HIGH-TEMPERATURE STRUCTURAL MATERIALS

EDITED BY R. W. CAHN, A. G. EVANS AND M. McLEAN

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Preface

The Royal Society of London for Improving Natural Knowledge, to give that august body its full name, every year arranges several Discussion Meetings at its headquarters in London on matters of broad scientific or engineering interest. The topics are chosen competitively from a large number of proposals, and each such Discussion Meeting is organized by a group of experts, at least one of whom is a Fellow of the Society. The papers presented, together with a record of the discussion that follows the papers, are published in an issue of the *Philosophical Transactions of the Royal Society*. Often, as here, the organizers also edit the proceedings. If the topic is judged appropriate, commercial publishers are then given an opportunity of publishing the proceedings as a book, thereby giving the subject matter a wider dissemination. In this manner, this book came to be published.

The organizers of this Discussion Meeting are all academics, being attached to Cambridge University (Cahn), Harvard University (Evans) and Imperial College, London (McLean). Three of the 13 speakers whose papers are presented here work in the industrial or Government sector, so the perspective is by no means exclusively academic. Also, as is customary on such occasions, various nationalities are represented: the authors of the papers printed here come from five countries, and from both sides of the Atlantic.

To summarize the objectives of the meeting, I cannot do better than repeat the synopsis prepared by my colleague, Professor McLean, for use in the original printed programme.

> The drive for increased efficiency of gas turbines, and other heat engines, has determined increasingly demanding specifications for future generations of high temperature materials. It is clear that the required performance, in relation to high-temperature strength and oxidation resistance, cannot be achieved by the incremental evolution of conventional materials, such as nickel-base superalloys. The meeting reviewed the characteristics and potential of a wide range of candidate superalloy replacements, such as ceramics intermetallics and their composites. Particular attention was devoted to the problems of processing and design with these materials.

One of the industrial contributions, by Dr Williams, General Manager of GE Aircraft Engines in Ohio, focuses attention on economic considerations, which are coming to take the centre of the stage. The scope and limitations of superalloys, the exploitation of thermodynamics and of quantum physics to predict phase diagrams and crystal structures, various aspects of mechanics and design, and reliability aspects of mechanical testing of both metals and ceramics, are some of the themes covered in the pages that follow.

We are pleased that Chapman & Hall have offered to bring these proceedings to a wide international readership, and commend the book to all those interested in load-bearing materials for use at high temperatures, certainly a very wide public.

Robert Cahn (on behalf of the Organizers)
July 1995

Contents

1

Nickel-base superalloys: current status and potential

By M. McLean

The evolution of nickel-base superalloys has occurred over about 50 years through a combination of alloy and processing developments to satisfy quite different service requirements of various components of the gas turbine. There is now a good general understanding of the mechanisms leading to the unusual mechanical properties of these precipitation strengthened materials. Although the scope for further significant improvements in the behaviour of nickel-base superalloys appears to be limited, it is unlikely that their full potential is yet being achieved in engineering applications. Progress towards the development and validation of constitutive laws describing fully anisotropic deformation is described.

1. Introduction

The development of nickel-base superalloys has, almost entirely, been motivated by the requirement to improve the efficiency, reliability and operating life of gas turbines. There have been other peripheral applications but, at present about 90% of superalloys produced are used in gas turbines for a range of applications, including aerospace, electricity generation, gas/oil pumping and marine propulsion. The differing requirements in specific parts of the engine and the different operating conditions of the various types of gas turbine have led to the development of a wide range of nickel-base superalloys with individual balances of high-temperature creep resistance, corrosion resistance, yield strength and fracture toughness. However, all of these materials have evolved from the Ni–Al–Ti–Cr precipitation strengthened alloy, Nimonic 80A, developed by Pfeill and his colleagues at the Mond Nickel Company around 1940 in response to Whittle's need for a suitable turbine blade material for the first British gas turbine for aircraft propulsion (Betteridge & Shaw 1987; Sims 1984).

The principal characteristics of nickel-base superalloys largely derive from the precipitation of an $L1_2$ ordered intermetallic phase, γ' $Ni_3(Al,Ti)$, that is coherent with the face-centred-cubic γ-nickel solid solution matrix (Stoloff 1987). The development of viable superalloys has been achieved by a combination of compositional modifications that control aspects of the γ/γ' relationship (γ' volume fraction, γ' solvus, γ/γ' lattice mismatch), the use of more conventional alloying approaches to solid solution strengthening and corrosion resistance, and the introduction of a range of novel processing techniques (directional solidification, single crystal technology, powder processing, mechanical alloying, HIPping, etc.). A full review of superalloy technology is beyond the scope of this paper which will present a personal view relating to the most important recent developments and future requirements.

2. Historical trends

The efficiency of operation of the gas turbine is largely determined by the combination of the temperature and pressure/volume of gas passing from the combustion chamber to the external environment to provide propulsion, or power to motivate other machinery. The materials available to be used in the turbine, particularly as turbine blades and discs, have to a large extent determined the operating conditions of gas turbines. The progressive improvement in the efficiencies of gas turbines has paralleled the increased temperature capabilities and strengths of successive generations of superalloys that have been specifically developed for these critical components, in particular turbine blades and discs. Indeed, much of the drive for superalloy substitutes, which is the major theme of the present meeting, derives from the same continuing requirement. We consider briefly the evolution of materials for turbine blade and turbine disc applications.

(a) *Turbine blades*

Materials for high-pressure turbine blades must be able to operate in the high-temperature gases emerging from the combustion chamber; they experience a combination of high temperatures and relatively low gas-bending and centrifugal stresses. In the half century since the development of the first precipitation strengthened superalloy (Nimonic 80) the temperature capability of nickel-base superalloys, as measured by the temperature at which a creep rupture life of 1000 h can be achieved with a tensile stress of 150 MPa, has progressively increased by about 7 K per year (figure 1*a*). The increase in the gas operating temperature has been much greater than this due to engineering innovations, such as blade and thermal barrier coatings, that allow the blades to operate in an environment in which the gas temperature exceeds the melting point of the alloys from which the blade is produced.

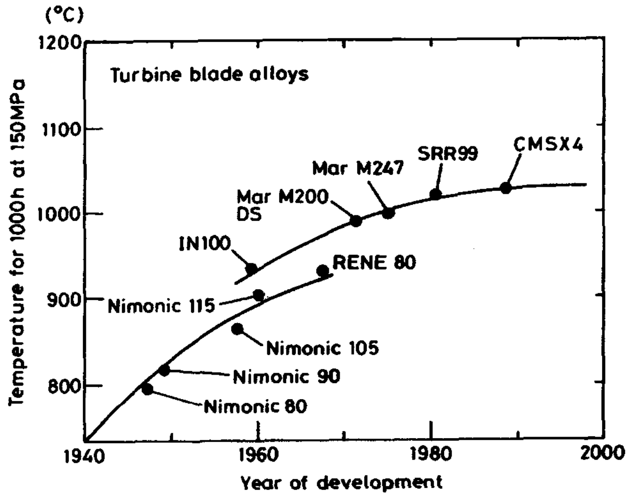
The strategies adopted in the development of turbine blade materials have depended on the service cycles for which specific engines were designed and where different failure mechanisms determine component life. However, there have been some common threads to this alloy development:

increasing γ' volume fraction (Al, Ti);
increasing γ' solution temperature (Co);
minimization of the γ/γ' lattice parameter mismatch;
solid solution strengthening (W, Mo, Ta, Re);
ductilizing additions (Hf, B).

Alloys with high chromium contents have been developed to give the enhanced oxidation/corrosion behaviour required for marine and industrial applications, but this has usually been achieved at the expense of mechanical performance. The development of reliable corrosion resistant coatings is rendering less important the need for alloys that are inherently oxidation/corrosion resistant.

As the alloys have evolved to give increased high-temperature strength, it has been necessary to develop new processing techniques to produce the turbine blades to acceptable tolerances and to maintain the required levels of ductility. The principal stages in this development can be summarized as follows.

(i) Forged blades were produced, and still are from some alloys, while there was a sufficiently wide heat treatment window, between the γ'-solvus and liquidus temperatures to allow reliable thermo-mechanical processing.



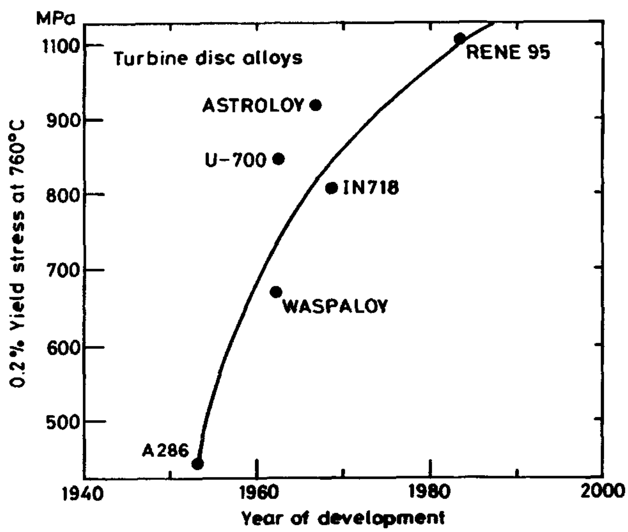


Figure 1. Trend in the improvement in superalloys for turbine blade and disc applications as a function of the year of introduction of the alloy. (*a*) Blade alloys temperature for 1000 h rupture life with 150 MPa stress. (*b*) Disc alloys. Yield stress at 850 °C.

(ii) Investment casting was introduced for alloys where forging was impracticable and where adequate ductility could be achieved. However, as the γ' volume fraction increased beyond about 50%, the ductilities became unacceptably low due to premature fracture at transverse grain boundaries.

(iii) Directional solidification, first used by Ver Snyder and co-workers by a modification of the investment casting process (see, for example, Ver Snyder *et al.* 1966), produced an elongated grain structure and a $\langle 001 \rangle$ crystal texture parallel to the solidification direction. The result has been an increase in creep ductility from less than 1% to more than 25% and considerable enhancement of the thermal fatigue resistance for alloys such as MarM 200.

(iv) Single crystal superalloys result from a fairly simple variant of the directional solidification process and is now state-of-the-art for advanced aerospace applications and is also being considered for large electricity generating plant.

It should be noted that processing changes have not always been in response to alloy development. Rather, alloy chemistry has often been adjusted to produce alloys tailored to the available processing technology. For example, the introduction of hafnium was to reduce the occurrence decohesion of longitudinal grain boundaries during directional solidification (Lund 1972). There is little or no inherent advantage of single crystal versions of the alloys produced by directional solidification; indeed, Piearcey *et al.* (1970) studied single crystal superalloys over twenty years ago. However, Gell *et al.* (1980) showed that by stripping the elements intended to modify the grain boundaries (C, B, Hf) it was possible to increase the liquidus temperature and allow more effective control of the γ' morphology through heat treatment. A wide range of superalloys specifically intended for use in the single crystal form has been and continues to be developed.

The most advanced single-crystal superalloy turbine blades are now operating at a homologous temperature $T/T_m > 0.85$. Although further developments will certainly take place, the melting point of nickel provides a natural ceiling for the temperature capability of nickel-base superalloys. Consequently, there is limited scope for further large increments in temperature capability of this class of alloys.

(*b*) *Turbine disc alloys*

The turbine disc operates at considerably lower temperatures than do the blades (about 850 °C compared to 1150 °C for blades in current aero-engines). Consequently creep deformation is relatively insignificant. The principal design requirements, to reduce engine weight and increase rotational speed, both lead to high stresses on the disc and alloy development has been designed to increase the yield strength and to inhibit crack initiation and growth, particularly in fatigue conditions. Figure 1*b* indicates the progressive increase in yield strength and fatigue resistance of this class of alloy.

With increasing yield strength there has been an associated decrease in fracture toughness. Some amelioration of this effect has been obtained through control of grain size; attempts at producing duplex grain morphologies (*necklace grain structures*) appear to have been abandoned as being impractical (Jeal 1986). However, in current advanced disc alloys the critical defect size for brittle fracture at service stresses is about 30 μm (Sczercenie & Maurer 1987). Since various inclusions or clusters of precipitate particles can constitute such a critical defect this places demands on non-destructive examination that are currently unattainable. The consequences of disc failure, particularly in aero-engines, require a viable quality assurance procedure.

Turbine discs are currently produced either by forging or by powder processing, although the former is more extensively used. In both cases quality is maintained through careful control of alloy cleanness at each stage of the process. The use of different secondary melting processes, on bar-stock initially produced by vacuum induction melting, is now standard procedure to control inclusion content. Vacuum arc refining (VAR), electro-slag refining (ESR), electron beam cold hearth refining (EBCHR) are all currently available as commercial processes producing

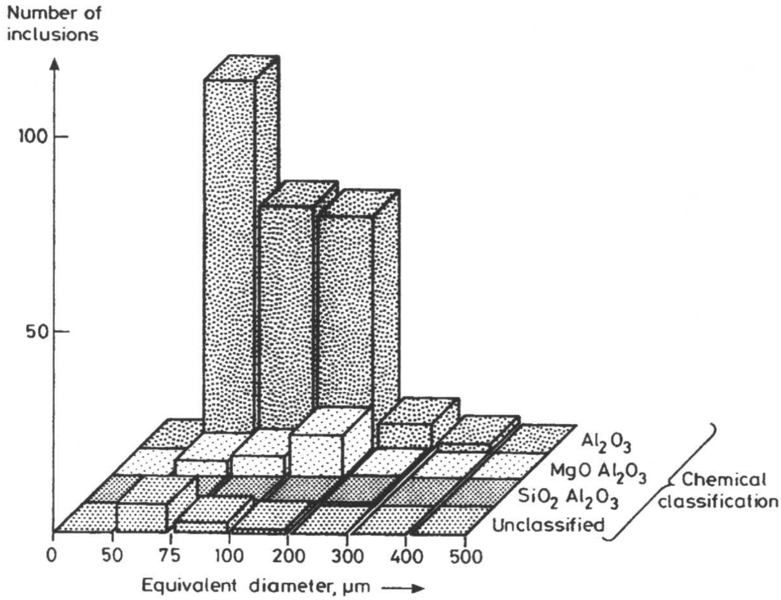


Figure 2. Size distribution of various types of inclusions found by analysis of the concentrated inclusions produced by electron beam button melting of the turbine blade alloy IN738LC (Chakravorty *et al.* 1987).

double, or triple, melted alloy (Patel & Siddal 1994). Because of the impracticability of characterizing the very low inclusion contents in these materials by conventional metallographic procedures or by mechanical tests on small specimens, novel approaches to evaluating very clean alloys are being developed. One such example is the electron beam button melting approach used by Quested & Hayes (1993) at the National Physical Laboratory which allows inclusions from 1 kg of alloy to be concentrated, identified and their size distributions determined (figure 2). A code-of-practice for use of the NPL approach to cleanness evaluation has been agreed by the leading UK producers of turbine disc materials (Quested, personal communication).

If replacement materials for superalloys are developed that allow a significant increment in turbine operating temperature, there will be a corresponding increase in the service temperature of the disc. This will require new disc alloys. There is certainly scope for the further development of superalloys for this purpose. However, alternative materials, such as structural intermetallics, could well supersede superalloys because of the attractions of weight savings through reduced density. Superalloys for discs are at a less mature stage of development than are those for blade applications.

3. Fundamentals of mechanical behaviour

There can be no doubt that the attractive mechanical properties of nickel-base superalloys derive directly from the disposition of a high volume fraction of the

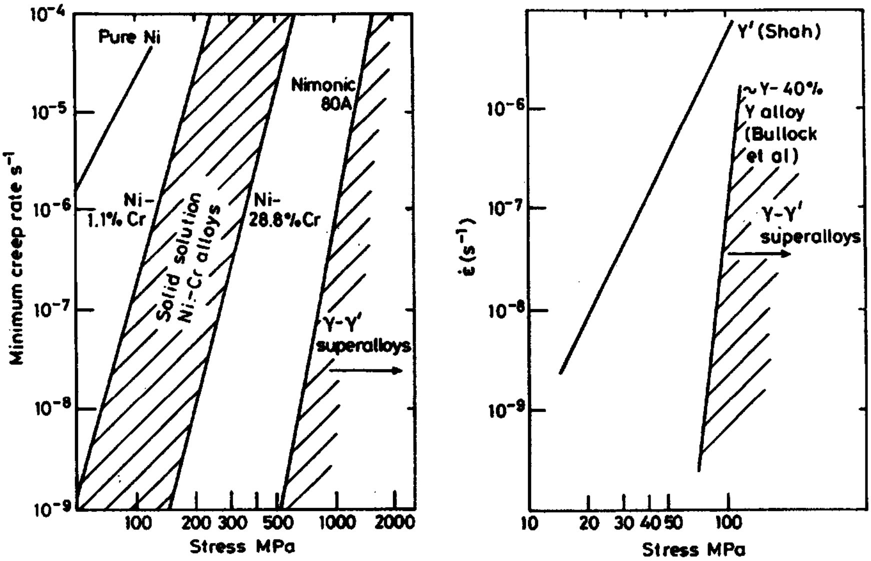


Figure 3. Comparison of the creep behaviour of (*a*) solid solution Ni–Cr alloys, (*b*) γ' Ni_3(Al,Ti) intermetallic compounds and (*c*) γ/γ' nickel-base superalloys.

coherently dispersed γ' precipitate (up to 70% by volume) in the γ-nickel matrix. However, in spite of extensive fundamental studies there is still no clear consensus on the mechanisms controlling the engineering performance in service conditions. Here we focus on a limited number of aspects of the mechanical behaviour of these materials that have been thought to be of particular importance.

Superalloys with high volume fractions of γ' show a similar anomalous rise in yield strength with increasing temperature as is exhibited by the monolithic $L1_2$ intermetallic phase (Stoloff 1987). Detailed analysis of this phenomenon has been carried out by a large number of authors, notably Paidar *et al.* (1984), and there is now a general consensus that it a consequence of thermally activated cross-slip onto cube planes that produces sessile dislocation segments that inhibit dislocation glide on octahedral planes. Hirsch (1992) has recently considered the detailed dislocation interaction that are occurring. Such considerations are likely to be important in service conditions where the yield stress is attained, or at least approached. However, design stresses will almost invariably be below the threshold for time-independent yield and γ' cutting is unlikely to be a significant factor during service.

In the sub-yield creep regime, relevant to turbine blades, it is clear that the creep performance of the duplex γ/γ' alloys is significantly superior either to (Ni,Cr) solid solution matrix or to the γ' Ni_3(Al,Ti) precipitated phase (figure 3). Consequently, the γ' behaviour cannot be taken as a limit to the alloy performance. Rather, the coexistence of the two phases requires the operation of a radically different deformation mechanism than would occur in either individual phase. Indeed at stress levels below those required for γ' shearing it is likely that dislocation activity is largely restricted to the γ matrix and this is supported

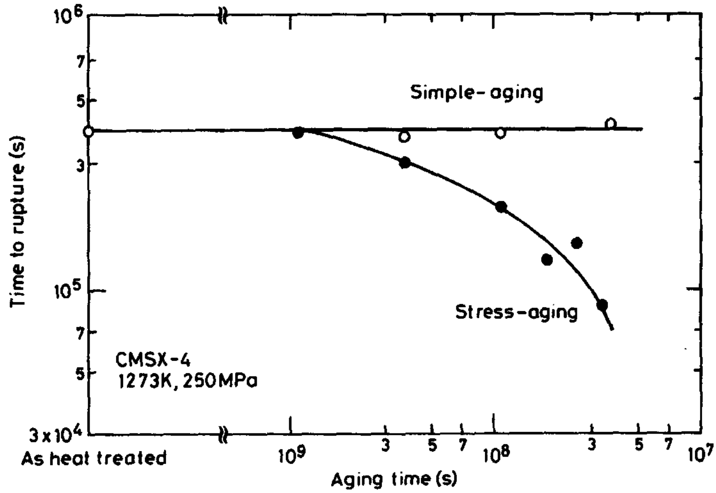


Figure 4. Comparison of the creep behaviour of the single crystal superalloy CMSX4 in two microstructural forms: (a) regular γ' morphology produced by commercial solution and ageing heat treatment and (b) rafted γ' morphology produced by heat treatment under stress (Kondo *et al.* 1994).

by transmission electron microscopy of creep deformed material (Henderson & McLean 1983). Dyson, McLean and co-workers (e.g. Ion *et al.* 1986; Dyson & McLean 1990) have developed a model of creep deformation that considers the dispersed particles to inhibit glide in the matrix: deformation occurs at a rate largely determined by dislocation climb and dislocations generated are mostly mobile leading to an increase in creep rate with accumulated plastic strain instead of the normal work-hardening exhibited by single-phase metals. This successfully accounts for a range of observations relating to the creep behaviour of superalloys that are not compatible with earlier models:

(i) Creep in both tension and compression exhibits a progressively increasing creep rate, rather than a steady state deformation rate.

(ii) Plastic prestrain of superalloys increases the creep rate relative to the unstrained material, rather than leading to strain hardening.

(iii) There is little difference in creep curves of superalloys produced under constant load and constant stress conditions, indicating the dominance of an intrinsic strain softening mechanism over the effect of increased stress due to reduction in cross-sectional area during tensile deformation.

(a) *Microstructural influences on mechanical behaviour*

An interesting microstructural feature of single crystal superalloys is the directional coarsening of the γ' particles that occurs during high-temperature ageing (greater than 1000 °C) in the presence of a small stress (Tien & Copely 1971). Plausible explanations have been given of the effect due to stress gradients generated as a result of differences in elastic and lattice constants of the γ and γ' phases. The rafted microstructures that develop in most commercial single crystal superalloys under tensile stresses have often been cited as the reason for their un-

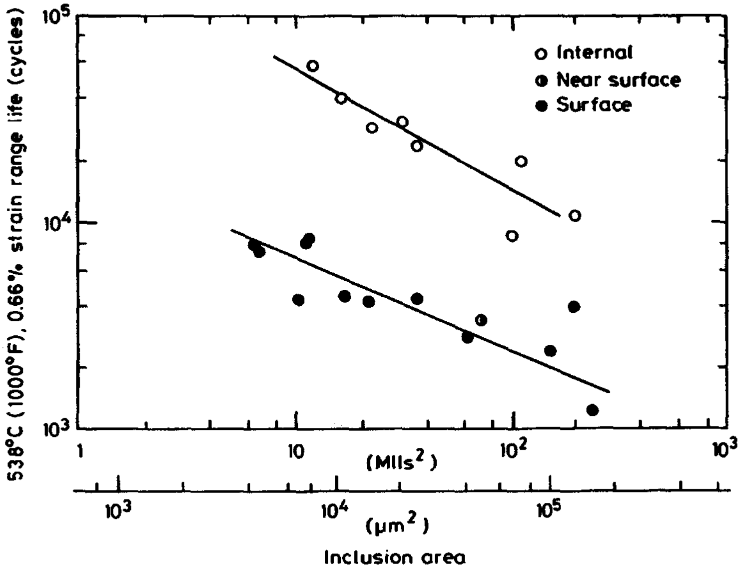


Figure 5. Variation in low cycle fatigue life with increasing volume fraction of inclusions in Rene 95 (Shamblen 1983).

expectedly good creep performance at temperatures in excess of about 1000 °C. However, it is now quite clear that the rafted γ' morphology is quite detrimental to the low and intermediate temperature creep behaviour (Caron *et al.* 1988; Kondo 1994). Figure 4, from the work of Kondo *et al.* (1994) clearly indicate that pre-rafting of the γ' reduces the rupture life relative to both the original material and that subject to conventional heat treatment. The benefits of a rafted γ' is now open to question particularly in the variable stress and temperature conditions likely to be experienced in service.

The importance of inclusions in controlling the low-cycle-fatigue life of turbine disc alloys has been demonstrated unambiguously in a number of studies. Shamblen (1993) for example, has deliberately added inclusions of known size and concentration to the alloy RENE95 and has shown a progressive decrease in cycles to failure with increasing inclusion volume fraction (figure 5). Pineau (1990) has paid particular attention to the problems of characterizing the fracture behaviour of materials with very low concentrations of defects. Mechanical testing of such materials must be carried out on a sufficiently large volume of material to ensure a high probability of the occurrence of defects characteristic of the component of interest.

4. Engineering considerations

The implementation of computer-aided design methods, to replace the traditional design codes, depends on there being a sufficiently sophisticated representation of the material behaviour. Whereas previous designs of gas turbine blades were based on simple measures of material performance, such as stress rupture life and minimum creep rate, in the future attempts will be made to numerically simulate the performance of a component in likely service cycles that will inevitably involve multiaxial stresses and variable stresses and temperatures. It is unrealistic to collect an experimental database to cover all possible options, particularly in the case of anisotropic materials such as single crystal superalloys. It is necessary to devise a reliable approach to the extrapolation/interpolation of a restricted database through the use of appropriate constitutive equations that can be incorporated in the design calculations. Several empirical approaches (Graham & Walles 1955; Evans & Wilshire 1987) have been successful in representing uniaxial creep databases, but these are difficult to extend to variable and multiaxial loading conditions.

The mechanisms of creep deformation of superalloys, described in the previous section, have been translated into such a set of constitutive equations using the general formalism of continuum damage mechanics. Here, the uniaxial creep rate $\dot{\epsilon}$ is expressed as a function of state variables (or damage parameters) that represent the current condition of the material, in particular of the structural and microstructural features that control the strength of the alloy. For the isotropic form of the model appropriate to superalloys, an acceptable fit of creep data can be obtained by using two state variables; S is a dimensionless internal stress that increases to a steady-state value of S_{ss} leading to primary creep and $\omega = (\rho - \rho_i)/\rho_i$ represents the increasing density of mobile dislocations ρ (ρ_i is the initial value). The isotropic creep behaviour is represented by the following set of three equations involving the two variables S, ω and four constants $\dot{\epsilon}_i$, where $\dot{\epsilon}$ has dimensions of s^{-1} and H, S_{ss}, C are all dimensionless (Ion *et al.* 1986; Dyson & McLean 1990):

$$\dot{\epsilon} = \dot{\epsilon}_i(1 - S)(1 + \omega), \quad \dot{S} = H\dot{\epsilon}_i(1 - S/S_{ss}), \quad \dot{\omega} = C\dot{\epsilon}. \tag{4.1}$$

The model has been extended by Ghosh *et al.* (1990) to represent anisotropic creep of single crystals by considering creep deformation to be restricted to specific slip systems and computing the total strain resulting from each shear displacement. A set of equations equivalent to equations (4.1), but expressed in terms of shear, rather than tensile, strains γ^k is required for each family of slip systems. Then the total displacement ϵ_{ij} from all N components of shear on the allowed system $(n_1n_2n_3)\langle b_1b_2b_3\rangle$ is given by

$$\epsilon_{ij} = \sum_{k=1}^{N} \gamma^k b_i^k n_j^k. \tag{4.2}$$

Here i, j represent the cube directions and k identifies one of the slip systems being considered: γ^k is the amount of shear on that system. An arbitrary crystal direction x will transform to a new orientation X, with a strain in that direction of $(\bar{X} - \bar{x})/\bar{x}$, where

$$\begin{bmatrix} X_1 \\ X_2 \\ X_3 \end{bmatrix} \begin{bmatrix} 1 + \epsilon_{11} & \epsilon_{12} & \epsilon_{13} \\ \epsilon_{21} & 1 + \epsilon_{22} & \epsilon_{23} \\ \epsilon_{31} & \epsilon_{32} & 1 + \epsilon_{33} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix}. \tag{4.3}$$

In the analysis dislocation activity is taken to occur on two families of slip systems, $\{111\}\langle\bar{1}10\rangle$ and $\{100\}\langle 011\rangle$. There is considerable evidence of the occurrence of