Physcial Metallurgy and Microstructure of Superalloys

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The definition of "superalloys" utilized in the classic textbook 'The Superalloys' which was edited by Sims & Hagel (Wiley, New York, 1972) has stood the test of time:

"A superalloy is an alloy developed for elevated-temperature service, usually based on group VIIIA elements, where relatively severe mechanical stressing is encountered, and where high surface stability is frequently required."

When significant resistance to loading under static, fatigue and creep conditions is required, the superalloys have emerged as the materials of choice for high temperature applications. This is particularly true when operating temperatures are beyond about 800°C. This is the case for gas turbines used for (i) jet propulsion, e.g. the 100,000 lb thrust engines used for powering large two-engined aeroplanes such as the Boeing 777, or the smaller 1,000 lb engines used for helicopter applications and (ii) electricity generation, e.g. the 250 MW gas-fired industrial gas turbine which can generate enough power to satisfy a large city, or a smaller 3 MW gas-fired generator suitable for back-up capability. However, as high temperature materials which are relatively expensive, the superalloys should be employed only after consideration of others which are available. When weight-saving is important, titanium alloys are used in preference to the superalloys but their poor oxidation resistance restricts their application to below about 700°C. For some electricity-generating power plant applications which rely upon superheated steam at about 565°C, high strength creep resistant ferritic steels are preferred on account of their lower cost. The superalloys come into their own particularly in extreme environments, when resistance to oxidation and corrosion is required; for this purpose, they are often used in combination with protective coatings.

The superalloys display an outstanding combination of high temperature strength, excellent creep rupture life, toughness and resistance to oxidation and corrosion. Moreover, these properties are maintained to elevated temperatures - in some cases to within a few hundred degrees of the melting temperature. The chemical compositions have been tailored over the past fifty years to make this so. For many high temperature applications, other materials are unable to match this combination of properties.

Constitution

Pure nickel has a density of about 8.9 g/cm3 - most superalloys have a density a little greater than this. The relative density - at 8.9 - is appreciably greater than that of other metals, e.g. iron at 7.8, titanium at 4.5 and aluminum at 2.7; thus the superalloys are relatively heavy alloys. This is a consequence of a relatively small interatomic distance in nickel, arising from the strong cohesion provided by the outer d-electrons - a strong characteristic of the transition metals. Nickel displays the face-centered cubic (FCC) crystal structure - and this confers the major advantage of the superalloys: considerable ductility and toughness which makes them highly suited for engineering applications. Moreover, the FCC crystal structure is stable from ambient to the melting temperature.

Superalloys are based on elements found in the long period of transition metals. They consist of various combinations of Ni, Fe, Co and Cr as well as lesser amounts of W, Mo, Ta, Nb, Ti, Al, Re, Ru, C and B and sometimes others. The three major classes of superalloys are the nickel-, iron- and cobalt-based alloys. In addition, a major sub-group, those that have metallurgical characteristics similar to nickel-base alloys but containing relatively large iron contents, are called the nickel-iron superalloys. Of these, the nickel-base superalloys are probably the most important and widely used although some nickel-iron superalloys such as IN718 are also frequently employed.

In the superalloys, the number of alloying elements is often greater than ten and consequently, if judged in this way, the superalloys are amongst the most complex of materials engineered by man. Although a wide variety of alloying elements are used, some broad statements can be made. Most of the alloying elements are taken from the d-block of transition metals. Perhaps not surprisingly, the behaviour of each alloying element and its influence on the phase stability depends strongly upon its position within the periodic table. A first class of elements includes nickel, cobalt, iron, chromium, ruthenium, molybdenum, rhenium and tungsten which prefer to partition to the austenitic γ and thereby stabilise it. These elements have atomic radii not very different from that of nickel. A second group of elements: aluminum, titanium, niobium and tantalum have very much greater atomic radii and these promote the formation of ordered phases such as the compound Ni_3(Al, Ta, Ti), known as ã'. Boron, carbon and zirconium constitute a third class that tends to segregate to the grain boundaries of the γ phase, on account of their atomic sizes which are very different from that of nickel. Carbide and boride phases can also be promoted. Chromium, molybdenum, tungsten, niobium, tantalum and titanium are particularly strong carbide formers; chromium and molybdenum promote the formation of borides.

In common with nickel, all superalloys possess the face-centered cubic (FCC) crystal structure and thus have four atoms per unit cell. This crystal structure is stable from room temperature to the melting temperature - for pure nickel this lies at 1455 deg C. This represents an effective upper-limit on the useable service temperature for the superalloys.

Phases

The major phases present in most nickel superalloys are as follows:

• Gamma, (γ): The continuous matrix (called γ) is a face-centered cubic (fcc) nickel-based austenitic phase that usually contains a high percentage of solid-solution elements such as cobalt, chromium, molybdenum, ruthenium and rhenium, where these are present, since these prefer to reside in this phase.

The gamma matrix phase in the superalloys possesses the face-centered cubic (FCC) structure - which deforms via the a/2<110> dislocation. Such dislocations are not perfect dislocations in the gamma prime or gamma double prime on account of their different crystallography. A consequence is that dislocations cannot easily enter precipitates of the gamma prime and gamma double prime phases - and a considerable strengthening effect arises.

• Gamma Prime (γ'): The primary strengthening phase in nickel-based superalloys is $Ni_3(Al,Ti)$, and is called γ'. It is a coherently precipitating phase (i.e., the crystal planes of the precipitate are in registry with the γ matrix) with an ordered L_{12} (FCC) crystal structure. In most nickel-iron superalloys, a related ordered phase γ" is preferred instead of γ'; this is rich in niobium.

The close match in matrix/precipitate lattice parameter (~0-1%) combined with the chemical compatibility allows the γ' to precipitate homogeneously throughout the matrix and have long-time stability. Interestingly, the flow stress of the γ' increases with increasing temperature up to about $650^{o}C$ ($1200^{o}F$). In addition, γ' is quite ductile and thus imparts strength to the matrix without lowering the fracture toughness of the alloy. Aluminum and titanium are the major constituents and are added in amounts and mutual proportions to precipitate a high volume fraction in the matrix. In some modern alloys the volume fraction of the γ' precipitate is around 70%. There are many factors that contribute to the hardening imparted by the γ' and include γ' fault energy, γ' strength, coherency strains, volume fraction of γ', and γ' particle size.

Extremely small γ' precipitates always occur as spheres. In fact, for a given volume of precipitate, a sphere has 1.24 less surface area than a cube, and thus is the preferred shape to minimize surface energy. With a coherent particle, however, the interfacial energy can be minimized by forming cubes and allowing the crystallographic planes of the cubic matrix and precipitate to remain continuous. Thus as the γ' grows, the morphology can change from spheres to cubes or plates depending on the value of the matrix/precipitate lattice mismatch. For larger mismatch values, the critical particle size where the change from spheres to cubes (or plates) occurs is reduced. Coherency can be lost by overaging. One sign of a loss of coherency is directional coarsening (aspect ratio) and rounding of the cube edges. Increasing directional coarsening for increasing (positive or negative) mismatch is also expected.

• Carbides and Borides: Carbon, added at levels of 0.05-0.2%, combines with reactive and refractory elements such as titanium, tantalum, and hafnium to form carbides (e.g., TiC, TaC, or HfC). During heat treatment and service, these begin to decompose and form lower carbides such as $M_{23}C_6$ and M_6C, which tend to form on the grain boundaries. These common carbides all have an FCC crystal structure. Results vary on whether carbides are detrimental or advantageous to superalloy properties. The general opinion is that in superalloys with grain boundaries, carbides are beneficial by increasing rupture strength at high temperature. Boron can combine with elements such as chromium or molybdenum to form borides which reside on the γ-grain boundaries.

• Topologically Close-Packed Phases (σ, μ, Laves, etc.): These are generally undesirable, brittle phases that can form during heat treatment or service. They usually form as plates (which appear as needles on a single-plane microstructure.) The cell structure of these phases have close-packed atoms in layers separated by relatively large interatomic distances. The layers of close packed atoms are displaced from one another by sandwiched larger atoms, developing a characteristic "topology." These compounds have been characterized as possessing a topologically close-packed (TCP) structure. Conversely, Ni_3Al (γ') is close-packed in all directions and is called geometrically close-packed (GCP). The plate-like structure negatively affects mechanical properties (ductility and creep-rupture.) σ appears to be the most deleterious while strength retention has been observed in some alloys containing μ and Laves. TCPs are potentially damaging for two reasons: they tie up γ and γ' strengthening elements in a non-useful form, thus reducing creep strength, and they can act as crack initiators because of their brittle nature. The compositions of the superalloys are chosen to avoid rather than to promote the formation of these compounds.

Superalloys work so well partly because of the high volume fraction of the intermetallic gamma prime phase which is effective at preventing dislocation movement at elevated temperatures, as are alloying elements (e.g. rhenium, molybdenum) which are added for their strengthening effects. (The role of Re in superalloy metallurgy has proved controversial. However, it is now known that Re - of all the transition metals - diffuses the slowest in nickel. It is likely therefore that diffusional processes - such as the thermally-activated glide and climb of dislocations which are responsible for creep degradation - are slowed when rhenium is added.) Also, elements such as aluminum and chromium are added to improve the oxidation and corrosion resistance; depending on which of these is preferred, the composition is chosen such that either an alumina-based or chromia-based scale is formed at temperature.

Microstructures vary from alloy to alloy. When the very best creep resistance is required, the gamma prime fraction is very high at about 0.70 and the grain boundaries are removed entirely - as in the single crystal superalloys. When greater ductility, toughness and defect tolerance is required then the fraction of the strengthening phases (gamma prime and gamma double prime) is substantially less - in the range 0.30 to 0.50. Some superalloys - such as IN625 - are hardened only by solid solution strengthening in which casr they are very soft.

Even the single crystal superalloys contain some carbon and boron. It has been found that the casting of single crystal superalloy turbine blading for industrial gas turbines (IGTs) - which is significant in size compared to that required for aeroengines - is very difficult to achieve in practice, without defects being introduced. Typical defects include low-angle grain boundaries. The incorporation of carbon and boron - for example in Cannon-Muskegon's CMSX-486 alloy - is done to give a measure of tolerance to grain boundaries.

A number of degradation processes occur during service exposure. Polycrystalline superalloys are prone to creep cavitation at grain boundaries. The gamma prime precipitates can coarsen with increasing time at temperature. In the single crystal superalloys the coarsening can be 'anisotropic' - an effect which is known as 'rafting'. In all cases, increasing damage is associated with an increase in dislocation density as work hardening occurs. Due to interaction with the environment, oxidation and/or corrosion is possible.