Lecture 12: High Temperature Alloys

Metallic materials capable of operating at ever increasing temperatures are in demand for power plant and aeroengine applications. But why do we need to increase the operating temperatures?

Thermodynamics

1. Energy is conserved. You cannot win – you can only break even.
2. You can only break even at absolute zero:

$$\text{efficiency} = \frac{T_H - T_L}{T_H - 0}$$

   where T_H is the highest absolute temperature, T_L the lowest absolute temperature in the operating cycle.
3. You cannot reach absolute zero.

Operating Conditions

Property	Aeroengine	Power Plant
Temperature	> 1000 °C	750 °C
Pressure	$\simeq 3$ bar	$350 - 370$ bar
Design life	10^4 h	2.5×10^5 h
$\sigma_{100{,}000\ h}$	10 MPa	100 MPa
Coating	Yes	No
Forced cooling	Yes	No
Single crystal	Yes	No

Table 1: An illustration of the potential differences between a turbine blade in the hot part of an aeroengine and one in the hottest part of a power plant. The stress is a 100,000 h creep rupture strength.

Power Plant Steels

Power plant contain components which can be 1–2 m in dimension. The steels used must therefore have sufficient hardenability to ensure uniform microstructures. The mechanism of creep deformation is the climb of dislocations over particles; the particles therefore control creep deformation.

Fe-0.1C–2.25Cr–1Mo wt% steel with a bainitic microstructure, but tempered at 700 °C for 10 h to obtain precipitates of M_2X, $M_{23}C_6$. This is a secondary hardened alloy. The chromium also gives the alloy some oxidation resistance but cannot be used at temperatures greater than 565 °C.

Fe–0.1C–9Cr–1Mo wt% for higher temperature applications (more oxidation resistant). Has a fine martensitic microstructure. After tempering contains mainly $M_{23}C_6$ carbides which are at the martensite boundaries and hence stabilise the plate microstructure and give a much greater creep resistance. Some alloys also contain Nb which forms fine and very stable NbC for long term stability. The solid solution strengthening from the large Cr concentration also improves the long term creep properties.

Coarsening

Coarsening is driven by surface energy. The surface to volume ratio for a spherical particle is $3/r$ where r is the particle radius. The particle therefore has an extra energy of $3\sigma/r$ where σ is the interfacial energy per unit area. It follows that (Fig. 58) the equilibrium compositions will be altered so that there will be a diffusion flux from the small to the large particles, leading to coarsening.

To minimise coarsening it is necessary to reduce the interfacial energy, to minimise the diffusion coefficient and to minimise the solubility of solute in the matrix so that diffusion gradients are small.

Aeroengine alloys

The key technology requirements for aeroengines are cost, weight, fuel consumption, polluting emissions, noise and reliability. Nickel base superalloys help achieve better fuel consumption and lower emissions by allowing the engine to operate at an optimally high temperature. The thermodynamic efficiency of an engine increases with the difference between the highest and lowest temperatures in its cycle, so increasing the

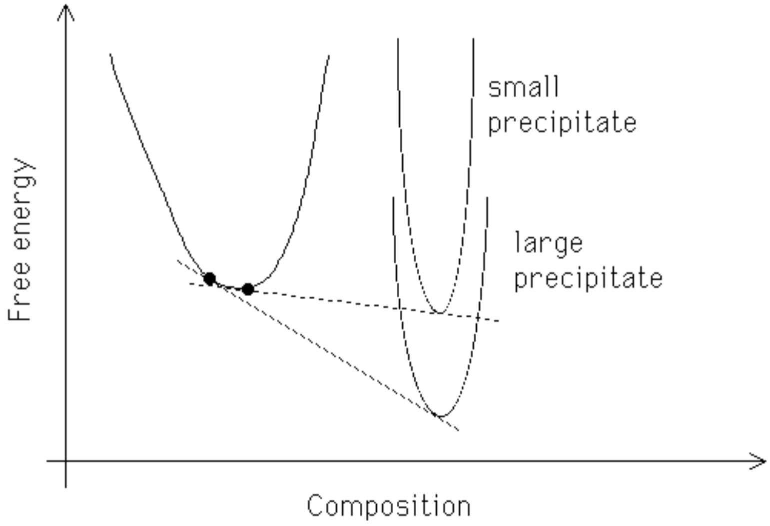

Fig. 58: Coarsening

temperature. However, too high a temperature increases the nitrous oxide emissions to unacceptable levels. The optimum highest temperature is believed to be about 1700 °C, which is far higher than is currently achieved in aeroengines.

Nickel base superalloys are two phase mixtures containing 40% γ and 60% γ' (Fig. 59). The γ is a disordered mixture of Ni and Al atoms with a c.c.p. crystal structure. The γ' has a stoichiometric composition Ni_3Al with a primitive cubic crystal structure with a motif of an aluminium atom at [0,0,0] and three nickel atoms at $[0,\frac{1}{2},\frac{1}{2}]$, $[\frac{1}{2},0,\frac{1}{2}]$ and $[\frac{1}{2},\frac{1}{2},0]$. The two phases are in a cube–cube orientation, *i.e.* their cell edges are exactly parallel. They are coherent.

The coherency is important because it implies a small interfacial energy and hence a reduced tendency to coarsen during exposure at elevated temperatures.

A real superalloy has a much more complicated chemical composition.

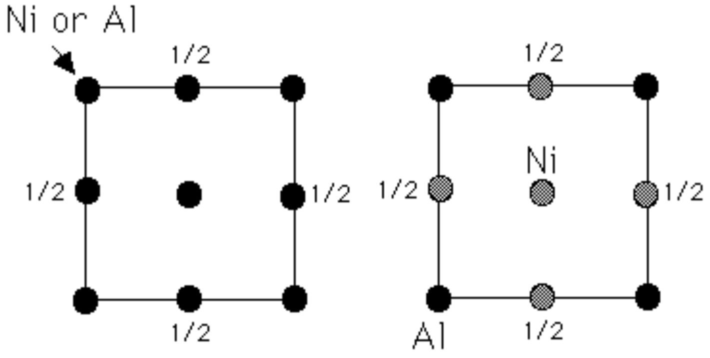

Fig. 59: γ and γ' cell projections

Titanium is added to form $\mathrm{Ni_3(Al, Ti)}$. The ratio of Al/Ti therefore determines the lattice parameter of γ', and can be adjusted to give coherency with γ.

Chromium is added for oxidation resistance and there may be additions of cobalt, rhenium, *etc.* to provide solid solution strengthening or to control the formation of detrimental compounds over the long term.

For turbine blade applications, the alloys may have an equiaxed structure, a directionally solidified structure or may be in the form of single–crystals. Any grain boundaries naturally assist diffusion so the creep strength increases as the processing tends towards single–crystals.

In all nickel base superalloys, the presence of the γ' phase hinders the motion of dislocations even though it is coherent with the matrix. This is because it has an ordered crystal structure. In γ the Burgers vector of a dislocation is $\frac{a}{2} < 1\ 1\ 0 >$; this is, of course, a lattice vector so that slip does not alter the crystal structure. However, for γ' $\frac{a}{2} < 1\ 1\ 0 >$ is not a lattice vector – $a < 1\ 1\ 0 >$ is the lattice vector for a primitive cubic lattice. It follows that the motion of an $\frac{a}{2} < 1\ 1\ 0 >_{\gamma}$ dislocation into the γ' will disrupt the order, leaving behind an anti–phase domain boundary. However, the passage of a second such dislocation through γ' on the same slip plane restores the order.

As a consequence, the penetration of γ' has to occur by pairs of γ dislocations. Such pairs are called 'superdislocations'. The requirement for pairing makes it more difficult for dislocations to penetrate the γ' and hence improves the resistance to creep deformation.

Intermetallic compounds

Ni_3Al

Ordered f.c.c. γ' phase, a major strengthening component of superalloys. Density only 7.5 $\mathrm{g\,cm^2}$ compared with about 8.5 for the nickel base superalloys. Because this is a strongly ordered phase, the atoms are unable to relax at the grain boundaries where different crystals meet. This makes the boundaries brittle giving very poor ductility. The addition of 0.1 at.% of boron disorders the grain boundary region (which remains crystalline), allows the atoms to relax and leads to a large improvement in ductility.

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

The most successful of the aluminides has a lamellar structure made up of alternating layers of an ordered hexagonal (D_{19}) $\mathrm{Ti_3Al}$ α_2 compound and ordered f.c.t. ($L1_0$) TiAl γ (Fig. 60). Ductility about 4-6% at ambient temperature. The γ aluminide tends to be more ductile. Density about 4.5 $\mathrm{g\,cm^2}$ and the aluminium makes them resistant to burning. The alloys have been extensively studied for aerospace and automotive turbochargers because of their high strength, low density and creep resistance. The γ phase forms with its most closely packed plane parallel to the basal plane of the α_2:

$$\{1\ 1\ 1\}_\gamma \| \ \{0\ 0\ 0\ 1\}_{\alpha_2}$$

$$<1\ 1\ 0>_\gamma \| \ <1\ 1\ \bar{2}\ 0>_{\alpha_2}$$

The lamellar microstructure is a direct consequence of this orientation relationship.

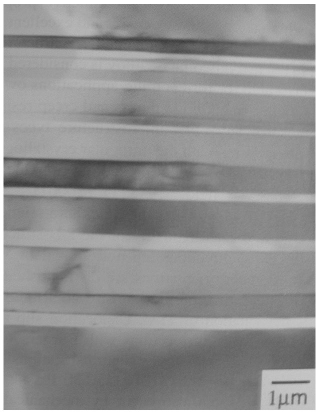

Fig. 60: Ti–48Al: lamellar microstructure (Kim and Maruyama, 2001)

Additional Resources

1. Dispersion strengthened:

   www.msm.cam.ac.uk/phase-trans/2005/ODS.html

2. Titanium metallurgy:

   www.msm.cam.ac.uk/phase-trans/2003/titanium.movies/titanium.html

3. Nickel–based superalloys:

   www.msm.cam.ac.uk/phase-trans/2003/Superalloys/superalloys.html

4. Heat–resistant:

   http://www.msm.cam.ac.uk/phase-trans/2002/creep.1.html

5. Alloys for nuclear fusion:

   www.msm.cam.ac.uk/phase-trans/2006/Irradiated_Steel/Irradiated_Steel.html