SUPERALLOYS

Superalloys are heat-resisting alloys based on nickel, nickel-iron, or cobalt that exhibit a combination of mechanical strength and resistance to surface degradation.

Superalloys are primarily used in gas turbines, coal conversion plants, and chemical process industries, and for other specialized applications requiring heat and/or corrosion resistance.

A noteworthy feature of nickel-base alloys is their use in load-bearing applications at temperatures in excess of 80% of their incipient melting temperatures, a fraction that is higher than for any other class of engineering alloys.

Applications of superalloys are categorized below; the bulk of tonnage is used in gas turbines:

- **Aircraft gas turbines**: disks, combustion chambers, bolts, casings, shafts, exhaust systems, cases, blades, vanes, burner cans, afterburners, thrust reversers
- **Steam turbine power plants**: bolts, blades, stack gas re-heaters
- **Reciprocating engines**: turbochargers, exhaust valves, hot plugs, valve seat inserts
- **Metal processing**: hot-work tools and dies, casting dies
- **Medical applications**: dentistry uses, prosthetic devices
- **Space vehicles**: aerodynamically heated skins, rocket engine parts
- **Heat-treating equipment**: trays, fixtures, conveyor belts, baskets, fans, furnace mufflers
- **Nuclear power systems**: control rod drive mechanisms, valve stems, springs, ducting
- **Chemical and petrochemical industries**: bolts, fans, valves, reaction vessels, piping, pumps
- **Pollution control equipment**: scrubbers
- **Metals processing mills**: ovens, afterburners, exhaust fans
- **Coal gasification and liquefaction systems**: heat exchangers, re-heaters, piping.
Nickel Base Superalloys

Nickel-base superalloys are the most complex, the most widely used for the hottest parts, and, to many metallurgists, the most interesting of all superalloys. They currently constitute over 50% of the weight of advanced aircraft engines.

The principal characteristics of nickel as an alloy base are the high phase stability of the face-centered cubic (FCC) nickel matrix and the capability to be strengthened by a variety of direct and indirect means. Further, the surface stability of nickel is readily improved by alloying with chromium and/or aluminum.

Chemical Composition

The nickel-base superalloys discussed below are considered to be complex because they incorporate as many as a dozen elements.

In addition, deleterious elements such as silicon, phosphorus, sulfur, oxygen, and nitrogen must be controlled through appropriate melting practices. Other trace elements, such as selenium, bismuth, and lead, must be held to very small (ppm) levels in critical parts.

Many wrought nickel-base superalloys contain 10 to 20% Cr, up to about 8% Al and Ti combined, 5 to 15% Co, and small amounts of boron, zirconium, magnesium, and carbon.

Other common additions are molybdenum, niobium, and tungsten, all of which play dual roles as strengthening solutes and carbide formers. Chromium and aluminum are also necessary to improve surface stability through the formation of Cr₂O₃ and Al₂O₃, respectively. The functions of the various elements in nickel alloys are as below.
# Role of elements in superalloys

<table>
<thead>
<tr>
<th>Effect</th>
<th>Iron base</th>
<th>Cobalt base</th>
<th>Nickel base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid-solution strengtheners</td>
<td>Cr, Mo</td>
<td>Nb, Cr, Mo, Ni, W, Ta</td>
<td>Co, Cr, Fe, Mo, W, Ta</td>
</tr>
<tr>
<td>Fcc matrix stabilizers</td>
<td>C, W, Ni</td>
<td>Ni</td>
<td>. . .</td>
</tr>
</tbody>
</table>

**Carbide form**

<table>
<thead>
<tr>
<th>Type</th>
<th>Iron base</th>
<th>Cobalt base</th>
<th>Nickel base</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC Type</td>
<td>Ti</td>
<td>Ti, Ta, Nb</td>
<td>W, Ta, Ti, Mo, Nb</td>
</tr>
<tr>
<td>M7C3 type</td>
<td>. . .</td>
<td>Cr</td>
<td>Cr</td>
</tr>
<tr>
<td>M23C6 type</td>
<td>Cr</td>
<td>Cr</td>
<td>Cr, Mo, W</td>
</tr>
<tr>
<td>M6C type</td>
<td>Mo</td>
<td>Mo, W</td>
<td>Mo, W</td>
</tr>
</tbody>
</table>

**Carbonitrides**

<table>
<thead>
<tr>
<th>Type</th>
<th>Iron base</th>
<th>Cobalt base</th>
<th>Nickel base</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(CN) type</td>
<td>C, N</td>
<td>C, N</td>
<td>C, N</td>
</tr>
<tr>
<td>Forms γ' Ni3 (Al, Ti)</td>
<td>Al, Ni, Ti</td>
<td>. . .</td>
<td>Al, Ti</td>
</tr>
<tr>
<td>Retards formation of hexagonal η(Ni3Ti)</td>
<td>Al, Zr</td>
<td>. . .</td>
<td>. . .</td>
</tr>
<tr>
<td>Raises solvus temperature of γ'</td>
<td>. . .</td>
<td>. . .</td>
<td>Co</td>
</tr>
<tr>
<td>Hardening precipitates and/or intermetallics</td>
<td>Al, Ti, Nb</td>
<td>Al, Mo, Ti(a) W, Ta</td>
<td>Al, Ti, Nb</td>
</tr>
<tr>
<td>Forms γ'' (Ni3Nb)</td>
<td>. . .</td>
<td>. . .</td>
<td>Nb</td>
</tr>
<tr>
<td>Oxidation resistance</td>
<td>Cr</td>
<td>Al, Cr</td>
<td>Al, Cr</td>
</tr>
<tr>
<td>Improves hot corrosion resistance</td>
<td>La, Y</td>
<td>La, Y, Th</td>
<td>La, Th</td>
</tr>
<tr>
<td>Sulfidation resistance</td>
<td>Cr</td>
<td>Cr</td>
<td>Cr</td>
</tr>
<tr>
<td>Increases rupture ductility</td>
<td>B</td>
<td>B, Zr</td>
<td>B(b), Zr</td>
</tr>
<tr>
<td>Causes grain-boundary segregation</td>
<td>. . .</td>
<td>. . .</td>
<td>B, C, Zr</td>
</tr>
</tbody>
</table>
Microstructure

The major phases that may be present in nickel-base alloys are:

- **Gamma matrix**, $\gamma$, in which the continuous matrix is an FCC nickel-base nonmagnetic phase that usually contains a high percentage of solid-solution elements such as cobalt, iron, chromium, molybdenum, and tungsten. All nickel-base alloys contain this phase as the matrix.

- **Gamma prime**, $\gamma'$, in which aluminum and titanium are added in amounts required to precipitate FCC $\gamma'$ ($\text{Ni}_3\text{Al}$, Ti), which precipitates coherently with the austenitic gamma matrix. Other elements, notably niobium, tantalum, and chromium, also enter $\gamma'$. This phase is required for high-temperature strength and creep resistance.

- **Gamma double prime**, $\gamma''$, in which nickel and niobium combine in the presence of iron to form body centered tetragonal (BCT) $\text{Ni}_3\text{Nb}$, which is coherent with the gamma matrix, while including large mismatch strains of the order of 2.9%. This phase provides very high strength at low to intermediate temperatures, but is unstable at temperatures above about 650 °C (1200 °F). This precipitate is found in nickel-iron alloys.

- **Grain boundary $\gamma'$**, a film of $\gamma'$ along the grain boundaries in the stronger alloys, produced by heat treatments and service exposure. This film is believed to improve rupture properties.

- **Carbides**, in which carbon that is added in amounts of about 0.02 to 0.2 wt% combines with reactive elements, such as titanium, tantalum, hafnium, and niobium, to form metal carbides (MC). During heat treatment and service, these MC carbides tend to decompose and generate other carbides, such as $\text{M}_{23}\text{C}_6$ and/or $\text{M}_6\text{C}$, which tend to form at grain boundaries. Carbides in nominally solid-solution alloys may form after extended service exposures.

- **Borides**, a relatively low density of boride particles formed when boron segregates to grain boundaries.

- **Topologically close-packed (TCP) type phases**, which are plate-like or needle-like phases such as $\sigma$, and $\mu$ that may form for some compositions and under certain conditions. These cause lowered rupture strength and ductility.
**Gamma Matrix (γ)**

Pure nickel does not display an unusually high elastic modulus or low diffusivity (two factors that promote creep rupture resistance), but the gamma matrix is readily strengthened for the most severe temperature and time conditions. Some superalloys can be used at 0.85 $T_m$ (melting point) and, for times up to 100,000 h, at somewhat lower temperatures. These conditions can be tolerated because of three factors:

- The high tolerance of nickel for solutes without phase instability, because of its nearly filled $d$-shell
- The tendency, with chromium additions, to form $\text{Cr}_2\text{O}_3$, thereby restricting the diffusion rate of metallic elements outward and the rate of oxygen, nitrogen, and sulfur inward
- The additional tendency, at high temperatures, to form $\text{Al}_2\text{O}_3$ barriers, which display exceptional resistance to further oxidation.

**Gamma Prime $\gamma'$**

It is an intermetallic compound of nominal composition $\text{Ni}_3\text{Al}$, which is stable over a relatively narrow range of compositions Fig. 1.

It precipitated as spheroidal particles in early nickel-base alloys, which tended to have a low volume fraction of particles. Later, cuboidal precipitates were noted in alloys with higher aluminum and titanium contents.

The change in morphology is related to a matrix-precipitate mismatch. It is observed that $\gamma'$ occurs as spheres for 0 to 0.2% mismatches, becomes cuboidal for mismatches of 0.5 to 1%, and is plate-like at mismatches above about 1.25%.

Tantalum, niobium, and titanium are effective solid-solution hardeners of $\gamma'$ at room temperature. Tungsten and molybdenum are strengtheners at both room an elevated temperatures, while cobalt does not solid-solution strengthen $\gamma'$.
Fig. 1 Nickel-aluminum phase diagram
**Gamma Double Prime γ”**

In which nickel and niobium combine in the presence of iron to form body centered tetragonal (BCT) Ni₃Nb, which is coherent with the gamma matrix, while including large mismatch strains of the order of 2.9%.

This phase provides very high strength at low to intermediate temperatures, but is unstable at temperatures above about 650 °C (1200 °F). This precipitate is found in nickel-iron alloys.

**Grain Boundary Chemistry**

The improvement of creep properties by very small additions of boron and zirconium is a notable feature of nickel-base superalloys. Improved forgeability and better properties have also resulted from magnesium additions of 0.01 to 0.05%. It is believed that this is due primarily to the typing up of sulfur, a grain boundary embrittler, by the magnesium.

However, boron and zirconium segregate to grain boundaries because of their large size misfit with nickel. Because, at higher temperatures, cracks in superalloys usually propagate along grain boundaries, the importance of grain-boundary chemistry is apparent.

Boron may also reduce carbide precipitation at grain boundaries by releasing carbon into the grains. Finally, the segregation of misfitting atoms to grain boundaries may reduce grain-boundary diffusion rates.

This effect was accompanied by the precipitation of several precipitates containing zirconium at grain boundaries. The creep strength increased significantly, and the fracture mode changed from intergranular to transgranular ductile rupture, with a corresponding substantial increase in ductility.

**Carbides**

In superalloys severe a number of functions. They often precipitate at grain boundaries in nickel alloys, whereas in cobalt and iron superalloys, intergranular sites are common.
Carbide Types and Typical Morphologies

The common nickel-base alloy carbides are MC, M$_{23}$C$_6$, and M$_6$C. MC usually exhibits a coarse, random, cubic, or script morphology.

The carbide M$_{23}$C$_6$ is found primarily at grain boundaries and usually occurs as irregular, discontinuous, blocky particles, although plates and regular geometric forms have been observed.

The M$_6$C carbides also can precipitate in blocky form in grain boundaries and less often in a Widmanstätten intragranular morphology.

MC Carbides

FCC in structure usually forms in superalloys during freezing. They are distributed heterogeneously through the alloy, both in intergranular and transgranular positions, often interdendritically. Little or no orientation relation with the alloy matrix has been noted.

MC carbides are a major source of carbon for subsequent phase reactions during heat treatment and service. In some alloys, such as Incoloy 901 and A286, MC films may form along grain boundaries and reduce ductility.

These carbides, for example, TiC and HfC, are among the most stable compounds in nature. The preferred order of formation (in order of decreasing stability) in superalloys for these carbides is HfC, TaC, NbC, and TiC.

In these carbides, M atoms can readily substitute for each other, as in (Ti, Nb)C. However, the less reactive elements, principally molybdenum and tungsten, can also substitute in these carbides. For example, (Ti, Mo)C is found in Udimet 500, M-252, and René 77.

It appears that the change in stability order cited above is due to the molybdenum or tungsten substitution, which weakens the binding forces in MC carbides to such an extent that degeneration reactions.

This typically leads to the formation of the more stable compounds M$_{23}$C$_6$ and M$_6$C-type carbides in the alloys during processing or after heat treatment and/or service.
Additions of niobium and tantalum tend to counteract this effect. Recent alloys with high niobium and tantalum contents contain MC carbides that do not break down easily during processing or solution treatment in the range of 1200 to 1260 °C.

**M\textsubscript{23}C\textsubscript{6} Carbides**

It is readily formed in alloys with moderate to high chromium content. They form during lower temperature heat treatment and service (that is, 760 to 980 °C) both from the degeneration of MC carbide and from soluble residual carbon in the alloy matrix.

When tungsten or molybdenum is present, the approximate composition of M\textsubscript{23}C\textsubscript{6} is Cr\textsubscript{21}(Mo, W)\textsubscript{2}C\textsubscript{6}, although it also has been shown that appreciable nickel can substitute in the carbide. It is also possible for small amounts of cobalt or iron to substitute for chromium.

The M\textsubscript{23}C\textsubscript{6} particles strongly influence the properties of nickel alloys. Rupture strength is improved by the presence of discrete particles, apparently through the inhibition of grain-boundary sliding.

Eventually, however, failure can initiate either by fracture of particles or by decohesion of the carbide/matrix interface. In some alloys, cellular structures of M\textsubscript{23}C\textsubscript{6} have been noted. These can cause premature failures, but can be avoided by proper processing and/or heat treatment.

**M\textsubscript{6}C carbides**

M\textsubscript{6}C carbides have a complex cubic structure. They form when the molybdenum and/or tungsten content is more than 6 to 8 at.%, typically in the range of 815 to 980 °C.

Typical formulas for M\textsubscript{6}C are (Ni, Co)\textsubscript{3}Mo\textsubscript{3}C and (Ni, Co)\textsubscript{2}W\textsubscript{4}C. M\textsubscript{6}C carbides are formed when molybdenum or tungsten acts to replace chromium in other carbides; unlike the more rigid M\textsubscript{23}C\textsubscript{6}, the compositions can vary widely.
Because M₆C carbides are stable at higher levels than are M₂₃C₆ carbides, M₆C is more commercially important as a grain-boundary precipitate for controlling grain size during the processing of wrought alloys.

**Carbide Reactions**

MC carbides are a major source of carbon in most nickel-base superalloys below 980 °C. However, MC decomposes slowly during heat treatment and service, releasing carbon for several important reactions.

The principal carbide reaction in many alloys is believed to be the formation of M₂₃C₆:

\[
MC + \gamma \rightarrow M_{23}C_6 + \gamma' \quad \text{or} \quad (Ti, Mo)C + (Ni, Cr, Al, Ti) \rightarrow Cr_{21}Mo_2C_6 + Ni_3 (Al, Ti)
\]

The carbide M₆C can form in a similar manner.

**Borides**

Small additions of boron are essential to improved creep-rupture resistance of superalloys. Borides are hard particles, blocky to half moon in appearance, that are observed at grain boundaries. The boride found in superalloys is of the form M₃B₂, with a tetragonal unit cell.

**TCP Phases**

In some alloys, if composition has not been carefully controlled, undesirable phases can form either during heat treatment or, more commonly, during service. These precipitates are known as TCP phases. Usually harmful, they may appear as long plates or needles, often nucleating on grain-boundary carbides.

Nickel alloys are especially prone to the formation of σ and μ. The formula for σ is (Fe, Mo)ₓ (Ni, Co)ᵧ, where 𝒙 and 𝒚 can vary from 1 to 7. Alloys containing a high level of body-centered cubic (bcc) transition metals (tantalum, niobium, chromium, tungsten, and molybdenum) are most susceptible to TCP formation.
The σ hardness and its plate-like morphology cause premature cracking, leading to low-temperature brittle failure, although yield strength is unaffected.

**Heat Treatment**

Wrought alloys are, first, solution treated to dissolve nearly all γ' and carbides other than the very stable MC carbides.

Typical solution treatments (for creep-limited applications) are in the range of 1050 to 1200 °C and may be followed by a second solution treatment at lower temperature.

Some γ' can form upon air cooling from the solution treatment temperature. Aging is then carried out in several steps to coarsen the γ' that is formed upon cooling, as well as to precipitate additional γ'.

A two-step aging treatment is commonly used, with the first treatment in the range of 850 to 1100 °C over a period of up to 24 h. Aging at one or more lower temperatures, for example at 760 °C (1400 °F) for 16 h, completes the precipitation of γ'.

The finer γ' produced in the second aging treatment is advantageous for tensile strength as well as for rupture life. Both solution and aging anneals are followed by air cooling.

Carbide distribution also is controlled by the heat treatment schedule. Modifications to the γ' heat treatment procedure often are required to avoid problems with carbide films at grain boundaries.

Therefore, a lower solution treatment temperature (about 1075 °C) is used to preserve the fine-grain as-worked structure with well-dispersed M₆C.
Iron Base Superalloys

Microstructure

Iron-base superalloys evolved from austenitic stainless steels and are based on the principle of combining a closed-packed fcc matrix with (in most cases) both solid-solution hardening and precipitate-forming elements.

The austenitic matrix is based on nickel and iron, with at least 25% Ni needed to stabilize the fcc phase. Other alloying elements, such as chromium, partition primarily to the austenite for solid-solution hardening.

The strengthening precipitates are primarily ordered intermetallics, such as $\gamma'$ $\text{Ni}_3\text{Al}$, $\gamma\text{Ni}_3\text{Ti}$, and $\gamma'' \text{Ni}_3\text{Nb}$, although carbides and carbonitrides may also be present.

Elements that partition to grain boundaries, such as boron and zirconium, perform a function similar to that which occurs in nickel-base alloys; that is, grain-boundary fracture is suppressed under creep rupture conditions, resulting in significant increases in rupture life.

Several groupings of iron-nickel alloys based on composition and strengthening mechanisms have been established.

Alloys that are strengthened by ordered fcc $\gamma'$, such as V-57 and A-286, and contain 25 to 35 wt% Ni, represent one subgroup. The $\gamma'$ phase is titanium-rich in these alloys, and care must be taken to avoid an excessively high titanium-to-aluminum ratio, resulting in the replacement of fcc $\gamma'$ by hexagonal close-packed (hcp) $\gamma$ ($\text{Ni}_3\text{Ti}$), a less effective strengthener.

A second iron-rich subgroup, of which Inconel X750 and Incoloy 901 are examples, contains at least 40% Ni, as well as higher levels of solid-solution strengthening and precipitate-forming elements.

Boron in quantities of 0.003 to 0.03 wt% and, less frequently, small additions of zirconium are added to improve stress rupture properties and hot workability.

Zirconium also forms the MC carbide ZrC. Another MC carbide, NbC, is found in alloys that contain niobium, such as Inconel 706 and Inconel 718.
Vanadium also is added in small quantities to iron nickel alloys to improve both notch ductility at service temperatures and hot workability.

Manganese and rare earth elements may be present as deoxidizers; rare earths also have been added to improve oxidation resistance.

Inconel 718 is one of the strongest (at low temperatures) and most widely used of all superalloys, but it rapidly loses strength in the range of 650 to 815 °C. This is probably due to the high lattice misfit associated with the precipitation of γ'' in the austenitic matrix.
Cobalt Base Superalloys

Wrought cobalt-base alloys, unlike other superalloys, are not strengthened by a coherent, ordered precipitate. Rather, they are characterized by a solid solution strengthened austenitic (fcc) matrix in which a small quantity of carbides is distributed.

Cobalt crystallizes in the hcp structure below 417 °C. At higher temperatures, it transforms to fcc. To avoid this transformation during service, virtually all cobalt-base alloys are alloyed with nickel in order to stabilize the fcc structure between room temperature and the melting point.

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.

Cobalt-base alloys generally exhibit better weldability and thermal-fatigue resistance than do nickel-base alloys. Another advantage of cobalt-base alloys is the capability to be melted in air or argon, in contrast to the vacuum melting required for nickel-base and iron-nickel-base alloys containing the reactive metals aluminum and titanium.

However, unlike nickel-base alloys, which have a high tolerance for alloying elements in solid solution, cobalt-base alloys are more likely to precipitate undesirable plate-like $\sigma$, and TCP phases.

Microstructure

Virtually all cobalt alloys are based on an fcc matrix obtained by alloying with 10% or more nickel. Iron, manganese, and carbon additions also stabilize the fcc phase, while nickel and iron additions improve workability.

Exerting the opposite hcp stabilizing tendency are other common alloying elements, such as tungsten, added primarily for solid-solution strengthening, and chromium, added primarily for oxidation and hot corrosion resistance.

Improved oxidation and corrosion resistance with 5 wt% Al have been noted in a few cobalt-base alloys.
Titanium additions also have been made in order to precipitate coherent, ordered Co₃Ti as a strengthening phase. Unfortunately, this phase is stable only to about 700 °C (1290 °F), which is much lower than for γ' Ni₃Al, Ti in Ni-base alloys.

As in the case of nickel-base alloys, a variety of carbides have been found in cobalt alloys. These include M₂₃C₆, M₆C, and MC carbides. In both L-605 and Haynes 188, M₆C transforms into M₂₃C₆ during exposure to temperatures in the range of 816 to 927 °C for 3000 h.

In addition to carbides, small quantities of intermetallic phases such as Co₃W, Co₂W, and Co₇W₆ have been found in L-605. Other alloys display the compounds CoAl, Co₃Ti, and Co₂(Ta, Nb, Ti).

However, it is unlikely that these phases contribute to the strengthening of the γ matrix. On the contrary, Co₇W₆ and Co₂(Ta, Nb, Ti) are TCP phases that are likely to cause the deterioration of mechanical properties.
Melting and Consolidation of Wrought Alloys

Superalloy ingots must be melted and cast with due regard for the volatility and reactivity of the elements present. Vacuum melting processes are a necessity for many nickel- and iron-nickel-base alloys because of the presence of aluminum and titanium as solutes. Cobalt-base alloys, on the other hand, do not usually contain these elements and, therefore, may be melted in air.

Melt Processes

The traditional processes used to produce superalloy components are identified in Fig. 2.

Fig. 2 Flow diagram of processes widely used to produce superalloy components
The VIM process produces liquid metal under vacuum in an induction-heated crucible. It is used as a primary melting step in the route to producing wrought and cast products, as well as near-net shape. Before being melted, the raw material can be refined and purified and its composition can be controlled. Vacuum induction melting has been widely used in the manufacture of superalloys, which must be melted under vacuum or in an inert gas atmosphere because of their reactivity with atmospheric oxygen and nitrogen.

The VAR process, a secondary melting technique, converts VIM-processed electrodes into ingots whose chemical and physical homogeneity have been significantly improved. In this process, a stub is welded to one end of an electrode, which is then suspended over a water-cooled copper crucible. Next, an arc is struck between the end of the electrode and the crucible bottom. Maintaining the arc generates the heat required to melt the electrode, which drips into the crucible and can subsequently be poured into molds. Many inclusions can be removed by flotation or chemical and physical processes before the molten material solidifies.

The ESR process, another secondary melting technique, may appear to be similar to the VAR process, but there are a number of differences. Remelting does not occur by striking an arc under vacuum. Instead, an ingot is built up in a water cooled mold by melting a consumable electrode that is immersed in a slag, which is superheated by means of resistance heating. Rather than operating in a vacuum, the process is conducted in air under the molten slag. During melting, metal droplets fall through the molten slag, and chemical reactions reduce sulfur and nonmetallic inclusions. Both ESR and VAR processes allow directional solidification of an ingot from bottom to top, yielding high density and homogeneity in its macrostructure, as well as an absence of segregation and shrinkage cavities.