a 'brittle' fracture with a minimum work of rupture. When the plates are separated by sliding, the work of rupture is increased by an amount equal to the frictional losses. Similarly when a crystal is fractured in a brittle manner the work of rupture is markedly increased due to the friction at planes of slip.

Small hard particles act as keys

Figure App 2.3 shows an ideal section through a crystal in which it is supposed that a hard, strong substance is dispersed in the form of substantially spherical particles. These particles are supposed to be about equal in size, but of course the

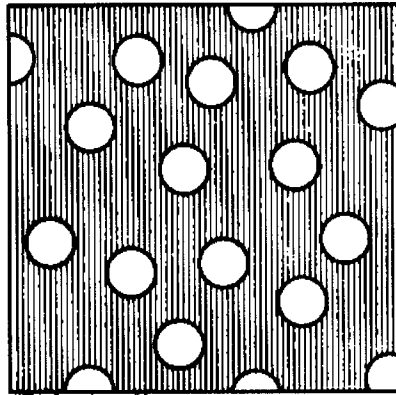


Fig. App. 2.3 Slip planes 'keyed' by hard particles.

circles cut by the plane of the section should be of different sizes according to the distance of this plane from the centers of the spheres. It will be noted that there is not a single plane of easy slip which does not encounter at least one of these hard particles. Under the action of an external load tending to produce slip along these planes, the hard particles must act as keys, mechanically obstructing any motion along the planes as a whole. The result is increased elastic limit, hardness and strength.

Now suppose all the hard particles to be gathered into a single large particle, as shown in Fig. App 2.4. Although the size and strength of the 'key' are greatly increased, there are many planes of weakness left without any reinforcement. The single large particle does not interfere with slip on these planes. It is easily seen

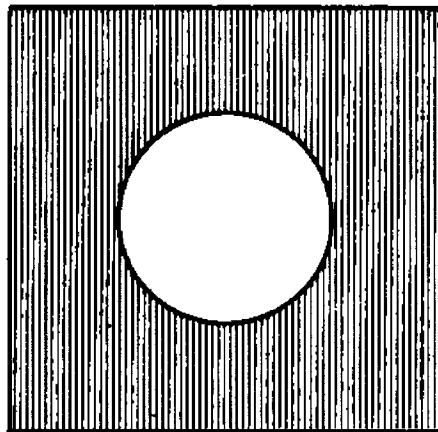


Fig. App. 2.4 Hard constituent gathered into a single large particle, leaving many planes without reinforcement.

that the strengthening effect of the hard particles increases with their *number* and not with their size. Even in case all possible planes of slip are keyed at some points, more effective slip interference must result from diminishing the size and increasing the number of the particles. We thus have the rule that the hardening effect of a given amount of hard dispersed substance is greater the smaller the particles. This rule must reach a limit as the particles approach atomic dimensions. We do not know how small a crystal may be and still possess the characteristic hardness and strength of the substance.

Let us consider the strength of true solid solutions or atomic dispersions from the point of view of the slip interference theory. Planes of weakness are present just as in the pure metal or solvent. At intervals the succession of atoms of solvent is interrupted by an atom of the solute. At each point where an atom of the solute occurs there is an increased bond, or, we might say, pressure, on the plane of potential slip, due to the greater force of attraction between the unlike atoms. This constitutes in effect a key, very much as do the crystalline particles of CuAl_2 in aluminum. The planes are seemingly 'spot welded' together by the atoms of the solute.

The experimental evidence indicates that the formation of crystalline nuclei of CuAl_2 in duralumin, from the solid solution of copper in aluminum, causes an increase in hardness and strength. If the key action of the atomically dispersed copper were equivalent to that of the crystalline particles of CuAl_2 , we should not expect this to be the case, since the hardness should increase as the number of keys increases. It is quite natural to suppose that the attractive forces of the copper and aluminum atoms for each other are not brought fully into play until the atoms are arranged in their most stable arrangement – that of the compound. The key formed by the little group of aluminum atoms surrounding the copper atoms in the solid solution is more easily sheared through than is a particle of crystalline CuAl_2 . The critical dispersion for maximum hardness should therefore consist of the smallest possible particles having the characteristic crystallinity of the compound. If we classify particles according to their diameters in terms of atoms, the following probably represents approximately the sizes involved:

1 atom diameter	solid solution	somewhat hard
10 atom diameters	critical dispersion	hardest
1,000 atom diameters	smallest particles	somewhat soft

Number of keys in a duralumin crystal

Let us take for an example the hardness changes in a duralumin alloy containing 4.5 per cent Cu. This alloy would contain 2 atoms per cent of copper or 8.33 weight per cent of CuAl_2 assuming that all of the copper is present as that compound. This would be at most 5.4 per cent CuAl_2 by volume: actually it is less than that amount, inasmuch as some of the copper will always be in solution. When the worked alloy is heated to a temperature at which all of the copper is in solution and then quenched, the hardness will be about 80 Brinell. The copper

is probably in atomic dispersion. On aging, the hardness can be increased to about 140 Brinell as the CuAl_2 precipitates and the particles reach critical size. By very slow cooling from high temperatures the hardness can then be reduced to about 50 Brinell. Such a hardness is produced only after the CuAl_2 particles have reached relatively large sizes.

Tensile strength varies with the hardness. The plasticity is the greatest in the freshly quenched condition and the least when the CuAl_2 particles are present in critical size. The high plasticity accompanying atomic dispersion of copper would be expected, because the areas of potential slip planes will depend on grain size only. The interference to slip is greater than in pure aluminum; it resides in the nature of greater pressure between the two slip surfaces, but the planes are relatively smooth.

An average sized grain of duralumin would have about 2,000,000,000 atoms of copper on each potential slip plane. Although we do not know exactly the percentage of the copper precipitating as CuAl_2 during aging, we can for convenience consider it as 75 per cent of that present. Assuming now that the CuAl_2 particles have reached an average size of one ten-millionth inch diameter there will still be 500,000,000 copper atoms on each of the above planes and in addition each plane will be keyed with the relatively hard CuAl_2 particles at 35,000,000 to 40,000,000 places. This condition corresponds nearly to critical dispersion. By the time the CuAl_2 particles have reached an average diameter of a hundred-thousandth of an inch, each of the above planes will be keyed in about 3,500 to 4,000 places; if the diameter were further increased one hundred times only about three planes out of eight would be keyed at all!

The presence of a given amount of hard substance in large particles produces excess slip interference locally, but leaves portions of the metal in a weak condition. Cohesion of the mass as a whole is therefore gained by subdivision of the key material into many particles distributed as uniformly as possible. The weak links of the chain of slip planes are thus strengthened at the expense of the strong ones. Plastic deformation in such a material produces an intricate system of slip planes determined by the number and size of the particles. In many places the slip cannot follow the easy crystallographic planes, but is forced to take place in unfavorable directions. The quantity of dispersed substance may be so great that the resistance to slip becomes equal to or greater than the direct rupturing strength of the atomic bonds, and brittleness accompanied by relatively great hardness will result.

In a high-carbon steel in which the cementite has been coarsely spheroidized an intricate system of slip planes or flow surfaces must be produced in this structure by plastic deformation: the slip avoids the cementite and the surfaces of slip are rough. The appearance is intricate as opposed to the systems of regular slip planes in nearly pure metals. As compared to critical size, the particles of cementite are very coarse. Each of the larger particles of cementite would have to be subdivided into about 1,000,000,000 particles to reach critical dispersion. The intricacy of the system of slip planes would correspondingly increase.

[N.B. The above paragraph was accompanied by some optical micrographs which have not been reproduced in the present text. – J.W.M.]

Adhesion between constituents

While the CuAl_2 and Fe_3C particles probably have rather strong adhesion for the aluminum and iron respectively, such adhesion need not obtain in order to produce hardening. Copper oxide often present in copper should have very little adhesion for the metal, but when it is present in the form of globules within the copper grains it produces a strengthening effect. Antisell* states that 0.2 per cent (1.8 per cent Cu_2O) oxygen increases the tensile strength of annealed copper over 10 per cent.

Thorium dioxide probably has little adhesion for tungsten, but when 1.5 per cent by volume is present as particles within the grains the tensile strength is increased in the temperature regions within which the metal is ductile. The presence of the thorium also has the effect of increasing the tensile strength more for a given amount of working below the annealing temperature than in pure tungsten. The cases of Cu_2O in copper and ThO_2 in tungsten are important, because they give positive evidence of the strengthening effect of these mixtures in which a weakening might be expected due to decrease of the effective cross-sections of the metals.

In all of the cases mentioned above the hardness has been produced by dispersing *hard* particles within relatively large grains of metal. We should not expect *soft* particles to produce hardening, because the 'keys' of soft substance would shear and thus assist rather than oppose slip. The term *soft* is used here in the relative sense only.

Similarity of Manganese Steel and Duralumin

The explanations of the hardening of duralumin and of hardening by grain refinement are so simple and logical that we should examine the phenomena of the hardening of steel from the same viewpoint. The fact that iron is capable of existing in at least two crystalline forms makes it difficult to differentiate between cause and effect and to appraise the true significance of the 'critical' changes. The case of duralumin might be equally difficult to understand if hardening by heat-treatment were accompanied by allotropic and visible structural changes. Hardening of duralumin does not involve an allotropic change, twinning, or even a refinement of grain.

Its study teaches us that a soft crystal of aluminum can be hardened by dissolving copper in it: that the aluminum copper solid solution can be further hardened by the precipitation of some of the copper into minute particles of CuAl_2 ; that maximum hardness is produced when the precipitated compound is present in particles of a small (critical) size, certainly much less in diameter than 1,000 atoms; that when the particles become larger than the critical size the hardness decreases as the particle size increases. The percentage increase in the hardness of duralumin by proper alloying and heat-treatment is comparable to that obtained in iron by alloying with carbon and heat-treatment.

* 'Relationship of Physical and Chemical Properties of Copper', Frank L. Antisell, *A.I.M.E., Bull.* 157.

If manganese steel containing from 1.0 to 1.5 per cent C and 13 per cent Mn is quenched from a high temperature, the structure existing at the high temperature is preserved at room temperature. The result is an aggregate of grains of austenite, which is in this case gamma iron with the carbon and manganese dissolved in it. The hardness is about 160 Brinell, a very substantial increase over pure alpha iron (75). The austenitic structure is stable unless the manganese steel is cold-worked or heated. The hardness increases on tempering and may reach about 500 Brinell after suitable heat-treatment. As the steel hardens it becomes magnetic, but not in proportion to the increase in hardness – in fact most of the hardening occurs before the steel has reached 2 per cent specific magnetism (iron equals 100 per cent), and before there is much visible change in the structure of the austenite.*

If a piece of this steel be heated to 1,100 deg. C. and cooled slowly, a network of carbide, presumably a mixture or solution of cementite and manganese carbide, is formed. Austenite at temperatures around 400 to 600 deg. C. is supersaturated with carbon, since the carbides precipitate around 500 deg. C. into particles large enough to be seen with a microscope. Since the dispersion of the carbon is atomic in the austenite, it does not offer maximum interference to slip. The austenitic manganese steel is therefore relatively soft and ductile: the carbon dispersion is sub-critical. The formation and precipitation of carbides into particles of visible size show that every size between molecular and visible must have obtained at some previous stage. The critical size or dispersion must have been reached prior to the appearance of the visible particles. Carbide of iron is magnetic and hence slight magnetism might appear on annealing, accompanied by a considerable increase in hardness, without producing a transformation of any appreciable amount of austenite into alpha iron. This latter transformation proceeds slowly, however, and its effect is superimposed on that resulting from the carbide precipitation.

Transformation into alpha iron produces an entire change in structure and a decided increase in magnetism, but the hardness may increase or decrease. Extended exposure to temperatures around 650 deg. C. eventually produces softening.

It is thus seen that in the early stages of hardening manganese steel the changes are strikingly similar to those found in the hardening of duralumin.

* *Metals and the Common Alloys*, S.L. Hoyt, pp.347–349.

APPENDIX 2 TO CHAPTER 2

THEORY OF DISLOCATION BOWING

[There follows an excerpt from Orowan's original exposition of his theory, which was presented during discussion at an Institute of Metals Symposium on Internal Stresses in Metals and Alloys, 1948.]

THEORY OF YIELD WITHOUT PARTICLE SHEAR

E. OROWAN

(*Inst. Metals Symposium on Internal Stresses* (1948), 451)

What is now the cause of the decrease of the yield stress after the critical particle size has been exceeded? Several special processes may lead to such an effect (e.g. the breaking away of the precipitate from the matrix lattice); in what follows, however, it should be pointed out that a decrease of the yield stress is bound to occur quite generally for a simple reason.

If the total volume of the precipitate is assumed to be constant, large distance between the particles means large particle size and hence the presence of extensive regions of negative internal stress around the particles which act as obstacles to advancing dislocation lines. Driven by the externally applied stress, a dislocation line will be held back at the regions of high negative stress around the precipitated particles, and it will bulge forward into the gaps between the particles (Fig. App 2.5).

As the applied stress increases, the line bulges more strongly (line B), and finally detaches itself from the obstacles, leaving them encircled by small closed dislocation lines (line C). If new dislocation lines come along, each repeats this process and leaves a new dislocation loop around the obstacles; the external stress needed to drive a dislocation line over the obstacles is not much higher for the second than for the first line if the number of encircled areas per unit of volume is not too high. The shear stress at an obstacle rises with the number of the encircling loops, and finally it is bound to overcome the resistance of the local internal stress, either by enforcing glide, or by tearing away the precipitated

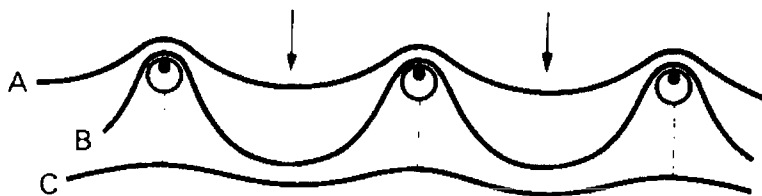


Fig. App. 2.5 Schematic representation of dislocations passing between widely spaced precipitates.

particle. Consequently, the yield stress of the material will be approximately equal to the shear stress necessary for forcing a dislocation line through a row of obstacles of spacing d . The calculation of this stress is quite similar to that of the air pressure necessary to blow a bubble from a capillary tube dipping into a liquid; the spacing of the obstacles corresponds to the diameter of the tube, the energy per unit length of the dislocation line to the surface energy of the liquid: the problem, however, is not three- but two-dimensional. The highest shear stress occurs when the bulge of the dislocation line is approximately a semicircle of radius $d/2$. From the formulae given by Nabarro at the bottom of *p.* 248 of his paper, it is easy to see that the shear stress needed for bending a dislocation line into a curve of radius r is Ga/r , where G is the shear modulus and a the interatomic distance in the glide direction. The yield stress of a material containing coarse precipitated particles of mean distance d is therefore

$$Y = 2Ga/d$$

This formula differs only by the factor 2 from the expression given by Sir Lawrence Bragg (*Nature*, **149** (1942), 512) for the yield stress of crystalline materials in which the free path of glide is restricted to the length d . It assumes, of course, that the barriers resisting the propagation of glide are so strong that they are not overcome before the bulge of the first dislocation line passing over them becomes approximately semicircular.

3 Fracture behaviour of aged alloys

3.1 INTRODUCTION

In our consideration of the effect of precipitate particles on fracture behaviour, we will consider the effect of particles on the *nucleation* of fracture, and then upon the *propagation* of such nuclei until total failure occurs. We will discuss in turn the processes of ductile rupture, intergranular fracture, fatigue, and stress-corrosion cracking.

The processes of fracture are affected by the movement of relatively large numbers of dislocations, and it appears that the nature of the *slip distribution* constitutes an important factor and so we will consider this subject first.

3.2 SLIP DISTRIBUTION IN ALLOYS CONTAINING PARTICLES

3.2.1 Heterogeneous and homogeneous slip

A given macroscopic amount of plastic strain can be distributed heterogeneously or homogeneously within a crystal. If one considers the case of slip on a single system, then Fig. 3.1 indicates the principal geometrical possibilities. Figure 3.1a defines a macroscopic shear strain ϕ , and Fig. 3.1b,c and d illustrate three ways in which slip processes on a single system can provide this macroscopic strain.

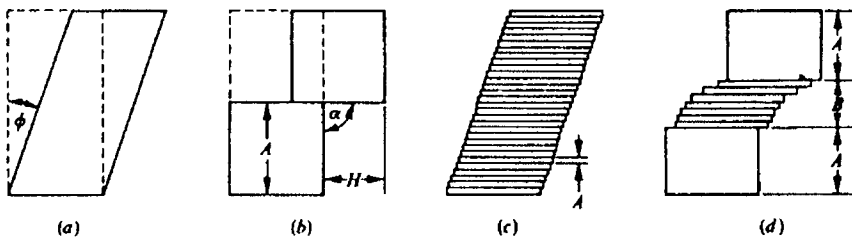


Fig. 3.1 Geometric possibilities for plastic deformation in a one-slip system. A is the step spacing; H is the height of the slip step; α is the angle between the slip plane and the crystal surface; B is the thickness of the slip band (after Hornbogen and Zum Gahr [1]).

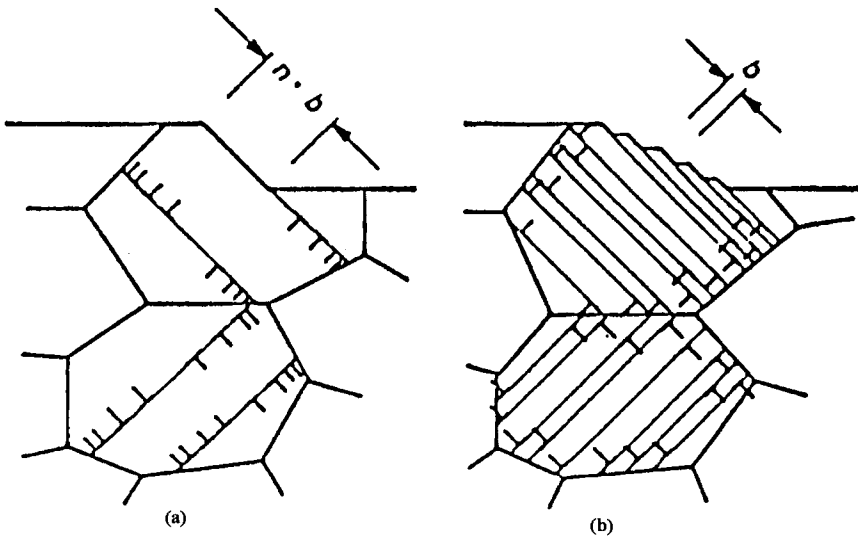


Fig. 3.2 Showing the effect of slip distribution in polycrystals upon the magnitude of strain concentrations where a slip band meets a grain boundary. (a) Heterogeneous slip and (b) homogeneous slip.

In Fig. 3.1b a slip step of height H has formed on a single plane, which makes an angle α with the crystal surface. In Fig. 3.1c the same macroscopic strain is effected by much smaller slip displacements upon many closely spaced planes, so that Figs 3.1b and c provide extreme examples of *heterogeneous or coarse slip* and *homogeneous or fine slip* distributions, respectively. Figure 3.2 illustrates diagrammatically the implication of these slip distributions upon the deformation of polycrystalline specimens. Sections perpendicular to the free surface are shown, with a single coarse slip step in Fig. 3.2a and many fine steps in Fig. 3.2b, analogous to the diagrams on Fig 3.1b and c for single crystals. Where the slip bands meet a grain-boundary, dislocation pile-ups occur. These will cause a local strain concentration, whose magnitude is dependent upon the number of dislocations per pile-up. The strain concentration where the slip band meets the grain boundary will be greater the greater the degree of slip heterogeneity.

In Fig. 3.1d, the shear strain is provided by a localized slip in a band of width B , the slip band spacing being A , and this corresponds to a situation intermediate between those illustrated in Fig. 3.1b and c in terms of slip heterogeneity.

3.2.2 The effect of particles on slip distribution

We have seen in Chapter 2 that, within a grain, an advancing dislocation either by-passes the particles it encounters or cuts through them. Above a certain critical particle diameter (d_c) Orowan looping takes place, and on further straining dislocation debris accumulates round the particles. This leads to work

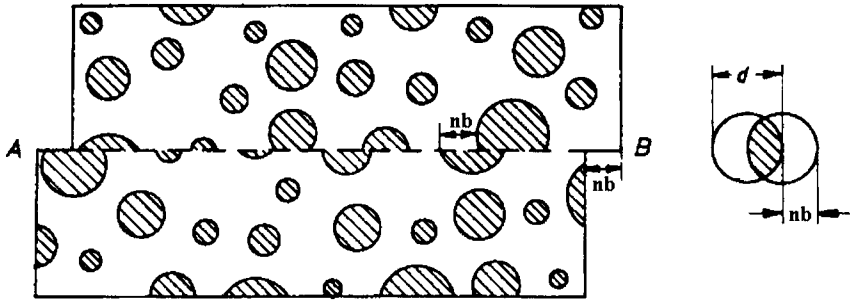


Fig. 3.3 An element of crystal containing particles (diameter d) which have been sheared by n dislocations of Burgers vector b in the slip plane AB. This is seen to reduce the cross-sectional area of the particles, thus making this slip plane softer than those which have not been sheared.

hardening of the slip plane upon which the dislocations have moved, thus favouring the operation of a different slip plane, i.e. slip tends to become *homogeneous*.

For particles smaller than d_c , the dislocations cut through them, as illustrated in Fig. 3.3. Cutting is seen to reduce the effective size of the obstacle. The weakened plane will continue to slip and deformation will be localized, i.e. become *heterogeneous* in nature. This is also known as *planar slip*.

Figure 3.4 summarizes the changes in local critical shear stress (τ_Y) in a single crystal as a function of the number of dislocations (n) that have passed a slip plane for the two situations discussed: for particle sizes where $d > d_c$, when local work hardening is observed leading to slip homogeneity, and also where $d < d_c$, and local work softening proceeds until $n = d/b$ when the particles are completely sheared and effectively destroyed.

3.2.3 The intensity of slip localization in polycrystalline material due to precipitate shearing

In polycrystalline material, whether or not a particular slip plane undergoes a net weakening with slip will depend on the relative intensities of two mechanisms: (a) the degradation of the particle strengthening with slip (Fig. 3.4); and (b) the strengthening effect of dislocation pile-ups (Fig. 3.2).

We have seen in Chapter 2 that the CRSS of alloys strengthened by shearable precipitates is often of the form

$$\tau_c = A \Delta^{3/2} \left(\frac{rf}{2T} \right)^{1/2} \quad 2.17$$

where A is a constant, and Δ is the particular dislocation/particle interaction term. The softening due to the cutting of particles by n dislocations on a

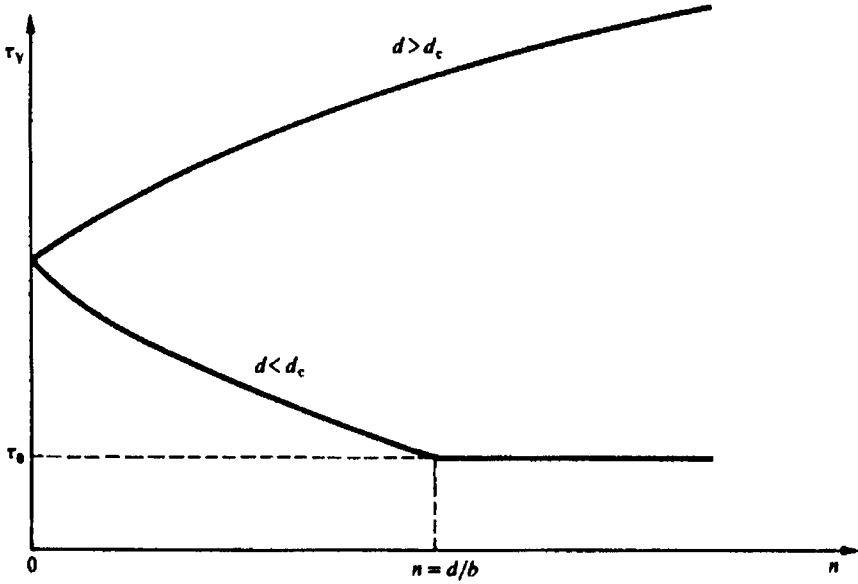


Fig. 3.4 The local critical shear stress (τ_Y) in a single crystal as a function of the number of dislocations, (n) that have passed a slip plane.

given plane can be modelled in equation (2.17) by using an effective particle radius, $r_{\text{eff}} = r - nb/2$ (so that when $n = 2r/b$ the particle is effectively destroyed).

We must also consider the strengthening effect of the dislocation pile-up at the grain boundaries (Fig. 3.2). This can be regarded as a superdislocation of Burgers vector nb , which will give a back stress at the grain centre. So by taking into account the strengthening effect of both the second-phase particles and the dislocation pile-ups, the shear strength (τ) of a particular slip plane in a polycrystal of grain sized has been written by Duva, Daeubler, Starke and Lütjering [2] as:

$$\tau = \tau_0 + C_p f^{1/2} (r - nb/2)^{1/2} + C_m nb/d \quad (3.1)$$

where τ_0 is the lattice friction stress of the matrix, C_p is a function of Δ , b and T (equation (2.17)), and C_m depends on the elastic properties of the matrix phase. The third term on the right can be regarded as the backstress at the grain centre due to the dislocation pile-up, which gives an approximate measure of the inhibiting effect of the pile-up on subsequent slip.

Duva *et al.* take N as an indicator of slip localization, being the number of dislocations that pass on a typical slip plane from the time deformation begins until local slip ends, and term it the *slip intensity indicator*. The larger the value of N , the coarser the deformation expected. They assume that if slip weakens a particular plane, slip will continue on that plane until it regains the strength it had

when the softening commenced, from the contribution of the pile-ups. Softening is indicated from equation (3.1) by the condition

$$\partial\tau/\partial n \leq 0$$

N is calculated for the two possible regimes:

(i) if $\partial\tau/\partial n \leq 0$ prior to deformation, then *softening occurs initially*, and continues as long as the inequality holds. Solving for r , the inequality is:

$$r \leq \frac{nb}{2} + f(d/2)^2 \left(\frac{C_p}{4C_m} \right)^2 \quad (3.2)$$

For sufficiently small particle size, therefore, slip will continue until τ again reaches its initial value giving

$$N = f^{1/2} r^{1/2} (d/2)(C_p/C_m.b) \quad (3.3)$$

(ii) If $\partial\tau/\partial n > 0$, *hardening occurs initially*, and continues as long as

$$r > (nb/2) + f(d/2)^2 (C_p/4C_m)^2 \quad (3.4)$$

holds. Those planes that happen to be more susceptible to slip will share the deformation until the first one begins to soften. Once this weakening has started, slip will continue until the resulting pile-ups cause the strength to return to the previous maximum value, giving

$$N = (2/b)(r + f(d/2)^2 (C_p/4C_m)^2) \quad (3.5)$$

Comparison with equation (3.3) shows that in this situation N increases linearly with r and f , and increases as the square of d .

3.2.4 The slip band spacing (S)

In the situation illustrated in Fig. 3.1d we will assume that ϕ is great enough for the particles to have been completely sheared on many different planes (Fig. 3.3), then

$$S = Nb/\phi \quad (3.6)$$

3.2.5 The influence of particle size on slip distribution

The effect of slip intensity N on particle radius r is illustrated in Fig. 3.5. For sufficiently small particle radius, equation (3.3) is applicable, and N is proportional to $r^{1/2}$, whereas for sufficiently large particles N increases linearly with r (equation (3.5)). Increasing N also implies an increase in S , the slip-band spacing according to equation (3.6).

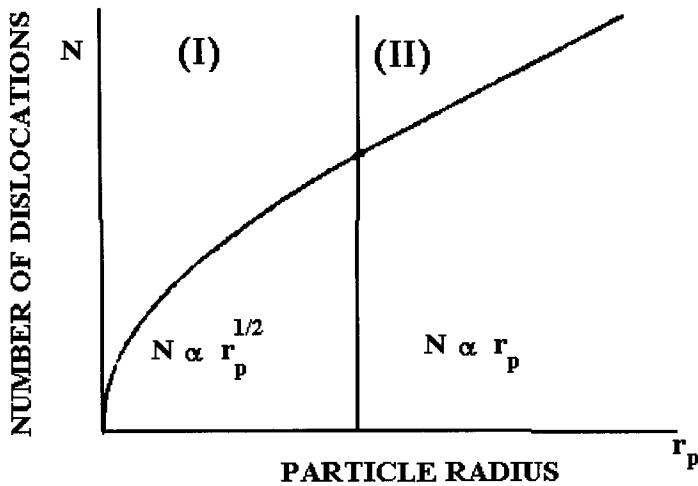


Fig. 3.5 Slip intensity versus particle radius [2]

The main effect of an inhomogeneous distribution of plastic strain on the mechanical properties is that the fracture stress can be reached locally in the region of strain concentration (Fig. 3.2), even if the overall (macroscopic) plastic deformation is still relatively small.

3.2.6 The control of slip distribution

Aside from the effect of second-phase particles, which we have discussed so far, it must be remembered that slip distribution may be influenced by a number of other factors including:

Stacking-fault energy. Low stacking-fault energy in a solid solution will promote the dissociation of the glide dislocations into widely separated partials which cannot cross-slip without re-association. This tendency will promote coarse planar slip.

Short-range order. The presence of short-range order will also tend to promote the planar glide of coupled dislocations with an associated APB.

Number of operating slip systems. The greater the number of slip systems operating, the fewer dislocations there will be per slip band, for a given applied strain, and so the more homogeneous the slip will tend to be.

Matrix grain size. The finer the matrix grain size, the greater the number of slip systems that will operate per grain, because of the 'complexity effect' associated with the local strain compatibility across the grain boundaries. There will thus be a general slip-homogenising effect as the grain size of a material is refined.

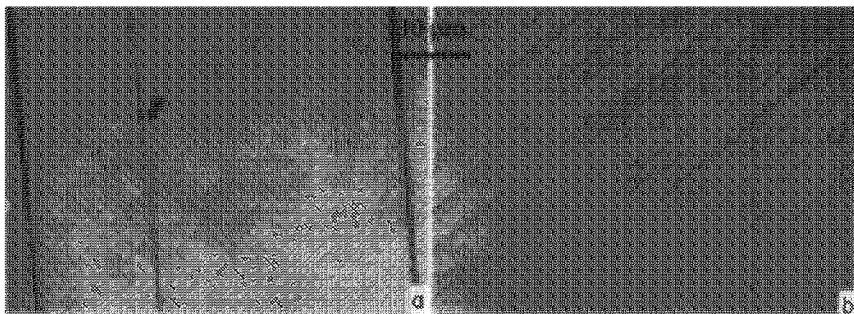


Fig. 3.6 Slip-line distribution revealed by light microscopy in Ti-16.8 wt% Al (a) annealed 100 hours at 750°C then deformed to fracture; (b) overaged by annealing 100 hours at 850°C then deformed 1% (after G. Lütjering and S. Weissman [3]).

There is thus scope in alloy design and processing for the control of the distribution of slip, in addition to that deriving from the effect of second-phase particles. Particle-control nevertheless remains the most powerful means available of changing the distribution of slip, and there are several approaches that can be employed:

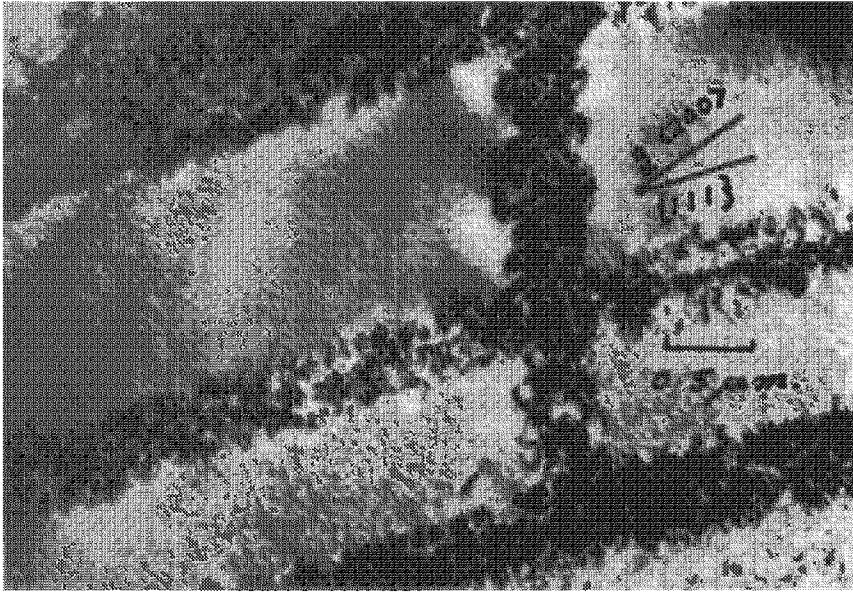
Overageing

This will promote the homogenization of slip by the process we have discussed earlier. It is possible to demonstrate the effect by studying the distribution of surface slip steps formed upon the polished surface of an alloy sample after ageing at different times and/or temperatures.

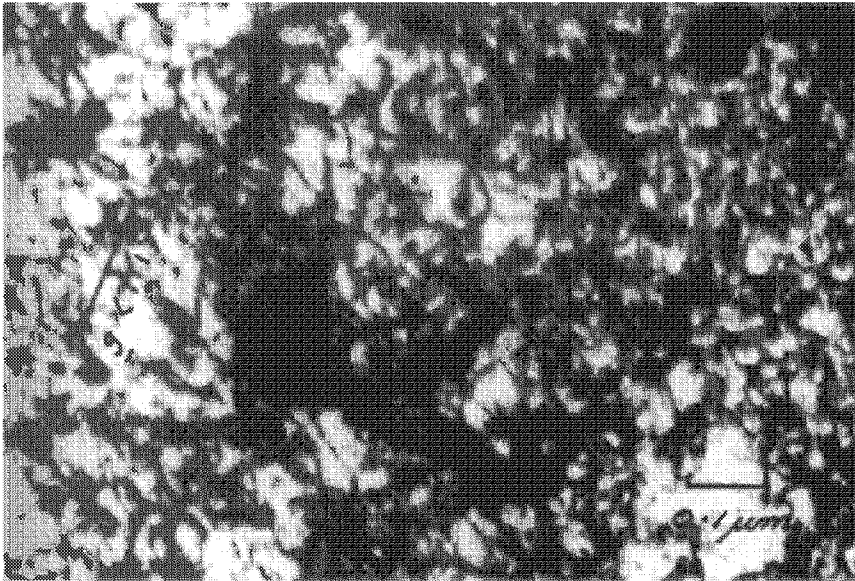
Thus the underaged sample of Fig. 3.6a, which contains only coherent particles within the grains, shows after deformation only relatively few slip steps, each with a large displacement. The overaged sample (Fig. 3.6b) contained partially coherent particles which exhibited the Orowan process when the sample was deformed. The surface is characterized by the presence of a large number of small slip steps that are homogeneously distributed over the entire surface of the sample.

Duplex ageing

Overageing produces slip homogenization at the expense of yield strength. In alloys of high precipitate volume fraction it is possible by duplex ageing to disperse the precipitate in two forms: the quenched alloy can be aged for a short time at a high ageing temperature to produce partial precipitation of a coarse dispersion to homogenize the slip, and this can be followed by a low temperature age to complete the precipitation to produce a high density of coherent zones, giving a structure of high yield strength. Duplex ageing can also be used to decrease the width of precipitate-free zones at grain boundaries.



(a)



(b)

Fig. 3.7 Electron micrographs showing dislocation distributions in plastically deformed Al–0.6 wt% Mg–1 wt% Si alloys in the peak-aged condition: (a) ternary alloy showing intense bands of dislocations; (b) alloy containing 0.5 wt% Mn. The dispersoid of α -Al₁₂Mn₃Si-phase homogenizes the dislocation distribution.

The production of two dispersed phases

Dispersoids As mentioned in Chapter 1, in many commercial aluminium alloys there is present an intermetallic dispersoid phase in addition to the ageing precipitate. A transition metal addition (e.g. Cr, Zr or Mn) is made which forms particles of intermetallic compounds (see Fig. 1.1) which not only maintain a fine grain size in the alloy during processing, but may also affect the deformation mode.

The effect is illustrated in Fig. 3.7 showing dislocation distributions in plastically strained Al–0.6 wt% Mg–1 wt% Si alloys in the peak-aged condition. The specimen shown in Fig. 3.7a is a simple ternary alloy, and the coherent Mg_2Si phase is sheared on yielding so that intense bands of dislocations are evident. Intense surface slip bands form, as in the Ti alloy of Fig. 3.6. The specimen of Fig. 3.7b is of a similar composition to that of Fig. 3.7a, except that it also contains 0.5 wt% Mn which is present as a dispersion of incoherent particles of the $\text{Al}_{12}\text{Mn}_3\text{Si}$ -phase. The specimen has also been aged to (the same) peak hardness, so that both the coherent hardening phase and the incoherent dispersoid are present. On plastic deformation the dislocation distribution in this specimen is much more homogeneous than in the ternary alloy.

Co-precipitation of two phases during ageing An example of this can be found in the Al–Li alloy 8090. This is age-hardened by precipitation of the metastable ordered δ' -phase (Al_3Li) which nucleates homogeneously throughout the matrix. The alloy also contains magnesium in addition to copper and lithium, and, upon ageing, the presence of semicoherent S' phase (Al_2CuMg) contributes to the strength, although δ' -remains the dominant strengthening phase. S' is not easily sheared by dislocations, so it promotes cross-slip and hence more homogenous deformation. In the underaged condition where S' precipitates have not grown to sufficient size to induce slip dispersal, planar slip may persist.

We will now consider the various possible fracture processes in turn and relate, where appropriate, the effect of slip distribution upon the various mechanisms.

3.3 FRACTURE UNDER TENSILE LOAD

3.3.1 Ductile fracture: microvoid coalescence

Failure in ductile solids arises from the concentration of plastic deformation into a localized region. An idealized model of the process is illustrated in Fig. 3.8a in which, under an applied tensile strain, simple shear occurs along a single slip line. The concentration of plastic strain cannot take place so long as the material is still work-hardening strongly. If two orthogonal slip lines are operative, then the process illustrated in the idealized model of Fig. 3.8b occurs, giving rise to simple necking. The processes illustrated in Figs 3.8a and b produce knife-edge or point failures, but in practice most ductile failures give much less than total reduction in area. This is because ductile rupture usually proceeds simultaneously from a number of holes or voids inside the material.

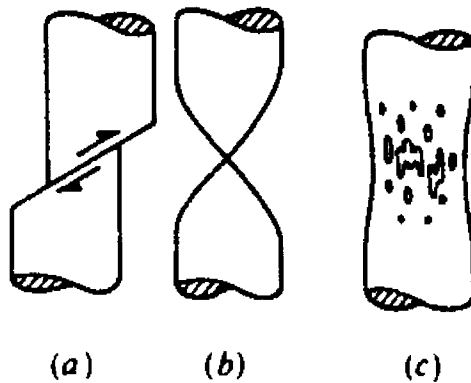


Fig. 3.8 The mechanisms by which a cylindrical tensile specimen may fail by ductile failure: (a) idealized simple shear; (b) idealized simple necking; (c) the void growth process.

The most fundamental discovery concerning the mechanism of ductile rupture in materials containing second-phase particles was that it is initiated by the generation of voids at the particles – either by decohesion of the particle/matrix interface or by cracking of the second-phase particles themselves. Tipper using optical metallography, was the first to show that the internal cavities originate at second-phase particles, and an excerpt from this classic paper appears in the Appendix to Chapter 3.

These cavities grow as the material is strained further, and ultimately they coalesce by an *internal necking* mechanism to give the dimpled fracture surface characteristic of ductile fracture. This void growth process is illustrated in Fig. 3.8c, and we will consider separately the nucleation and the growth of such internal voids during the ductile rupture of precipitation-hardened materials.

Nucleation of voids at particles

There have been many investigations reporting void nucleation at second phases, with particle sizes ranging from μm to nm in scale. It has been generally observed that while inclusions with large aspect ratio may undergo multiple internal fracturing, equiaxed inclusions almost always nucleate holes by interfacial separation. The number of voids increases with increasing strain, and it is further found that large particles usually nucleate voids earlier than small particles.

The problem of non-equiaxed particles, whose behaviour depends on their shape and orientation in addition to their size and spacing, is a complex one, and will not be discussed here. We will thus confine our attention to the process of void nucleation at equiaxed particles, regarding them as rigid and plastically non-deformable.

There are numerous models of varying complexity that have been put forward to describe the void nucleation process: the process appears to be influenced by:

- (i) *energy criteria*, in that a necessary condition for nucleation is that the elastic strain energy released by the particle is at least equal to the energy of the newly created surfaces. This condition is by no means sufficient, and is likely to be satisfied at the very onset of plastic deformation for particles greater than a few tens of nm in diameter. The work of decohesion will be dependent on the specific surface energy γ , which may be written as

$$\gamma = \gamma_m + \gamma_p - \gamma_i$$

where γ_m is the surface energy of the matrix, γ_p that of the particle and γ_i that of the particle/matrix interface. The magnitude of γ is thus dependent on the value of γ_i , so that non-coherent interfaces (large γ_i) will be easier to separate than coherent ones (low γ_i);

- (ii) *local stress criteria*, namely the attainment of a critical normal stress (σ_c , related to γ) at the particle/matrix interface;
- (iii) *local strain criteria*, which can be established through the relationship of the total plastic strain to the stresses acting.

For the case of small (radius $r < 1 \mu\text{m}$) spheroidal particles, dislocation models [4,5] have been employed to estimate the critical strain ε_1^n required to nucleate microvoids by particle decohesion:

$$\varepsilon_1^n = Kr (\sigma_c - \sigma_m)^2 \quad (3.7)$$

where K is a material constant related to the volume fraction of particles, and σ_m the macroscopic mean-normal stress.

Support for equation (3.7) is shown in Fig. 3.9, in which $\sqrt{\varepsilon_1^n}$ is plotted against σ_m for a number of spheroidized steel specimens having approximately the same volume fraction of carbide particles of similar radius. The data extrapolate to give a value for σ_c of 1200 MPa, which is within the range of values estimated for carbide/interface strengths for steels.

For particle sizes greater than $1 \mu\text{m}$, continuum plasticity models have been developed to describe the microvoid nucleation process, leading to an expression for the critical condition for microvoid nucleation:

$$\bar{\sigma} + \sigma_m = \sigma_c \quad (3.8)$$

where $\bar{\sigma}$ is the maximum tensile stress on the inclusion interface. The primary difference between this expression and that for sub-micron particles (equation (3.7)) is that the parameters are all independent of particle radius. In real materials, however, large particles usually decohere prematurely, and this may well arise because in hot-working processes such particles are subject to severe damage and fragmentation, leading to partial debonding of the particle/matrix interface.

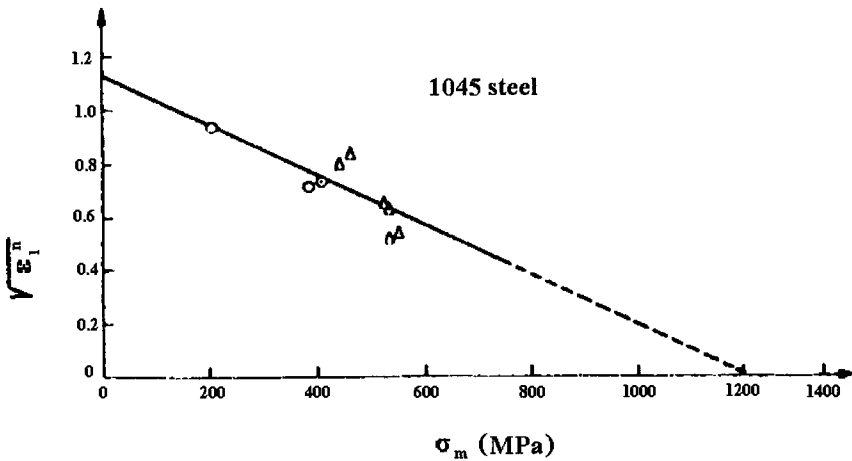


Fig. 3.9 The critical microvoid nucleation strains for various mean-normal stresses in a spheroidized 1045 steel, plotted according to equation (3.7) (after G. Le Roy, J.D. Embury, G. Edwards and M.F. Ashby [6]).

Growth and coalescence of voids

Under most practical conditions the spacing of the microvoids is large compared with their diameter, and so there is no initial interaction between their local stress and strain-rate fields.

There is a localized concentration of stress and strain, so that with continuing plastic flow of the matrix, the microvoid undergoes changes in volume and in shape which amplifies the imposed strain (Figs 3.10a and b).

The independent growth of voids is terminated when the load on the ligaments between the voids reaches the plastic limit load. The strain then localizes to the ligament, and the material fails with little additional strain outside the ligament. The ductile fracture surfaces are formed by the sudden catastrophic coalescence of microvoids by a process of localized 'internal necking' of the intervoid matrix (Fig. 3.10c).

The final fracture surface, corresponding to the result of the processes illustrated in Fig. 3.10 consists of an array of dimples, each dimple containing a particle. This is confirmed experimentally, as illustrated in Fig. 3.11. Some particles are attached to the mating fracture surface.

A simple theory due to Brown and Embury [7] leads to a good description of the microstructural features controlling the void coalescence strain (ϵ_g). Their approach neglects the important effects of stress triaxiality, and a more sophisticated approach due to Thomason [8] gives a better correlation with experimental values of ductility as a function of initial porosity.

Brown and Embury's treatment accounts semi-quantitatively for much of the data, however, and is amenable to comparison with a variety of microstructures. After the voids are nucleated (Fig. 3.10a) it is assumed that they grow by plastic

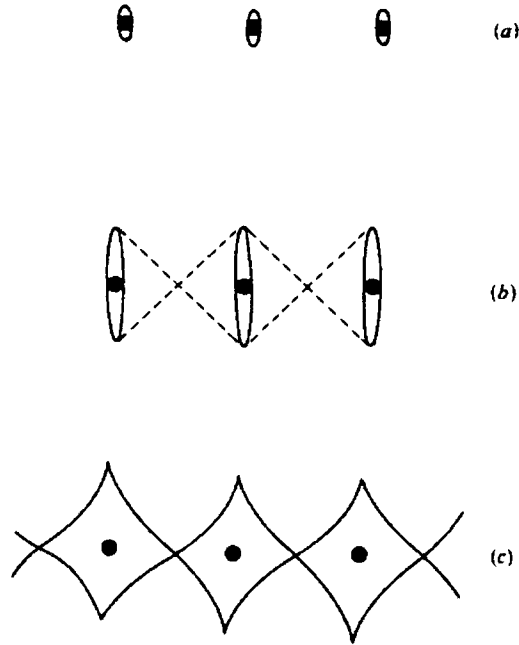


Fig. 3.10 The growth (a) and (b), and coalescence (c) of voids at particles during ductile failure.

extension – although the ductile matrix between neighbouring voids cannot suffer very large local deformations because it is under plastic constraint by the surrounding material. Because of its strain-concentrating effect, a spherical void will elongate initially at a rate of about twice that of the specimen itself. As it extends and becomes ellipsoidal, it grows more slowly until, when very elongated, it extends at the same rate as the specimen itself.

When the voids have been extended so that the spacing of neighbouring voids becomes equal to their length (Fig. 3.10b), a plastic slip line field can be constructed between the voids, as indicated in the diagram, so that the plastic constraint preventing local deformation is removed. Ductile fracture will now ensue: it is assumed that the contribution of this final linking strain to the total reduction in area will be very small.

The tensile strain required to cause the voids to grow to the unstable configuration can be estimated. If the diameter of the particles is $2r$, then $2r$ is also the size of the void when it is nucleated. If the particle spacing is λ , then a void length λ is required to enable the slip line field to be constructed (Fig. 3.10b). If the voids elongate at a rate which, on average, is faster by a factor C than the rate of extension of the specimen itself ($1 < C < 2$), then we may write the true strain to coalescence as

$$\varepsilon_g = C^{-1} \ln (1 + e_g) \quad (3.9)$$

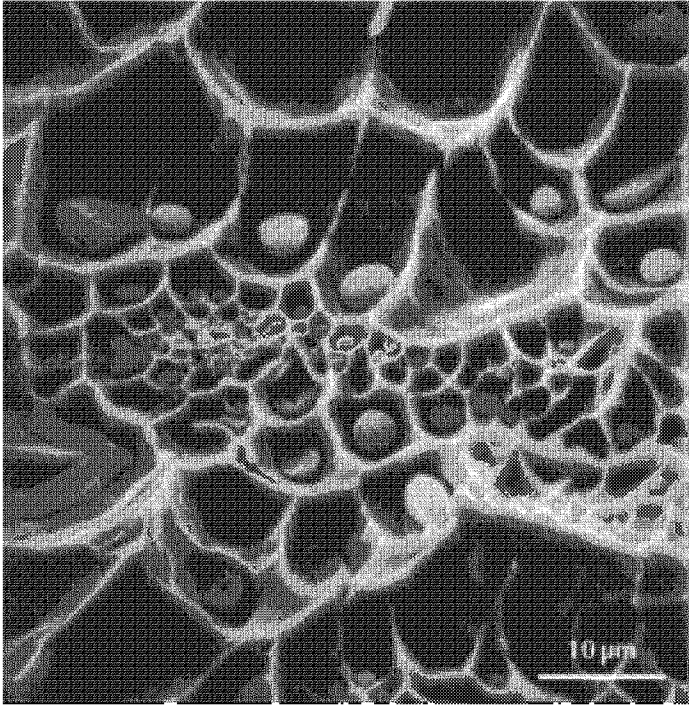


Fig. 3.11 Ductile fracture surface of low-carbon steel containing sulphide particles showing the relationship between the particle size and the ductile cusp size (courtesy of T.R. Gladman).

where

$$e_g = (\lambda - 2r)/2r$$

i.e.

$$\lambda = 2r (1 + e_g) \quad (3.10)$$

Since the fracture path is approximately a plane, λ is identified with the mean two-dimensional or planar spacing of the particles. As discussed in Chapter 1, we may write

$$\lambda = N_s^{-1/2} - 2r_s$$

where $r_s = \sqrt{(2/3)}r$. If the volume fraction of the particles is f , then $N_s = f/(\pi r_s^2)$, and appropriate substitution in equation (3.10) gives

$$2r (1 + e_g) = r (\sqrt{(2\pi/3f)} - \sqrt{(8/3)}) \quad (3.11)$$

Equation (3.11) indicates that the growth strain becomes zero above a critical volume fraction of $f = 0.159$, which is when a slip line can be drawn between neighbouring *particles* even in the absence of voids. For volume fractions greater than 0.159, therefore, the fracture strain is controlled entirely by the *nucleation* strain (e_n).

Substituting from equation (3.11) for $(1 + e_g)$ in equation (3.9) to give the true strain, we have

$$\varepsilon_g = C^{-1} \ln (\sqrt[3]{(\pi/6f)} - \sqrt[3]{2/3})$$

and we may write the total strain to failure as

$$\begin{aligned} \varepsilon_f &= \varepsilon_n + \varepsilon_g \\ &= C^{-1} \ln (1 + e_g + e_n) \end{aligned}$$

that is

$$\varepsilon_f = C^{-1} \ln (\sqrt[3]{(\pi/6f)} - \sqrt[3]{2/3} + e_n) = \ln (A_0/A_f) \quad (3.12)$$

where A_0 and A_f are the initial and final cross-sectional areas of the specimen, respectively. The fracture strain is seen to be inversely proportional to $f^{1/2}$.

Figure 3.12 illustrates the data of Edelson and Baldwin [9] for some dispersion-strengthened copper-based alloys which appear to be in qualitative accord with the model. In technological materials, the effect of small strengthening particles and macroscopic inclusions is not additive in defining f in equation (3.12), and since decohesion of the large particles may occur at very low strains, the large voids so formed may serve to limit the volume of material which needs to be strained to ε_f . Another shortcoming of Brown and Embury's model is that it fails to include the effect of the formation of zones of concentrated shear. For example, in a material which exhibits inhomogeneous slip distribution, a ductile crack may (depending on the degree of slip inhomogeneity) propagate along slip bands in the matrix. Localized shear of this kind can cause holes to coalesce at relatively small macroscopic strain, giving failure by 'void sheeting' and an associated low fracture toughness.

Void-sheet formation is observed in the 2000 and 7000 series of aluminium alloys. Although large voids are initially created by the fracture of large intermetallic constituent particles, and some of these voids coalesce by impingement, the more widely separated voids coalesce by the formation of void sheets. The void sheets are composed of smaller voids which are nucleated by decohesion at the interface between the matrix and submicrometre-sized dispersoids in the structure. The fracture surfaces are usually formed at $\sim 45^\circ$ to the tensile axis, and exhibit a duplex population of dimple sizes, as would be expected from the above mechanism.

Transgranular shear fracture has also been observed in Al–Li sheet alloys with a very strong texture. By introducing slip dispersing precipitates by alloy modification and by thermomechanical ageing, the ductility of these materials can be improved.

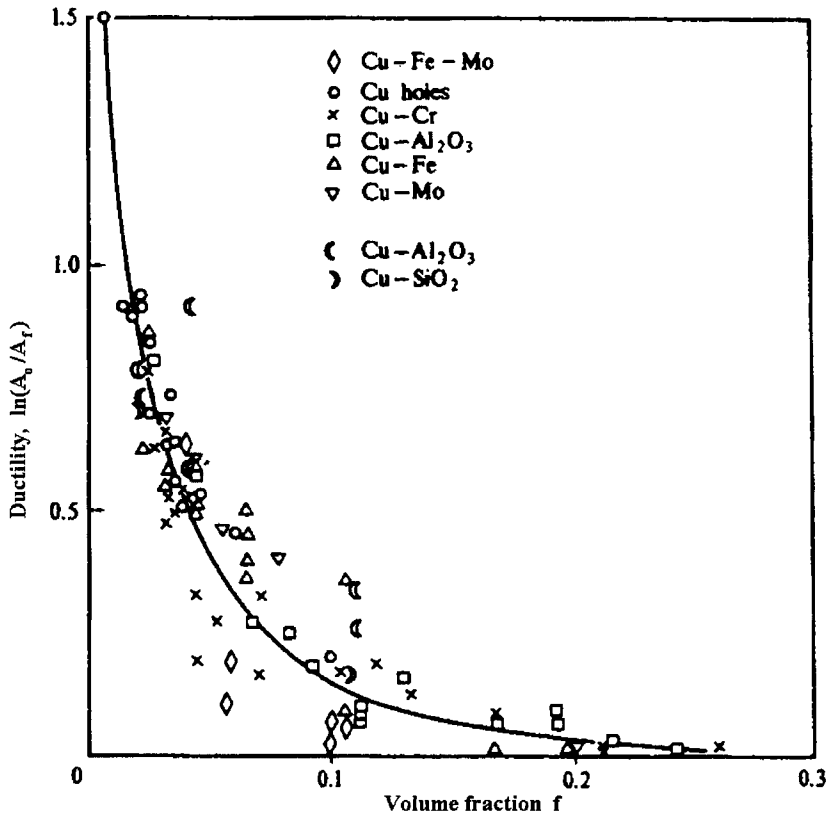


Fig. 3.12 A combined plot of ductility of several copper-based dispersion hardened alloys versus volume fraction (after B.I. Edelson and W.M. Baldwin [9]).

3.3.2 Grain-boundary ductile fracture (GBDF)

Another type of void-sheet formation, that can also lead to a reduction in toughness, arises from the nucleation of voids at particles that are on or near grain boundaries. This again can provide a low-energy fracture path through the material. The phenomenon of grain-boundary ductile fracture (GBDF) at room temperature in precipitation hardened alloys has been recognized for a very long time.

Figure 3.13a illustrates the intergranular nature of the fracture surface obtained in an Al-Mg-Si alloy aged to peak hardness. At higher magnification (Fig. 3.13b) the fracture surface is seen to be covered with fine cusps, which confirms that the micromechanism of fracture is by microvoid coalescence associated with particles in the grain boundaries.

There are at least three important effects that influence grain-boundary failure in such alloys.

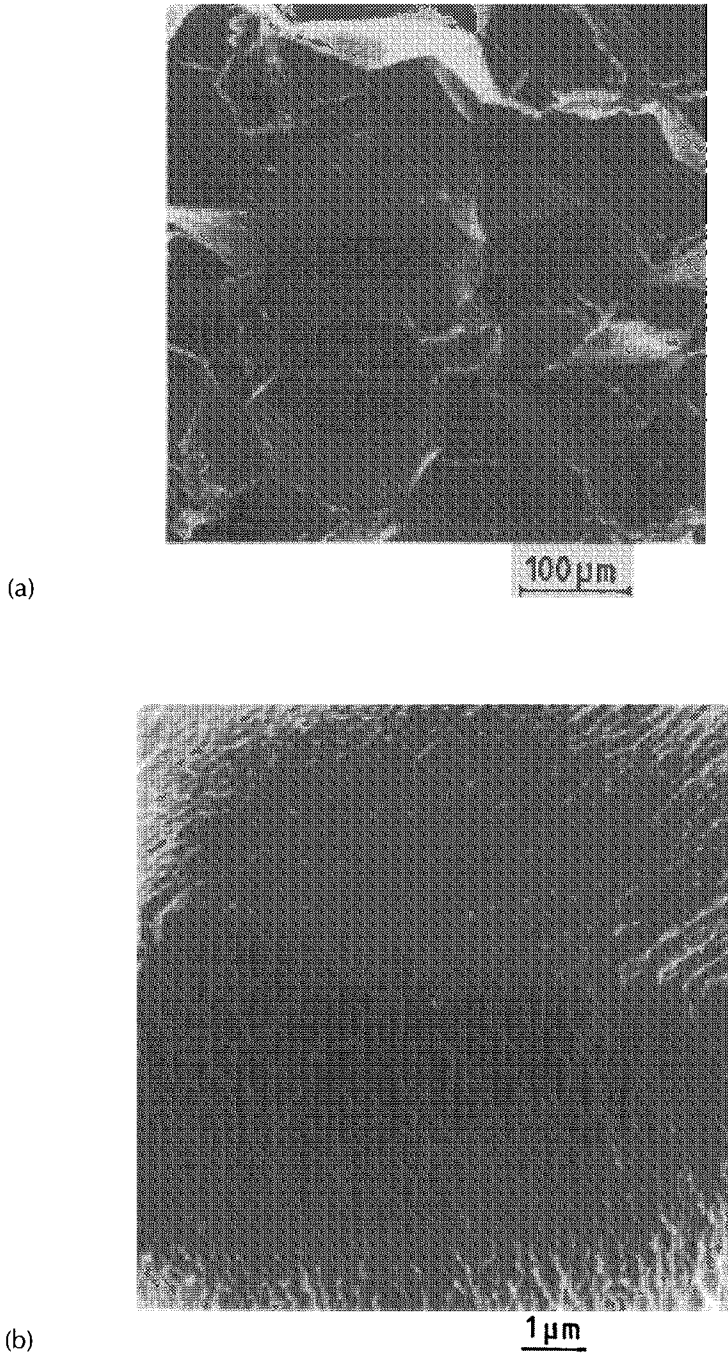


Fig. 3.13 SEM of fracture surface of Al–0.6 wt % Mg – 1 wt % Si alloy aged to peak hardness: (a) showing intergranular nature of the fracture path, and (b) at higher magnification showing the presence of ductile cusps.

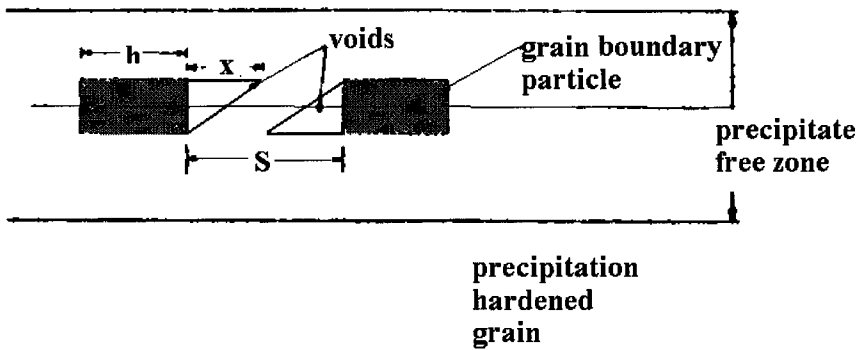


Fig. 3.14 Schematic diagram illustrating the process of grain-boundary fracture resulting from the initiation and growth of voids at grain-boundary precipitates.

The incidence of co-planar particles lying on the grain-boundary

The age-hardening treatment results in precipitates being heterogeneously nucleated on the grain boundaries. Where the grain-boundary precipitates are formed from the same solute additions as the matrix precipitates (as in the case of aluminium alloys, for example), the existence of a pfz is an inevitable consequence of the formation of grain-boundary precipitates. In contrast, in the precipitation-strengthened nickel-based alloy MAR-M200, the aged microstructure consists of the γ' -phase in the matrix and carbides in the grain boundaries, with no pfz being present. It is thus possible to study the effect of such particles with and without the presence of a pfz.

D.J. Embury and E. Nes [10] have developed a simple model for predicting the shear strain for grain-boundary fracture (γ_f) in materials containing a high area fraction (f_a) of incoherent grain-boundary precipitates in a pfz of unspecified width as illustrated in Fig. 3.14. When f_a is sufficiently large, the growth of voids does not involve the spread of plasticity much further than the precipitate dimensions, so the pfz width can be ignored.

If the particles are of length h and spacing S , a shear displacement x enables a shear strain $\gamma = x/h$ to be defined. Plastic collapse can occur when voids are able to join at $x = S/2$, so the strain to failure $\gamma_f = S/2h$.

If the areal fraction of precipitates is approximated as

$$f_a = \left(\frac{h}{S + h} \right)$$

then

$$\gamma_f \approx \frac{1}{2}(f_a^{-1/2} - 1) \quad (3.13)$$

There is ample experimental evidence that a high area of grain-boundary particles is very detrimental to toughness and ductility and leads to GBDF.

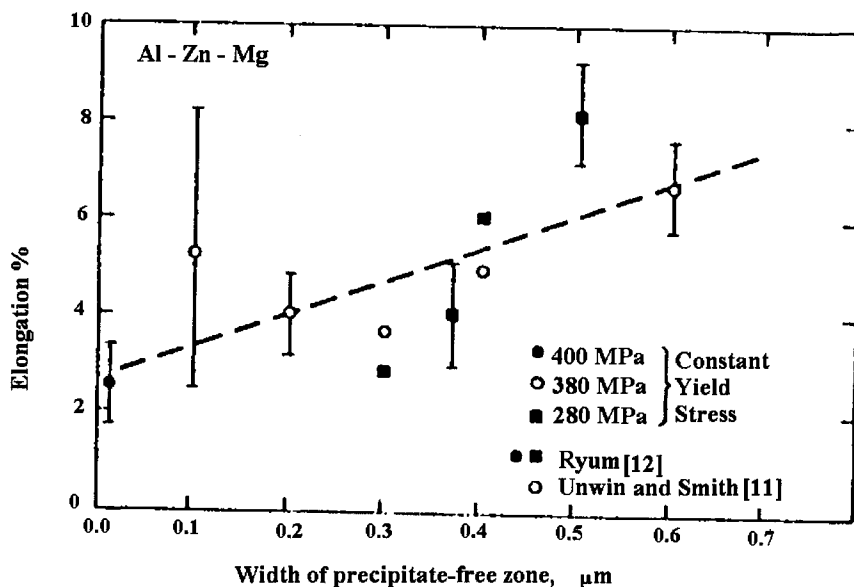


Fig. 3.15 Variation of tensile ductility with increased width of precipitate-free zone. (Open symbols: P. N. T. Unwin and G.C. Smith [11]; Closed symbols: N. Ryum [12].)

The occurrence of localized grain-boundary shear in the soft pfz regions

There are many observations of localized strain at soft pfz. TEM studies have revealed high dislocation densities in the pfz in samples that have been lightly deformed, and measurement of grain-boundary offsets suggest that localized grain-boundary shear strains in the pfz may be up to ten times greater than the imposed tensile elongation.

It is to be expected that the extent of grain-boundary strain localization will increase with the difference between the flow stress in the precipitation-strengthened matrix and that in the soft pfz. The difference will be at its maximum for the alloy aged to peak hardness.

It must be borne in mind that general plastic yielding of the soft pfz should not be expected because of the plastic constraint provided by the adjacent precipitation-hardened matrix, although there will be no plastic constraint against shear *parallel to the grain boundary plane*. It is thus reasonable to conclude that localized pfz shear is likely to augment GBDF by promoting grain-boundary void growth.

Several studies have investigated the influence of pfz width on fracture strain, and Fig. 3.15 shows the data from Unwin and Smith and from Ryum using Al-Zn-Mg alloys. They suggest a rather small increase in tensile ductility with increased width of the pfz.

Matrix slip localization that can cause high stress concentrations at the slip band termination at the grain boundary

It might be expected that this effect can also promote the grain-boundary fracture process – particularly in alloys containing grain boundary particles. The peak-aged specimen illustrated in Fig. 3.13 exhibits planar slip, but this inhomogeneous deformation mode can be modified by the introduction of intermetallic dispersoid phases. Thus the addition of 0.5 wt % Mn gives rise to the dispersoids of the $\alpha\text{-Al}_{12}\text{Mn}_3\text{Si}$ -phase (see Fig. 1.1); the presence of these incoherent particles has the result of homogenizing the dislocation distribution compared with the ternary alloy. The peak-aged Mn-free alloy exhibits about 1% elongation to fracture in a tensile test, but the peak-aged dispersoid-bearing material has an elongation to fracture of about 13%. The number of dislocations per slip band is reduced (both because of the homogenized slip and also because the dispersoid maintains a finer grain size in the material), so that failure will not be nucleated until considerably higher macroscopic strains have been applied. It should, however, be emphasized that the experimental evidence available suggests that the process of matrix strain localization, and the control of planar slip, do not play as great a role in promoting or inhibiting GBDF as control of the grain size.

3.3.3 Fracture toughness

We have so far considered fracture processes in tensile specimens, therefore involving both the nucleation and propagation of the fracture. The integrity of any engineering structure depends, however, upon the fracture toughness of the material from which it is made. Assessing this property involves establishing the conditions under which a sharp crack begins to propagate through the material. We will first define the various fracture toughness parameters.

Fracture toughness parameters

Linear elastic crack tip field In an infinite body containing a central, through-thickness crack of length $2a$, the Griffith relationship states that elastic fracture will occur at a critical value of the potential energy release rate per unit thickness, known as the **toughness**:

$$G_c = 2 \gamma \quad (3.14)$$

where 2γ is the elastic ‘work to fracture’, being the surface energy per unit area.

An alternative form of equation (3.14) makes use of the relationship between the stress intensity factor (K) and energy release rate (G). For tensile loading across the crack faces (mode I), this relationship is:

$$G = \alpha K^2/E \quad (3.15)$$

where $\alpha = 1$ in plane stress and $(1 - \nu^2)$ in plane strain: μ is Poisson's ratio and E is Young's modulus. The critical value of stress intensity factor corresponding to equation (3.14) is known as the **fracture toughness**:

$$K_c = \sigma_f (\pi a)^{1/2} \quad (3.16)$$

where σ_f is the fracture stress of the body. Substituting equation (3.16) into equation (3.14) yields

$$\sigma_f = (EG_c/\pi a)^{1/2} \quad (3.17)$$

Non-linear behaviour at the crack tip Most metals do not fail in a completely elastic manner, but only after some local yielding has occurred at the crack tip. Provided that the non-elastic region is small compared with the dimensions of the specimen and of the crack, it is possible to calculate the potential energy release rate using elastic theory. Much of the energy absorption in the form of strain-energy in the dislocations in the plastic zone, is concerned with this local plasticity. Equation (3.14) thus becomes

$$G_c = 2 \gamma + \gamma_p \quad (3.18)$$

where γ_p is a plastic work term.

The size and shape of the plastic zone at the tip of a propagating crack can be calculated, and Fig. 3.16 illustrates schematically such a zone under conditions of (a) plane stress and (b) plane strain (e.g. as at a crack tip in the centre of a thick sheet or plate). The radius $r(\theta)$ of the plastic zone in polar co-ordinates is given by an expression of the form:

$$r(\theta) = f(\theta) \cdot K^2/(4 \pi \sigma_y^2) \quad (3.19)$$

where $f(\theta)$ is a function of θ dependent upon the state of stress, and σ_y is the tensile yield stress. The dimensions of standard test-pieces are specified in such a way that the size of the plastic zone is much smaller than the distance the crack has to propagate (the 'ligament width') in the uncracked specimen, so that linear elastic analyses may acceptably employed. A second requirement of the test-piece is that its thickness is sufficient to ensure plastic constraint at the crack tip, to provide conditions of plane strain. Under these conditions, the critical stress intensity for crack propagation under mode I stressing is termed K_{Ic} . The size of the plastic zone is seen to be dependent upon the yield stress of the material (equation (3.19)), and in order to ensure that the toughness does correspond to 'plane strain', the standards specify that the specimen thickness B is greater than $2.5 (K_{Ic}/\sigma_y)^2$.

In circumstances of extensive plasticity, an alternative toughness parameter has been proposed, namely the *crack tip opening displacement* (CTOD), usually given the symbol δ . The CTOD is obtained from the reading of a clip-gauge placed across the crack mouth, and under conditions of fracture a critical value of δ_c is determined. The toughness may then be obtained from the relation:

$$G_c = \sigma_y \delta_c \quad (3.20)$$

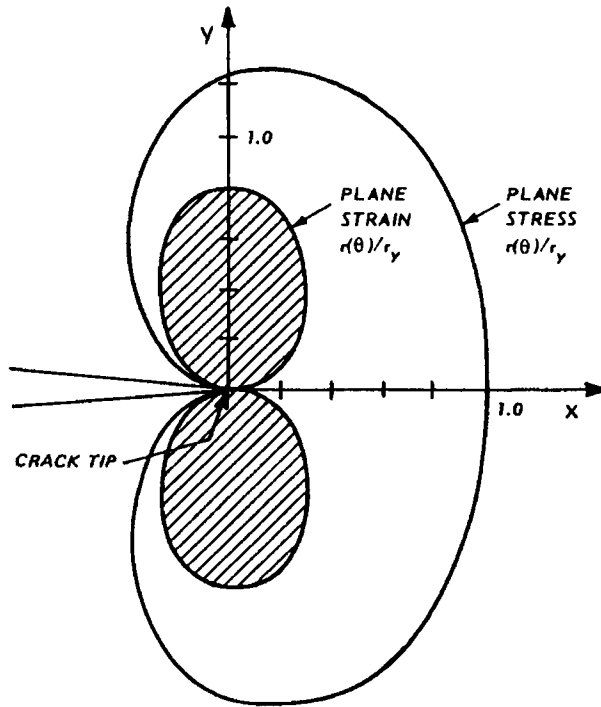


Fig. 3.16 The shape of the plastic zone at the tip of a propagating crack under conditions of (a) plane stress, and (b) plane strain.

The principle of CTOD testing is then that G_c may be measured in a body which has undergone extensive yielding where linear elastic fracture mechanics cannot be applied. δ_c may thus be associated with the coalescence of voids formed around second-phase particles to give ductile rupture.

The J Integral Materials which behave in a non-linear elastic manner have their energy release rate characterized by the parameter J , which is the non-linear equivalent of the potential energy release rate G . In a linear elastic material J would be identical to G , and the reader is directed to the British Standard BS 7448:1991 which describes methods for the determination of K_{Ic} , critical CTOD and critical J values of metallic materials.

The relation between fracture toughness and yield strength of precipitation-hardened alloys

It is generally observed that as the strength level of alloys is increased by alloy composition, fabrication and by ageing treatment, the fracture toughness values decrease. It is clear from Fig. 3.17 that increasing time of ageing from the underaged (UA) up to the peak-aged (PA) condition always leads to a monotonic

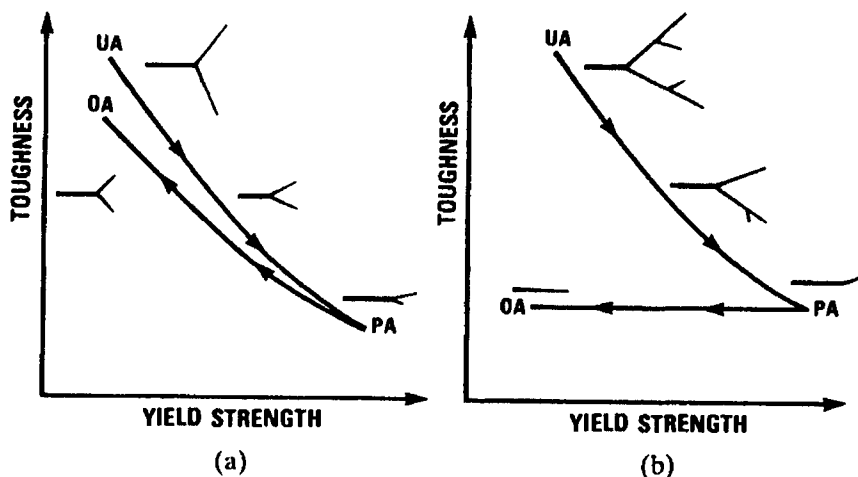


Fig. 3.17 Schematic representation of the variation in fracture toughness with tensile yield stress for (a) alloys in which the *matrix* microstructural changes dominate fracture, and (b) alloys where *grain-boundary* precipitates dominate fracture. Changes in the crack geometry accompanying the changes in toughness are also indicated (after A.K. Vasudevan, R.D. Doherty and S. Suresh [13]).

decrease in fracture toughness. Overageing (OA) can lead either to a significant restoration of toughness (in those alloys in which the *matrix* microstructural changes appear to dominate fracture, such as the 2xxx and 7xxx alloys), or to little or no increase of toughness (in those alloys where *grain-boundary* precipitate microstructure appear to dominate fracture, such as Al–Li alloys of high Li content, and Al–Mg–Si alloys).

There appear to be four major metallurgical factors that control the toughness of commercial age-hardening alloys.

- (i) *The volume fraction of coarse Fe-, Si- and Cu-rich constituents* arising during ingot casting. The main effect of powder-metallurgical processing seems to be a significant reduction in the size of these constituents, which improves their fracture toughness.
- (ii) *The presence of dispersoid phases*, due to the addition of transition elements such as Mn, Cr and Zr. These, as we have discussed, control the post working grain shape, and the degree of recrystallization.
- (iii) *The area fraction of non-coherent grain-boundary precipitates*, in those alloys which fail intergranularly. We have seen that the tensile ductility decreases as this parameter increases (Fig. 3.15), and the fracture toughness is affected in the same way. One important way in which the density of such phases may be decreased is by control of the quench-rate during processing.

We have discussed earlier the problem of quench sensitivity: more grain-boundary precipitation occurs during slow quenching prior to the final ageing treatment. This effect is particularly noticeable in thick section products. In such specimens the fracture toughness is always lower the slower the quench rate.

Another way of decreasing the density of grain-boundary precipitates, in some alloys, is by stretching prior to ageing. The dislocations act as nuclei for precipitation within the grains (see Section 1.2.3), so that the amount of precipitation within the grains is increased, and the amount on the grain boundaries is consequently decreased.

- (iv) *The degree of slip heterogeneity.* The tendency to concentrate strain on particular planes due to the shearing of coherent precipitates will promote planar slip deformation.

During the fracture process, the geometry of the growing crack dramatically influences the toughness. In the UA condition, planar slip will be dominant, and this often promotes a tendency for *crack branching*, with failure along slip bands where the shear strain is localized. The tendency for crack branching decreases with ageing time, as this is accompanied by an increase in the area fraction of the grain boundary precipitates. A branched crack has a lower effective crack-tip stress intensity than a linear crack of the same length under the same applied K_I , so crack branching leads to an apparent enhancement in the measured fracture toughness. The types of crack branching observed in different microstructures are shown schematically in Fig. 3.17.

Modelling fracture toughness in materials showing transgranular rupture

Attempts have been made to make a quantitative link between microstructure and fracture toughness, and one simple example, due to Hahn and Rosenfield, will be outlined. They considered the events in the crack tip plastic zone (Fig. 3.16), in a material containing second-phase particles. Events similar to those illustrated in Fig. 3.10 take place, and their model is based on the concept that the critical step in the crack extension process occurs when the crack tip opening displacement (δ_c) is of a comparable dimension to the width of the unbroken ligament separating the cavitated particles. Thus if λ is the spacing of these particles, then the Hahn and Rosenfield criterion may be written as

$$\lambda = \delta_c \quad (3.21)$$

If the mean volume spacing of the particles is expressed in terms of their volume fraction f and diameter d , as discussed in Chapter 1, i.e.

$$\lambda = d (\pi f/6)^{1/3}$$

substitution in equations (3.20) and (3.15) gives:

$$K_{Ic} = [2\sigma_y E (\pi/6)^{1/3} d]^{1/2} f^{-1/6} \quad (3.22)$$

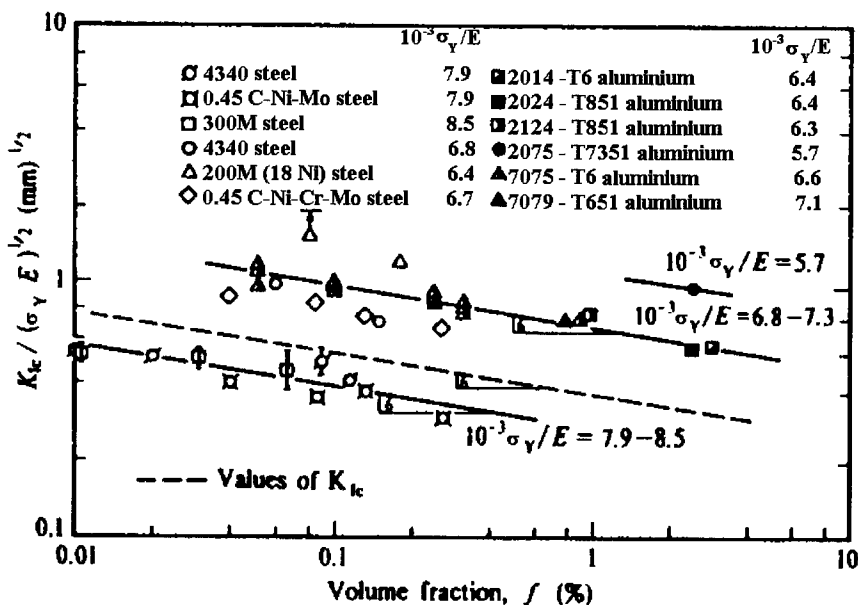


Fig. 3.18 Influence of the volume fraction, f , of large ($\geq 1 \mu\text{m}$) size second-phase particles on the plane strain fracture toughness of commercial alloys (after G.T. Hahn and A.R. Rosenfield [14]).

Figure 3.18 illustrates the application of equation (3.22) to data for a number of materials containing coarse inclusions, notably a range of commercial aluminium alloys and steels. There appears to be good experimental agreement with the predicted linear relationship between K_{Ic} and $f^{1/6}$. Equation (3.22) does not give a satisfactory description of the effect of other material parameters, however. Firstly, K_{Ic} is predicted to increase as $\sigma_y^{1/2}$, whereas the observed behaviour is as indicated in Fig. 3.17, with the fracture toughness falling with rising yield strength. Secondly, the toughness does not increase with increasing size, d , of void-nucleating particles – in fact the opposite effect has been found in steels of the same yield strength containing identical inclusion spacings differing only in size. It must be concluded that models using a single fracture plane and a single value of d are gross oversimplifications of the fracture process. The statistical nature of the distribution of inclusion size, shape and spacing, and the absence of fundamental models relating void nucleation, growth and coalescence to microstructural features and materials properties have limited progress in this area.

Modelling fracture toughness in materials showing intergranular rupture

During an isothermal ageing sequence, many precipitation-hardening alloys exhibit a condition in which the interior of the grains is highly hardened while the grain boundary and its environment (the pfz) is very soft. This tendency, and thus

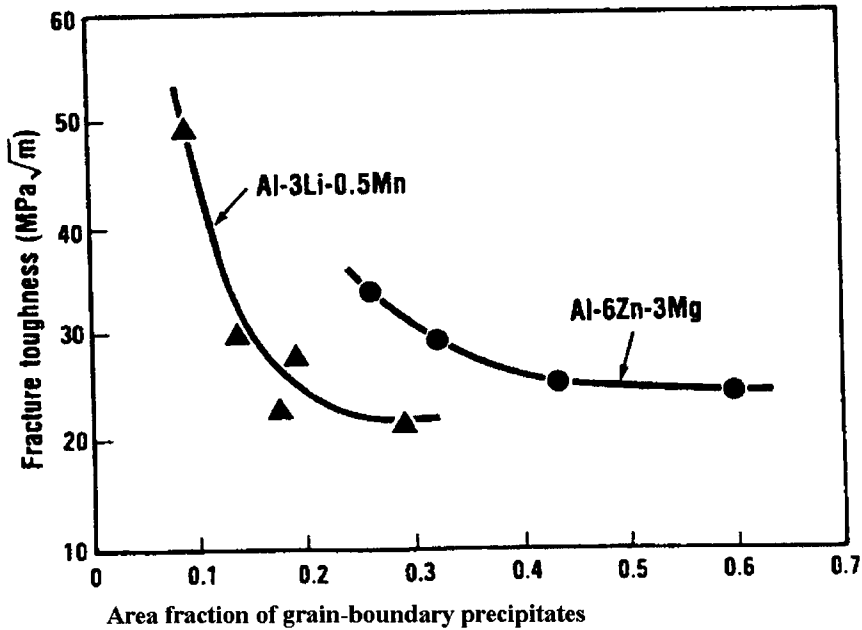


Fig. 3.19 Variation in plane strain fracture toughness with area fraction of grain-boundary precipitates, at constant matrix yield strength, for Al-3 wt% Li-0.5 wt% Mn, and Al-6 wt% Zn-3 wt% Mg alloys (after A.K. Vasudevan and R.D. Doherty [15], and P.N.T. Unwin and G.C. Smith [11]).

the inhomogeneity of distribution of strain between grain interior and pfz is maximized close to the maximum of the yield stress of the bulk alloy.

The intergranular failure strain, ε_{ci}^* , is likely to be dependent upon the area fraction f_i of particles in the grain boundaries. In most precipitation-hardened alloys, incoherent particles form there by heterogeneous nucleation (see Chapter 1), and by analogy with equation (3.12) one may write

$$\varepsilon_{ci}^* = C^{-1} \ln (\sqrt{(\pi/6f)} - \sqrt{(2/3)} + e_n) \quad (3.23)$$

Many microscopic investigations have shown that the local area fraction, f_i , can be very high, which then leads to small values of ε_{ci}^* , even in a very soft and ductile matrix. This in turn leads to a low value of K_{Ic} , as shown by Vasudevan and Doherty [15] who studied specimens of a high purity Al-3 wt% Li-0.5 wt% Mn alloy which were first aged to different times so that the size and area fractions of the grain-boundary δ -phase could be varied significantly. These microstructures were δ' -reverted (see Section 1.2.6) and re-aged to a fixed underaged condition which produced microstructures that contained different amounts of grain-boundary δ but with nearly identical matrix δ' , and that exhibited constant yield strengths.

Figure 3.19 shows the variation in plane strain fracture toughness measurements as a function of the area fraction of grain-boundary precipitate for this alloy and

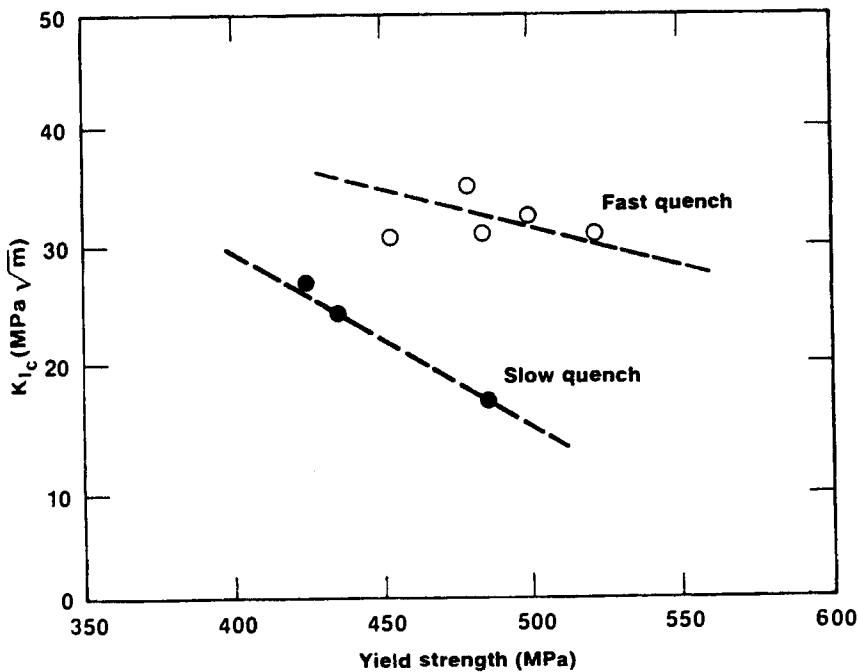


Fig. 3.20 Effect of quench rate on the plane strain fracture toughness of 7075 alloy plate aged to different yield strengths (after D.S. Thompson [16]).

also for an Al-6 wt% Zn-3 wt% Mg alloy for which Unwin and Smith employed a different method of heat-treatment to vary the amount of grain-boundary precipitates at nearly constant strength. The two alloys have very different compositions, yield strengths and also sizes of grain-boundary precipitates, but they exhibit full intergranular fracture and show a similar trend of a large loss of toughness as the area fraction of grain-boundary precipitate increases.

The significance of grain-boundary precipitation on toughness is also apparent in commercial alloys if slow quench rates are applied which allow more grain-boundary precipitation to occur prior to the final ageing treatment. This effect is particularly severe in thick section products where it is difficult to achieve fast quenching following solution heat-treatments. An example of this effect is shown in Fig. 3.20 in the case of 7075 alloy plate at different yield strengths.

In summary therefore, we may conclude that the toughness levels of age-hardenable alloys generally decrease as the strength level is raised by alloying and heat-treatment. Once peak strength is reached for a particular alloy, some improvement in toughness may be obtained by overaging, although the overaged strength-toughness curves generally lie below the underaged strength-toughness curves, as illustrated schematically in Fig. 3.17.

This is due to the presence of coarse grain-boundary precipitates and pfzs in the overaged condition which lead to an increased incidence of low-energy intergranular failure.

3.4 FAILURE OF PRECIPITATION-HARDENED ALLOYS DURING FORMING

3.4.1 Crystallographic texture effects

The relationship between formability and microstructure in the case of aluminium alloys has been reviewed by B.A. Parker [13], to which reference should be made for a fuller account of this topic than that which follows.

We will confine our discussion to sheet forming, although some of the conclusions may be applicable to other operations. Lack of formability may be defined not simply by fracture during forming, where the important parameters in precipitation-hardened alloys are those we have discussed in the previous sections, but also by the possibility of the product being too thin in some regions for the end use of the product. The latter effect is determined by the normal anisotropy of the sheet, which is described in terms of the r -value (the ratio of the width to the thickness strain in a tensile test), and by the planar anisotropy (the Δr value obtained by measuring the r values at 0, 45 and 90 degrees to the rolling direction of the sheet). Both of these parameters are related to the crystallographic texture of the grains in the sheet.

It is reasonable to expect that spherical and/or incoherent precipitates should have no effect on texture-induced anisotropies, while plate and rod-like precipitates (confined as they are to specific crystallographic planes) should result in some changes in the plastic anisotropy.

For aluminium alloys, the most common directional precipitates are those on either {100} or {111} habit planes, and it appears that {100} precipitates act to eliminate texture-induced plastic anisotropy, while {111}-type precipitates tend to reinforce it. The work of P. Bate, W.T. Roberts and D.V. Wilson [17] on Al–Cu alloys with {100} habit plane precipitates, demonstrates that the magnitude of the change depends on the aspect ratio and volume fraction of the precipitates and in the peak-aged condition these precipitates can almost totally eliminate texture effects, as shown in Fig. 3.21.

Here, the solution-treated material and the alloy overaged (48 h at 350°C) to contain coarse, roughly equiaxed particles of θ -phase show the theoretically expected variation of texture with angle to the rolling direction. When the alloy is aged (24 h at 200°C, or 4 h at 300°C) to contain θ' -plates with {100} habit plane, nearly isotropic behaviour is produced, as indicated by r values.

3.4.2 The effects of precipitates

If a dispersion of fine ($< 0.01 \mu\text{m}$ diameter) particles is cut by moving dislocations, we have seen that there is a tendency for the deformation to be concentrated into intense slip bands. This inhomogeneous slip distribution may provide a mechanism for the initiation of a premature shear failure, or assist in the nucleation of grain boundary cracks. The presence of non-deformable particles of intermediate size ($\sim 0.1 \mu\text{m}$) tends to homogenize the slip, and may also increase the work-hardening rate, because of the presence of geometrically necessary dislocations. This will have beneficial effects upon formability,

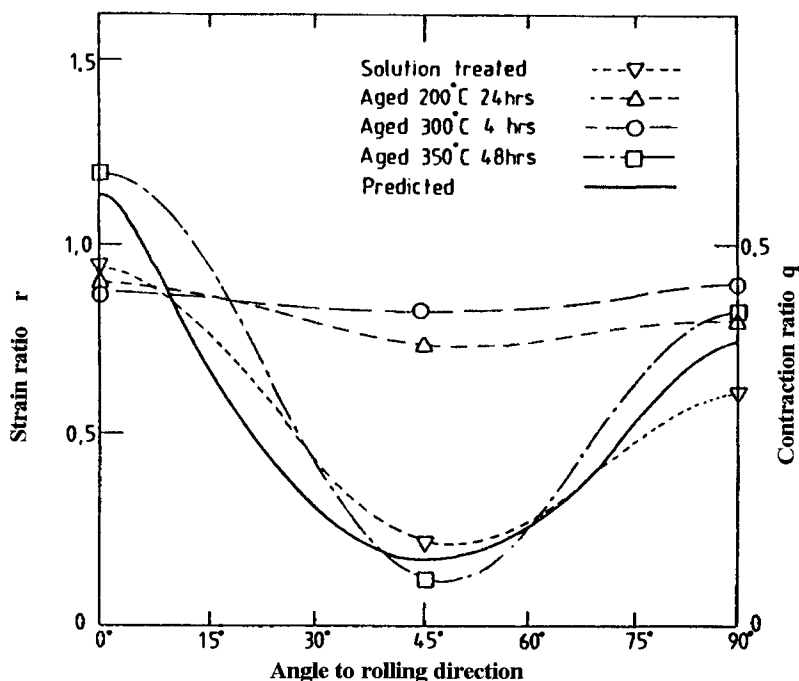


Fig. 3.21 Variation of r with test direction in Al-4 wt% Cu in the solution treated and aged conditions, compared with predictions of texture analysis (after P. Bate, W.T. Roberts and D.V. Wilson [17]).

whereas still larger particles ($> 5 \mu\text{m}$) may lead to fracture initiated by failure of the particle or their interface with the matrix.

An ideal microstructure for formable alloys should therefore exhibit a high work-hardening rate, it should contain no particles larger than $3\text{--}5 \mu\text{m}$, and it should not form intense slip bands. The latter requirement would be met if deformable precipitation-hardening particles were absent, or alternatively, if a duplex particle structure is present with fine particles for strength and larger (undeformable) particles to homogenize the slip. Additionally, the crystallographic texture should show negligible planar anisotropy and have $\{111\}$ planes parallel to the rolling plane.

3.5 FATIGUE OF PRECIPITATION-HARDENED ALLOYS

3.5.1 The endurance ratio

It is well established that the age-hardening process in many alloys, which has a large effect upon the tensile strength, may have relatively little effect upon the

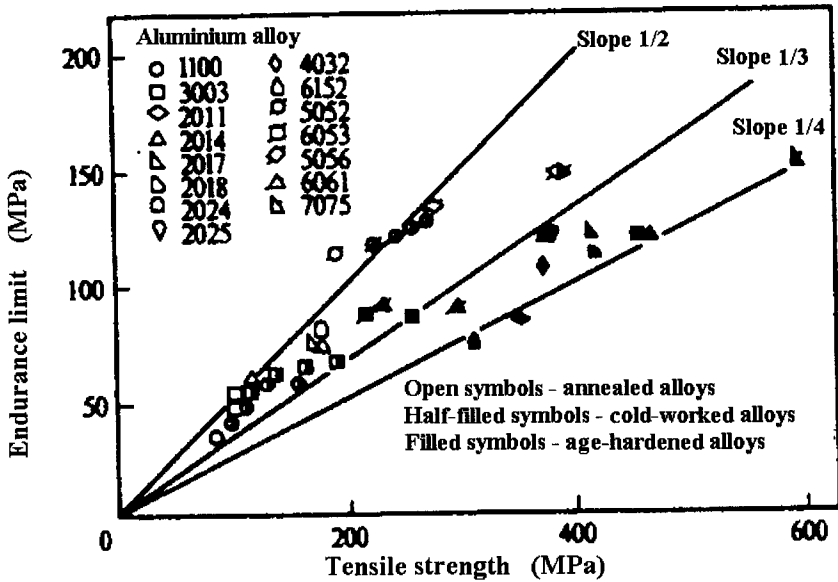


Fig. 3.22 Variation of the 10^8 cycles endurance limit with tensile strength for different aluminium alloys (after A.J. McEvily, J.B. Clark, E.C. Utley and W.H. Herrnsstein [18]).

fatigue strength. This results in a low value of the *endurance ratio*, i.e. the ratio of the fatigue stress giving failure in 10^7 or 10^8 cycles to the ultimate tensile stress (UTS).

Figure 3.22 illustrates the variation of the 10^8 cycles endurance limit with UTS for different aluminium alloys. This shows that for annealed alloys a ratio of about 0.5 is obtained, which is similar to that obtained in pure metals. Cold working gives rise to a ratio of 0.33 and age-hardening to a ratio of only 0.25. The value of the endurance ratio for a given alloy changes during heat-treatment, being a minimum when aged to peak hardness. These effects may be understood more readily if we examine the cyclic stress behaviour of these materials.

3.5.2 Cyclic stress-strain behaviour

When a metal or alloy is cycled through a constant or varying strain amplitude, large changes may occur in its flow stress. Depending upon the metal and its processing history, a metal's deformation resistance may increase (cyclic hardening), decrease (cyclic softening) or remain essentially unchanged (cyclic stability). Cyclic stress-strain response (CSSR) is the term used to describe the relationship between the flow stress and the cyclic strain over the entire life range.

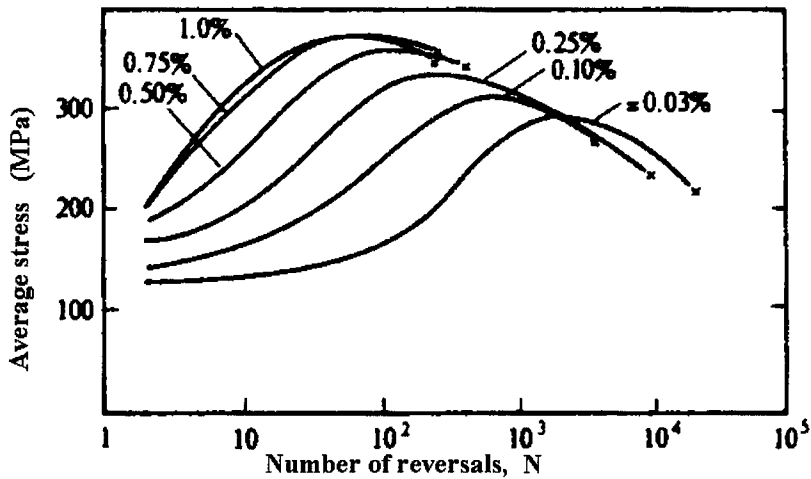


Fig. 3.23 Cyclic response curves at different plastic strain amplitudes for Al-Cu alloys aged to contain the θ'' phase (after C. Calabrese and C. Laird [19]).

- 1 *Single phase alloys* usually cyclically harden when tested in the annealed condition and soften when they are in the cold worked condition. The reason for this behaviour is related to the nature and stability of the dislocation substructure of the material. For an annealed material, the dislocation density is low. As a result of plastic strain cycling the dislocation density increases rapidly resulting in significant cyclic hardening. When a metal has a high initial dislocation density, as in cold-worked metal, subsequent strain cycling causes a rearrangement of dislocations into a configuration that offers less resistance to deformation, that is, the material strain softens.
- 2 In the case of *age-hardened alloys*, when the hardening particles are coherent and so closely spaced that dislocations are constrained to cut them, then considerable work hardening is caused by the first few cycles of strain, followed by softening. Figure 3.23 refers to Al-Cu, and illustrates the CSSR for material when aged to contain the coherent θ'' phase. Initial cyclic hardening up to a maximum or saturation value is followed by marked softening to failure.

The initial hardening arises due to an increase in dislocation density and due to precipitate-dislocation interactions. The subsequent cyclic softening is associated with the formation of *persistent slip bands* (PSBs), along which deformation is concentrated. (These bands persistently reappear at the same location during continued cycling, even after some material is removed by surface re-polishing.) Several mechanisms have been proposed for the origin of precipitate damage leading to softening and strain localization into PSBs, these include:

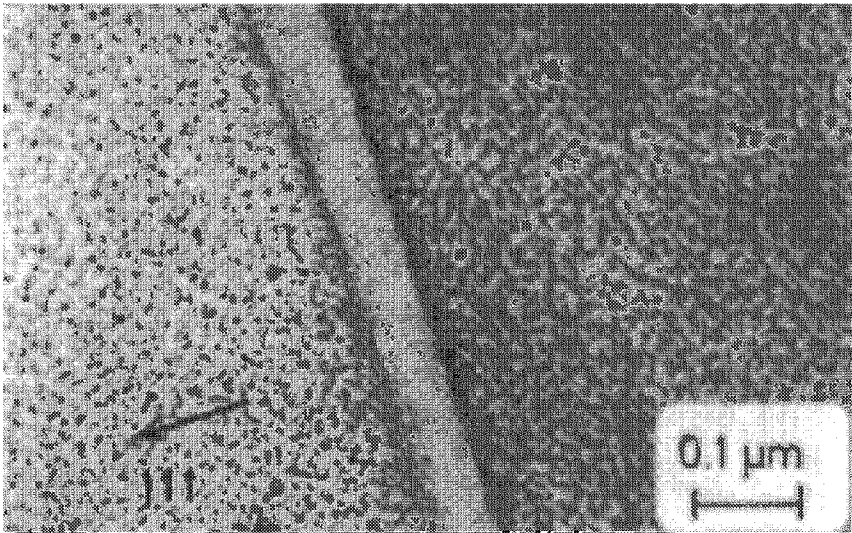


Fig. 3.24 PSB in fatigued Al–Ag containing spherical GP zones (E. Kohler, D. Steiner and V. Gerold [20]).

(i) *Reversion*

It is suggested that cyclic straining causes the dislocations to pass backwards and forwards through the coherent precipitates, so reducing them to below the critical size for stability. It is suggested that a high concentration of point defects are present in the slip bands during fatigue, leading to enhanced diffusion rates – the stability of the high vacancy concentration being maintained by solute–vacancy interaction. A high concentration of vacancies would greatly accelerate the diffusion of solute away from the subcritical precipitates.

In precipitation-hardened alloys the PSBs are very narrow – their width being below 100 nm, compared with 1–2 μm for single-phase materials. Figure 3.24 shows a TEM image of a PSB in an Al–Ag alloy containing spherical GP zones. The primary dislocations are out of contrast, and the narrow PSB is visible because of the disappearance of the zones.

(ii) *Precipitate disordering*

Many age-hardened systems contain precipitates of an ordered phase (e.g. γ' precipitates in nickel-based superalloys), and plastic deformation can disorder the precipitate if the flow is not fully reversible. Localized softening and PSB damage will ensue without precipitate dissolution being necessary. Dissolution may occur *subsequently*, however, as a consequence of the disordering, since the disordered precipitates will have a higher free energy and thus a higher solubility than the more stable ordered precipitates.

(iii) *Overaging*

It has been suggested that the combined action of fatigue-induced dislocations and vacancies may induce overageing, i.e. the replacement of

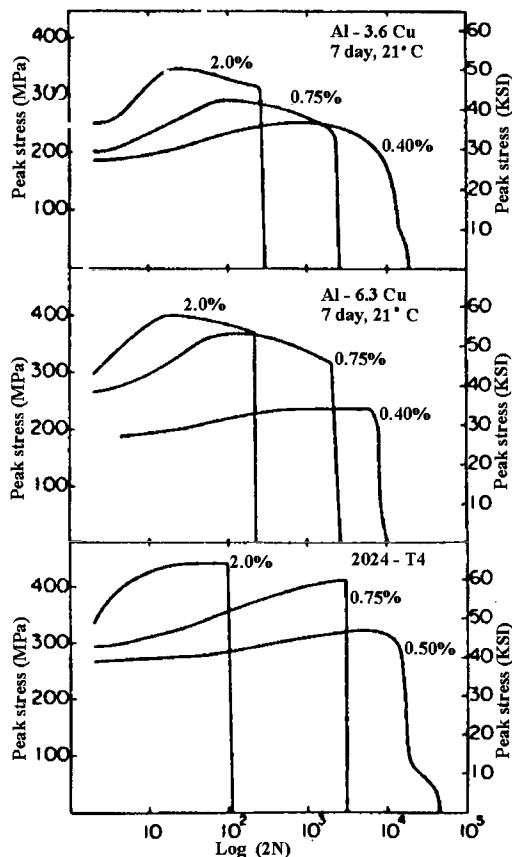


Fig. 3.25 Stress amplitude versus reversals ($2N$), at constant strain amplitude, in binary Al–base Cu alloys and in 2024 aluminium alloy aged at room temperature (after M.E. Fine and J.S. Santner [21]).

the metastable precipitates by more stable and more widely spaced precipitates.

- 3 *The effect of precipitate type upon CSSR.* Figure 3.25 illustrates the effect of various types of dispersion in an aluminium alloy upon cyclic softening. Three different Al–Cu alloys were chosen: Al–3.6 wt% Cu; Al–6.3 wt% Cu; and a commercial 2024 alloy. Each alloy was tested in the naturally aged condition: the Al–3.6 wt % Cu had only GP1 present, the Al–6.3 wt% Cu had both GP1 and undissolved 5 to 10 μm diameter θ particles, and the commercial 2024 had GP zones, dispersoids and inclusions present. In Fig. 3.25a, the alloy with only GP1 zones present shows cyclic hardening followed by softening at all strain levels, which is consistent with the data of Fig. 3.23. In Fig. 3.25b the alloy with both GP1 and θ particles exhibits hardening followed by softening only

at large and intermediate strains. No softening was observed at low strains. The interpretation is that at high strains the GP1 zones are cut sufficiently to disorder the structure and the alloy softens. At low strains the large θ particles homogenize the strain and thus prevent the localization of the strain required to soften the structure in the active slip bands. In Fig. 3.25c, the 2024-T4 shows no softening at any strain level: this is because the dispersoids present in commercial Al alloys are very effective at homogenizing the slip distribution.

3.5.3 Fatigue crack nucleation

Precipitation-hardened alloys do not appear to exhibit essentially different mechanisms of formation of fatigue crack nuclei from pure metals, when transgranular crack nucleation is considered. Naturally, crack initiation in commercial alloys can be from coarse inclusions, which are often in the form of intermetallics produced by impurity elements. The local stress concentration at the inclusion concentrates slip in the adjacent matrix, leading to the formation of fatigue crack nuclei. Thus, in aluminium alloys for aerospace applications, a low iron content is specified in order to minimize the occurrence of such constituent particles.

In the absence of such heterogeneities, the interface between a PSB and matrix serves as a preferential site for fatigue crack nucleation. Resistance to fatigue failure is thus likely to be higher in those materials which do not exhibit severe localization of plastic strain, and slip homogenization by means of dispersoids has been shown to inhibit the nucleation of fatigue cracks in age-hardened alloys.

Figure 3.26 shows three $S-N$ curves for a series of Al–Mg–Si alloys in the peak-aged condition. All the alloys were free from coarse iron-bearing constituent phases, whose effect might have been to swamp the effects of the dispersoid particles, and were processed to produce comparable grain sizes. MTS was essentially of pure ternary composition, ML and MH contained increasing volume fractions of the α -Al₁₂Mn₃Si dispersoid phase, of size approximately 0.1 μm (see Fig. 1.1). It may be seen in Fig. 3.26 that the dispersoid-bearing material exhibits an increased fatigue life at all stresses, and may be accounted for by the homogenization of slip by the dispersoid particles.

Finally, the nucleation of fatigue cracks at grain boundaries occurs under the influence of embrittling environments (which preferentially attack grain boundaries and any particles that may lie upon them). In age-hardened alloys, the presence of a pfz will clearly enhance the susceptibility for this type of failure.

3.5.4 Fatigue crack growth (FCG)

Fracture mechanics is employed to express the influence of stress, crack length and geometrical conditions upon the rate of fatigue crack propagation. The FCG data is plotted in the form of crack growth per cycle (da/dN) versus ΔK curves, where for tensile fatigue ΔK refers to the range of mode I stress intensity factors

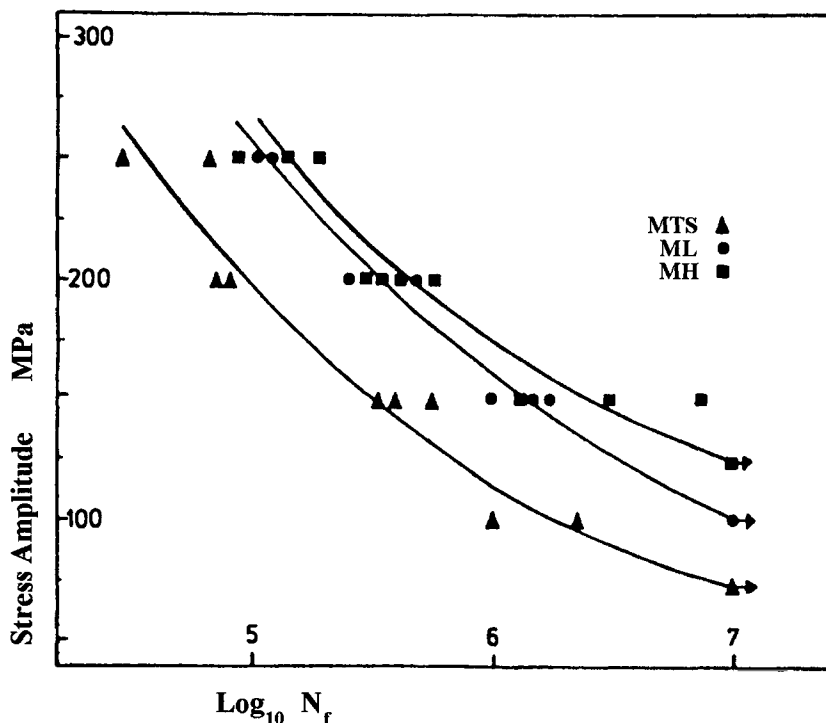


Fig. 3.26 *S-N* curves for pure ternary Al-Mg-Si alloys (MTS) and alloys containing volume fractions of 0.22 (ML) and 0.61 (MH) of the Mn-bearing dispersoid phase.

in the stress cycle (i.e. $\Delta K = K_{\max} - K_{\min}$). $K_{\min}/K_{\max}$ is known as R , the *load ratio*.

Figure 3.27 illustrates schematically the form of crack growth curve obtained in the case of most engineering alloys. The curve is seen to be essentially sigmoidal in form: over the central, linear portion (regime B in Fig. 3.27) the FCG rate is observed to obey the Paris power law relationship:

$$da/dN = C (\Delta K)^m$$

where C and m are constants. Here there is often little influence of microstructure and mean stress (R value) on the FCG rate.

In regime C (Fig. 3.27) FCG rates increase rapidly to final fracture. This corresponds to $K_{\max}$ in the fatigue cycle achieving the fracture toughness, K_c of the material.

In regime A, the average FCG rate becomes smaller than a lattice spacing, and this suggests the existence of a threshold stress intensity range, K_{th} , below which the crack remains essentially dormant. The value of K_{th} is highly sensitive to

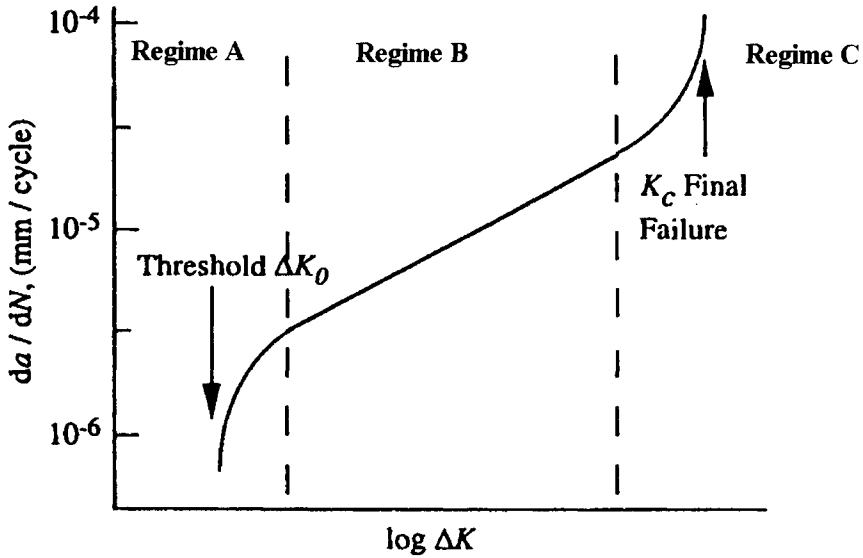


Fig. 3.27 Schematic illustration of fatigue crack growth curve.

microstructure and also to the value of R . For example, the presence of incoherent second-phase particles in the grain boundary, and their associated pfzs, can accelerate the rate of FCG by interface decohesion. Since the rate of crack advance is slow in the near-threshold region, the value of K_{th} also exhibits an increased sensitivity to environmental effects.

The FCG life of a structural member is often dominated by the propagation of cracks at low values of ΔK , so the factors influencing near-threshold FCG are clearly of great importance.

The size and shape of the plastic zone at the tip of a propagating fatigue crack can be calculated, and by analogy with equation (3.19), the radius r_s of the 'static' plastic zone is given by an expression of the form:

$$r_s = A (K_{max}/\sigma_y)^2$$

and the cyclic or fatigue plastic zone size, r_f , will be given by:

$$r_f = A' (\Delta K/\sigma_y)^2$$

where A and A' are constants and σ_y is the tensile yield stress. These plastic zone sizes may be correlated with microstructural features, such as the grain size.

The effect of slip distribution on near-threshold crack propagation

Even when the value of r_f at the tip of a near-threshold crack is the same for two different microstructures (with the same grain size), different thresholds may be

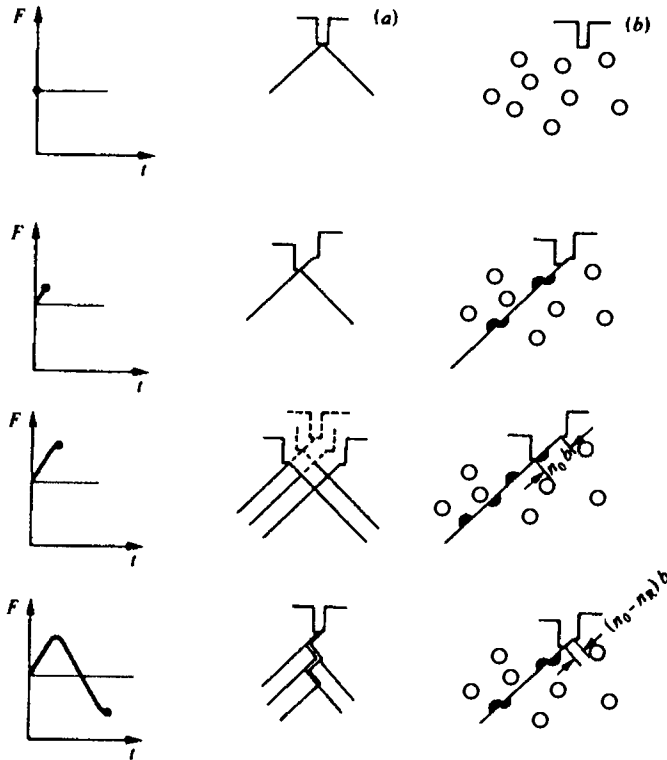


Fig. 3.28 Schematic representation of crack propagation during one cycle in (a) an overaged alloy, the microstructure tending towards homogeneous deformation, and (b) peak-aged and underaged alloys, the microstructure tending towards inhomogeneous deformation (after E. Hornbogen and K.H. Zum Gahr [22]).

observed because of differences in slip distribution. For example, if specimens of a given alloy are underaged and overaged to the same yield stress, the *underaged* alloy, containing coherent precipitates, will exhibit inhomogeneous, planar slip leading to crack propagation along a single slip system. The single shear failure promotes a highly serrated and tortuous crack path, with the wavelength of crack path tortuosity being of the order of the grain size. The *overaged* alloy will exhibit homogeneous slip, and cracks will propagate in a planar transgranular manner, showing no tortuosity.

The presence of a tortuous crack path will tend to retard the rate of fatigue crack growth, by the process of *roughness-induced crack closure*. Crack growth rates are not only influenced by the conditions ahead of the crack tip, but also by the degree of the crack face contact behind the crack tip. Premature contact between the faces of the crack will cause a reduction in the apparent 'driving force' for fatigue crack advance. If crack closure occurs at a stress intensity range value of $\Delta K_{\text{closure}}$, then the effective stress intensity range, ΔK_{eff} , will be:

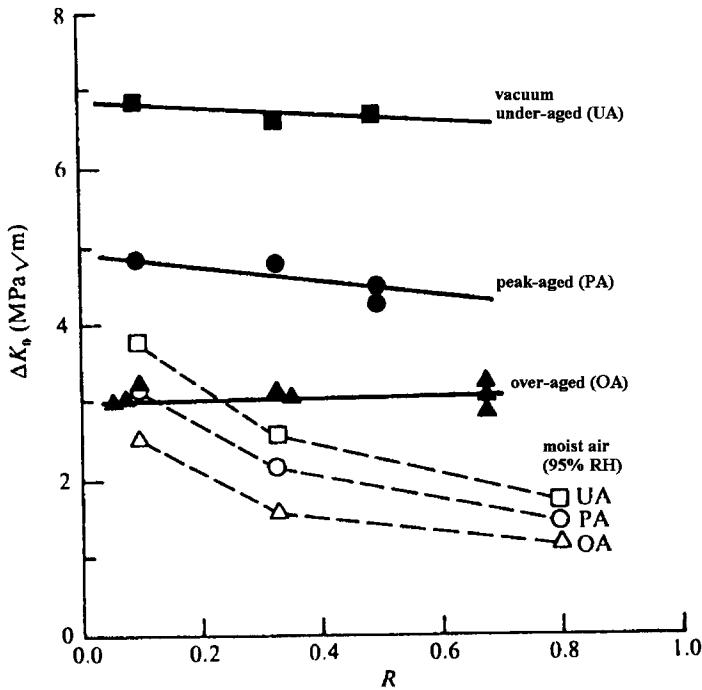


Fig. 3.29 Variation of ΔK_{th} as a function of the load ratio, R , for underaged and overaged conditions of a 7075 aluminium alloy. Both microstructures have the same yield strength and grain size (after S. Suresh [23]).

$$\Delta K_{eff} = \Delta K_{applied} - \Delta K_{closure}$$

The degree of slip heterogeneity will not only tend to change the crack path tortuosity, but also the degree of kinematic irreversibility of cyclic slip, when the crack tip plastic zone size is less than the grain size. The effect is shown schematically in Fig. 3.28, which represents crack propagation during one cycle in (a) an overaged alloy, in which there is a tendency for homogeneous deformation; several slip planes and two slip directions are shown to be operating, and (b) peak-aged and underaged alloys, where the microstructure has a tendency towards inhomogeneous deformation, here the slip in one plane and system allows partial reversal of the primary crack propagation event. If n_0 is the number of dislocations of Burgers vector b in the slip plane that produces slip steps at the crack tip, then if all of them contribute to crack propagation, we may write the growth velocity:

$$da/dN = C n_0 b$$

where C is a dimensionless parameter which takes into account the orientation of the slip plane to the macroscopic direction of crack propagation. If, during the

second half of the fatigue cycle say, n_R dislocations move backwards on exactly the same plane, they will not contribute to the progress of the crack, giving

$$da/dN = C (n_0 - n_R) b$$

This process is another contribution to the observed reduced crack growth velocity in material in which heterogeneous slip processes operate in the near-threshold region.

Figure 3.29 shows this effect, and also illustrates that underaged and overaged microstructures of an aluminium alloy with the same yield strength and grain structure can also exhibit vastly different ΔK_{th} values in both vacuum and moist air.

Finally, it must be pointed out that there is inadequate fundamental knowledge about the optimum size and distribution of precipitates required for maximum resistance to fatigue failure. A mixture of small coherent particles to give strength, and larger dispersoids to homogenize strain distribution may be the most effective, but this will only be so if one can assume that no local weaknesses develop in PFZs or at particle/matrix interfaces.

3.6 STRESS-CORROSION

Materials are known to fail under stress when the *initial* stress intensity level is considerably below K_{Ic} . This is because cracks are able to grow to a critical size at which the stress intensity level is increased to the critical value. The processes whereby such crack extension occurs in the presence of an applied stress in an aggressive environment are referred to collectively as *environmentally-assisted cracking* (EAC). Two important examples are *stress-corrosion cracking* (SCC), and *hydrogen embrittlement* (HE), and they arise from the conjoint action of the stress and the environment. The stress may be externally applied, or may be internal, residual stresses. An applied fluctuating stress can lead to *corrosion fatigue*. The environment may be an aggressive liquid (e.g. salt solution), or even moist air, whose moisture content may by dissociation be a source of hydrogen atoms.

In order to quantify EAC processes, the rate of crack advance (da/dt) is monitored as a function of the instantaneous value of the stress intensity. Cracked specimens are tested in Mode I (crack opening mode), and in general the data are represented on plots of $\log da/dt$ versus K , and they take the form shown schematically in Fig. 3.30.

Three distinct crack growth regimes are shown, although all may not be present in a given alloy. In region I, da/dt is strongly dependent on K , and the slope of this part of the curve may be steep enough to define a value of K_{IEAC} , i.e. a level of K_I below which da/dt become vanishingly small. In region II the rate of crack growth appears to be relatively independent of the prevailing level of K . The crack extension rate is still strongly dependent on the environment, however. Experimental data suggest that true 'plateau velocities' rarely occur, but crack velocities fluctuate, with an overall tendency for the mean velocity to

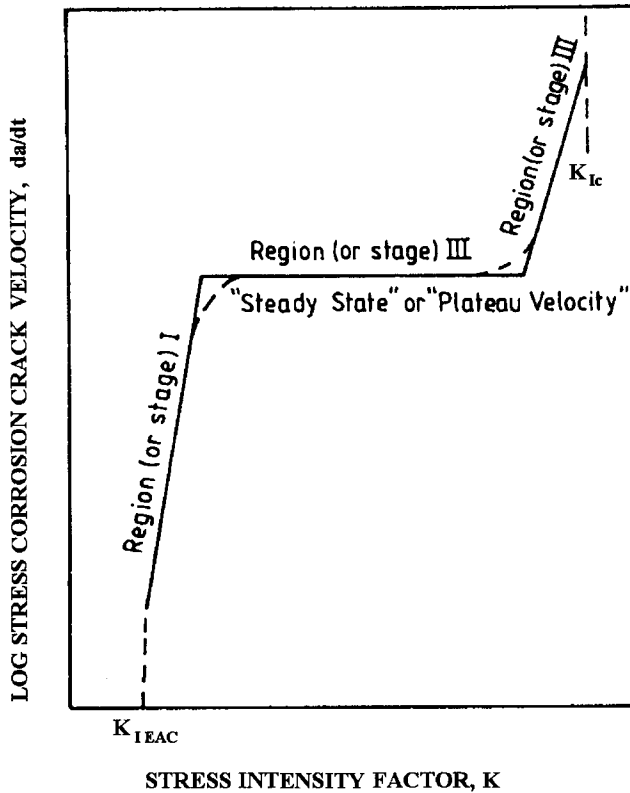


Fig. 3.30 Diagram showing three stages of environment-assisted cracking under sustained loading in an aggressive environment. Lower and upper limits of the plot are determined by K_{IEAC} and K_{Ic} respectively.

increase with increasing K . Finally, in region III, da/dt is strongly K -dependent, and in the limit the crack grows unstably as K approaches K_{Ic} .

The effect of the environment is such that the ratio K_{IEAC}/K_{Ic} is very small, typically 0.05! We will confine ourselves to a consideration of the behaviour of age-hardening aluminum alloys in the following discussion.

3.6.1 Stress-corrosion of high-strength aluminum alloys

Pure aluminium is immune to stress-corrosion, whereas aluminium binary or ternary alloys containing copper, magnesium, zinc or lithium can all be susceptible. Generally speaking, an alloy's potential susceptibility to SCC tends to increase as the total solute in solid solution increases, and the microstructural condition (as influenced by aging) is also known to influence SCC.

As solution-treated (provided no significant room temperature ageing has occurred), the 2xxx, 7xxx and 8xxx series of aluminium alloys are immune to SCC. As shown schematically in Fig. 3.31, aluminium alloys are most

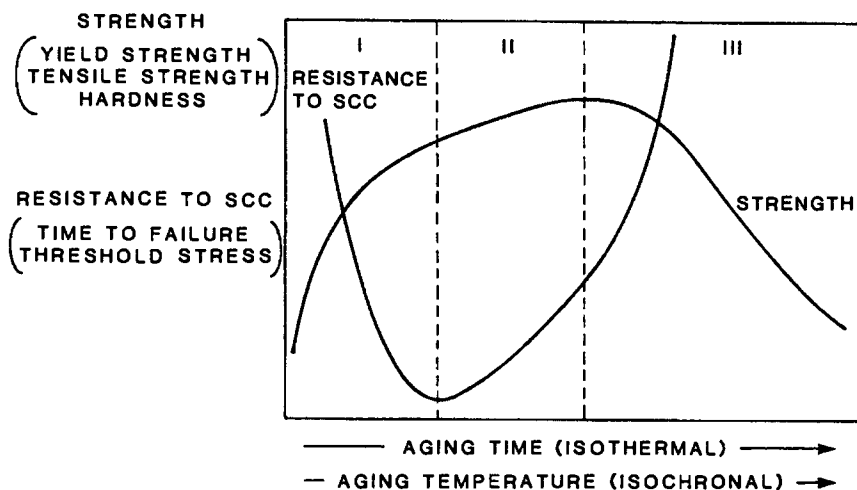


Fig. 3.31 Schematic representation of the change in resistance to SCC and strength as a function of ageing time or ageing temperature (after M.O. Speidel [24]).

susceptible when slightly below peak strength, when planar slip and strain localization are most pronounced. As the alloy is overaged, the SCC susceptibility progressively decreases. SCC is almost exclusively intergranular in nature in aluminium alloys, and although numerous detailed mechanisms have been proposed for the phenomenon in various alloys, two basic theories have evolved. One regards SCC as highly localized anodic dissolution of the alloy under the combined influence of stress and the environment. The other approach suggests that atomic hydrogen enters the alloy, and this causes embrittlement and loss of ductility.

A review of the current SCC mechanisms has been given by Holroyd, Vasudevan and Christodoulou [13] to which reference should be made for more detailed information. These authors conclude that mechanistic interpretation of the SCC of high-strength aluminium alloys remains controversial and much systematic work remains to be done.

There are complex interactions between an alloy's microstructure and its SCC behaviour. While some effects may be attributed to changes in slip distribution in the matrix, there is recent experimental evidence that grain boundary precipitation and local chemical composition in the grain boundary pfz can play an additional and more important role during SCC.

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FURTHER READING

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APPENDIX TO CHAPTER 3

THE ROLE OF DISPERSED SECOND PHASES ON THE DUCTILE FRACTURE PROCESS

[An excerpt from a paper follows, which was presented in 1948 by Dr Constance F. Tipper at a conference on The Fracture of Solids organised by the British Rheologists' Club under the Chairmanship of their President, Professor N. F. Mott FRS. Opening this conference Professor Mott pointed out that quite apart from its practical importance, fracture was the most interesting property of solids to the theoreticians because it is the least understood property, no progress having been made beyond the 1924 Griffith crack theory.]

Dr Tipper described some experimental work on the brittle fracture and the ductile fracture of mild steel. It is the latter work we quote below, and it shows the importance of second-phase particles on the nucleation of ductile fracture. It is now known that the same process operates over a very large range of particle size, and so the work identifies for the first time a very important general fracture mechanism, one which is particularly relevant to particle-hardened alloys.]

THE FRACTURE OF METALS

C. F. TIPPER, MA, DSc

Metallurgia **39** (1949) 133–137

[After discussing the metallography of brittle fracture, an account is given of the fracture of material in a ductile condition]

Diagrammatic drawings are given in Fig. App. 3.1. No. (1) shows the two parts fully separated; (2) represents a section before the point of visible cracking on the surface; and (3) near the end of the fracture where the metal is divided into separate sections. The mean fracture path is still perpendicular to the direction of loading. in No. (4) the mean fracture path is at 45° to the direction of pulling, a change which takes place in very ductile steels and results in the typical appearance of most fractures in mild-steel plate.

[The paper continues]

In ductile steels the holes almost certainly originate by the drawing away of the metal from non-metallic inclusions. This process may begin at an early stage, probably at the yield point. Fig. App. 3.2 shows such a hole forming round an inclusion. Separation has hardly begun in the lower inclusion. Near the main fracture, the holes become so large that the inclusions generally drop out during the preparation of the section (Fig. App. 3.3).

The influence of structure on mechanical properties, apart from composition is well known. It is only necessary to mention the lower values for elongation and more especially reduction in area in a tensile test and the energy absorbed in

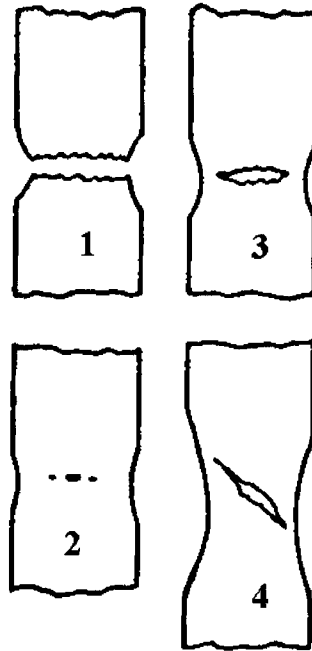


Fig. App. 3.1 Diagram of ductile fracture processes.

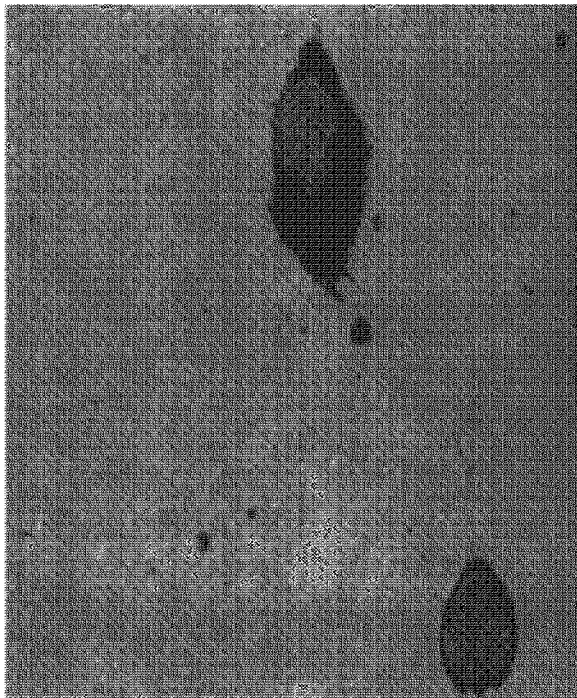


Fig. App. 3.2 Hole forming round inclusion. $\times 800$

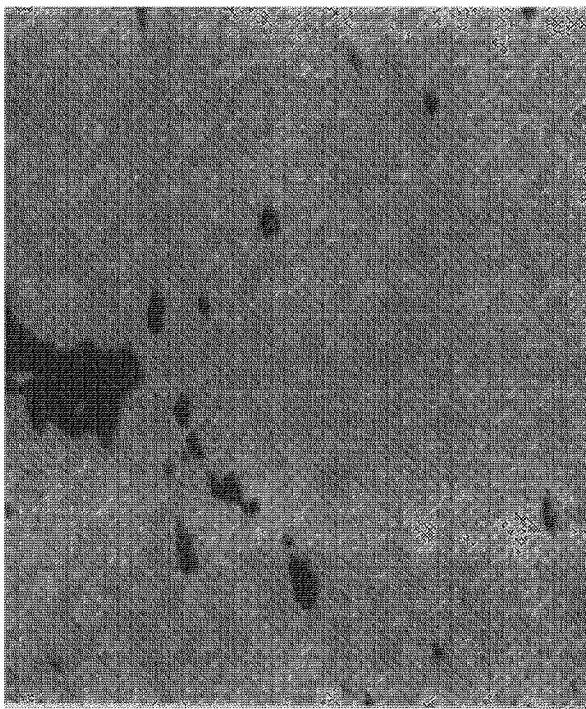


Fig. App. 3.3 Holes formed round inclusions tend to lie at 45° lines to direction of loading. $\times 80$

impact tests when the test-pieces are cut across the direction of rolling. Since inclusions are elongated by the working they are more dangerous when they are placed with their long axis perpendicular to the principal tensile stress. In the position also, there are more 'ways through' for the advancing fracture of whatever type. Cracks meeting an inclusion or hole may be diverted or stopped if the discontinuity affords relief of stress, so that inclusions may act in two capacities.

At what stage do cracks and fissures form? It has been suggested above that separation between metal and non-metallics may begin at the yield point. Separation would be expected to increase rapidly at the point when a neck forms in a tensile test-piece or near a notch. Hence, Bridgman's observations on the increase in ductility caused by testing under high hydrostatic pressure, and the large extension obtainable in wire-drawing and rolling may be regarded merely as the results of closing the flaws.

These observations refer chiefly to the fracture of mild steel, but they can be applied to explain the fracture of all polycrystalline aggregates, since internal flaws are necessarily present, although differing in both sizes and form.

4 The strength of aged alloys at elevated temperature

Aged aluminium alloys have the highest specific strengths of all commercially available engineering alloys at temperatures up to 100°C. At higher temperatures, however, the mechanical properties decline rapidly. Up to, say, 200°C, this is due to coarsening of the fine precipitates and, as the temperature increases further, to their progressive dissolution. This has serious implications for using such alloys for supersonic transport aircraft (SST). Concorde was designed to fly at Mach 2.05, where the general structural temperatures arising from aerodynamic heating are anticipated to be in the range 90° to 100°C, with some locations reaching 127°C. At Mach 2.4 these temperatures would range from 160° to 220°C, which would prohibit the use of conventional ingot metallurgy aluminium alloys, and require the aircraft to be constructed from, for example, more expensive titanium alloys, although some experimental age-hardened Al–Cu–Mg–Ag alloys with high Cu:Mg ratios have been successfully developed which contain the relatively stable Ω phase. These maintain their high mechanical properties at temperatures below 200°C.

It is the so-called nickel-based *superalloys* that provide the most important example of precipitation-hardened materials for use at elevated temperatures, though their relatively high density precludes their use as airframe and skin materials. The particles are coherent with the matrix, with closely matching lattice parameters, so that the interfacial energy (the driving force for particle coarsening) is minimized.

We will consider in general terms the strengthening mechanisms in precipitation-hardened systems at elevated temperatures, firstly when particle by-pass occurs (where the properties of the particle itself are irrelevant), and secondly when particle shearing occurs.

4.1 STRENGTH OF MICROSTRUCTURES WHERE PARTICLE BY-PASS BY DISLOCATIONS OPERATES

It is convenient to study model systems consisting of single crystals hardened with oxide particles when attempting to understand the interaction of dislocations with particles as a function of temperature. Because of the low solubility and high stability of such particles, their distribution remains virtually constant at high temperatures, in contrast to particles of intermetallic phases precipitated from supersaturated solid solution, which will tend to coarsen in size and to return into solution in the matrix. There has been considerable work on the high temperature strength of internally oxidized copper crystals, and Fig. 4.1, which refers to copper containing spherical particles of SiO_2 , is typical of the results obtained, and these are discussed below.

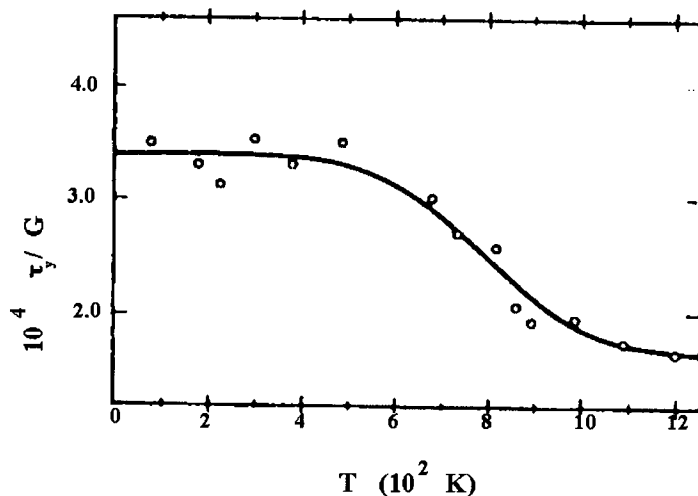


Fig. 4.1 The modulus-corrected yield stress as a function of testing temperature for copper – 0.41 vol % SiO_2 (courtesy of G.J. Lloyd).

4.1.1 Changes in yield stress with temperature

In Fig. 4.1, the shear yield stress/shear modulus ratio is plotted as a function of test temperature between 77 K and 1200 K. At low temperatures the curve is horizontal, indicating that in this range the variation of the Orowan stress with temperature is mainly due to change in the matrix shear modulus (equation (2.19)). However, as the temperature rises, a substantial fall in yield stress occurs, and this is attributed to ‘climb’ of dislocations around the particles.

It is significant that these crystals retain a large fraction of their strength at temperatures that are close to the melting point of the copper matrix. The minimum flow stress is found to be approximately one-half of the Orowan stress observed at low temperature. During plastic deformation, it is assumed that the dislocations remain in their slip planes, but at yield they locally ‘climb’ over the particles as illustrated in Fig. 4.2.

When a dislocation does climb locally over a particle it must increase its line length. This requires energy, and explains why the yield stress increment due to

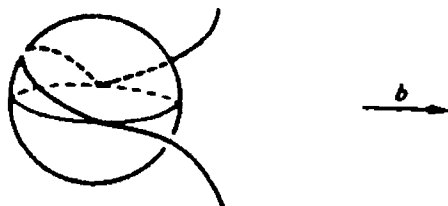


Fig. 4.2 An edge dislocation climbing over a spherical particle.

the particles in precipitation-hardened crystals does not become vanishingly small as the temperature approaches the melting point of the matrix. Whether or not climb occurs will depend on the applied strain rate and on the temperature of deformation. Calculations suggest that when all the particles are by-passed by local climb, the expected yield stress would be about one-half of the Orowan stress, as is observed experimentally. This has implications in the design of materials required to exhibit a high yield stress at elevated temperatures, in that the yield stress increment due to the particles would still be expected to be proportional to that predicted by the Orowan equation in terms of the spacing and volume fraction of the dispersion (equation (2.20)).

4.1.2 Changes in the rate of work hardening with temperature

Work on model systems again provides the clearest evidence of the changes in work-hardening rate with increasing temperature, and an electron metallographic study of deformed single crystals has, furthermore, enabled an understanding to be gained of the micromechanisms of deformation.

We will take as our model system single crystals of Al–0.5 wt% Si–0.45 wt% Cu. These may be solution-treated and aged to produce equiaxed silicon particles within a solution-hardened matrix. The crystals contain a volume fraction of 0.31% of Si particles of mean planar diameter of $0.097\ \mu\text{m}$ with a mean planar interparticle spacing of $1\ \mu\text{m}$. Figure 4.3a illustrates the changes in the form of the shear stress–shear strain curves observed as the testing temperature is increased from 77 K to 493 K. The curves show a parabolic region up to strains of 30%, and the orientation of the crystals was such that this range of deformation involved essentially primary slip activity. Figure 4.3b shows the temperature dependence of the parabolic work-hardening rate ($d\tau/d\varepsilon^{1/2}$). A very high temperature sensitivity is apparent, especially in the temperature region 300 to 500 K.

TEM examination of the deformed crystals revealed marked changes in the primary dislocation structure between specimens deformed at elevated temperatures, especially in the temperature range where there is a large reduction in the work-hardening rate. Whereas after low temperature deformation, dislocation debris is present, indicating by-pass by Orowan looping; after deformation at 463 K few dislocations are seen in association with the particles. This recovery process has been considered theoretically by Hirsch and Humphreys [2], and their model, based on processes involving dislocation pipe diffusion, appears to account well for the observed dramatic loss of work hardening encountered at a relatively low temperature.

4.2 YIELD STRENGTH OF MICROSTRUCTURES WHERE PARTICLE SHEARING BY DISLOCATIONS OPERATES

We will take nickel-based superalloys as our example for this class of precipitation strengthening. The term ‘superalloy’ was introduced in the late 1950s to describe those materials with high mechanical strength at high temperatures, primarily used for the aircraft gas turbine engine. They can

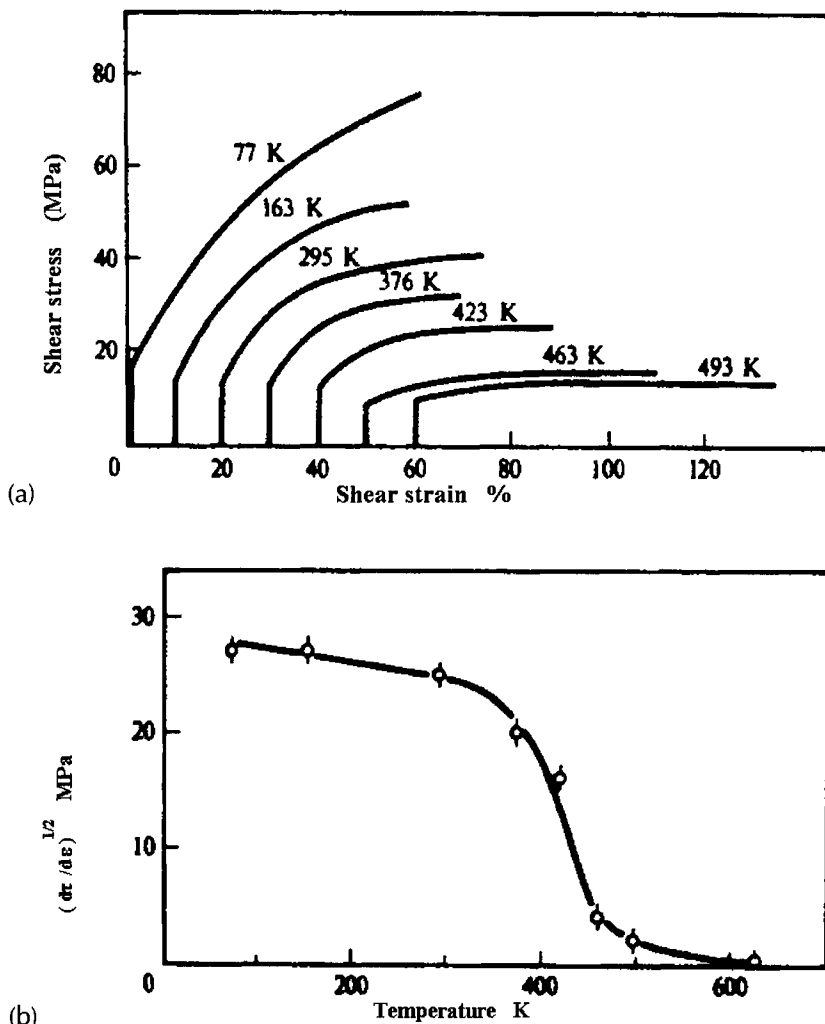


Fig. 4.3 (a) Shear stress–shear strain curves for aluminium crystals containing 0.31 vol % of Si particles, tested between 77 K and 493 K. (b) Temperature dependence of the parabolic work-hardening rate of the crystals whose stress–strain curves are shown in Fig. 4.3(a). (After A.T. Stewart and J.W. Martin [1].)

generally be divided into three main groups according to the main element which forms the matrix:

- nickel base,
- nickel-iron base and iron base,
- cobalt base.

The physical metallurgical principles underlying superalloy development have been described in great detail in numerous excellent reviews which cover the subject more comprehensively than the present text.

In nickel-based superalloys the microstructure consists of a fcc, oxidation-resistant Ni–Cr matrix, strengthened by $L1_2$ – type ordered γ' ($\text{Ni}_3(\text{Al},\text{Ti})$) precipitates. The degree of oxidation resistance may be impaired if, in highly alloyed superalloys, the Cr content has to be reduced in order to prevent the formation of the embrittling *sigma phase*, however. With regard to the precipitate phase, we discussed in Section 2.3.1 the mechanism of order strengthening at room temperature, involving the formation of antiphase boundaries within the particles and the movement of paired dislocations in the slip plane. The importance of this class of alloy for elevated temperature applications lies in the observation that the flow stress of the γ' particles *increases* with increasing temperature.

4.2.1 The effect of ordered precipitates

Figure 4.4 shows the temperature dependence of the 0.2% yield stress of a series of Ni–Cr–Al alloys containing various volume fractions of γ' , together with that for the γ -phase and γ' -phase alone. Three distinct types of behaviour can be

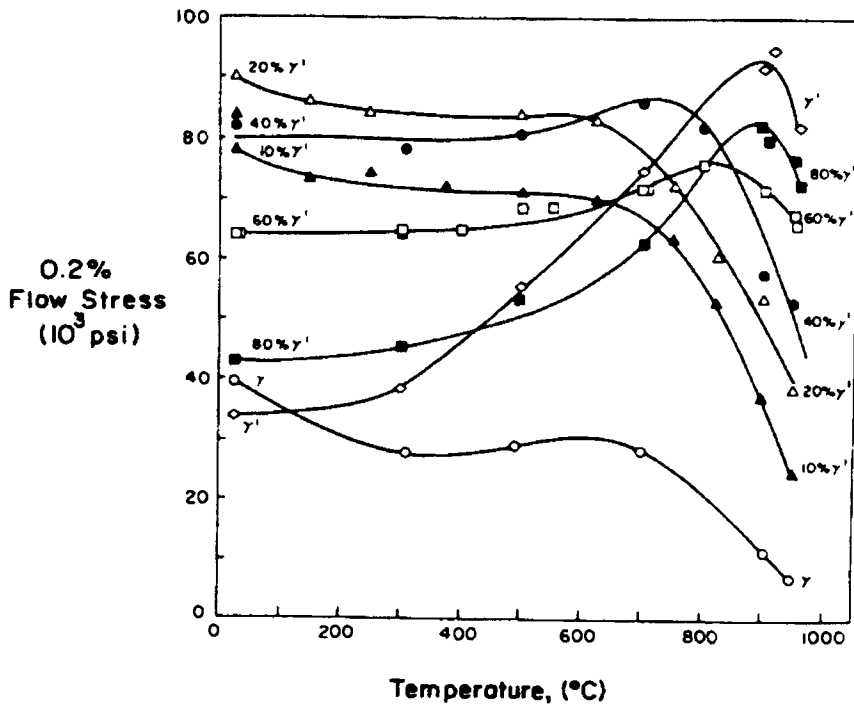


Fig. 4.4 Temperature dependence of the 0.2% yield stress of Ni–Cr–Al alloys containing various volume fractions of γ' , after P. Beardmore, R.G. Davies and T.L. Johnston [3].

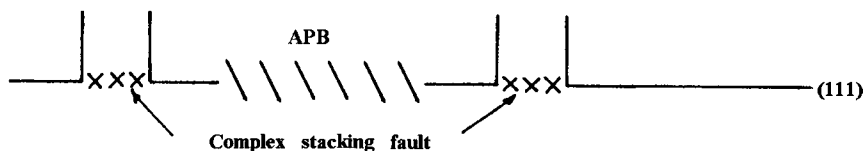


Fig. 4.5 Dissociated dislocation scheme for two $\frac{1}{2} \langle 101 \rangle$ dislocations coupled by an antiphase boundary (APB) lying on the (111) plane of an ordered crystal lattice.

identified – alloys with a low volume fraction of γ' initially exhibit a flow stress which is independent of temperature, followed by a rapid reduction in strength above about 700°C, high volume fraction γ' alloys exhibit comparatively low strength at low temperatures, increasing to a maximum at about 800°C to 900°C and then decreasing again. Intermediate γ/γ' show an initial constant flow stress at an intermediate strength level, followed by an increase and then a decrease.

(a) *The single-phase solid solution* shows a decrease in flow stress with increasing temperature which is comparable to the decrease of the shear modulus, and is thus to be expected.

(b) *The anomalous yield behaviour of the γ' phase.* Ni_3Al forms one of a group of A_3B intermetallic compounds that exhibit anomalous strengthening, i.e. the yield strength increases with increasing temperature. One consequence of the ordering of the fcc structure is that the unit Burgers vector (BV) is $\langle 101 \rangle$, which is twice as large as that of the disordered counterpart ($\frac{1}{2} \langle 101 \rangle$). $\langle 101 \rangle$ is not the shortest lattice translation vector for the ordered material, which is $\langle 100 \rangle$.

Dissociation of dislocations of $\langle 101 \rangle$ unit Burgers vector into paired $\frac{1}{2} \langle 101 \rangle$ dislocations (termed *superdislocations*) connected by a ribbon of antiphase boundary (APB) takes place in a manner analogous to that illustrated in Fig. 2.10. These may each further dissociate into Shockley partials (*superpartials*) by a similar process to that encountered in unit fcc dislocations in disordered lattices, and this is sketched in Fig. 4.5.

The superpartials are separated by complex stacking-faults (CSFs) which have high energy, and consequently exhibit very small partial separation on $\{111\}$. These dissociated structures have stacking-fault components cross-slipped on to lower energy planes and they have been shown to control the glide behaviour and are at the source of the anomalous strengthening of the Ni_3Al phase in isolation, and also in high γ' volume fraction two-phase alloys. These theories are complex, and have recently been reviewed by F.R.N. Nabarro and H.L. de Villiers (*The Physics of Creep*, London, Taylor and Francis, 1995) to which reference should be made for full details.

The models are based on the thermally activated locking of screw superdislocations when they cross-slip from a glissile $\{111\}$ plane to a sessile $\{010\}$ plane. This 'Kear–Wilsdorf' lock is illustrated in Fig. 4.6, and it is a sessile, low energy, non-planar configuration for superdislocations. The driving force for cross-slip arises from the anisotropic nature of the APB energy, which is a minimum for $\{100\}$. Cross-slip events are distributed along the dislocation

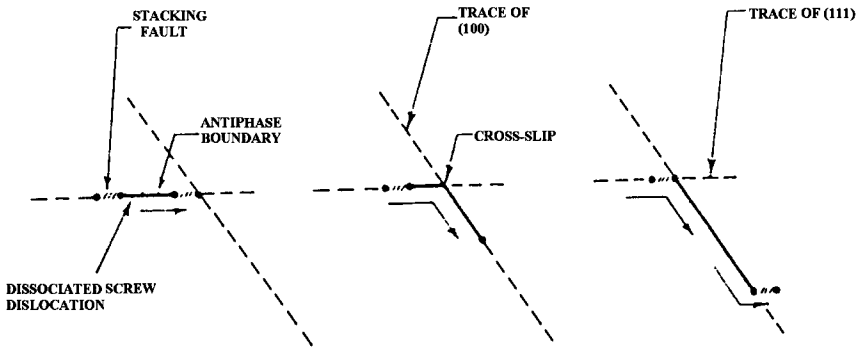


Fig. 4.6 Cross-slip pinning mechanism: the dislocation cross-slips on to (010) due to the lower APB energy and is locked in this configuration.

line and an enhanced probability of cross-slip at increased temperature results in an increase in the flow stress.

The eventual decrease in yield stress which is seen as the temperature continues to increase is commonly associated with macroscopic yielding on the primary cube slip plane (001), and it occurs when some critical value for the resolved shear stress on the (001) [110] system is reached.

(c) *The behaviour of two-phase γ/γ' material.* As is apparent from Fig. 4.4, at 900°C or more the flow stress is a function of f , the volume fraction of γ' -phase – the strongest alloy being that consisting of 100% γ' . In the highest temperature range all the two-phase alloys consisted of 0.5 μm diameter γ' particles in a weak γ matrix. Alloys with large f of γ' are deformed by particle shear, and those with small f are deformed by bowing of unpaired dislocations in the γ matrix.

In the lower range of temperature, the data of Fig. 4.4 cannot be interpreted by a single model of yielding over the entire range of γ' volume fractions. This is because in the alloys containing a low volume fraction of coarse γ' , the matrix also contained a hyperfine ($\sim 10\text{ nm}$) precipitate of γ' which formed upon cooling from the ageing temperature (950–900°C). The precipitation hardening of the γ -phase arising from these fine particles leads to a high yield stress in the lower temperature range, but since these fine particles redissolve at temperatures over 700°C, the γ is weakened and the flow stress drops rapidly.

4.3 CREEP BEHAVIOUR OF PRECIPITATION-HARDENED ALLOYS

At low temperatures materials usually deform by dislocation glide, and as the temperature increases other mechanisms of flow become possible. Dislocations can climb as well as glide, grains slide over each other at grain boundaries, vacancies diffuse. Thus, in a polycrystalline solid, there are many distinguishable mechanisms by which it can flow. In one range of stress and temperature one of

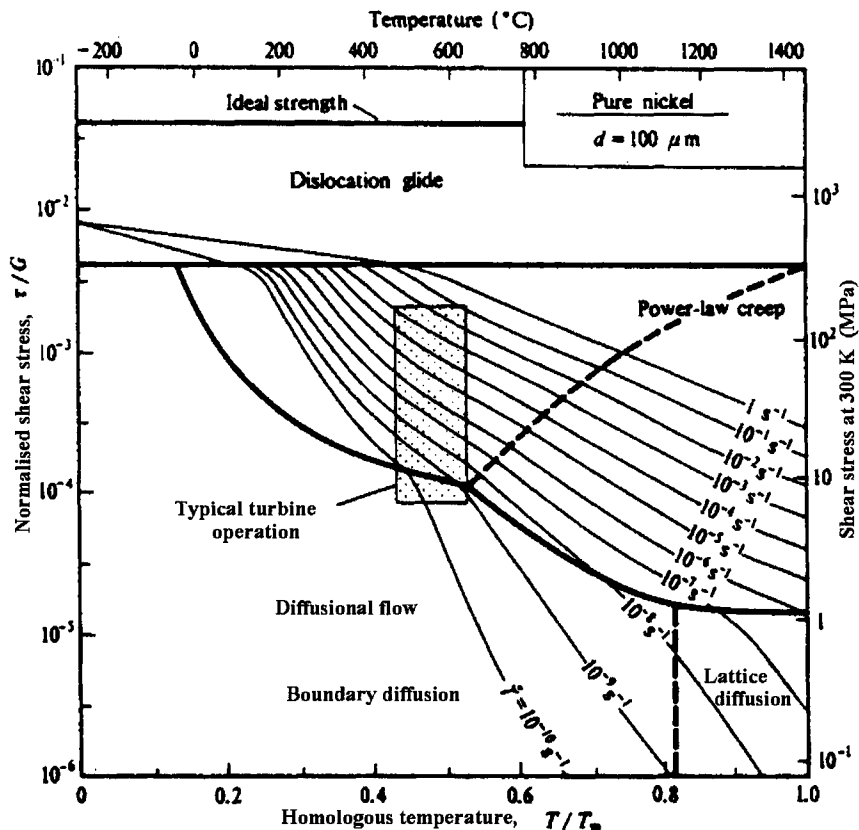


Fig. 4.7 The deformation mechanism map for pure nickel of grain size $100\text{ }\mu\text{m}$. The shaded box indicates the typical stresses and temperatures to which a turbine blade was subjected at the time of the construction of the map (after H.J. Frost and M.F. Ashby [4]).

these flow mechanisms tends to dominate, in another range a different mechanism will prevail. This 'landscape' of deformation mechanisms is most conveniently surveyed with the aid of an Ashby deformation mechanisms map.

4.3.1 Deformation mechanism maps

The Ashby map is a commonly used method of representing the regions of temperature and stress in which different creep mechanisms dominate. Figure 4.7 is such a map for pure nickel with a grain size of $100\text{ }\mu\text{m}$. It shows the fields in which a given flow mechanism will be dominant, and the strain-rate due to all the mechanisms acting together. The coordinate axes are temperature T normalized with respect to the melting point T_m , and normalized shear stress, τ/G , on a

logarithmic scale. The maximum overall strain allowed in the engines of civil aircraft is approximately 1% in 10 000 hours, i.e. a strain rate $3 \times 10^{-10} \text{ s}^{-1}$, although local strains may be considerably higher. The lowest strain contour shown in Fig. 4.7 is 10^{-10} s^{-1} , and the shaded box indicates the typical stresses and temperatures to which a turbine blade was subjected at the date when the map was constructed.

Figure 4.7 illustrates that at low temperatures, flow is confined to the *dislocation glide* field, slip being the dominant mechanism. Above $0.3 T_m$, the dislocations can climb as well as glide, and the flow has different characteristics known as *power law creep*. The creep rate ($\dot{\epsilon}$) can be described by the semi-empirical equation

$$\dot{\epsilon} = AD (\sigma/E)^n \quad (4.1)$$

where A is a material parameter, n is the stress exponent, D is the diffusivity and E is Young's modulus at the respective temperature. In metals there are two subgroups of power law creep: at higher temperatures lattice diffusion is the dominant transport mechanism; but at lower temperatures dislocation core-diffusion becomes the more efficient process.

Finally, at still higher temperatures *diffusional flow* by the motion of single ions permits deformation in a polycrystal at a rate which depends strongly on grain size. Like power law creep, two subgroups exist, corresponding to diffusion occurring predominantly through the grains (Nabarro–Herring creep) or round their boundaries (Coble creep). The following combined constitutive equation describes diffusional creep:

$$\dot{\epsilon} = 14 \frac{\sigma \Omega}{kT d^2} D_v \left(1 + \frac{\pi \delta D_b}{d D_v} \right) \quad (4.2)$$

where Ω is the atomic volume, d is the grain size, k is Boltzmann's constant, T is the absolute temperature, D_v is the volume diffusion coefficient, D_b is the boundary diffusion coefficient, and δ is the effective thickness of a boundary for diffusional transport.

Diagrams such as Fig. 4.7 are limited to the description of *steady-state* flow, and this is the type of creep to which we will confine our attention in the present section.

4.3.2 The suppression of dislocation (power law) creep

Intrinsically high creep strength is observed in materials in which diffusion is slow, and in which dislocations are poor sinks or sources for point defects. The first of these is achieved in covalent elements and compounds, and materials of high melting point. The second is an attribute of a low stacking-fault energy, since the core attachment or detachment kinetics are slowed when dislocations are widely dissociated.

Further reduction in power law creep may be achieved by metallurgical control designed to slow both glide and climb. Solute and particle hardening may reduce

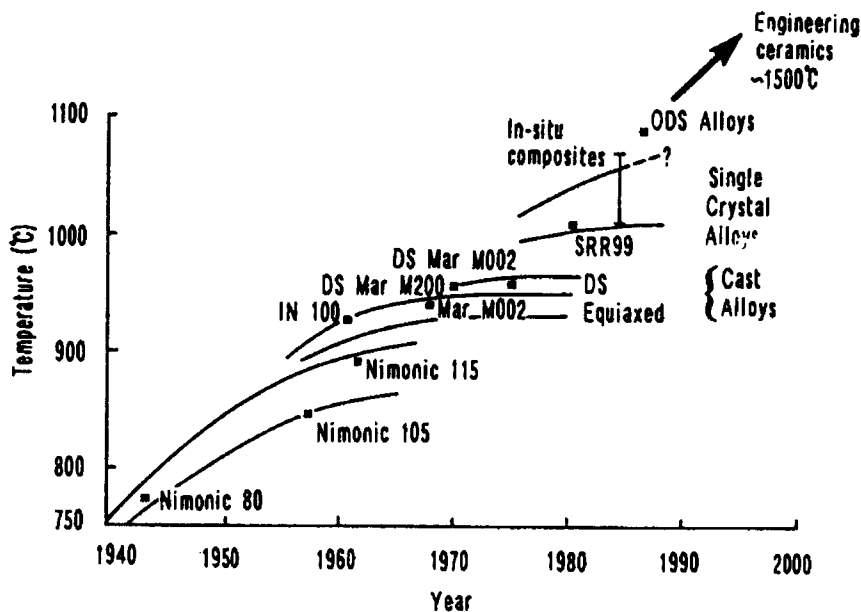


Fig. 4.8 Increased temperature capability of nickel-based superalloys, shown as the temperature for 1000 hour life at a stress of 150 MPa, as a function of the year of introduction (after M. McLean, in Khan, T. and A. Lasalmonie [5]).

the former. Climb is slowed by alloying which lowers the diffusivity, lowers the stacking-fault energy and which introduces an internal or threshold stress. A grain-boundary precipitate will also have the effect of pegging the boundaries and thus suppressing grain-boundary sliding; they may also result in interlocked and extremely wavy grains with a large resistance to sliding motion.

Nickel-based superalloys exhibit high resistance to creep because of the coherency strains set up between the precipitates and the matrix and because of the high temperature strength of the γ' -phase already discussed in detail. Solid solution strengthening by Cr, Co, Mo, W and Ta is the other major source of high temperature strength, and control of grain-boundary structure in superalloys is largely practised through precipitation of substituted chromium and tantalum carbides.

It is obvious from the preceding discussion that by sophisticated alloy design, dislocation creep may be very effectively inhibited. Historically there has been a continuous development in the temperature capability of nickel-based superalloys, this is illustrated in Fig. 4.8 as the temperature for 1000 hour life at a stress of 150 MPa, as a function of the year of introduction into service.

The earliest developments were aimed primarily at increasing the size and volume fraction of the γ' -phase, but by the late 1950s the improved creep strength had led to alloy compositions which were difficult to forge, and casting became the favoured processing route thereafter.

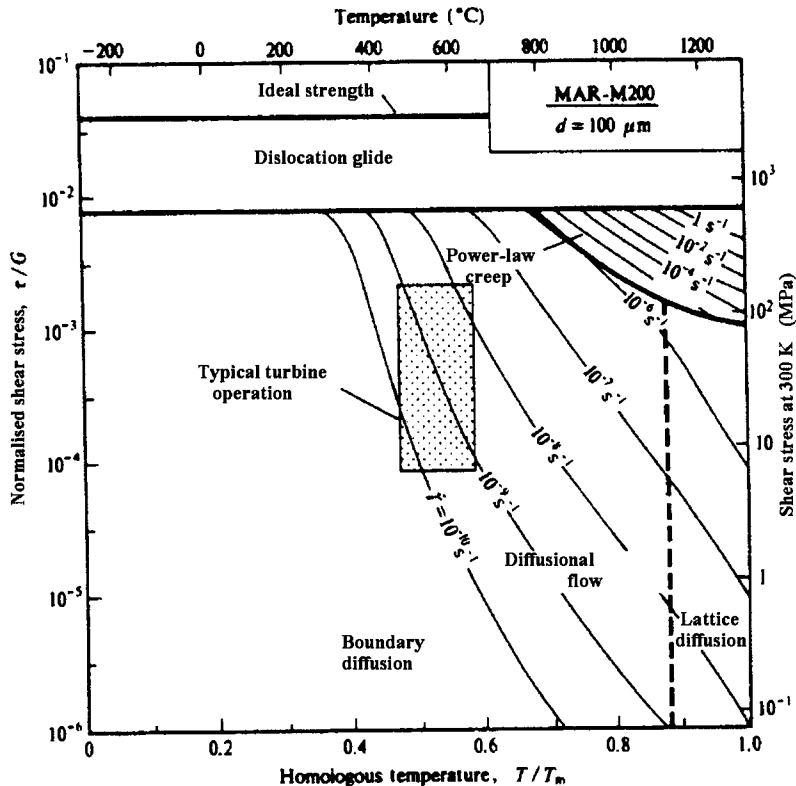


Fig. 4.9 The deformation mechanism map for the cast superalloy MAR-M200 of grain size $100\text{ }\mu\text{m}$. The shaded box indicates the typical stresses and temperatures to which a turbine blade was subjected at the date when the map was constructed (after H.J. Frost and M.F. Ashby [4]).

Figure 4.9 shows the Ashby map for an older generation alloy – Mar M200, a cast alloy of grain size $100\text{ }\mu\text{m}$, which was used in industrial turbines. This illustrates the effectiveness of the combination of many methods of strengthening. The alloy contains about 60% Ni; the addition of W and Co provides solid-solution strengthening, and γ' provides precipitation strengthening. By comparison with Fig. 4.7, the Ashby map for pure nickel of the same grain size, it is clear that solution strengthening and precipitation hardening have raised the yield stress and have drastically curtailed the rate of power law creep. In comparison with pure nickel, the creep rate of a turbine blade has been reduced by five orders of magnitude and the mechanism of flow has changed from power law creep to diffusional creep. It should however be borne in mind that with the passing years since the map was constructed this 'typical' box is now unrealistic, and when describing the conditions under which blades are used in more modern engines, the box should be moved upwards and to the right in order to describe the required capabilities of the

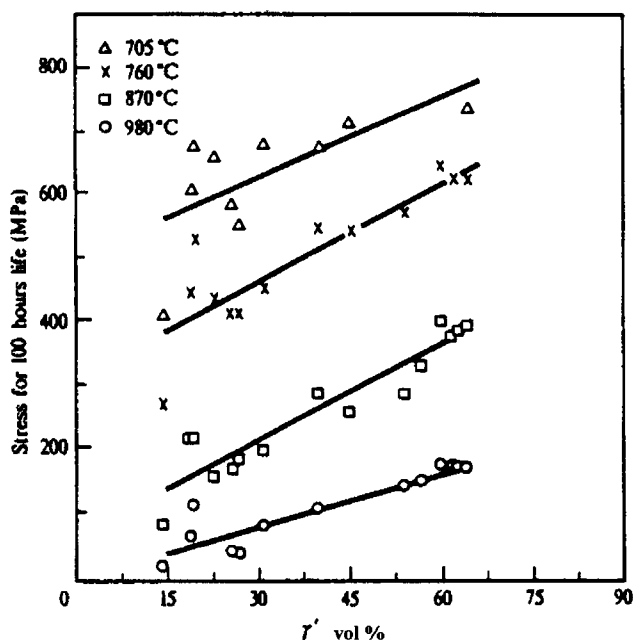


Fig. 4.10 The relationship between stress-rupture properties and volume fraction of γ' -phase for a variety of nickel-based superalloys (after R.F. Decker [6]).

material. The upper temperature limit is now approaching $0.8T_m$, so that dislocation creep mechanisms are encountered.

Figure 4.10 illustrates the relationship between stress-rupture properties and volume fraction of γ' for a variety of nickel-based superalloys. All γ' -hardened alloys show reduced strength at high temperatures because of the re-resolution of the γ' precipitate, whereas alloys hardened by an insoluble dispersion of, say, an oxide do not have this characteristic. Thoria-dispersed, or TD nickel is an early example of the latter type of alloy which was manufactured from chemically reduced powders. The material typically contained about 2 wt % of thoria, the particle diameter varying between 10 and 100 nm, with interparticle spacing of less than 30 nm.

Figure 4.11 shows the 1000 h specific rupture strength as a function of temperature for TD nickel. In comparison with Mar M200, for example, it can be seen that the creep rupture strength is much lower at intermediate temperatures, but, because of the stability of the thoria dispersion, the rate at which its strength falls with increasing temperature is much slower than that of the more conventional superalloys. The result is that above 1100°C TD nickel is stronger than Mar M200. Unfortunately TD nickel had inadequate oxidation resistance, and was also very expensive to manufacture, so that its industrial applications were limited in number.

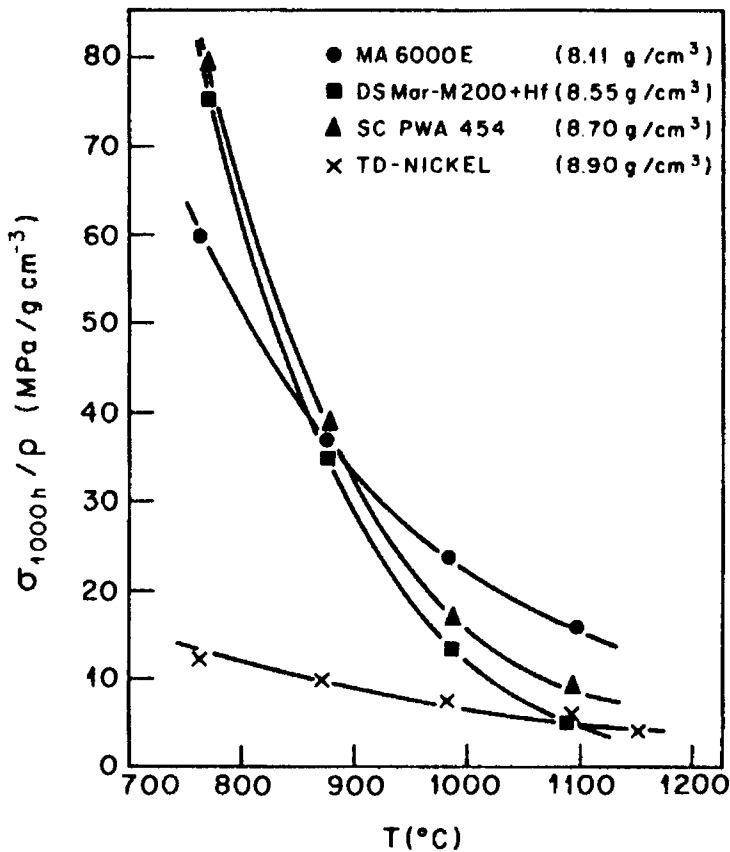


Fig. 4.11 Comparison of the 1000 h specific rupture strength of a number of nickel-based superalloys: directionally solidified MAT-M200 + Hf, single crystal PWA 454, TD nickel, and mechanically alloyed MA 6000. After R.C. Benn, L.R. Curwick and G.A.J. Hack [7].

As mentioned in section 1.1.1, a more recent development has been the employment of the powder-metallurgical technique of *mechanical alloying* to produce superalloys strengthened by both an oxide dispersion (ODS) and a γ' precipitate phase. The introduction of an insoluble oxide such as yttria (Y_2O_3) reduces the dependence upon the γ' phase for strength at the highest temperatures.

4.3.3 Multiphase strengthening: mechanically alloyed materials

MA6000 is a nickel-based superalloy strengthened by both γ' precipitates (60% by volume) and a dispersion of yttria (1.1 wt %). Its creep rupture strength (Fig. 4.11) is superior to that of the strongest cast alloys at very high temperatures;

below 900°C, however, MA6000 is surpassed by some of the very best cast superalloys.

A plot of log (stress) against log (time to fracture) for MA6000 is linear at high stresses and short lifetimes, but bends upwards at low stresses and long lifetimes. Extrapolation from short-term high-stress creep tests to long-term low-stress applications can be done with a considerable margin of safety. This effect is thought to arise from the presence of the yttria dispersion introducing a 'threshold stress' effect.

Threshold stress

Electron microscopy has revealed that, after creep deformation, dislocations may become attached to the 'departure side' of incoherent (yttria) particles: it appeared as if a stress were required to pull the dislocations off the particles. It has long been recognized that there is an attractive interaction between a dislocation and a *void*, and that such an interaction would lead to a threshold stress below which dislocations would be unable to detach themselves from the voids. If the boundary between the matrix and the particle could sustain normal tractions but not tangential tractions, a dislocation would feel a force of attraction, because the freely slipping surface would allow some components of the stress field of the dislocation to relax. If k is the ratio of the line energy of a dislocation segment in the particle/matrix interface to its line energy in the matrix, then when $k = 1$ there is no threshold stress. $k = 0$ corresponds to the situation when the particle has become detached from the matrix and behaves as a void. Arzt has calculated that the creep rate will fall rapidly to zero when the stress falls to $(1 - k^2)^{1/2}$ of the Orowan stress. Rösler and Arzt [8] point out that mechanically dispersed particles are likely to be incoherent, with small values of k and large activation energies for detaching dislocations, while precipitated particles are likely to be at least partially coherent, with k close to unity and small activation energies.

4.3.4 Diffusion creep in particle-hardened alloys

Figure 4.9 suggests that in general, as dislocation creep is suppressed by sophisticated alloy design, diffusional creep will tend to dominate as components are exposed to higher and higher temperatures in service. It is well established that the deformation of pure metals at low stresses and elevated temperatures can occur by the stress-directed diffusion of vacancies. As mentioned in Section 4.3.1, for polycrystalline materials two major mechanisms occur, as indicated in Fig. 4.9, and described by equation (4.2), namely Nabarro–Herring creep and Coble creep.

In either case, a higher than normal concentration of vacancies occurs at grain boundaries transverse to a tensile stress, and a lower than normal concentration at longitudinal boundaries. This concentration gradient leads to a flow of vacancies from the transverse to the longitudinal boundaries, causing an opposite flow of atoms that creates the tensile strain in the direction of the stress. It is important to realize that grain-boundary sliding is an integral part of diffusional

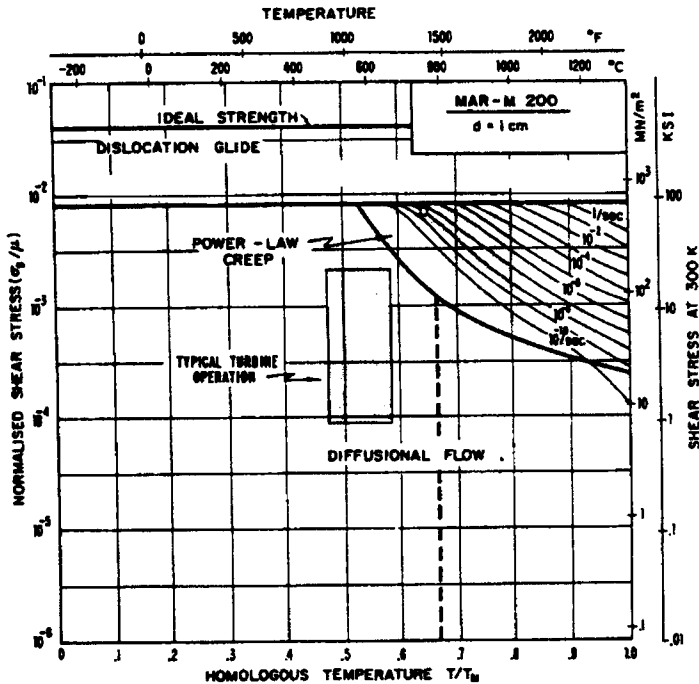


Fig. 4.12 The deformation mechanism map for the cast superalloy MAR-M200 of grain size 1 cm. As in Fig. 4.9, the shaded box indicates the typical stresses and temperatures to which a turbine blade was subjected at the date when the map was constructed (after H.J. Frost and M.F. Ashby [4]).

creep, and equation (4.2) describes the grain-boundary sliding of a polycrystal with diffusional accommodation.

Equation (4.2) indicates that diffusional creep is grain-size dependent, and a material's resistance to this type of deformation may be increased by increasing the grain size. Figure 4.12 shows an Ashby map for MAR M200 of 1 cm grain size, and comparison with Fig. 4.9 indicates the degree to which diffusion creep has been suppressed by this microstructural change. This principle is one underlying reason for the development of single crystal turbine blades, see Fig. 4.8.

The mechanically alloyed ODS superalloys are also heat-treated in order to increase their grain size: the process is known as 'zone annealing', and it involves passing the material through a temperature gradient under controlled conditions. This produces a structure of large elongated grains – the grains can be several millimetres in length, with grain aspect ratios (GAR) ranging from 5 to 10.

Under the conditions of diffusion creep, precipitates should take no part in the process and merely act as inert markers, so that boundaries on which atoms are deposited will show a precipitate-free zone of the deposited matrix, while

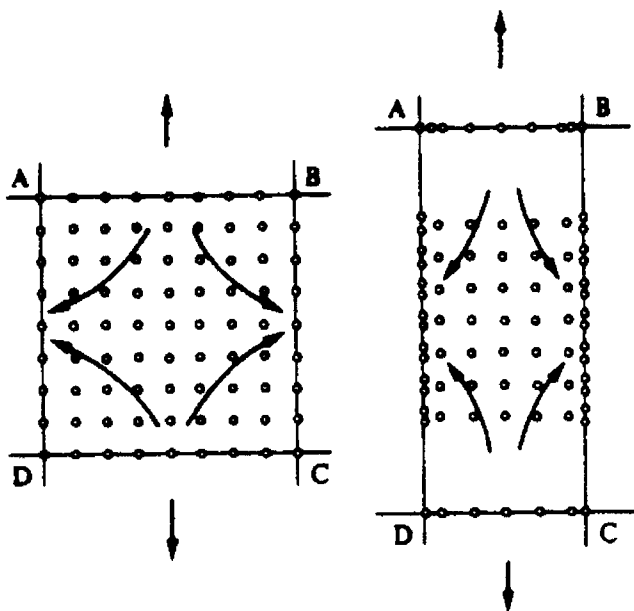


Fig. 4.13 Schematic representation of the effect of diffusional creep on particle distribution in a two-phase alloy.

boundaries from which matrix atoms are removed will become rich in the precipitate phase. This is shown schematically in Fig. 4.13, in which the stress axis is vertical and the arrows indicate the general direction of vacancy flow. Development of such microstructural inhomogeneities has been frequently reported, particularly in the magnesium-based alloys used in low-temperature nuclear reactors, such as Magnox ZR55, where zones denuded of zirconium hydride precipitates have been found adjacent to those grain boundaries which were normal to the applied tensile stress.

There is considerable evidence that dispersoid phases may inhibit diffusional creep. Harris *et al.* creep-tested sintered Mg powder which contained particles of MgO, and their data, together with those for ZR55 for a test temperature of 400°C are shown in Fig. 4.14. The logarithm of the grain-size compensated creep rate is plotted against the logarithm of the stress, and the theoretical creep rate according to equation (4.2) is shown. Although it is clear that there is a significant inhibition of diffusional creep in the ZR55 at low stresses, the creep rates of the sintered Mg/MgO powder are as much as seven orders of magnitude lower than those predicted by the equation. Several explanations have been suggested for this effect, including:

- 1 The dispersoids reduce the efficiency with which boundaries can emit or absorb vacancies. This may arise if the dispersoids prevent the collapse inwards of grain boundaries.

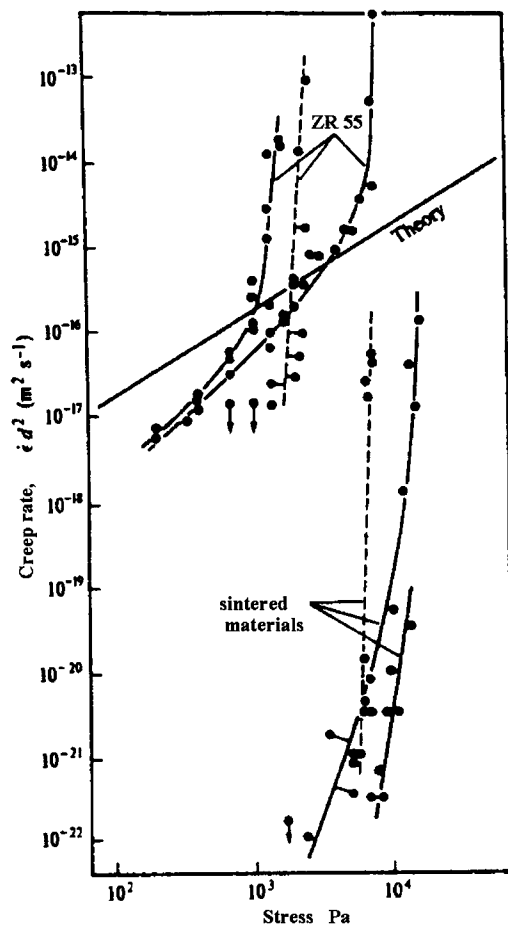


Fig. 4.14 Grain-size compensated creep rate plotted against stress for ZR55 and sintered magnesium products at 400°C. After Harris, J.E., Jones, R.B., Greenwood, G.W. and Ward, M.J. [9].

- 2 Dispersoids result in interlocked and extremely wavy grains with large resistance to sliding motion.
- 3 As the grains change their shape by creep, the boundaries move and as they do so they drag the particles with them. If a particle is to move, then it is necessary for particle atoms to move into the vacant lattice sites formed by the removal of matrix atoms. The rate at which particle migration occurs is then controlled by the slower of the two processes – either the diffusion of matrix atoms or of particle atoms. As many of the particles have high melting points, it is likely that the latter may become rate-controlling. This is consistent with the observation that the more refractory the particles are, the more effectively they inhibit diffusion creep.

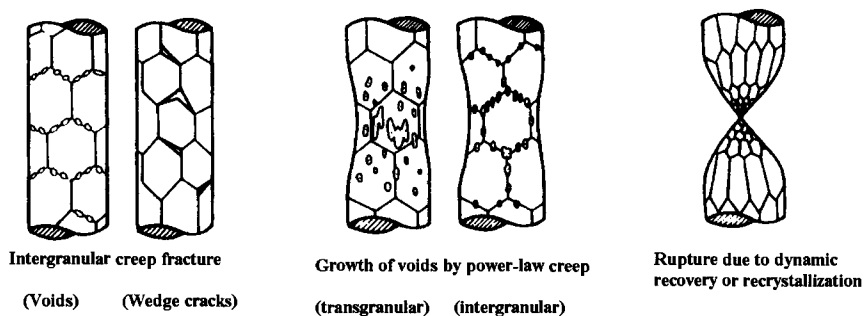


Fig. 4.15 A simple classification of fracture mechanisms in the temperature range ($> 0.3 T_m$) in which materials creep (after Ashby, Gandhi and Taplin [10]).

4.4 HIGH-TEMPERATURE FRACTURE OF PRECIPITATION-HARDENED ALLOYS

Ashby *et al.* have classified fracture mechanisms at elevated temperatures as shown in fig. 4.15 – shown in order of increasing ductility. If no other fracture mechanism intervenes, a material pulled in tension becomes mechanically unstable and deformation becomes localized in a neck and continues until the cross-section has gone to zero. This is *rupture*, and may arise at high temperature in precipitation-hardened alloys when most of the dispersed phases have gone into solution, and when high rates of recovery relieve the stress at inclusions. Dynamic recrystallization permits rapid local stress relief, and often gives rise to rupture.

Transgranular creep fracture arises from the operation of low-temperature ductile fracture processes in the creep regime: holes nucleate at inclusions within the grains and grow as the material creeps until they coalesce to give a fracture path.

Intergranular creep-controlled fracture is observed at lower stresses and longer times to fracture. Grain boundaries slide, and wedge-cracks or voids grow on boundaries lying roughly normal to the tensile stress axis.

There are numerous mechanisms of failure in a sample of a superalloy in a tensile or creep test. They may differ between materials which are strengthened by incoherent oxide particles and those in which the dislocations interact with ordered, coherent particles. New mechanisms of failure may occur under fatigue conditions, and there can also be an interaction between creep and fatigue.

The failure mechanism in creep of a given alloy may change as the minimum creep rate is altered by different applied stresses, and we will use Ashby fracture maps to survey the observed behaviour. We will firstly consider failure mechanisms in γ' -strengthened superalloys, then in oxide dispersion-strengthened (ODS) materials, and finally in mechanically alloyed material containing dispersions of both γ' and oxides.

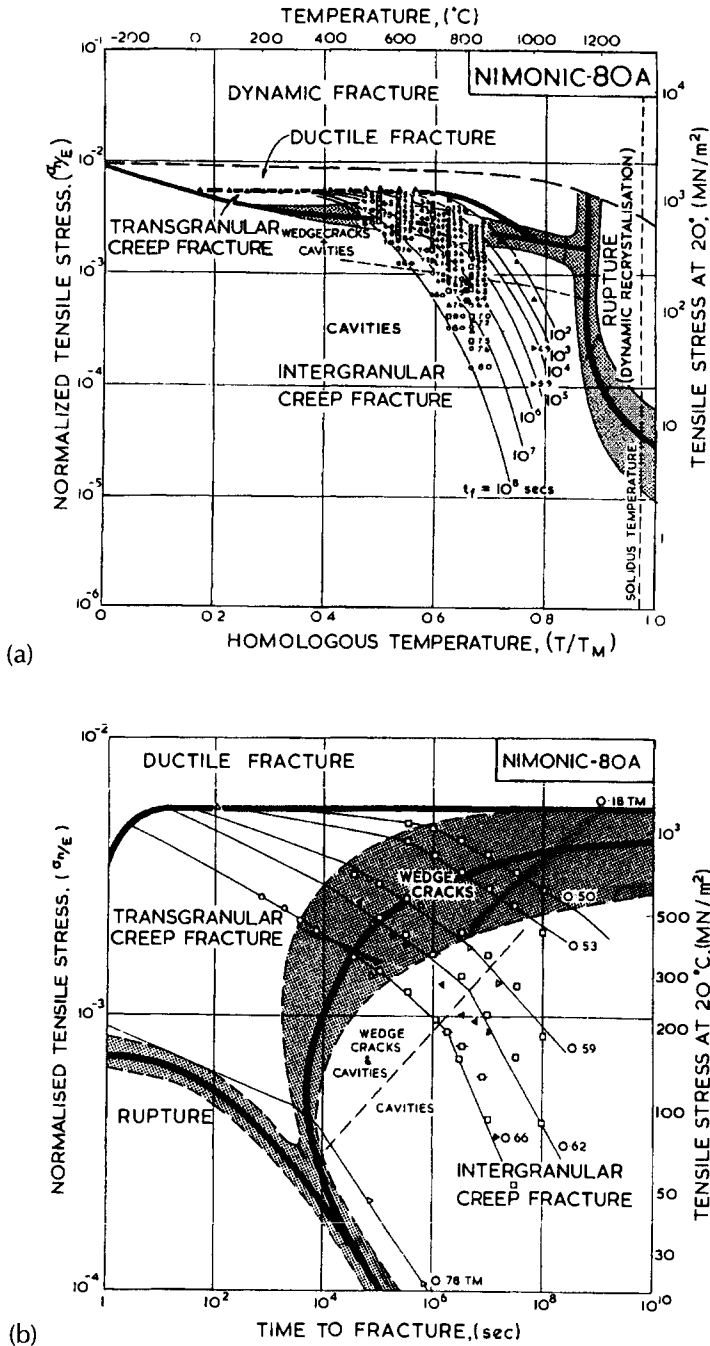


Fig. 4.16 The Ashby fracture maps for the nickel-based superalloy Nimonic 80A showing (a) the fracture mode and lifetime as functions of stress and temperature, and (b) the fracture mode and temperature of test as functions of lifetime and stress (after Ashby, Gandhi and Taplin [10]).

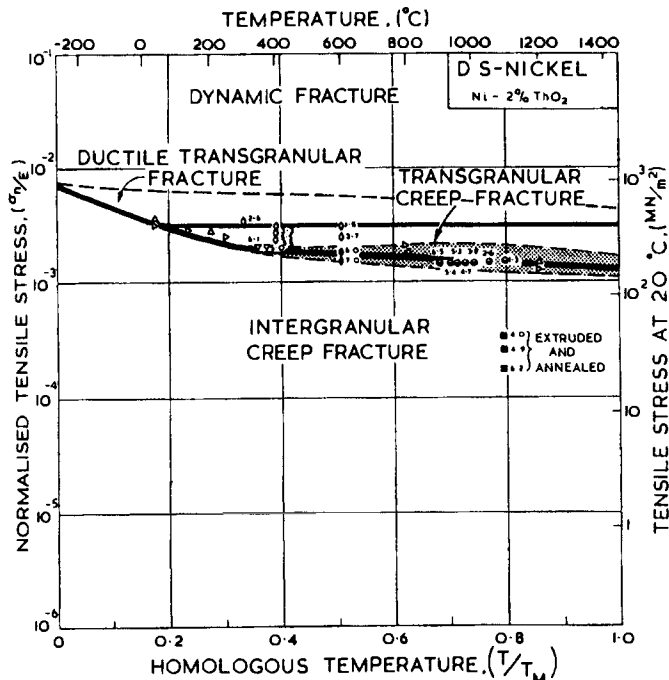


Fig. 4.17 The Ashby fracture map for nickel containing 2 vol % of finely dispersed ThO_2 (DS nickel) (after Ashby, Gandhi and Taplin [10]).

4.4.1 Fracture in γ' -strengthened alloys

Figure 4.16 illustrates Ashby diagrams showing the fracture mode and lifetimes of Nimonic 80A, which is the nickel-based superalloy from which most superalloys in use today have evolved. The heat-treatment consists typically of a solution heat-treatment at 1080°C followed by ageing at 700°C which leads to precipitation of γ' in a solution-strengthened matrix. A dispersion of carbide precipitates is formed at the grain boundaries, which help to suppress grain boundary sliding.

At high stresses in the temperature range 600 to 900°C (0.55 – $0.75 T_M$), fracture is observed to be transgranular. As the stress is reduced, the material shows wedge-shaped cracking and the fracture becomes increasingly intergranular. Below 240 MPa, the fracture mode changes from wedge cracks to voids which appear to nucleate on carbide particles, and fracture is completely intergranular.

Although rupture has not been observed, it is predicted in the range shown in Fig. 4.16, since both the γ' and the grain-boundary carbides return to solution as the temperature is raised to, say, 1150°C . Above $0.9 T_M$, therefore, the alloy is a single-phase solid solution, and dynamic recrystallization and failure by rupture is to be expected.

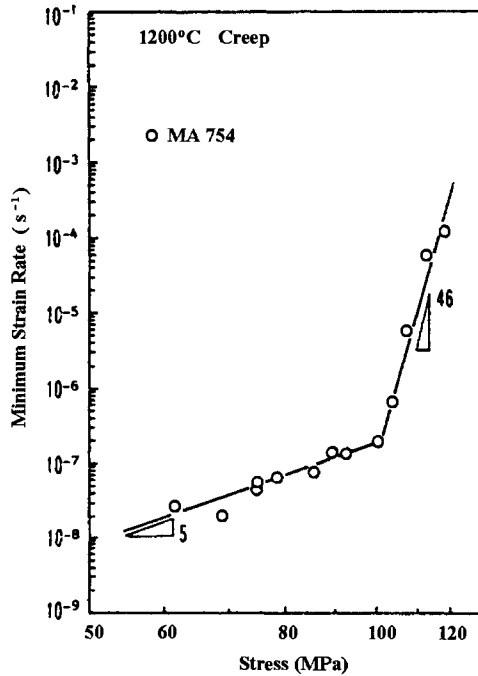


Fig. 4.18 The minimum creep rate of the ODS superalloy MA 754 at 1200°C as a function of stress (after J.J. Stephens and W.D. Nix [11]).

Since failure usually occurs by the growth and coalescence of voids, any treatment which removes voids is likely to improve the creep life of the material. Hot isostatic pressing (HIP) may thus be applied to single crystal superalloys in order to remove any microporosity formed during solidification, and HIP may successfully 'rejuvenate' used turbine blades in which damage is already apparent.

4.4.2 Fracture in ODS alloys

Dispersion-strengthened nickel (DS nickel) is an alloy with an exceptionally stable microstructure. It consists of small grains of almost pure nickel, elongated in the direction in which the material was worked. The grain shape is stabilized and the material strengthened by a fine (40 nm diameter) dispersion of ThO₂, and Fig. 4.17 shows an Ashby fracture map for this alloy.

The ThO₂ particles are stable up to the alloy's melting point, and they suppress dynamic recrystallization completely, so, in contrast to Nimonic 80A, rupture is not to be expected at the highest temperatures and strain-rates.

A more modern ODS alloy, MA 754 is strengthened by solution hardening and by a fine dispersion of yttria particles, shows similar pattern of fracture behaviour to that of the DS nickel in Fig. 4.17. As shown in Fig. 4.18, MA 754 exhibits a

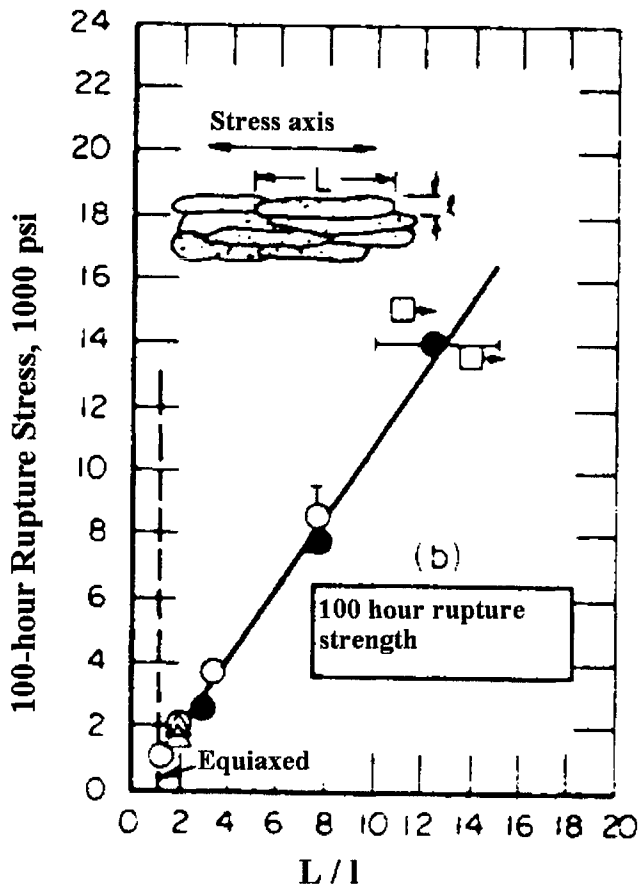


Fig. 4.19 The effect of the grain aspect ratio (GAR) in DS nickel alloys on the 100 h rupture strength properties at 1100°C (after B.A. Wilcox and A.H. Clauer [12]).

steady-state creep rate proportional to the fifth power of the stress up to a fairly well-defined stress, and then increases much more rapidly.

Creep fracture in the low stress regime of Fig. 4.18 is intergranular, cavities are formed on those grain boundaries perpendicular to the tensile axis, and after a process of microvoid coalescence the fracture surface is roughly perpendicular to the tensile axis. At higher stresses, plastic flow is homogeneous, fracture is transgranular and the fracture surface is smooth and oblique to the tensile axis.

The grain aspect ratio (GAR) is defined as the ratio of the grain dimension (L) parallel to the tensile stress direction to the grain dimension (l) perpendicular to the tensile stress direction, as illustrated in Fig. 4.19, and the creep life has been found to be dependent upon this parameter.

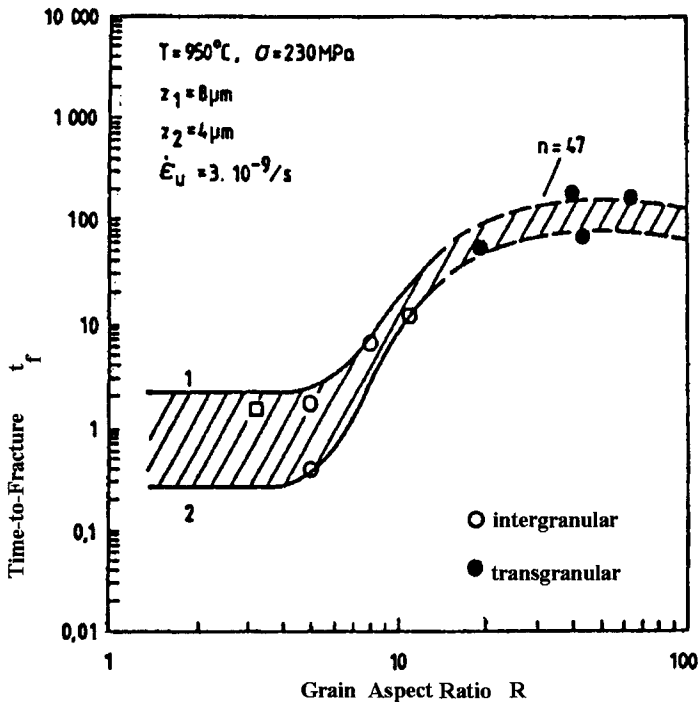


Fig. 4.20 Rupture time as a function of grain aspect ratio (GAR) for MA6000 at 950°C and 230 MPa (after H. Zeizinger and E. Arzt [13]).

In ODS alloys, the elongated grain shape imparts resistance to creep fracture, provided the specimen is stressed parallel to the long dimension of the grains. For intergranular fracture to occur, the long, interlocked grains must pull apart, giving a fracture surface which looks fibrous. This type of decohesion is more difficult at large GARs because of the large area over which grain-boundary sliding has to occur. Instead, the large grains fracture in a transgranular manner perpendicular to the tensile axis; the creep strength is therefore enhanced because grain-boundary sliding is inhibited. This effect is exploited in directionally solidified (DS) components such as turbine blades (see figure 4.11).

4.4.3 Fracture in mechanically alloyed material containing both γ' and oxide (MA 6000)

The effect of grain aspect ratio (GAR) has been explored in some detail in the case of the ODS mechanically alloyed material MA 6000, which is strengthened by both γ' and yttria.

Figure 4.20 shows the strong grain-shape sensitivity in this material, and also indicates the transition from intergranular to transgranular fracture as the GAR exceeds about 20. Small regions of equiaxed grains produced by recrystallization

may act as fracture nuclei, with typical nucleation times smaller than 10% of the time-to-fracture. It therefore appears that, in order to realize the full potential of dispersion strengthening in ODS alloys, fine grain regions must be eliminated.

4.4.4 Fatigue of precipitation-hardened alloys at elevated temperatures

Nickel-based superalloys will again be the principal class of material considered in the context of fatigue at elevated temperatures. We will again consider precipitations of the γ' -phase and of oxide dispersions, both individually and in combination.

High-temperature low-cycle fatigue (HTLCF)

LCF is an important consideration in turbine disc materials which operate at high stresses in the intermediate temperature range, and it is also an important variable determining the life of turbine blades operating in the high temperature range, but at lower stresses. The cyclic life is determined by the initiation of cracks of a certain size (e.g. 0.8 mm) by the linking up of microcracks, and their propagation under cyclic load.

Time-dependent effects such as oxidation and creep explain why all superalloys show a marked decrease in lifetime with increasing temperature, as illustrated in Fig. 4.21, though short-term mechanical properties such as flow stress, tensile strength and tensile ductility remain essentially constant.

The two most tractable microstructural influences upon LCF life are the grain morphology and the slip characteristics of the alloy as determined by the nature of any precipitates/dispersoids present. As indicated in Fig. 4.21, at lower temperatures microcracks form on slip bands, which are formed by heterogeneous planar slip. The extent of slip band cracking depends on the grain size, and if the grain size is reduced, as in the case of powder-metallurgically produced material, the amount of slip displacement per band becomes smaller, and the rate of microcrack formation is reduced. Defects such as hard second-phase particles and pores will then control crack initiation. Microstructures containing fine γ' and having optimum tensile strength lead to the longest fatigue lives. LCF lives can thus be increased by an increased solution heat-treatment (SHT) temperature, which increases the amount of γ' that can subsequently be precipitated. Increasing the rate of cooling from the SHT temperature increases the degree of supersaturation, and thus increases the volume fraction of fine γ' particles. Careful control has to be exercised in the processing of nickel-based disc alloys however, and it is generally carried out below the γ' solvus to prevent excessive and inhomogeneous grain growth due to dissolution of those primary γ' particles that pin the grain boundaries. The benefits gained in terms of precipitation strengthening can be offset by a reduction in grain-boundary strengthening; excessive cooling rates lead to poor LCF properties in these components due to cracking of the carbide particles during the quench.

Above a temperature of approximately $0.5T_M$ intergranular fracture dominates, although the transition is shifted to lower temperatures with decreasing frequency, since time-dependent oxidation of grain boundaries will become more

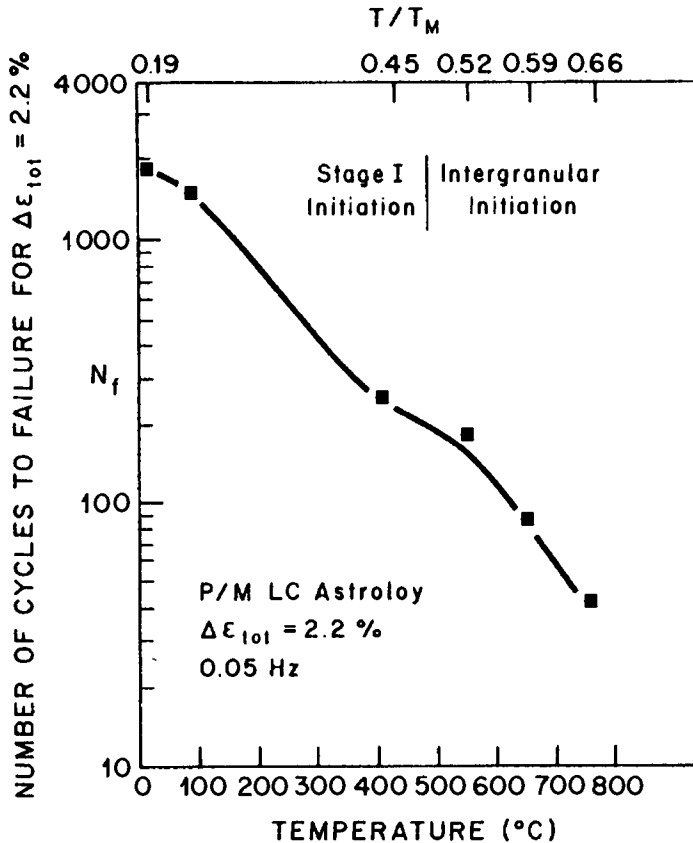


Fig. 4.21 The variation of number of cycles to failure with temperature for a powder-metallurgical low carbon Astroloy tested at constant total strain range of 0.022 (after Runkle J.C., and Pelloux, R.M. [14]).

important. Microstructurally this means that it is no longer the strength of the matrix which controls the fracture behaviour, but the strength of the grain boundaries. It is found that in this temperature regime the best results are obtained with a microstructure designed to minimize grain-boundary sliding – consisting of slightly serrated grain boundaries containing both $M_{23}C_6$ carbides and primary γ' particles.

ODS superalloys This class of material contains a dispersion of non-shearable particles, sometimes in addition to γ' and sometimes alone. The presence of such phases virtually eliminates the occurrence of coarse, concentrated slip bands typical of γ' -strengthened superalloys under HTLCF conditions. Stage I cracks, which develop from coarse slip bands in non-ODS alloys, have not been observed in, for example, MA6000 or MA 754, under any conditions of temperature and strain rate. The oxide particles lead to a dispersal of slip in the

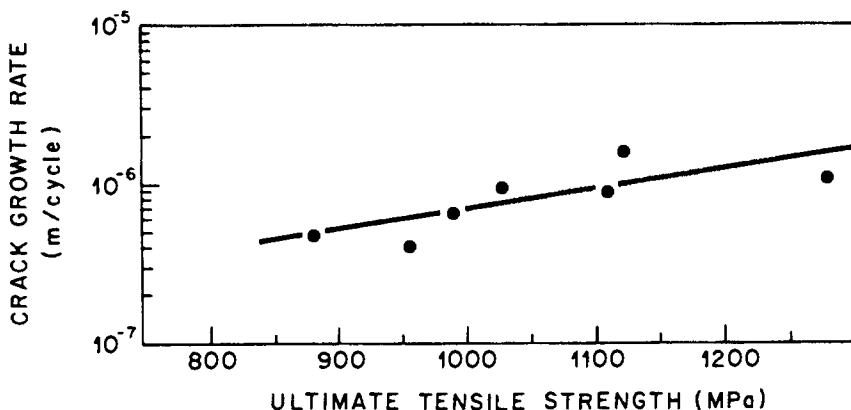


Fig. 4.22 Fatigue crack growth rates for seven different nickel-based superalloys tested at 650°C in air at $\Delta K = 30 \text{ MPa m}^{1/2}$ (after G.H. Gessinger [15]).

alloy, leading to homogenization of plastic glide. This high degree of strengthening obtained within the grain interiors of ODS superalloys enhances the susceptibility of grain boundaries to various damage processes. The highly elongated grain structure present in these superalloys counters this effect, although, as in the case of creep deformation already discussed, pockets of small included grains are the weakest link in the microstructural chain, and LCF crack initiation is usually found to be associated with them.

High-temperature fatigue crack growth (HTFCG)

As in crack initiation, the mode of fracture which will control the rate of crack propagation is a function of temperature, time (and frequency), stress ratio, hold time and environment. At lower temperatures, the rate of FCG is mainly a power law function of ΔK divided by the elastic modulus. As the temperature increases to above $0.5T_M$, the FCG rate increases more rapidly and microstructural parameters, such as grain size, and time-related parameters determine the FCG rate. There is a general trend that fine-grained materials show higher FCG rates than coarse-grained alloys. Especially at low ΔK values, microstructure and grain size become important parameters for FCG.

The effect of gross mechanical properties on FCG is the opposite to their effect on HTLCF crack initiation. Generally, the cyclically strongest alloy has the highest FCG rate.

Figure 4.22 illustrates this tendency by plotting for seven different nickel-based superalloys tested under identical conditions their HTFCG rates as a function of their UTS. This effect of microstructure on FCG rates is strongest at low ΔK , when the size of the *reversed plastic zone* at the crack tip is small.

The extent of the plastic zone, r_p , directly ahead of the crack tip is proportional to the square of K . In mode I,

$$r_p = \frac{1}{3\pi} \left(\frac{K_I}{\sigma_y} \right)^2 \text{ for plane strain, and}$$

$$r_p = \frac{1}{\pi} \left(\frac{K_I}{\sigma_y} \right)^2 \text{ for plane stress}$$

The size of the cyclic plastic zone (r_c) is derived by replacing K_I by ΔK and σ_y by $2\sigma_y$, so that for plane stress,

$$r_c = \frac{1}{\pi} \left(\frac{\Delta K}{2\sigma_y} \right)^2$$

The microstructure will influence the FGC rates at low values of ΔK , when the reversed plastic zone size is less than the grain size. As soon as r_c exceeds the grain size, secondary crack formation will commence, and the microstructure itself will have minimal effect. Crystallographic crack growth is therefore expected at low ΔK , changing to a striated growth mode with increasing stress intensity range.

Optimization of the microstructure for resistance to fatigue at elevated temperatures must reconcile the requirements for both HTLCF and HTFCG. Precipitates which promote slip homogenization enhance the resistance to HTLCF, but would not be expected to have a significant effect upon FCG. A fine grain size enhances resistance to HTLCF, but gives the highest FGC rates; this once led to the use of turbine disc alloys with a microstructure consisting of a 'necklace' of fine grains surrounding each of the grains of a relatively coarse-grained matrix, although this approach has been abandoned in recent years in favour of a uniform 30–50 μm grain size material.

When testing in air at high temperature, and a propagating fatigue crack encounters a grain boundary, embrittlement of that boundary occurs through local oxidation. The extent of this damage increases as the test frequency is decreased, since the duration of the tensile part of the cycle is increased. This can lead to an anomalous *deceleration* of HTFCG if a crack is propagating in a plane perpendicular to an array of parallel, planar high-angle grain boundaries.

This is encountered in, for example, directionally recrystallized MA6000 (which contains 2.5 vol% of finely distributed yttria particles in addition to 50 vol% of the γ' -phase) where the length of the grains can extend up to several centimetres. Experiments in which transgranular HTFCG in a direction perpendicular to the axis of these grains has been studied, and this anomaly is observed as the test frequency is reduced, as shown in Figure 4.23 (a), which shows the FCG rate curves for three test frequencies of 10, 1 and 0.1 Hz at 850°C in air. The FCG rates at 1 and 10 Hz are similar, with the former exhibiting slightly faster growth at low values of da/dN , which arises from oxidation enhancing the growth per cycle. The 0.1 Hz curve shows considerable reduction in FCG rate, with odd plateaux appearing at high levels of ΔK . This effect was shown to arise from the development of secondary cracking arising from the growing fatigue crack being diverted along the high-angle grain boundaries lying

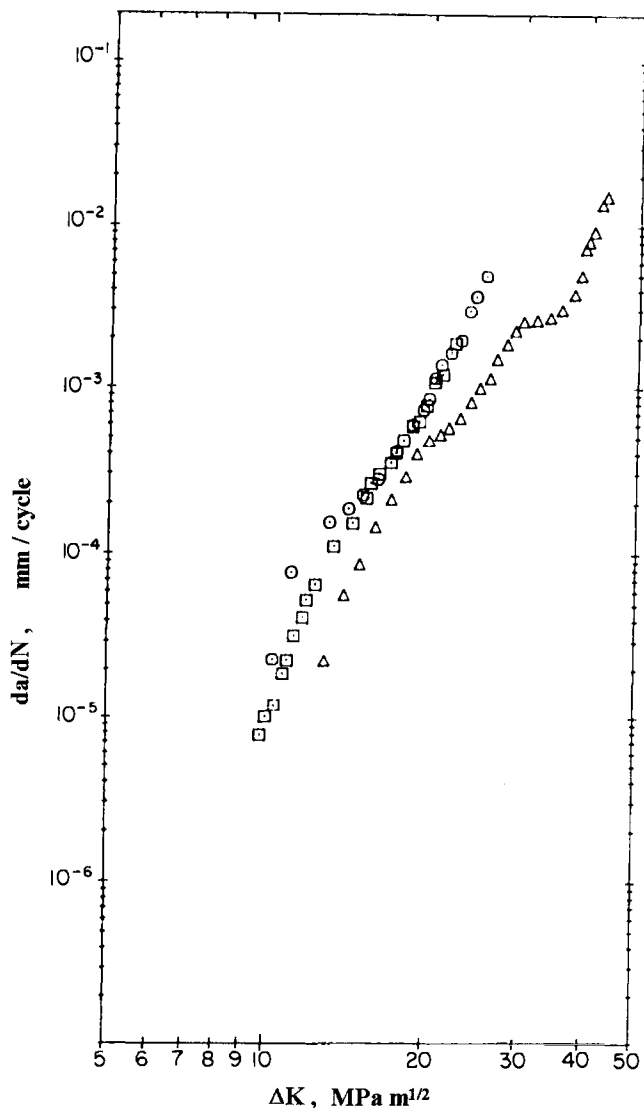


Fig. 4.23 (a) The effect of frequency on the HTFCG rate in MA 6000 at 850°C in air: □ 10 Hz, ○ 1 Hz and △ 0.1 Hz.

perpendicular to its direction of propagation. At this low frequency, when the crack tip arrives at a large-angle grain boundary there is time for oxygen diffusion to take place along the boundary. On subsequent cycles, a secondary crack nucleates along the boundary and then propagates by a combination of further oxidation and mechanical tearing. This is clear in Fig. 4.23 (b), which shows the crack being deflected in a direction perpendicular to its original direction of growth, which has led to a sharp deceleration in FCG rate.

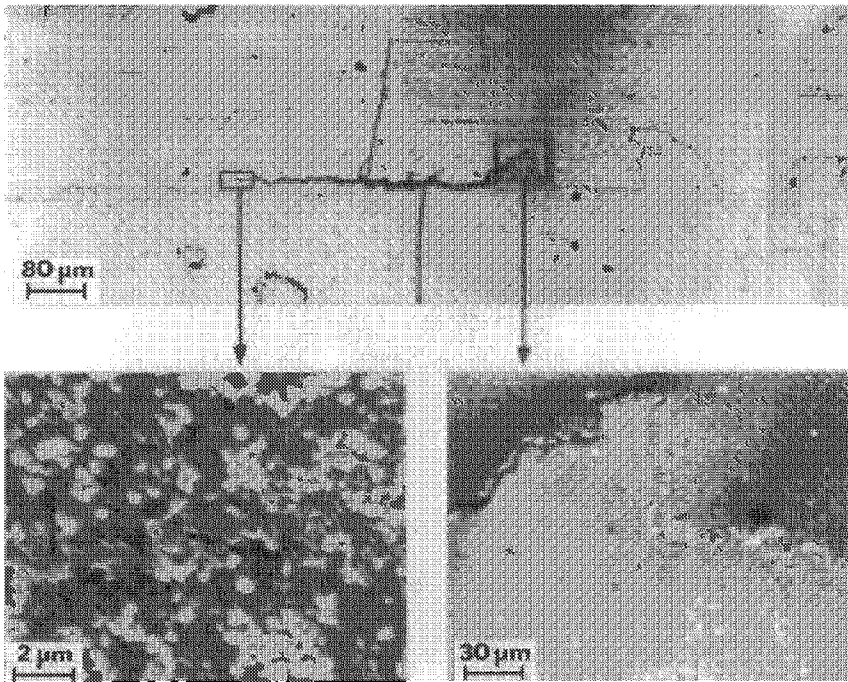


Fig. 4.23 (b) Cross-section through a crack formed at 850°C and 0.1 Hz. The main fatigue crack growth direction is upwards on the micrograph: lateral deflection along a grain boundary is evident (after A. Tekin and J.W. Martin [16]).

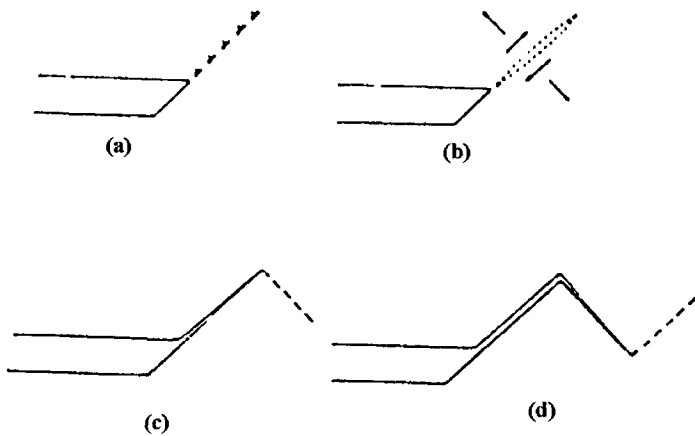


Fig. 4.24 Schematic representation of HTFCG in a single crystal by the nucleation of a small crack on the slip plane.

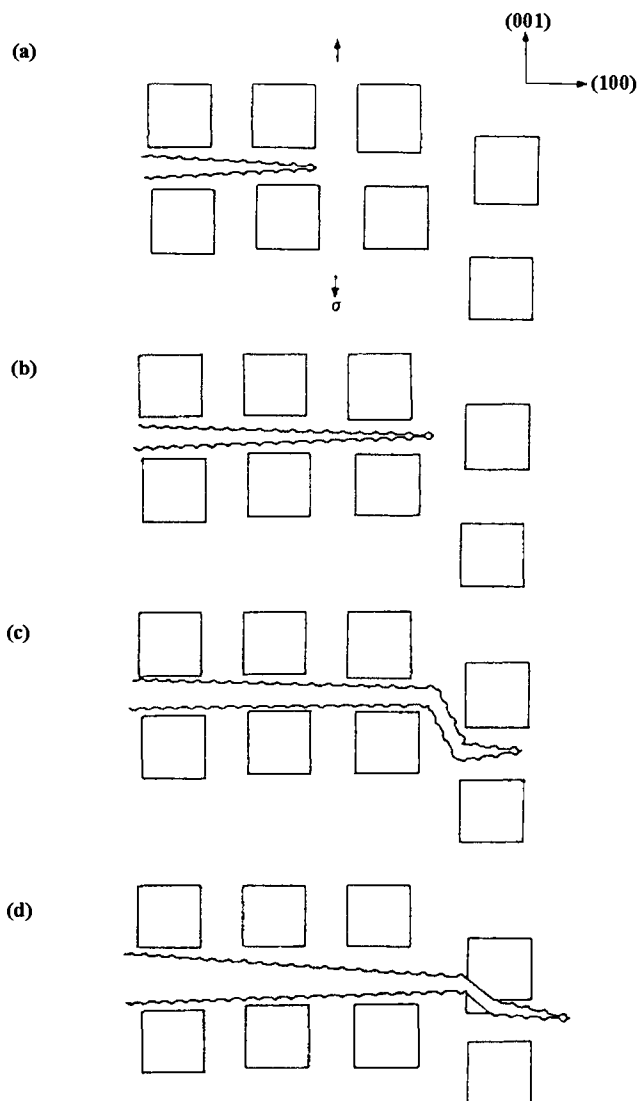


Fig. 4.25 Schematic representation of HTFCG in a single crystal by crack advance on {001} due to the constraints of the surrounding cuboidal γ' -phase. On encountering a γ' precipitate, either (c) by-passing or (d) shear of the particle may occur.

Single crystal superalloys Single crystal superalloys demonstrate the influence of microstructure on HTFCG without the complication of grain-boundary effects. Such crystals are usually grown with a [001] longitudinal axis, and are heat-treated to contain a homogenous microstructure of fine cuboidal γ' in a γ matrix. Typical alloys would contain up to 80% of such cuboids with an edge length of

250 nm. FCG testing has tended to concentrate on the influence of temperature and frequency on the fatigue response of specimens having macroscopic {001} crack planes.

In these materials, Stage I crack propagation has been found to occur at temperatures up to the range 600–750°C. The Stage I fracture plane is {111}, and it forms as shown schematically in Fig. 4.24 by a mechanism involving the shearing of the γ' -phase.

With an increase in test temperature, the matrix becomes softer than the γ' -particles and the crack propagation path changes from one of precipitate cutting to propagation through the matrix along a 'soft' {001} propagation path, as indicated schematically in Fig. 4.25. When the crack front encounters a γ' particle, either local bypassing or shearing of the particle may occur, with crack bifurcation being commonly observed.

In general, reducing the frequency and increasing the temperature enhances crack-tip shielding at low ΔK s due to increasing oxide-induced crack closure.

Henderson and Martin [17] have reported an orientation-dependent HTFCG response at 650 and 850°C in a single crystal superalloy SRR99. The fracture face appearance for each orientation studied was influenced by the relationship between the crack front and the slip systems available for crack tip shear. At the higher temperature the best FCG resistance was found for those orientations most able to accommodate crack tip shear by cuboidal slip activity.

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APPENDIX TO CHAPTER 4

THE ANOMALOUS INCREASE IN FLOW STRESS WITH INCREASING TEMPERATURE EXHIBITED BY Ni_3Al

[An extended excerpt follows from the paper by Davies and Stoloff which identifies the retention of strength at high temperature of aged Ni–Al alloys as arising from the unusual strength properties of Ni_3Al . They correctly conclude that the phenomenon arises from a lattice effect, but section 4.2.1 gives a more recent interpretation of the process. Most of the units used by the authors remain unchanged: note that $1 \text{ psi} = 6.9 \times 10^{-3} \text{ MPa}$].

ON THE YIELD STRESS OF AGED Ni–Al ALLOYS

R.G. DAVIES AND N.S. STOLOFF

(Transactions of the Metallurgical Society of AIME **233** (1965) 714–719)

A study has been made of the effect of different dislocation–particle interactions upon the temperature dependence of the flow stress of aged Ni–14 at.pct Al alloy. It is observed that when the dislocations bow between widely spaced ($\sim 200 \text{ nm}$) coherent Ni_3Al particles the flow stress decreases with increasing temperature in the normal way.

However, when the dislocations cut closely spaced ($\sim 50 \text{ nm}$) particles the flow stress is independent of temperature from -100 to $+600^\circ\text{C}$, due to a balance between softening of the matrix and an increase in strength of the particles with increasing temperature. The retention of strength at high temperatures of commercial nickel-base alloys, which are strengthened by the precipitation of a phase based on Ni_3Al is thought to be due to the unusual strength properties of Ni_3Al . The flow stress of Ni_3Al increases continuously from -196°C to a maximum at $\sim 600^\circ\text{C}$. It is concluded from a series of thermal-mechanical tests that the sevenfold increase in flow stress over this temperature interval is due to a lattice effect and is not diffusion-controlled.

The flow stress of precipitation- or dispersion-hardened materials depends on the resistance to dislocation motion within the matrix and the extra energy required for dislocations to bow between or to cut particles. If the dislocations bow between the particles or if the strength of the cut particles is constant with temperature, then the flow stress of the precipitation-hardened alloy must decrease with increasing temperature due at least to the decrease in elastic modulus of the material. There will be softening also from thermally activated cross-slip or climb, offering an additional degree of freedom for dislocations to avoid particles. For example, in the case of nickel containing a dispersion of thoria,[1] which most probably deforms by dislocations bowing between particles, the flow stress decreases by about 50 pct between 25° and 650°C . In Al–Cu alloys [2] aged to produce the θ'' precipitate, dislocations cut the particles, and the flow stress decreases by about 20 pct between -269° and 25°C .

However, many commercial high-temperature nickel-based alloys, for example Inconel-X and Udimet-700, [3] exhibit little or no decrease in flow stress with increasing temperature up to about 700°C. A characteristic feature of these alloys is that they are strengthened by the precipitation of a phase based upon Ni_3Al . Guard and Westbrook [4] and Flinn [5,6] have shown that Ni_3Al (and alloys in which a third element such as molybdenum or iron is substituted for part of the aluminium) is unusual in that the hardness and flow stress increase with temperature to a maximum at about 600°C. For the flow stress of a precipitation-hardened alloy to be independent of temperature we propose that the particles must be cut by dislocations moving through the matrix and that the strength of the particle must increase with increasing temperature. Theories of precipitation hardening do not take into account the flow stress of the dispersed particles that are cut during deformation; the only dissipative process usually considered [7] is the creation of interface within the particle and between the precipitate and matrix.

The purpose of the present investigation has been to study in detail the temperature dependence of the flow stress of a nickel-base alloy strengthened by the precipitation of Ni_3Al in two structural conditions such that when deformation occurs it does so by dislocations (*a*) bowing between the particles and (*b*) cutting the particles, respectively. A simple binary Ni-14 at. pct Al alloy was chosen because considerable information is already available for this system concerning phase equilibria and precipitation reactions and rates. [8] Dislocation-precipitate interactions in the binary alloy should be similar to those in the more complex commercial alloys. In addition, the mechanical and physical properties of Ni_3Al were studied in detail in the hope of elucidating the mechanism by which the strength increases with increasing temperature up to 600°C.

EXPERIMENTAL PROCEDURE

For the study of the effect of precipitation of Ni_3Al upon the temperature dependence of the flow stress, an alloy containing 14 at. pct Al was utilized; a Ni-8 at. pct solid solution alloy was employed as a comparison material. Vacuum-cast ingots were hot-rolled at 1000°C and cylindrical compression samples, 0.20 in. diam by 0.40 in. high, were prepared from the $\frac{1}{4}$ -in.-diam rod. Specimens were recrystallized and solution-treated at 1000°C for $\frac{1}{2}$ hr and then water-quenched. A preliminary study revealed that, when the Ni-14 at. pct alloy was aged for 1 hr at 700°C, significant precipitation hardening was obtained, and that the structure was free from grain boundary discontinuous precipitation; an overaged condition was produced by annealing the aged specimens at 850°C for 1 hr.

To circumvent the difficulties involved in the hot rolling and swaging of Ni_3Al , compression samples, $\frac{1}{4}$ in. square by $\frac{1}{2}$ in. high were cut directly from a vacuum-cast ingot having the composition Ni-25 at. pct Al. After a homogenization treatment at 1200°C for 5 days the ingot had a grain size of approximately

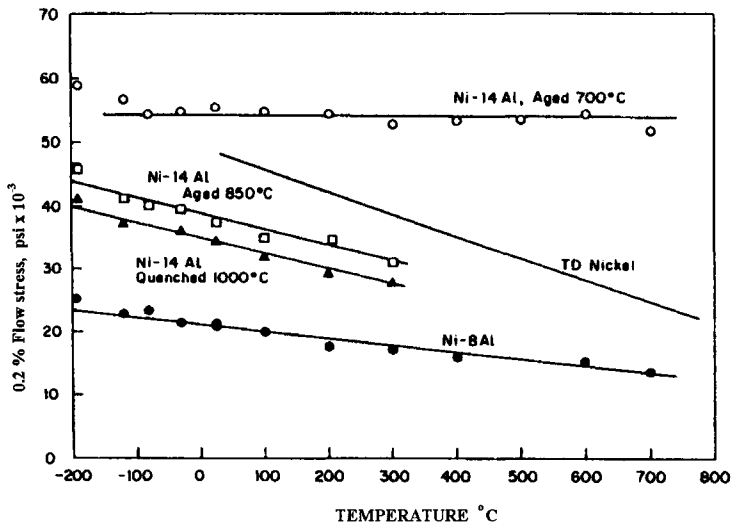


Fig. App. 4.1 – The flow stress as a function of temperature for several nickel-based materials; the data for TD Nickel is taken from Ref 1.

0.020 in. Elevated-temperature compression tests were carried out in a resistance furnace in air and low-temperature tests were performed in constant-temperature baths. An Instron machine was utilized with a crosshead rate of 0.01 in. per min. Thin foils for electron microscopy were prepared from the Ni-14 at. pct Al alloy by electropolishing 0.003-in. thick strip in a nitric acid-methyl alcohol solution. The foils were examined in a Hitachi HU-11 electron microscope operating at 100 kV.

RESULTS AND DISCUSSION

(1) *Aged Ni-14 at. pct Al alloy.* The change in flow stress with temperature for the Ni-14 at. pct Al alloy in several heat-treated conditions is shown in Fig. App 4.1. After aging at 700°C, this alloy exhibited the highest flow stress which, surprisingly, remained constant between -100° and 600°C. For the condition producing by ageing at 850°C, the strength fell linearly with temperature at a rate equal to the softening of samples solution-treated at 1000°C and quenched.

Also shown in Fig. App 4.1 are flow-stress data for nickel containing a dispersion of thorium [1] (TD Nickel)* and for the Ni-8 at. pct Al alloy, both of which, over the temperature range studied, are metallurgically stable structures. The strength of these materials decreased with increasing temperature at approximately the same rate as for the quenched Ni-14 at. pct Al alloy.

*TD Nickel – E.I. duPont de Nemours trade name for thorium-dispersed nickel.

The interparticle spacing and dislocation configurations were investigated using electron transmission microscopy. Micrographs of foils aged at 850°C and deformed several percent at 25°C revealed precipitates with an interparticle spacing of 200 nm to 250 nm. Contrast effects due to coherency strains can be seen around the Ni₃Al particles. Phillips *et al.* [9] also have observed coherent precipitates in an aged Ni–12.7 at.pct Al alloy. [*This is not reproduced in the present excerpt; it also showed dislocations in tangles, indicating that they had cross-slipped around and bowed between the particles. J.W.M.*]

For the condition of dislocation bowing between particles the yield stress, σ , is, to a first approximation, [7] given by

$$\sigma = \sigma_M + 2\mu b/l \quad [1]$$

where σ_M is the yield stress of the matrix, μ the shear modulus, b the Burger's vector, and l the interparticle spacing. For Ni–14 at. pct Al alloy aged at 850°C, σ_M is approximately 21,000 psi (the flow stress of the Ni–8 at.pct Al alloy), and $2\mu b/l$ is calculated to be 22,000 psi. The flow stress, σ , therefore should be 43,000 psi at 25°C; this is in good agreement with the observed value of the flow stress of 38,000 psi. For the TD Nickel the interparticle spacing is ~ 120 nm, [1] and then $2\mu b/l \sim 44,000$ psi and $\sigma_M \sim 3000$ psi; the calculated flow stress, 47,000 psi, is again in good agreement with the measured value at 25°C. The example of TD Nickel, with its low value of σ_M , illustrates the importance of interparticle spacing in determining the flow stress. To produce a high yield stress simply by the addition of hard inert second phase, the interparticle spacing must be of the order of a few tens of nm.

Electron transmission micrographs of foils aged at 700°C and deformed at 25°C revealed that the dislocations were in planar arrays and the interparticle spacing was 40 to 60 nm [*omitted in this excerpt, J.W.M.*]. Planar arrays of dislocations often are observed in the early stages of precipitation hardening, since when the coherent particles are closely spaced it required less energy for the dislocations to cut the particles than to bow between them. To bow dislocations between these particles 40 to 60 nm apart would require a stress of $\sim 120,000$ psi, but before this stress is reached the dislocations cut the particles and so remain in planar arrays. [*Reference to a second micrograph is omitted at this point, JWM.*]

Thus, when the dislocations are cutting the Ni₃Al particles, the flow stress is independent of temperature from -100° to 600°C . As pointed out in the introduction, this can only be understood if the strength of the particle increases with increasing temperature. [*A further section of the text is omitted here, JWM.*]

It is desirable to attempt to define the properties of Ni₃Al in detail. In particular, understanding of the mechanism by which Ni₃Al can increase in strength might lead to development of age-hardening systems based on other particles with similar properties.

(2) *Properties of Ni₃Al.* The flow stress of Ni₃Al over the temperature range -196° to 1000°C is shown in Fig. App 4.2. The results are in very good agreement with those reported by Flinn [6] for the temperature range 25° to 1000°C and corroborate the maximum in the flow stress at $\sim 600^\circ\text{C}$. However,

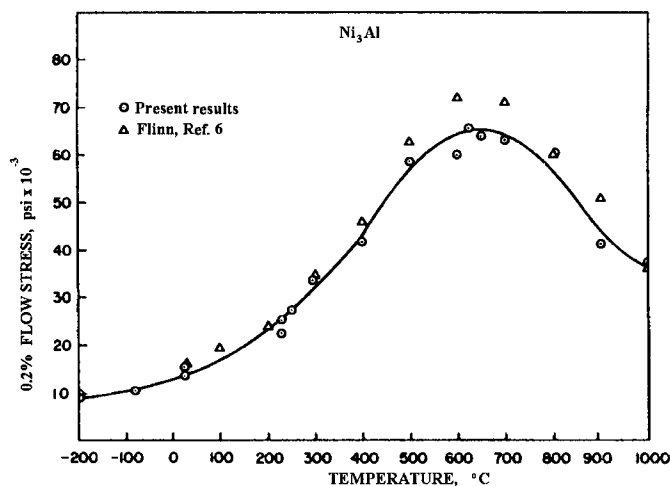


Fig. App. 4.2 Flow stress as a function of temperature for Ni₃Al.

there is the additional important observation that the flow stress increases continuously from -196°C ; the increase in strength between -196° and 600°C is sevenfold.

Explanations for the increase in strength of Ni₃Al at high temperatures have been based on two types of diffusion-controlled phenomena. Guard and Westbrook [4] proposed that strain ageing occurs due to the presence of the interstitial impurities carbon, nitrogen, and oxygen. Flinn [5], on the other hand, suggested that the flow stress increases by a mechanism involving the diffusion-controlled climb of a superlattice dislocation. Superlattice dislocations are pairs of unit dislocations connected along the $\{111\}$ slip plane by a strip of antiphase boundary. The lattice is restored by movement of these dislocation pairs. However, should climb of one dislocation occur, so that the antiphase boundary is on $\{100\}$ (the lowest-energy boundary), a higher stress will be needed to drive each unit dislocation through the lattice.

The observation that the flow stress increases uniformly between -196°C and 25°C , Fig. App 4.2, suggested that a diffusion process is unlikely, since 25°C is $<0.2T_m$, and climb or strain ageing is not likely to occur at such low temperatures. However, to eliminate any possibility that diffusion was involved, a further series of tests were carried out. To examine whether strain ageing occurs during deformation, a sample was strained 10 pct at 600°C at a very slow crosshead rate (0.002 in. per minute); the stress-strain curve was quite smooth, whereas if strain ageing occurs during the test a serrated curve is to be expected. Strain ageing should give rise to negative strain sensitivity, but no strain-rate sensitivity was observed upon increasing the crosshead speed 100 times at 240° and 625°C . Additional evidence for the lack of strain-ageing effects was obtained when no increase in flow stress was observed subsequent to straining and holding at 230°C for up to 2 hr.

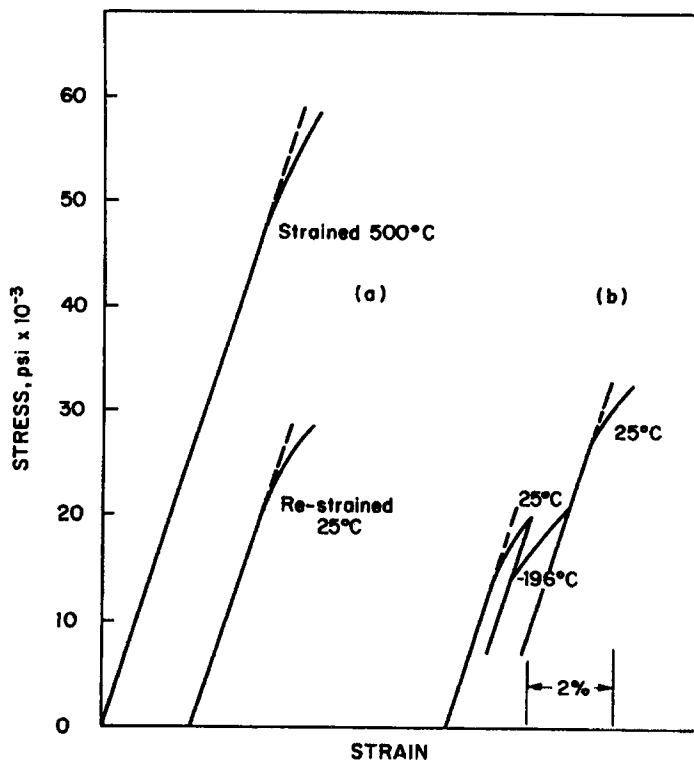


Fig. App. 4.3 The effect of temperature on the flow stress of a Ni_3Al specimen: (a) strained at 500°C and restrained at 25°C and (b) cycled between 25°C and -196°C.

The strain-rate sensitivity and ageing test results described above were not in accord with the Flinn mechanism, since diffusion-controlled climb effects would be enhanced at low strain rate rates or during long ageing times. An additional test to determine the effect of ageing was carried out by prestraining a sample at 25°C, annealing for 1 hr at a series of temperatures between 200° and 500°C to permit climb to occur, and retesting at 25°C. Each of these tests would be expected to lead to an increase in strength upon retesting if the climb mechanism were operative. However, no increase in flow stress was observed; in fact there was considerable recovery upon annealing above ~350°C. It may be concluded from this series of tests that neither a dislocation-climb nor a strain-ageing mechanism can explain the unusual behaviour of Ni_3Al .

The possibility was then considered that precipitation might occur during tests at high temperatures or by internal oxidation. However, the flow stress of samples annealed for 1 hr at 500°C, 600° and 700°C was no different from that obtained from specimens either air-cooled or quenched from 1000°C. Also, samples strained at 500°C, rapidly cooled, and retested at 25°C showed no retention of the high-temperature strength; see Fig. App 4.3a. Since the

strength at high temperatures cannot be retained at low temperatures, precipitation or internal oxidation cannot be taking place. Similarly, a mechanism involving thermally-activated cross-slip of superlattice dislocations, as recently suggested by Flinn, [12] would be expected to lead to a permanent increase in strength. Finally, to show that the flow-stress increase for different samples from the original ingot was not a reflection of some systematic variation in composition along the original ingot, a single sample was strained at 25°C, cooled to -196°C, strained further, and then warmed to 25°C and restrained again; see Fig. App 4.3b. It is clear that the strength of the sample is a function of the temperature and of strain hardening due to dislocation accumulation during each strain cycle.

[The authors next describe the deformation behaviour of Ni₃Al at 25°C, observing cross-slip and intersecting slip, and both intergranular and transgranular cracking. They also measured the elastic modulus and specific heat of this phase as a function of temperature in order to elucidate the increase in strength with temperature].

It is concluded from the mechanical and physical measurements that the increase in flow stress with increasing temperatures due to a lattice effect. It has been proposed [15] that in Ni₃Al there is a lattice interaction with dislocations as a result of the mixed nature of nearest neighbours together with a strong ordering tendency of the alloy. As the temperature is increased and the forces in the lattice increase, this interaction of the dislocations with the lattice becomes stronger, and hence the stress required to move the dislocation will also increase until a temperature is reached at which thermally activated processes become important and lower the flow stress. As far as is known the observed behaviour is unique to Ni₃Al, but it is expected that the flow stress of other ordered alloys of the Cu₃Au type should be relatively insensitive to temperature below the critical ordering temperature, and, in fact, this has been observed for Cu₃Au. [16]

SUMMARY AND CONCLUSIONS

A study of the deformation of aged Ni-14 at. pct Al alloy has shown that, when dislocations bow between the coherent Ni₃Al particles, the flow stress decreases with increasing temperature in the normal way. However, when the interparticle spacing is such that the particles are cut by the dislocations, the flow stress is independent of temperature from -100° to +600°C, due to a balance between the softening of the matrix and the increase in strength of the Ni₃Al particle with increasing temperature. It is proposed that a similar dislocation-particle interaction is responsible for the excellent high-temperature properties of commercial nickel-based alloys which are strengthened by the precipitation of a phase based upon Ni₃Al. It has been shown that the flow stress of Ni₃Al increases continuously from -196° to a maximum at ~600°C, there is a seven-fold increase in strength over this temperature

interval. From a series of thermal-mechanical tests, it is concluded that the anomalous increase in strength with increasing temperature of Ni_3Al is due to a lattice anisotropy effect and not to a diffusion-controlled mechanism.

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12. P.A. Flinn: *The Strengthening of Metals*, D. Peckner, ed., p. 219, Reinhold Publishing Corp., 1964.
13. E.M. Savitskii: *Mechanical Properties of Intermetallic Compounds*, p. 87, John Wiley and Sons, Inc. 1960.
14. R.G. Davies and N.S. Stoloff: *Phil. Mag.* 1964, vol. 9, p. 349.
15. T.L. Johnston, A.J. McEvily, Jr., and A.S. Tetelman: *Conferences on High Strength Materials*, Berkeley, California, June, 1964, to be published.
16. R.G. Davies and N.S. Stoloff: submitted to *Phil. Mag.*, 1965.

Appendix

1 PHASE DIAGRAMS OF SOME RELEVANT SYSTEMS

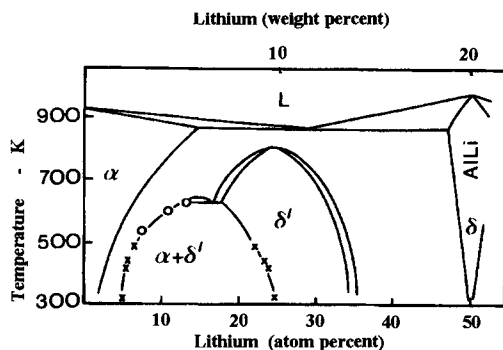


Fig. App. 1 The Al-rich end of the Al-Li phase diagram proposed by Gayle and Vander Sande (*Bull. Alloy Phase Diagrams*, 5 (1984), 19).

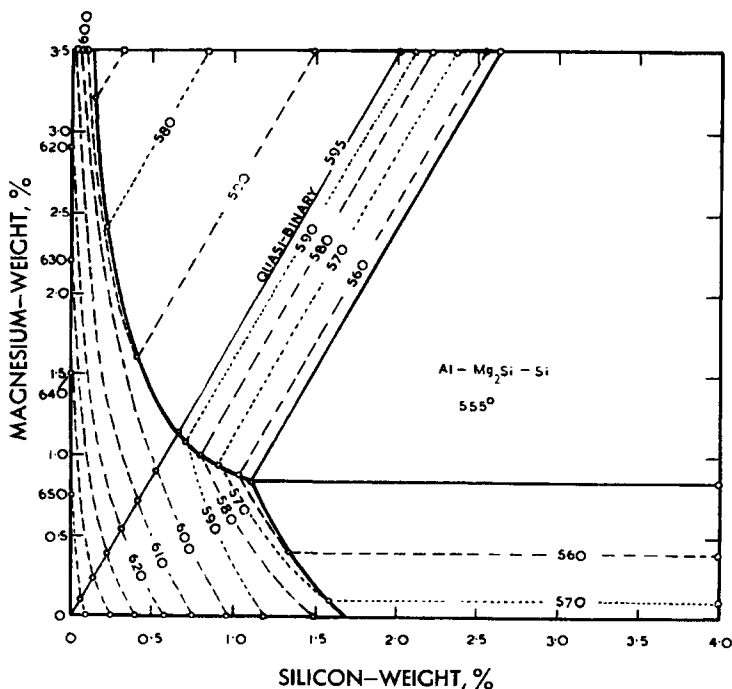


Fig. App. 2 The Al corner of the Al-Mg-Si phase diagram showing the limits of solid solubility as a function of temperature (courtesy of the Aluminium Development Association).

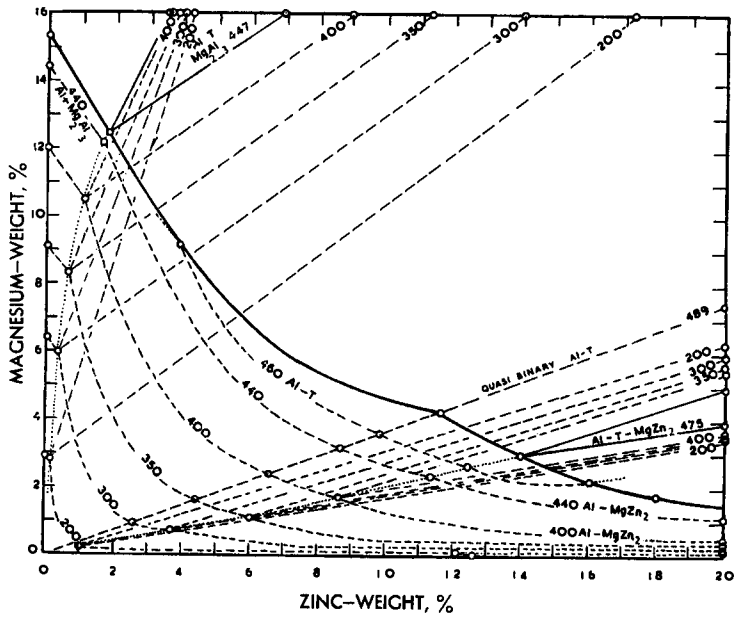


Fig. App. 3 The Al corner of the Al – Zn – Mg phase diagram showing the limits of solid solubility as a function of temperature (courtesy of the Aluminium Development Association).

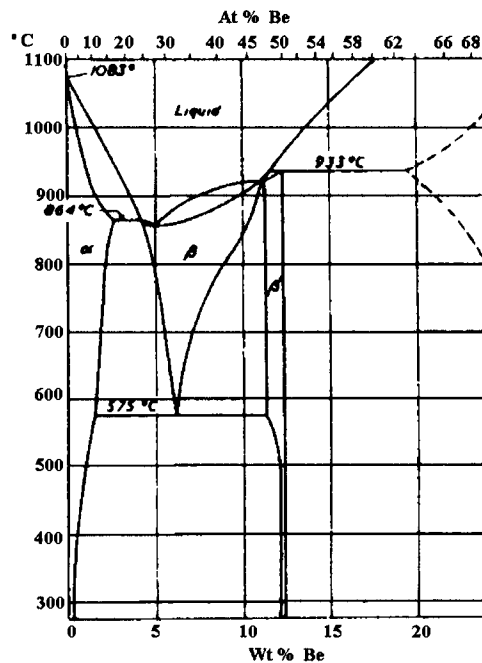


Fig. App. 4 The copper-rich end of the Cu – Be phase diagram.

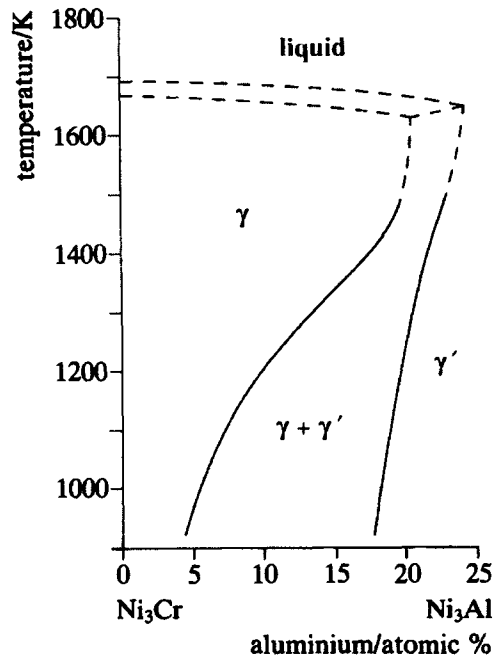


Fig. App. 5 The pseudo-binary Ni_3Cr – Ni_3Al phase diagram.

2 SOURCES OF ALLOY PROPERTY DATA

- 1 ASM *Metals Handbook*, 10th edition (1990), ASM International, Metals Park, Columbus, Ohio, USA.
- 2 *Smithells Metals Reference Book*, 7th edition (1992) (ed. E.A. Brandes), Butterworth-Heinemann, London UK.
- 3 Database software

There is a rapidly increasing number of computer-based alloy information systems available, and only a small selection of them is given here. The Materials Information Service of the Institute of Materials publish an updated list of PC based Materials Databases, from whom copies are available at 1, Carlton House Terrace. London SW1Y 5DB.

Data on individual metals and alloys are available as follows:

The Copper Development Association: Copper and copper alloys.

Nickel Development Institute: Stainless steels.

Aluminium Federation: 'Aluselect'.

MPR Publishing Services Ltd.: Powder metallurgy (PM) Selector.

On-line data for metallic aerospace materials are available in the form of Design Tables from *Military Handbook*, MIL-HDBK-5F. This is a numeric database

containing mechanical and physical properties of metals and alloys for aerospace vehicles and structures, including aluminium, beryllium-copper, iron-chromium-nickel, steels and titanium. Properties include elastic moduli, tensile and fatigue data.

3 ALLOY DESIGNATION (IADS)

Although precipitation hardening is encountered in a wide range of both ferrous and non-ferrous alloys, it is the large family of *wrought aluminium-based* alloys which has been most widely studied in this context. An International Alloy Designation System (IADS) is employed for these materials, and an outline of this system is given in the table below, and references to particular aluminium alloy systems in the text uses this designation.

4-digit series (xxxx)

Each wrought alloy is assigned a four-digit number of which the first digit is determined by the major alloying elements(s) present, thus:

<i>Series</i>	<i>Main alloying elements</i>
1xxx	Unalloyed aluminium (99% Al minimum)
2xxx	copper
3xxx	manganese
4xxx	silicon
5xxx	magnesium
6xxx	Mg and Si
7xxx	zinc
8xxx	others

Temper or heat treatment

Suffix letters and digits are added to the alloy number in order to specify the mechanical properties of the alloy and the way in which the properties were achieved, thus:

<i>Suffix letter</i>	<i>Basic condition</i>
F	as-fabricated
O	annealed wrought products
H	cold-worked (strain hardened)
W	solution heat-treated
T	heat-treated (stable)
<i>Suffix digits</i>	<i>Secondary treatment</i>
First digit	
1	Partial solution plus natural ageing
2	Annealed (cast products only)
3	Solution plus cold work

4	Solution plus natural ageing
5	Artificially aged only
6	Solution plus artificial ageing
7	Solution plus stabilizing
8	Solution + cold work + artificial ageing
9	Solution + artificial ageing + cold work
<i>Second digit (H only)</i>	Degree of cold work.

Recourse to detailed specifications or to manufacturers' literature is suggested when several digits are included in the temper designation. But a simple example would be 6061-T6, which would describe an Al-Mg-Si alloy solution heat-treated followed by artificial ageing.

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