The anomalous yielding effect broadly speaking, it arises for the following reason. Upon deformation, the applied stress, the anisotropy of the anti-phase boundary energy and further contribution from the elastic anisotropy combine to promote the *cross-slip* of segments of the γ' superpartial dislocations from the {111} slip plane to the cross-slip plane {001}.

The cross-slipped segments represent *microstructural locks* since they resist deformation – they cannot move without trailing APBs behind them and are thus immobile. These are known as Kear–Wilsdorf locks after the researchers who first proposed their existence. The hardening is increasingly prevalent as the temperature rises, due a component of the cross-slipping process which is thermally activated. Beyond the peak stress, slip-line trace analysis has revealed that the mode of slip deformation changes





Creep

The solutes were observed to have a profound effect on the creep resistance, with Au and Rh being the most and least potent strengtheners, respectively. The amount of primary creep strain was found to increase in the order rhodium (4%), iridium (5%), palladium (6%) and gold (8%) compared with nickel at 2%;

Creep strengthening in nickel alloys by precipitation hardening

The presence of the γ' phase, which is promoted by alloying with Al, Ti and Ta, has a

profound influence on the creep resistance of the nickel alloys

Provided the stress level is not too high (in which case the γ' particles are sheared),

the performance is improved substantially.

In alloys with γ' fractions of approximately 0.17, 0.18, 0.32 and 0.62, respectively;

(creep measured for 1000 h creep life at 137 MPa), the last of these alloys is better

than the first by about 120 C.

Single-crystal superalloys for blade applications

Operating conditions for the high-pressure turbine blades in a large civil turbofan engine.

The temperature of the gas stream is about 1750 K, which is above the melting temperature of the superalloys from which the blades are made.

The high-pressure shaft develops a power of about 50 MW – hence, with about 100 blades, each extracts about 500 kW, which is sufficient to satisfy the electricity requirement of about 500 homes.

Each row of blades is expected **to last at least 3 years**, assuming they operate at 9 h/day. This is equivalent to about 5 million miles of flight, or ~500 circumferences of the world. The blades rotate at an angular speed, ω , of more than 10 000 revolutions per minute, so that the tip velocity is greater than 1200 km/h.

The stresses experienced by the blades, which are largely centrifugal in nature due to the significant rotational speeds, are considerable; if the blade cross-section is assumed to be uniform, the stress, σ , at the blade root is approximately given by

$$\sigma = \int_{r_{\text{root}}}^{r_{\text{tip}}} \rho \omega^2 r \, \mathrm{d}r = \frac{\rho \omega^2}{2} \left(r_{\text{tip}}^2 - r_{\text{root}}^2 \right)$$

where ϱ is the blade density. If the blade length is 10 cm and the mean blade radius is

0.5 m, the stress at the blade root is given by

 $\sigma = 9000 \times (100 \times 2\pi)2 \times (0.552 - 0.452)/2 = 180 \text{ MPa}$

Since the cross-sectional area is, in general, no greater than a few square centimetres,

this is equivalent to the weight of a heavy truck hanging on each blade.

Castings were fabricated with the presence of different angle grain boundaries. The data indicate that for an applied stress of 300 MPa at 850 C, a perfect single crystal has a stress rupture life in excess of 10 000 h; however, a grain boundary of misorientation $\theta = 7^\circ$ reduces the creep life to 100 h. When $\theta > 10^\circ$, the creep life is only a few hours.

This is one reason why so-called 'grain-boundary-tolerant' single-crystal superalloys have recently become available – these contain the grain-boundary strengtheners such as carbon and boron.

Under creep loading of about 200 MPa and 980 C, the removal of the transverse grain boundaries increases the creep ductility from below 5% to in excess of 25%. *In single-crystal form, the creep life is improved to greater than 100 h from about 70 h for the directionally solidified, columnar-grained structure.*

Fig. 3.11. Evolution of creep strain with time for the superalloy Mar-M200 under loading of 206 MPa and 982 °C, in the conventionally cast (equiaxed) state, the directionally solidified (columnar) state and the single-crystal form [8].

The practice of investment casting: directional solidification

The investment shell mould sits on a copper chill plate of about 14 cm diameter. Since the diameter of the chill plate is small, as little as 5 kg of charge needs to be melted.

This size is sufficient for five HP turbine blades for a civil jet engine to be produced simultaneously, or alternatively 20 for a smaller helicopter engine.

The mould is withdrawn at the programmed rate. In practice, a high thermal gradient of typically 4000 K/m is achieved, which is sufficient to produce cast microstructures of dendritic form; the primary dendrite arm spacing is then in the range 100–500 μ m. The cooling time between the critical temperatures of 1400 C and 1000 C is typically about 20 minutes.

Optimisation of the chemistry of single-crystal superalloys

- The chemistry of the single-crystal superalloys has been refined in order to improve the properties displayed.
- Of note is the introduction of significant additions of Re ($\leq 6\%$), and the reduction of Ti and Mo to low concentrations.

(1) <u>Proportions of γ' -forming elements such as Al, Ti and Ta should be high, such</u> <u>that the γ' fraction is ~70%</u>.

Why is 70% an appropriate figure? creep deformation on the microscale is restricted to the γ channels which lie between the precipitates of γ' . Thus, creep dislocations do not penetrate the γ' precipitates. **It follows then that a reduced fraction of** γ **yields improved properties.**

The optimum microstructure

A second point is that the creep performance does not increase monotonically as the γ' fraction is increased – thus, an alloy with 70% γ' performs better than one with 100% γ' . This implies a strong strengthening effect from the γ/γ' interfaces, which impart resistance to creep deformation. This effect has been confirmed by measuring the creep rupture lives of a series of alloys containing various fractions of γ' of *identical composition*

Fig. 3.29. Variation of the creep rupture lives of the single-crystal superalloys TMS-75 and TMS-82+, as a function of the amount of γ' phase [27]. The creep rupture life is largest when the γ' fraction is about 70%. (Courtesy of Hiroshi Harada.)

There is another consideration. There should exist a sufficient solutioning window, ΔT , below the melting temperature, across which γ is the only stable phase. This is necessary because, after solidification, heat treatment is required to remove residual microsegregation and eutectic mixtures rich in γ' . This puts the γ' precipitates into solution; during subsequent exposure to lower temperatures, the γ' develops a uniform microstructure with an optimum precipitate size. The heat treatment for a typical single-crystal superalloy would involve a solutioning of 8h at 1314 C, a primary age of 4h at 1140 C followed by a secondary age of 16 h at 870 C The solutioning window is about 50 C, which is rather small; this emphasises the need for precise temperature control during heat treatment. Since the solutioning window is expected to decrease as the γ' fraction is increased, the heat treatment of the higher-strength alloys is a delicate process.

(2) <u>The composition of the alloy must be chosen such that the γ/γ' lattice misfit is</u> <u>small; this minimises the γ/γ' interfacial energy so that γ' coarsening is restricted</u>.

When the misfit is small, less than about 0.5%, the γ ' particles are cuboids. The precipitates become spherical as the magnitude of the misfit increases, since coherency is lost.

Experiments indicate that the expansion coefficient of γ' is considerably less than that of γ ; thus, the lattice misfit becomes more negative as the temperature increases, implying that the misfit, δ , can be either positive or negative. A consequence of a variation in δ , followed by a change in temperature, are *misfit stresses* which are present even when the externally applied load is zero. Consider the SRR99 single-crystal superalloy. Assuming that the γ/γ' interfaces are forced into elastic coherence, it follows that the γ' particles are constrained in a state of hydrostatic tension, and that the γ channels separating them are in a state of biaxial compression.

Fig. 3.31. The γ/γ' microstructures displayed by four experimental single-crystal superalloys of varying chemistries [28]. Note the correlation between the γ' morphology and the estimated values of the lattice misfit, δ . (Courtesy of Pierre Caron.)

There is some evidence, that alloys of negative misfit possess greater creep resistance than those with positive misfit

Fig. 3.34. Schematic illustration of the coherency stresses to be expected in a nickel-based superalloy when the misfit, δ , is negative. (Courtesy of Hael Mughrabi.)

(3) <u>Concentrations of creep-strengthening elements, particularly Re, W, Ta, Mo and</u> <u>Ru, must be significant but not so great that precipitation of topologically close-</u> <u>packed (TCP) phases is promoted</u>

The major differences between the chemistries of first-, second- and thirdgeneration alloys lies in the addition of Re. Thus, a strong creep-strengthening effect can be attributed to Re. The elements W and Ta appear to be less potent, with Cr and Co having little effect.

 $Co \to Cr \to Ta \to W \to Re$

The best strengtheners thus appear to be those which diffuse the slowest in nickel.

In practice, there is a limit to the concentrations of the refractory elements which can be added. Excessive quantities of Cr, Mo, W and Re promote the precipitation of intermetallic phases which are rich in these elements (4) The composition must be chosen such that surface degradation through exposure to the hot, working gases is avoided.

The thermodynamics of formation of the important oxides NiO, Cr_2O_3 and Al_2O_3 . The Gibbs energies of formation indicate that Al_2O_3 is the most stable of the three, NiO the least, with Cr_2O_3 between the two.

However, of equal relevance in practice are the kinetics of oxidation.

NiO has a high concentration of nickel vacancies and thus forms very rapidly with voids and microcracking prevalent – thus it is friable, which promotes spallation and hence sustained attack. Cr_2O_3 , is less so, but at elevated temperatures it is oxidised to the gaseous CrO_3 , with a significant rate of oxidation.

For these reasons, designed is always to be alumina formers. To ensure this, the aluminium content was chosen to be around ~6 wt%.

The Al content is 5-6 wt.

Additions of rare-earth, such as **Hf**, **La and Y**, are beneficial – **since they bind strongly** with S, which is inevitably present at impurity levels. It is now known that S present in the superalloys has a strong influence on the oxidation resistance - due to its solubility in the oxide scale and its likely segregation to the metal/scale interface. This explains the considerable emphasis placed by the alloy manufacturers on reducing the S levels of superalloy melts; sulphur should be restricted to 10–20 ppm, although recent melt desulphurisation techniques have allowed residual levels to reach less than 1 ppm on a routine basis I aval Contaminant

Containinain	Level
Na+K	1
V	0.5
Pb	1
F_2	1
Cl ₂	1500
S	10 000

From the point of view of microstructure, Ni superalloys are complex.

The fcc matrix, known as γ *, mainly consists of nickel,*

cobalt, iron, chromium and molybdenum. Figure 2 The strength of superalloys are due to the hardening precipitates known as γ' (Ni3Al based L12 structure)

> In some nickel – iron superalloys such as IN718 and IN706, which contain niobium, they are hardened by γ '' (Ni3Nb based D022 structure)

Major phases in Superalloys

 γ (gamma) = <u>face-centered-cubic</u> (FCC) nickel-based continuous matrix with high percentage of solid solution elements (Co, Cr, Mo, and W)

 γ ' = gamma prime Ni₃X precipitate (X = AI, Ti and Si)

- Same crystal structure (FCC)
- Similar lattice parameter (coherent precipitate)
- Ni₃X ordered FCC structure

Major phases in Superalloys

The major phases present in the nickel-base superalloys:

- γ (gamma) phase the continuous matrix of FCC.
- γ' (gamma prime) phase the major precipitate phase
- Carbides –various types, mainly $M_{23}C_6$ and MC. M = metal
- γ'' (gamma double prime) phase Ni and Nb combine to form a BCT Ni₃Nb coherent precipitate found in Ni-Fe alloys.
 - Provides strength at low and intermediate temperatures
 - Unstable above 650 ° C
- Borides formed at grain boundaries
- Topologically close-packed (TCP) type phases-

Superalloys

Microstructure and Strengthening Mechanisms

Strengthening mechanisms in superalloys:

- Solid solution strengthening (Mo and W)
- Addition of elements, e.g., Co which decrease the solubility of others to promote precipitation of intermetallics
- Al and Ti to form ordered FCC intermetallic precipitates of γ ' -phase [Ni₃AI], [Ni₃Ti]
- Carbides on grain boundaries (pin boundaries to stop shear) i.e. control grain boundary sliding
- Small additions of B and Zr which segregate to the grain boundaries and retard sliding process and grain boundary diffusional process
- Large grains; columnar grains; single crystal to stop grain boundary shear

Major phases in Superalloys

- Solutes in nickel based superalloys: Cr, Al, Ti
- Two-phase equilibrium microstructure: gamma (γ) and gamma-prime (γ ') Ni3AI.

0.

Ni

Melting point is not a reliable guide to the temperature capability of Fe-, Ni-, and Co-base superalloys.

Although Ni possesses the lowest melting point of the three alloy bases, it has by far the highest temperature capability under moderate-to-high stresses.

Co-base alloys, may display good creep rupture properties around 1000 °C. This may best be seen by means of comparative Larson-Miller plots for superalloys.

Also, cobalt-base alloys display superior hot corrosion resistance at high temperatures, probably a consequence of the considerably higher chromium contents that are characteristic of these alloys.

Co-based superalloys

Vitallium is a trademark for the first Co-based superalloy (1930)

an alloy of 60% Co, 20% Cr, 5% Mo, and traces of other substances.

The alloy is used in dentistry because of its light weight and resistance to corrosion. It is also used for components of turbochargers because of its thermal resistance.

Stellite is a range of Co-Cr alloys designed for <u>wear</u> resistance. It may also contain **W** and a small but important amount of **C**. It is a <u>trademarked name</u> of the <u>Deloro Stellite Company</u> and was invented by <u>Elwood Haynes</u> in the early 1900's as a substitute for flatware that stained (or that had to be constantly cleaned).

Cobalt-based superalloys are used due to their good weldability and hot corrosion resistance. These alloys have higher strength at high temperatures than Ni-based alloys and also have excellent resistance to thermal fatigue, oxidation, and corrosion. These alloys have **Co** as the principal alloying element, with significant amounts of Ni and Cr and smaller amounts of W, Mo, Nb, Ta, and sometimes Fe. They are mainly hardened by carbide precipitation. Alloys hardening by carbide precipitation contain between 0.4 and 0.85% carbon. Such superalloys consist of an austenitic matrix (fcc) and a variety of precipitated phases such as primary carbides $(M_3C_2, M_7C_3, and MC)$ and coarse carbides $(M_{23}C_6)$ and GCP types phases (geometrically compact phases) such as and (Ni₃Al) and TCP (topologically close packed) type phases , or $(Cr, Mo)_x(Ni, Co)_y$.

Co-based superallovs

- At room temperature Co: HCP crystal structure
- At 417°C Co undergoes an allotropic transformation and changes to an FCC structure
- Typical composition
 - 50-60 %Co
 - 20-30 %Cr
 - 5-10 %W
 - 0.1-1 %C
- Strengthening:
 - solid solution strengthening
 - carbide precipitation
- Lower strength of cobalt alloys at intermediate temperatures due to a lack of γ^I

Co-based alloys, unlike other superalloys, are not strengthened by a coherant, ordered precipitate. Rather, they are characterized by a solid solution strengthened austenitic (fcc) matrix in which a small quantity of carbides is distributed. (Cast cobalt alloys rely upon carbide strengthening to a much greater extent.) Cobalt crystallizes in the HCP structure below 417 C. At higher temperatures, it transforms to FCC. To avoid this transformation during service, virtually all Co-base alloys are alloyed with Ni in order to stabilize the FCC structure between room temperature and the melting point.