Tungsten in Superalloys

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Superalloys are unique high temperature materials used in gas turbine engines which display excellent resistance to mechanical and environmental degradation. Tungsten is a key alloying element in many of these alloys. This article will summarise the demands of the gas turbine engine and show the requirement for high temperature materials. The metallurgy of superalloy systems will be explained and the compositions and manufacturing processes used will be outlined. A range of applications will be considered but particular emphasis will be placed on the turbine blade alloys that contain up to ~ 10 weight % tungsten.

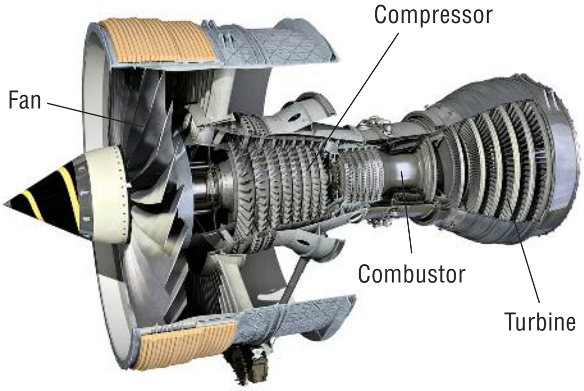


Figure 1: Rolls-Royce Trent Engine. © Rolls-Royce plc

1 Gas turbine engines

Gas turbine engines are used for aero-engines and power generation equipment. There are a number of variants on the basic design, one of which is the turbofan used for propulsion of civil aircraft. The layout of a Rolls-Royce Trent turbofan engine is shown in **Figure 1**.

Incoming air is squeezed in the compressor thus increasing its pressure. The compressed air enters the combustor, where it is mixed with fuel and ignited. The hot gases are allowed to expand through a turbine, which extracts the mechanical work required to drive the compressor via a shaft. At the front of the engine is a fan. Air passes through the fan and bypasses the core of the compressor, combustor and turbine. The thrust from the air that passes through the fan drives the aircraft forward. High bypass ratios minimise noise and fuel consumption.

Many criteria influence the design of gas turbine engines for aerospace application. Above all, safety is paramount. There are requirements for reliability and reduced cost of operation, including a requirement for low fuel consumption. There are increasing environmental pressures to reduce noise impact and for reduced emissions of NO_x and CO_2. Since 1950, the industry has developed products offering a ~4x reduction in noise and a ~70% reduction in fuel burn (**Figure 2**). However, with continued growth in flight numbers and a growth in environmental pressures, this trend needs to continue.

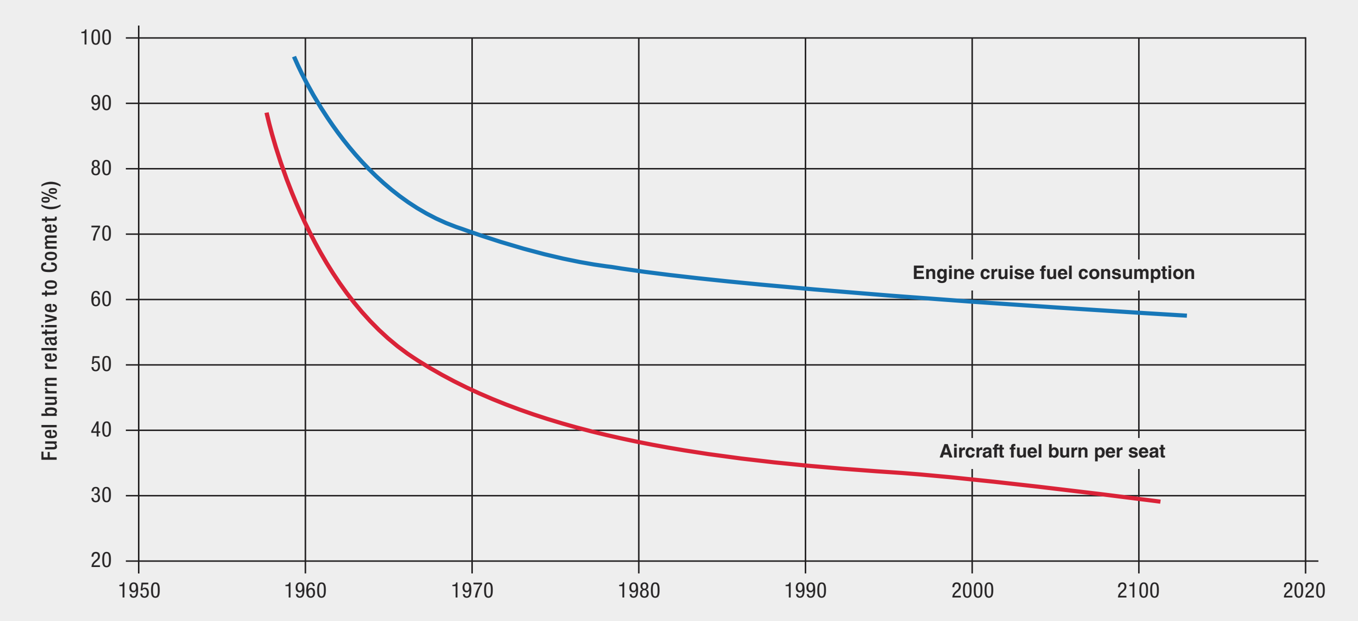


Figure 2: Reductions in fuel burn of civil aircraft since the Comet (derived from Air Transport Action Group).

A key design feature that leads to reduced fuel consumption is the turbine entry temperature (TET), ie the temperature of the hot gases entering the turbine. The performance and fuel efficiency of the engine is raised as the turbine entry temperature is raised [1]. This requirement drives the need for high temperature materials.

2 Nickel-based superalloys

A number of factors combine to make nickel a good base for high temperature materials. Nickel displays the FCC crystal structure and is therefore both tough and ductile. This structure is stable across the temperature range and therefore no phase transformations occur. The FCC structure brings low rates of self-diffusion helping to impart creep resistance. Nickel has sufficient abundance in relation to demand to mean it has a reasonable cost in contrast, for example, to the platinum group metals. The density is 8.907 g/cm³ and is often reduced through alloying with aluminium. This is significantly lower than refractory and platinum group metals. Nickel can also be alloyed with many other elements, including tungsten, allowing the development of stable high temperature materials.

Since the use of the first nickel-chromium alloys in the 1940s, a wide variety of alloys has been developed with different balances of cost, density and mechanical and environmental properties in different temperature ranges. A wide variety of manufacturing techniques have been employed, including forging, casting and powder metallurgical routes. Specialised techniques including single crystal casting have been developed. Depending on the composition, the alloys can consist of a number of phases.

The gamma phase (denoted γ) has the FCC structure and in nearly all cases forms a continuous phase in which the other phases reside. It contains significant concentrations of elements when present including tungsten, cobalt, molybdenum, rhenium and chromium that segregate to this phase.

Many alloys are precipitation hardened through the gamma prime precipitate, denoted γ´. This is a primitive cubic

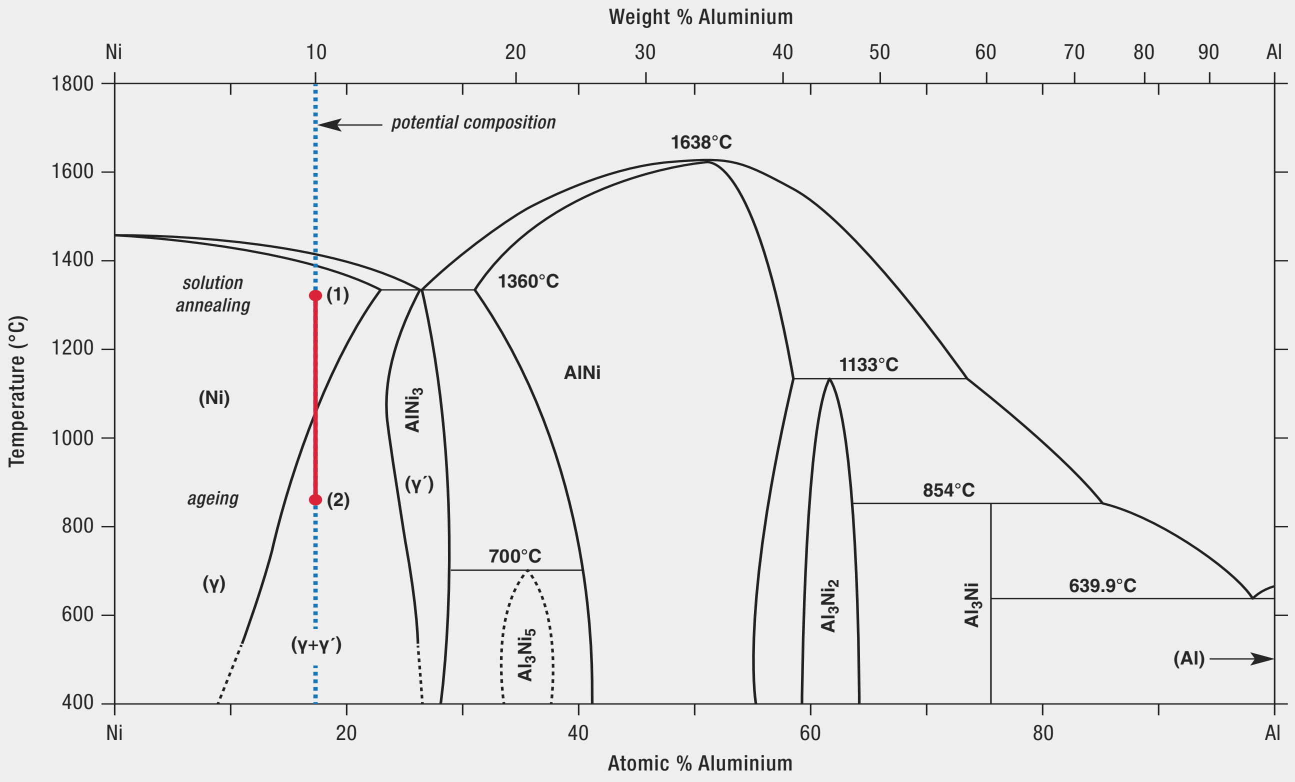


Figure 3: Ni-Al phase diagram showing potential composition that can be solution heat treated in a single phase field (point 1 along the composition line) and subsequent ageing (point 2 within the γ+γ´ phase area).

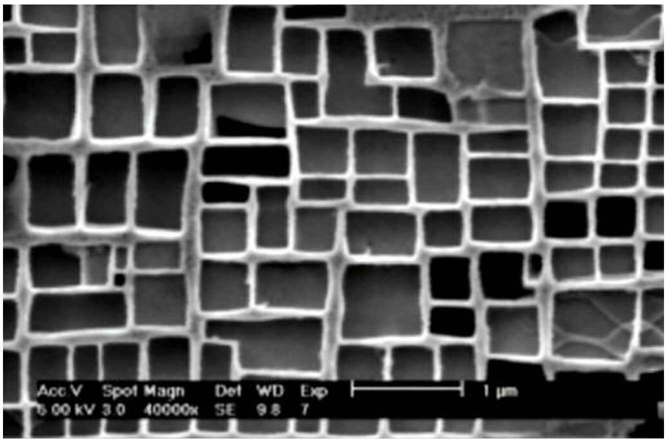


Figure 4: Showing γ´cuboidal precipitates in a single crystal alloy with γ channels between the precipitates forming the continuous phase. © Rolls-Royce plc

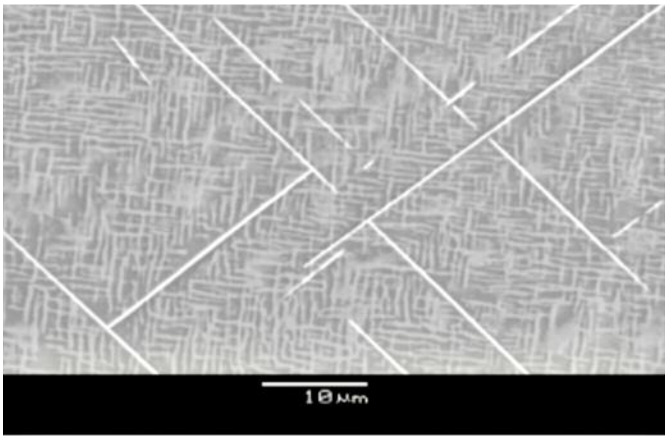


Figure 5: TCP phases in an experimental single crystal alloy. The phases form as plates that appear as needles in section. © Rolls-Royce plc

intermetallic phase with the $L1_2$ structure often coherent with the matrix. It is rich in elements including aluminium, titanium, tantalum and niobium. The nickel-aluminium phase diagram is shown in **Figure 3**. Phase relationships are clearly modified by alloying but many alloys have a single phase region that allows dissolution of the γ´ phase and subsequent precipitation during an ageing cycle at the preferred size. In some nickel-iron alloys and those rich in niobium, a related phase γ´´ which is body centred tetragonal is formed.

The volume fraction of the γ´ phase used varies significantly. The cast turbine blade alloys have volume fractions approaching 70% at room temperature (**Figure 4**). The γ´ precipitates form along {100} planes of the metallic matrix.

Various carbides and borides form in superalloys, the type depending on the alloy composition and processing conditions employed. The role of carbides and borides has been the subject of some debate. The phases and the elements show a preference for presence at the grain boundary and are considered to have a potent effect on the rupture strength via inhibition of grain boundary sliding. Carbon and boron are present in most superalloys but can be omitted from single crystal alloys that do not contain grain boundaries.

Topologically close packed (TCP) phases are undesirable phases (**Figure 5**). These phases have complex lattice structure and are based on chromium, tungsten, molybdenum and rhenium. The kinetics of formation can be slow and the phases can form on exposure in service (thousands of hours >750°C), a phenomenon sometimes referred to as metallurgical instability. They reduce the strength of the material by denuding the γ matrix of strengthening elements. These phases form a limit to the alloying of nickel-based superalloys.

Environmental resistance is provided through alloying with chromium and aluminium. These elements promote the formation of Cr_2O_3 and Al_2O_3 oxides at different temperature regimes.

3 Tungsten in superalloys

The key role of tungsten is as a solid solution strengthening element. Tungsten, molybdenum and more recently rhenium have been the key elements added to superalloys for solid solution strengthening.

Some work on systematic investigation of solid solution strengthening has been published e.g. in references 2 and 3. These papers examined the effects on tensile strength of single phase solid solution strengthened nickel using modelling and experimentation. Both papers demonstrated that of the elements that segregate to the gamma phase tungsten and molybdenum demonstrate the most potent strengthening effects. The data shown in **Figure 6**, for example, show that these two elements are more potent than chromium. However, chromium is added to superalloys to enhance environmental resistance.

Superalloy compositions have been defined, based on combinations of empirical understanding, experimentation and modelling with modelling becoming more prominent in

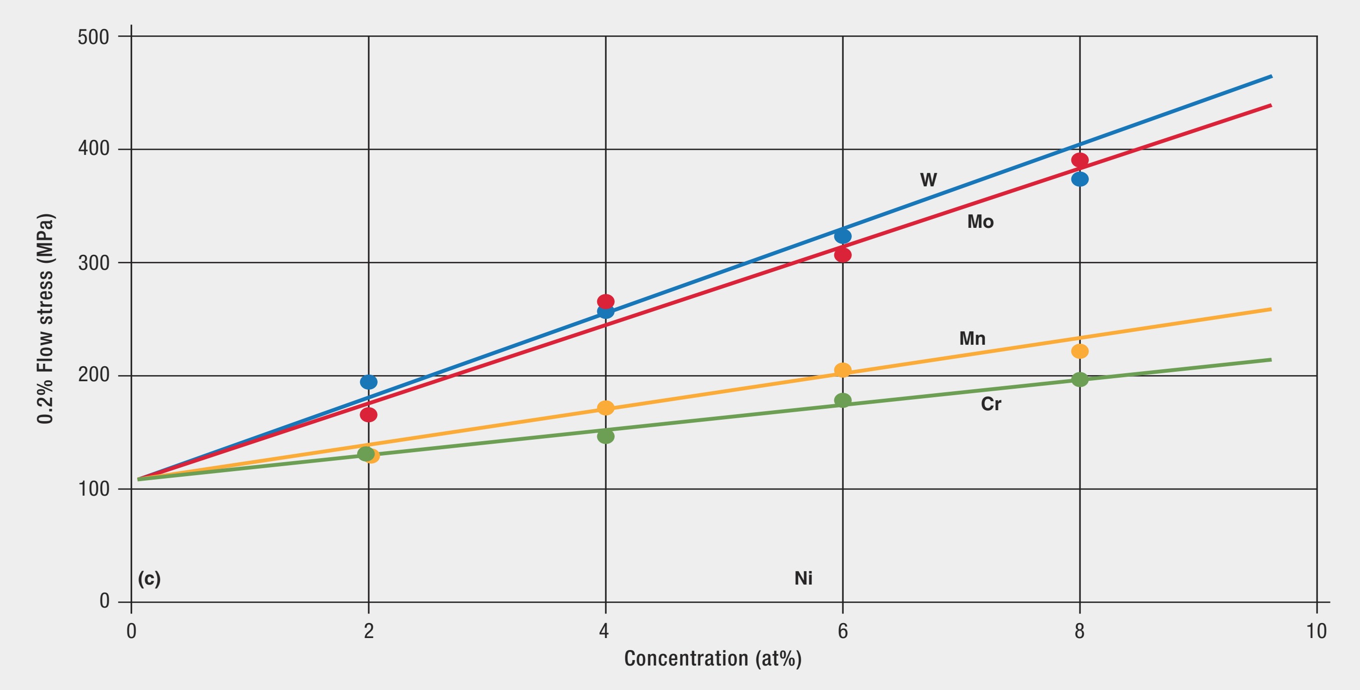


Figure 6: Changes in the 0.2% flow stress (the stress required to produce a 0.2% plastic deformation in the material) at 77K of binary nickel with additions [2].

recent years. There is no definitive consensus within the superalloy community on whether molybdenum or tungsten should be the preferred addition to strengthen the alloy against tensile and creep deformation and a different answer might be expected at different temperatures.

Alloy design involves balancing many requirements. Both tungsten and molybdenum form the damaging TCP phases and the effect on alloy stability needs to be determined. The lattice mismatch between the gamma and gamma prime phases influences the creep behaviour at some conditions and the additions of elements that segregate to both phases control this. Tungsten does increase the density more than molybdenum on an equi-atomic basis.

4 Turbine aerofoil alloys

As stated above, the turbine entry temperature (TET) is an important driver to reducing fuel consumption. On a modern gas turbine engine the values of TET can be above 1500°C and the trend of increasing TET values will continue. The blades extract approximately 500 kW each. The loading on each blade is equivalent to the weight of a heavy truck hanging on each blade. This requirement is met by cast nickel-based superalloys that are internally cooled as the gas temperatures are above the melting points of the alloys, typically between 1260 and 1400°C.

The cooling of turbine blades is illustrated in **Figure 7**. Cool air is passed through the inside of the blade. The air follows a tortuous path through the inside of the blade, thus allowing the air to absorb heat and cool the blade. In the hottest region of the turbine, components are 'film-cooled' –

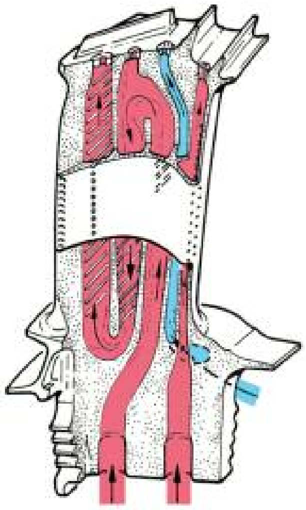


Figure 7: Cooling configuration in a high pressure turbine blade. © Rolls-Royce plc

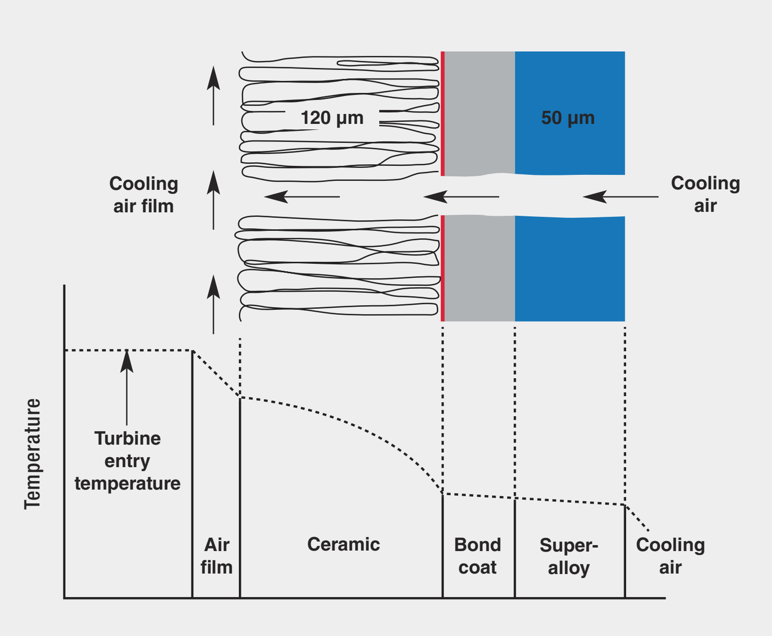


Figure 8: Illustrating temperature drop through a thermal barrier coating.
© Rolls-Royce plc

Figure 9: Thermal barrier coated HP blade.
© Rolls-Royce plc

small holes are drilled through the surface of the blade to allow a protective film of cooling air to ‘bleed’ over the outer surface of the blade.

Further reductions in metal temperature are possible using thermal barrier coatings (**Figures 8 and 9**). A ceramic layer is deposited onto the metal which, by virtue of its low thermal conductivity, reduces the metal temperature. The ceramic layer is deposited onto a bond coat which provides an oxidation resistant layer. It is thereby possible to provide a materials system that has a combination of high temperature mechanical properties and environmental resistance.

Manufacture of turbine blades

There are many forms of superalloy present within a gas turbine engine and processing methods vary widely, dependent on the necessary properties of each specific part. Turbine blades are often produced using the investment casting process.

This process usually starts with ingots of alloy barstock of the desired chemistry. The barstock manufacturer needs to control the purity of the raw elemental additions closely as trace element levels, particularly in single crystal alloys, are controlled to tight levels. An alternative source for the barstock manufacturer is termed ‘revert’. Scrap castings and the runners and risers from the casting process can be segregated by the foundry and returned to the barstock manufacturer for blending with elemental additions.

The vacuum investment casting process is illustrated in **Figure 10**. A wax model of the casting is prepared by injecting molten wax into a die. For hollow blades, the wax is formed around a ceramic core which is a replica of the internal cooling passages required. The individual models are arranged in clusters connected by wax models of the risers and runners. Next, an investment shell is produced by dipping the wax assembly into a ceramic slurry consisting of zircon, alumina and silica. The wax is then removed, usually by heating in a steam autoclave leaving an internal cavity in the mould that is the shape of the required casting including the internal passages. The mould is then pre-fired to increase its strength and is then ready for casting.

The casting process is discussed in more detail below. After solidification is complete, the shell is removed and the internal ceramic core is leached out by chemical means using a high pressure autoclave. If required, the blades are then heat treated and all blades are inspected for grain structure prior to release.

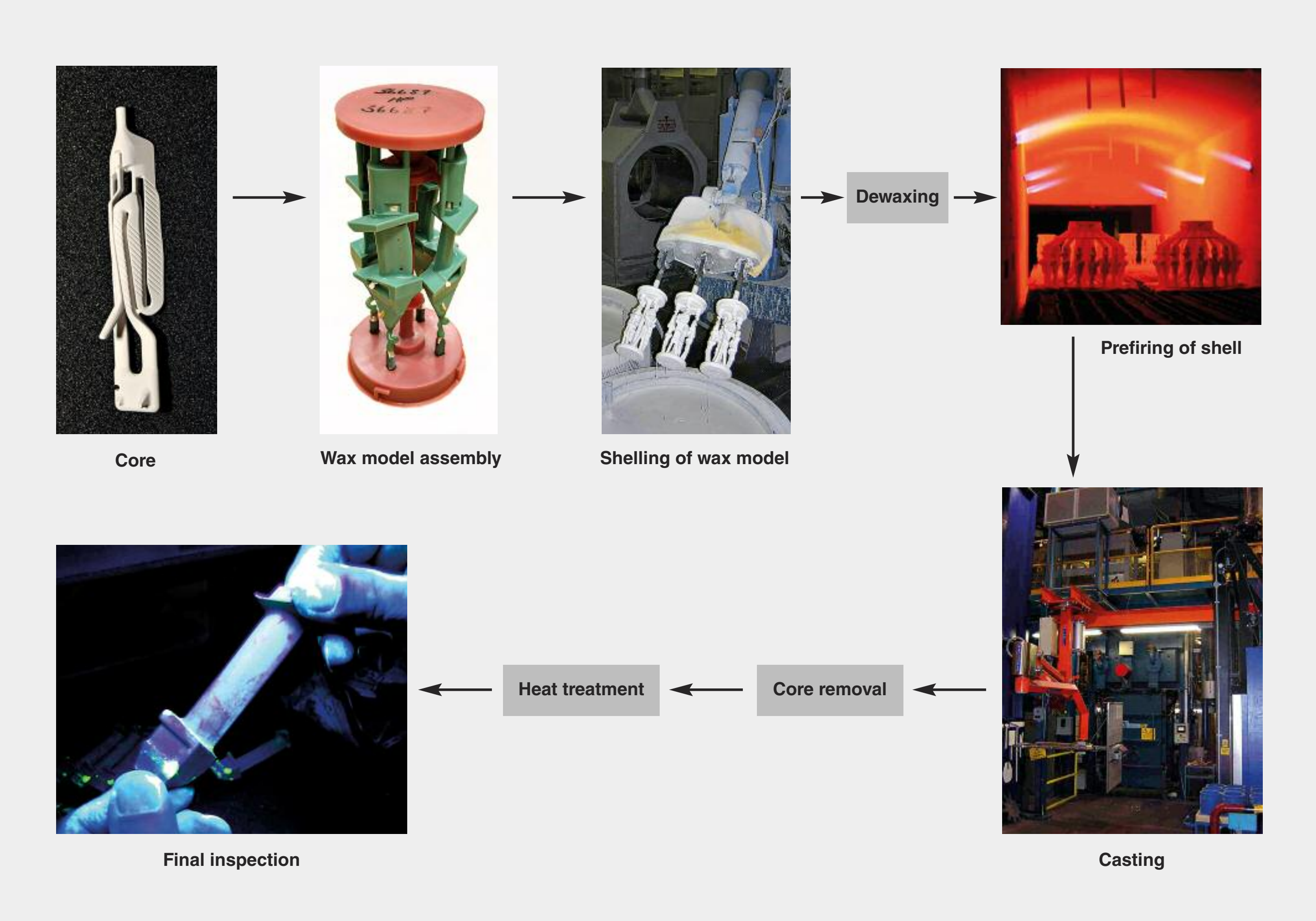


Figure 10: The investment casting process. © Rolls-Royce plc

Cast blades can be manufactured with different grain structures (**Figure 11**). Initially blades were manufactured with a random crystal structure. Further improvements in mechanical strength can be gained by directional solidification where large columnar grains are formed approximately parallel to the blade axis so that transverse boundaries are absent. An extra benefit of the natural solidification direction is <100> and this does give the best overall combination of properties. Another development is the single crystal process in which grain boundaries are removed entirely.

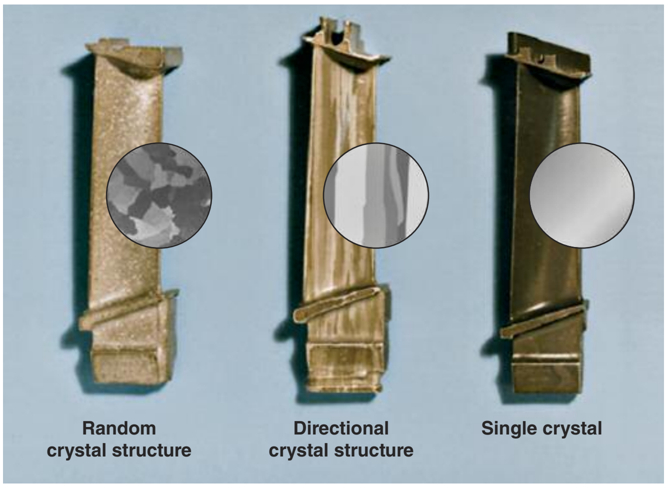


Figure 11: Cast turbine blade grain structures. © Rolls-Royce plc

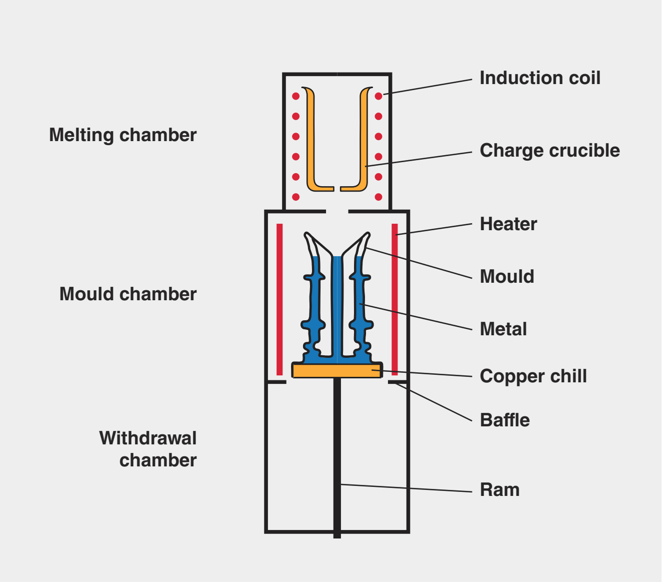


Figure 12: Directional casting process in small bore casting furnace. © Rolls-Royce plc

Directional solidification is illustrated in **Figures 12** and **13**. After pouring the metal, the mould is withdrawn at a controlled rate from the furnace. A speed of a few inches per hour is typical so the liquid/solid interface progresses gradually along the casting starting at the base. One way to produce a single crystal is to make a grain selector at the base of the wax mould, typically in the form of a pig tail. Only a single grain enters the cavity of the casting which is then in monocrystalline form.

Figure 14 demonstrates the advances in material capability and turbine entry temperature with time. Materials capability is plotted as the temperature for a creep rupture life of 1000 hours at a stress of 137MPa. Turbine entry temperature is plotted for various Rolls-Royce civil engines. Material capability has consistently improved with time. The benefits of reduced metal temperature through cooling and the application of thermal barrier coatings are shown as the increases in turbine entry temperature require both the improvements in materials capability and the benefits of reduced metal temperature.

Turbine blade alloy compositions are shown in **Table 1**. Many of these alloys have an excellent balance of properties that allow them to find application in a range of aero engines and also in gas turbine engines for applications such as power generation.

Tungsten has generally been preferred to molybdenum for these alloys. In addition to the general balances discussed above, oxidation resistance may be a factor. Molybdenum alloys are considered to have inferior oxidation resistance although direct comparisons are not readily available.

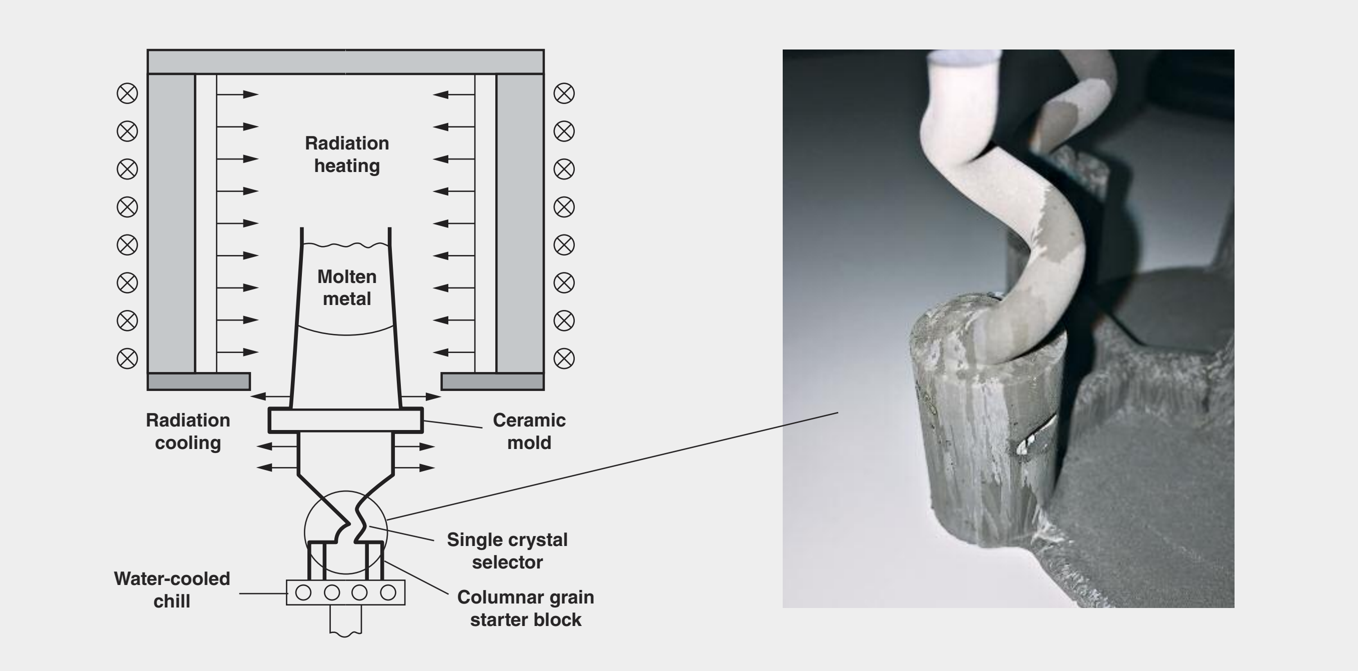


Figure 13: Single crystal (SX) casting process. © Rolls-Royce plc

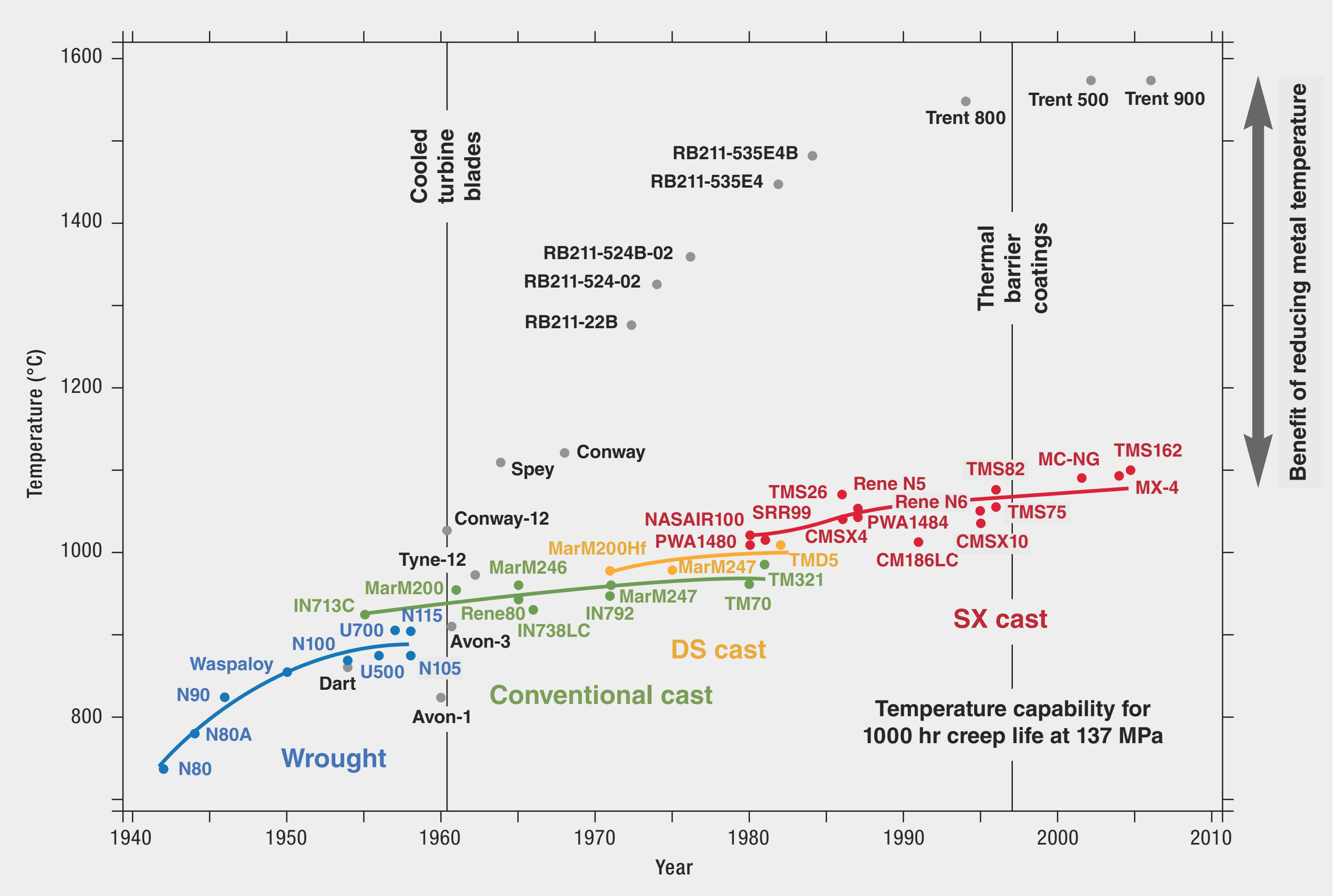
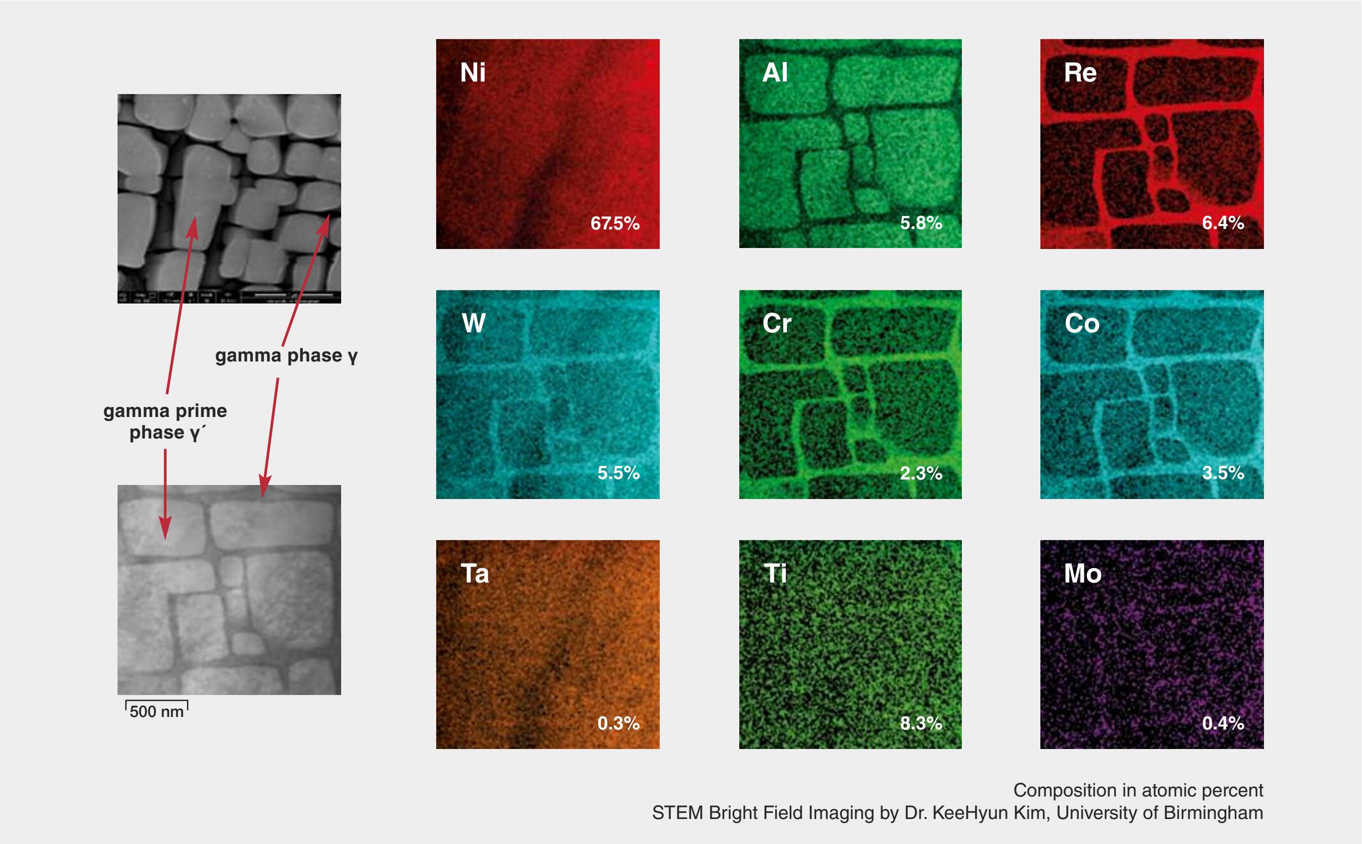


Figure 14: Advances in temperature capability and turbine entry temperature with time. © Rolls-Royce plc

Table 1: Turbine blade alloy compositions (weight %, balance Ni)

Alloy	Type	Co	Cr	Mo	W	Re	Al	Ta	Ti	Nb	Hf	C	B	Zr
IN738	Cast	8.5	16	1.75	2.6	–	3.4	1.75	3.4	0.9	–	0.11	0.01	0.04
IN713	Cast	–	12	4.5	–	–	5.9	–	0.6	2.0	–	0.05	0.01	0.10
CM247LC	Cast	9.3	8.0	0.5	9.5	–	5.6	3.2	0.7	–	1.4	0.07	0.015	0.010
Mar-M-002	Cast	10.0	8.0	–	10.0	–	5.5	2.6	–	–	1.4	0.15	0.015	0.03
CMSX-3	SX	4.8	8.0	0.6	8.0	–	5.6	6.3	1.0	–	0.1	–	–	–
SRR99	SX	5.0	8.0	–	10.0	–	5.5	2.8	2.2	–	–	–	–	–
CMSX-4®	SX	9.6	6.4	0.6	6.4	3.0	5.6	6.3	1.0	–	0.1	–	–	–
CMSX-8®	SX	10.0	5.4	0.6	8.0	1.5	5.7	8.0	0.7	–	0.2	–	–	–
PWA1484	SX	10.0	5.0	2.0	6.0	3.0	5.6	9.0	–	–	0.1	–	–	–
Rene N5	SX	8.0	7.0	2.0	5.0	3.0	6.2	7.0	–	–	0.15	–	–	–
CMSX-10®	SX	3.0	2.0	0.4	5.0	6.0	5.7	8.0	0.2	–	0.03	–	–	–



Composition in atomic percent
STEM Bright Field Imaging by Dr. KeeHyun Kim, University of Birmingham

Figure 15: Elemental segregation in CMSX-10 following heat treatment. © Rolls-Royce plc

For example, in papers reporting both the development of CMSX-10 and CMSX-by Cannon-Muskegon Corporation it was stated that the low molybdenum levels were a factor in achieving good oxidation resistance [4, 5]. Tungsten segregates to the γ phase although it is present in the γ´ phase. **Figure 15** shows the elemental segregation in CMSX-10 between the phases after heat treatment.

Rhenium is an alloying addition in many turbine blade alloys. It has been found that this element is a very potent solid solution strengthening element in superalloys. However, it is a bi-product of copper and molybdenum production. The cost of the element fluctuates but is generally high and the supply is limited. For reasons of cost and availability, use of rhenium is restricted to where maximum benefit can be gained. Where rhenium is added the levels of tungsten and/or chromium have been reduced. This ensures the alloys are stable against the formation of TCP phases.

5 Alloys for other applications

Turbine discs are amongst the most critical components in the engine. The primary function of the turbine disc is to provide a fixture for the turbine blades located in the gas stream (**Figure 16**). The complete assembly of blades and discs then transmits power to the fan and compressor via shafts which run along the length of the engine. In modern engines, temperatures at the rim can approach 650°C or beyond and rotational speeds can be of the order of 10,500 revolutions per minute.

Turbine discs are produced by the machining of superalloy forgings. Two manufacturing processes are available to produce the billets for forging. The first is the cast and wrought route. An ingot is produced by vacuum induction melting, electro-slag refining and vacuum arc remelting. This ingot is thermo-mechanically worked. The second involves powder metallurgy. Here vacuum induction melting is used as before, followed by remelting and inert gas atomisation to produce the powder. A billet for extrusion is produced by hot isostatic pressing and extrusion. The more heavily alloyed materials have to be produced by the more expensive powder route due to the levels of segregation that arise during melt processing.

Photographs of the disc manufacturing process are shown in **Figure 17**.

Some compositions are given in **Table 2**. Waspaloy and Udimet 720 are cast and wrought alloys whilst the other alloys are powder alloys. It can be seen that the tungsten levels in these alloys are lower than those in blade alloys. Even the most advanced alloys also have lower gamma prime volume fractions (~50%) and higher levels of chromium compared to turbine blade alloys. The higher chromium levels are required for corrosion resistance. One factor that leads to lower tungsten levels in disc alloys is the need to control the density. Turbine discs can account for about 20% of the weight of the engine on a modern turbofan engine. Discs alloys tend to have a density of around 8.0 g/cm^3 whilst the turbine aerofoil alloys often have densities in the range 8.5–9.1 g/cm^3.

Figure 16: Showing turbines blades attached to a disc rim. © Rolls-Royce plc

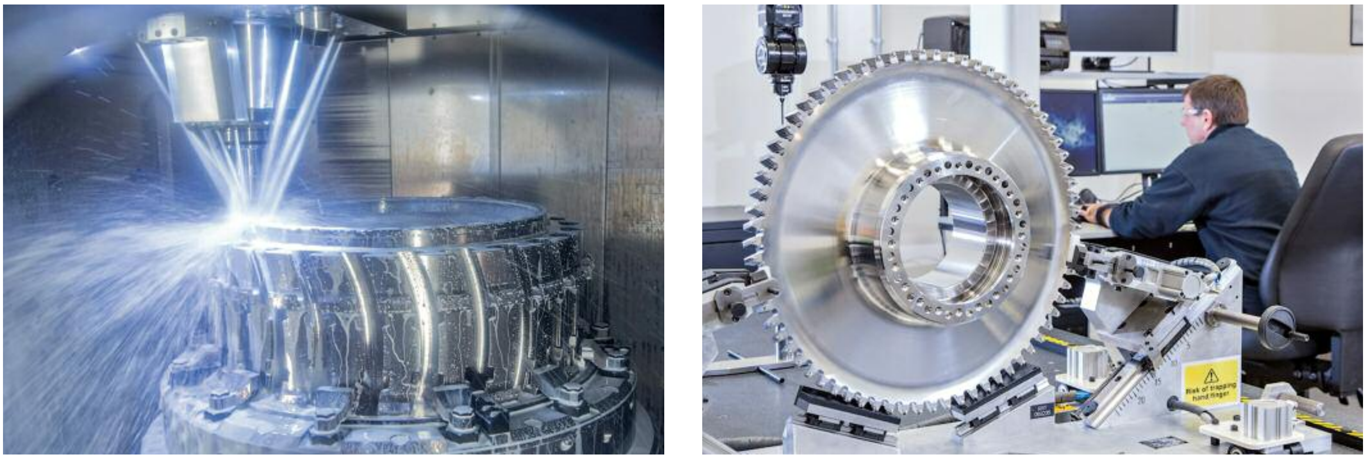


Figure 17: Advanced aerospace disc manufacturing facility. © Rolls-Royce plc

Table 2: Disc alloy compositions (weight %, balance Ni)

Alloy	Co	Cr	Mo	W	Al	Ta	Ti	Nb	Hf	C	B	Zr
Waspaloy	13.5	19.5	4.3	–	1.3	–	3.0	–	–	0.08	0.006	–
Udimet 720 LI	15.0	16.0	3.0	1.25	2.5	–	5.0	–	–	0.025	0.018	0.05
RR1000	18.5	15.0	5.0	–	3.0	2.0	3.6	1.1	0.5	–	–	–
Rene 95	8.0	14.0	3.5	3.5	3.5	–	2.5	3.5	–	0.15	0.010	0.05
Rene 88DT	13.0	16.0	4.0	4.0	–	–	3.7	0.7	–	0.03	0.015	0.03
Rene 104	18.2	13.1	3.8	1.9	3.5	2.7	2.5	1.4	–	0.03	0.03	0.05

Table 3: Alloy compositions (weight %, balance Ni)

Alloy	Co	Cr	Mo	W	Fe	Al	Ta	Ti	C	B	Zr
C 263	15.9	16.0	3.0	1.25	–	2.5	0.75	5.0	0.03	0.02	0.05
Haynes® 230®	–	22.0	2.0	14.0	–	0.3	–	–	0.01	–	–
Haynes® 242®	2.5	8.0	25.0	–	2.0	0.25	–	–	0.15	0.003	–

The alloy compositions shown in **Table 3** can be used for a variety of applications including sheet fabrications and casings. These alloys are generally quite low in tungsten and have lower gamma volume fraction than blade and disc alloys. Haynes 230 is an exception and the tungsten level is the highest of any regularly used nickel base superalloy. This material relies entirely on solid solution strengthening. It finds wide application for combustor components, such as combustion cans, transition ducts, flame holders, liners, thermocouple shields, etc.

6 Cobalt-based alloys

Cobalt-based superalloys also find application although their use is not as widespread as nickel-based alloys. Two examples are Stellite 31 and Haynes 188 and the compositions are shown in **Table 4**.

Applications of cobalt based alloys

Tungsten is added to these materials for solid solution strengthening. Chromium is added for environmental resistance. Nickel stabilises the FCC solution against transformation to a HCP phase at lower temperatures. Carbon leads to the formation of carbides that provide some dispersion hardening. Carbides and borides strengthen grain boundaries. The lanthanum and silicon additions to Haynes 188 are believed to improve oxidation resistance.

Cobalt-based alloys do not have the high temperature strength and oxidation resistance of high gamma prime volume fraction nickel-based alloys. Cobalt based are used for static (non-rotating) parts, for example in the combustor.

7 Emerging alloy systems

For many years the materials community has sought to develop replacement systems for nickel-based superalloys. Success has been partial; ceramic matrix composites show great promise and titanium aluminides are finding application at the rear of LP turbines where temperatures are relatively low. However, the Ni-Al system, with the combination of mechanical and environmental properties that can be produced, has been shown to be superior to other contenders.

One possible system is emerging and includes tungsten as a key alloying element. Work on the cobalt-rich corner of the Co-Al-W ternary revealed the presence of a γ-γ' phase field based on Co-Co_3(Al, W) [6] (**Figure 18**). The intermetallic phase has the $L1_2$ structure and has approximately equi-atomic amounts of aluminium and tungsten. Since the emergence of this system, significant volumes of research have been performed across the world on alloying effects, thermodynamic modelling and determining mechanical and environmental properties. Some of the alloys are showing similar behaviour to non-rhenium single crystal alloys up to ~900C°. At present, oxidation does seem to be a challenge for this system. Overall it must still be regarded as a speculative system.

Summary

Tungsten is a key alloying element in nickel-based superalloys, with alloys for turbine blade application containing up to ~10 weight % tungsten. Nickel-based superalloys are going to continue to be the material of choice for high

Table 4: Cobalt-based alloy composition (weight %, balance Co)

Alloy	Cr	W	Ni	C	B	Si	La
Stellite 31	25.5	8.0	10.5	0.5	0.005	–	–
Haynes® 188	22.0	14.0	22.0	0.1	0.01	0.35	0.03

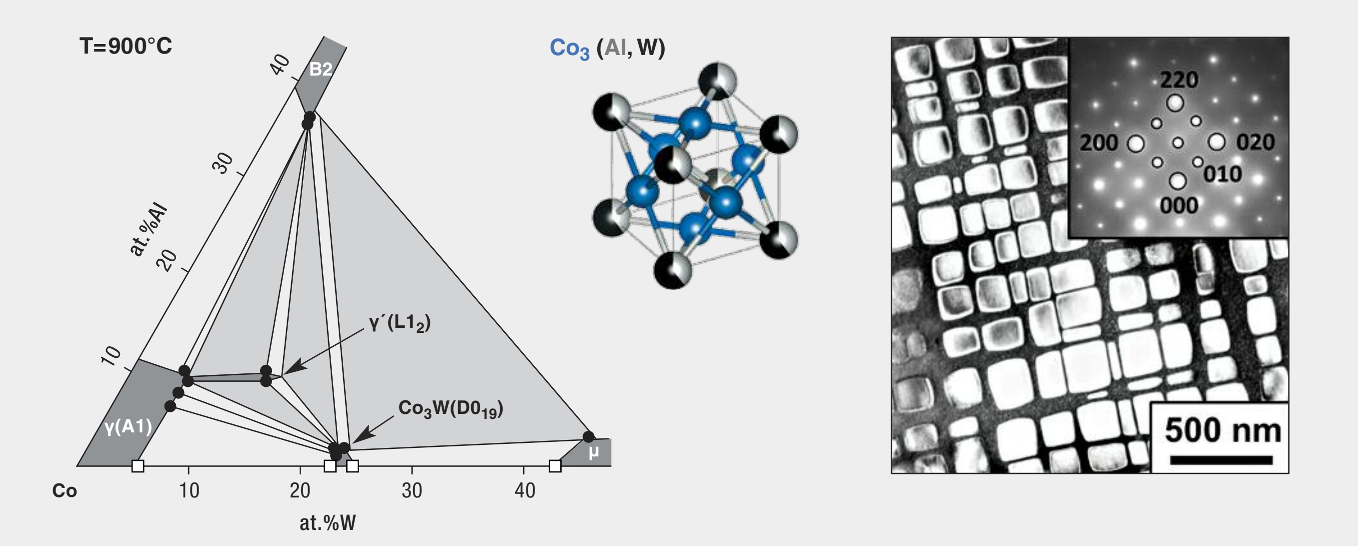


Figure 18: Cobalt-rich corner of Co-Al-W ternary phase diagram showing γ-γ´ phase field (left) [6]; dark field TEM image and diffraction pattern of a Co-9Al-9W-alloy (at.%) obtained by solution annealing and subsequent ageing at 900°C for 200 h (right). Courtesy of C. H. Zenk, F. Pyczak & S. Neumeier, University Erlangen-Nürnberg, Germany

temperature application in gas turbine engines for the foreseeable future and tungsten will continue to be a key alloying element.

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Further reading

For a comprehensive review of superalloys, the reader is referred to The Superalloys – Fundamentals and Applications by Roger C Reed, Cambridge University Press 2006.

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