

Nickel Based Superalloys – Properties and Their Applications

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Abstract:

The term "Superalloy" was first used shortly after World war II to describe a group of alloys developed for use in turbo-superchargers and aircraft turbine engines that required high performance at elevated temperatures. The range of applications for which superalloys are used has expanded to many other areas and now includes aircraft, gas turbines, rocket engines, chemical, and petroleum plants. They are particularly well suited for these demanding applications because of their ability to retain most of their strength even after long exposure times at temperatures above 650 °C. Their versatility stems from the fact that they combine this high temperature strength with good low-temperature ductility (and/or formability) and excellent surface stability.

Key words: Nickel based superalloy, composition, properties, applications.

1. Brief History of Superalloys

Superalloys are based on Group VIII B elements of the periodic table and usually consist of various combinations of Fe, Ni, Co, and Cr, as well as lesser amounts of W, Mo, Ta, Nb, Ti, and Al. The three major classes of superalloys are nickel, iron, and cobalt-based alloys. Among these, nickel base superalloy development has witnessed large number of comprehensive programs internationally. In response, the Mond Nickel Company (now International Nickel Ltd.) produced Nimonic alloy 75 in 1941, and shortly thereafter developed the age hardenable Nimonic alloy 80. These alloys were modifications of the then existing 80% nickel - 20% chromium alloy, which in the case of Nimonic alloy 80 employed the additions of titanium and aluminium to achieve age hardening by precipitation of γ' , the FCC coherent intermetallic phase $Ni_3(Al, Ti)$. In the United States, the γ' - precipitate hardened Monel nickel-copper alloy K-500 had been in commercial production since 1928, and age hardenable nickel since 1934. Beginning in 1939, a series of nickel-chromium-iron alloys were developed at the Huntington alloy products division of International Nickel Company, and heat treatment producers involving solution treatment and precipitation hardening treatment were developed to maximize their high temperature strength. These alloys were based on the solid solution high temperature alloy, Inconel alloy 600, and involved addition of aluminium and titanium to obtain γ' hardening. The addition of 1% columbium then created the widely used Inconel X-750 [1]. During the late 1940s, Waspalloy and alloy M-252 were developed by Pratt and Whitney Aircraft and the General Electric Company, respectively. Haste alloy X is a solid solution strengthened sheet alloy used in combustion cans and afterburner liners in a variety of turbines. Rene 41 is also available as a high strength precipitation hardened sheet alloy, often used in welded conditions, though welding is difficult and fabrication has suffered from the problems of susceptibility to cracking in post weld treatment (strain age cracking). Inconel alloy 718, a rather unique iron containing alloy, provides moderate temperature high strength as well as good resistance to strain age cracking in welding.

Superalloys exhibit excellent mechanical strength and creep resistance at elevated temperatures, in addition to good surface stability, phase stability as well as high oxidation and corrosion resistance [2]. Hence, they have been used in several high temperature applications, particularly when in sheet form as front panels for the thermal protection systems [2,3]. Other notable applications of these alloys include space components, blades and vanes in turbine engines, critical part of rocket engines, submarines, nuclear reactors, chemical processing vessels and heat exchanger [2-6]. Nickel base alloys are the most complex, the most widely used for the hottest parts, and to many metallurgists, the most fascinating of all superalloys. Their use extends to the highest homologous temperature of any common alloy system, and they currently comprise over 50% of the weight of advanced aircraft engines. Now the advent of aircraft engines requiring materials for long periods of service and their use in industrial gas turbines for peaking electrical power generation needs, a combination of the following properties is critical: creep resistance, fatigue resistance, thermal fatigue resistance, low thermal expansion, high modulus, and low density. Thus machines such as aircraft engines for advanced transport systems aimed at 5000-40000h life and the industrial turbines aimed at 5000-100000h life. This is the prime consideration of many factors to ensure high performance and reliability in service. To deal with these problems new tools and new metallurgical strategies are being developed, and hence nickel-based superalloy metallurgy is showing significant scientific enlightenment [7].

2. Science behind the Development of Nickel-base Superalloys.

2.1. Chemical composition

The nickel base superalloys mainly consist of three different classes of elements. The first class consists of elements that prefer and make up the face centered cubic (FCC) austenite matrix. These are from group V, VI and VII and include nickel, cobalt, iron, chromium, molybdenum, tungsten, and vanadium. The second class of elements partition to and make up the γ' precipitate Ni_3Al . These elements are from Groups III and IV and are very odd sized in atomic diameter. Boron, carbon, and zirconium make up a third class of elements that segregate to grain boundaries. As shown in the Fig.1 these three major classes of elements have two sub-classifications, one includes the carbide formers: chromium, molybdenum, tungsten, vanadium, columbium, tantalum, and titanium.[8].

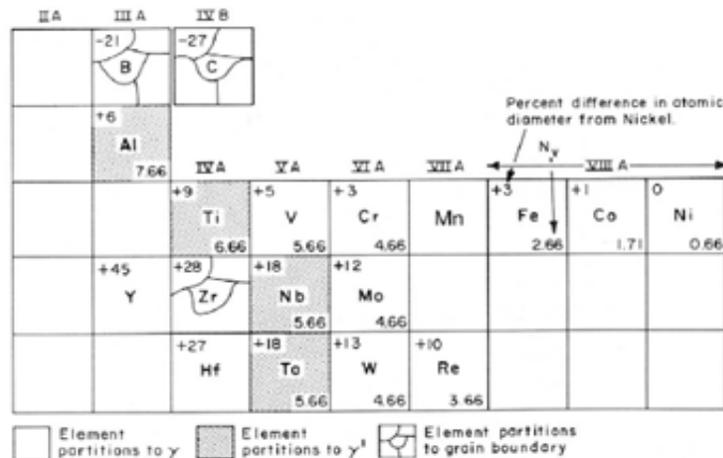


Fig: 1 Main alloying elements and element partitions in the constitution of Ni-base alloys [8]

Table 1: Compositions of wrought Nimonic and other high temperature alloys [13].

Alloy	Composition, in Wt. %												Others, if any	Nickel
	C	Si	Cu	Fe	Mn	Cr	Ti	Al	Co	Mo	B	Zr		
Nimonic 75	0.08	1.0	0.5	5.0	1.0	18.0	0.2	0.3	2.0	0.3	0.001	0.05		Bal.
	0.15	max	max	max	max	21.0	0.6	max	max	max	max	max		
Nimonic 80A	0.04	1.0	0.2	1.0	1.0	18.0	1.8	1.0	2.0	0.3	0.0015	0.04		Bal.
	0.10	max	max	max	max	21.0	2.7	1.8	max	max	0.005	0.10		
Nimonic 81	0.05	0.5	0.2	1.0	0.5	30.0	1.8	0.9	2.0	0.3	0.002	0.06		Bal.
		max	max	max	max				max	max				
Nimonic 90	0.05	1.5	0.2	1.0	1.0	18.0	2.0	1.15	15.0	0.3	0.0015	0.04		Bal.
	0.13	max	max	max	max	21.0	2.7	1.65	18.0	max	0.005	0.10		
Nimonic 105	0.12	1.0	0.2	1.0	1.0	13.5	0.9	4.5	18.0	4.5	0.004	0.07		Bal.
	0.16	max	max	max	max	15.75	1.5	4.9	22.0	5.5	0.008	0.14		
Nimonic 115	0.12	0.4	0.2	1.0	1.0	14.0	3.5	4.5	13.0	3.0	0.12	0.03		Bal.
	0.20	max	max	max	max	16.0	4.5	5.5	16.5	5.0	0.20	0.06		
Nimonic 263	0.04	0.4	0.2	0.7	0.2	19.0	1.9	0.3	19.0	5.6	0.001	0.02		Bal.
	0.08	max	max	max	0.6	21.0	2.4	0.6	21.0	6.1	max	max		
Inconel 600	0.08	0.25		8.0	0.5	15.5								76.0
Inconel 718	0.06	0.35	0.1	Bal.	0.35	19.0	0.9	0.6	1.0	3.0	0.003		Nb+Ta 5.25	52.5
		max	max		max				max					
Inconel 751	0.05	0.25		7.0	0.5	15.5	2.3	1.2					Nb 0.95	72.5
Inconel X - 750	0.04	0.3	0.5	7.0	0.7	15.0	2.5	0.9	0.5	0.3		0.03	Nb+Ta 1.0	Bal.
			max						max	max				
Incoloy 903	0.05	0.2	0.5	Bal.	0.2	0.2	0.2	0.9	14.5	0.2	0.005		Nb+Ta 3.0	37.5
	max	max	max		max	max				max				
Incoloy 904	0.05	0.25	0.35	Bal.	0.4	0.1	1.4	0.05	14.0	0.2				32.2
	max	max	max		max	max				max				
AEREX™ 350	0.015					17.0	2.0	1.0	25.0	3.0	0.015		W 2.0 Ta 4.0 Nb 1.1	Bal.
Inconel 713	0.12					12.5	0.8	6.1		4.2	0.012	0.1	Nb 2.0	Bal.
Rene 125	0.11					8.5	2.5	4.8	10.0	2.0			W 8.0 Ta 3.8	Bal.
Waspaloy™						18.7	3.0	1.3	13.4	4.0				Bal.

Nickel-based alloys can be either solid solution or precipitation strengthened. Solid solution strengthened alloys, such as Hastelloy X, are used in applications requiring only modest strength. Most nickel-based alloys contain 10-20% Cr, up to 8% Al and Ti, 5-10% Co, and small amounts of B, Zr, and C. Other common additions are Mo, W, Ta, Hf, and Nb. In broad terms, the elemental additions in Ni-base superalloys can be categorized as being (i) γ formers (elements that tend to partition to the matrix), (ii) γ' formers (elements that partition to the γ' precipitate), (iii) carbide formers and (iv) elements that segregate to the grain boundaries. Elements which are considered γ formers are groups V, VI, and VII elements such as Co, Cr, Mo, W and Fe. The atomic diameters of these alloys are only 3-13% different than Ni (the primary matrix element). γ' formers come from groups III, IV, and V elements and include Al, Ti, Nb, Ta, Hf. The atomic diameters of these elements differ from Ni by 6-18%. The chemical

composition of different wrought nimonic and other high temperature alloys [9] are shown in Table 1.

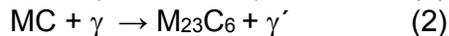
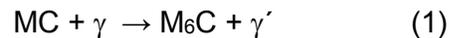
2.2. Structure and microstructure

The major phases present in most nickel superalloys are as follows [9]:

Gamma (γ): The continuous matrix (called gamma) is a face-centered-cubic (fcc) nickel-based austenitic phase that usually contains a high percentage of solid-solution elements such as Co, Cr, Mo, and W.

Gamma Prime (γ'): The primary strengthening phase in nickel-based superalloys is $\text{Ni}_3(\text{Al,Ti})$, and is called gamma prime (γ'). It is a coherently precipitating phase (i.e., the crystal planes of the precipitate are in registry with the gamma matrix) with an ordered L1_2 (fcc) crystal structure. The close match in matrix/precipitate lattice parameter ($\sim 0-1\%$) 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 °C. In addition, γ' is quite ductile and thus imparts strength to the matrix without lowering the fracture toughness of the alloy.

Carbides: Carbon, added at levels of 0.05 - 0.2 wt. %, 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 carbides begin to decompose and form lower carbides such as M_{23}C_6 and M_6C (where M represents Ti, Ta or Hf), which tend to form at the grain boundaries. These common carbides all have 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 as they are seen mostly to increase rupture strength at high temperature. The dominating reactions for formation of these two carbides are:



M' and M'' can be substituted with chromium, cobalt, nickel or molybdenum. All these carbides have fcc crystal structure and increase the rupture strength at high temperature.

Topologically Close-Packed Phases: These are generally undesirable brittle phases that can form during heat treatment or service. The cell structure of these phases has 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 (gamma prime) is close-packed in all directions and is called geometrically close-packed (GCP). TCP phases (σ , μ , Laves, etc.) usually form as plates (which appear as needles on a single-plane microstructure). The plate-like structure adversely affects mechanical properties (especially ductility and creep-rupture). Sigma 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 non-useful forms, thus reducing creep strength; and, they can act as crack initiators because of their brittle nature.

2.3. Physical and Mechanical Properties of Ni-base Superalloys

2.3.1. Density

The density of superalloys falls within the range 7.75 to 9.25 gm/cm³. As a class, the iron base alloys have the lowest density, owing to the density advantage of iron over nickel and cobalt. Nickel base alloys cover a wider range of densities, as they vary widely in alloy content. For example, the density of IN-100(60% Ni) is 7.75 gm/cm³, because of the large amount of low-density aluminum and titanium present, whereas some experimental nickel base alloys containing large amounts of high density tungsten and tantalum have densities as high as 9.0 gm/cm³. Tungsten and tantalum are major additions to cobalt base alloys and contribute significantly to their densities, which range from 8.6 gm/cm³ to 9.25 gm/cm³. Density is a particularly important consideration in the design of rotating components to minimize centrifugal stress.

2.3.2. Thermal expansion

Nickel and cobalt base alloys have similar thermal expansion coefficients, which are lower than those of austenitic iron base alloys. Gas turbines are designed to operate most efficiently with close tolerances; therefore, thermal expansion is an important design factor. In some cases it is necessary to match coefficients in mating components, whereas in others a low coefficient is preferred to minimize thermal stresses, which causes buckling and thermal fatigue cracking.

2.3.3. Thermal conductivity

Thermal conductivity of superalloys is only 10 to 30% that of pure iron, nickel, or cobalt, owing to the effect of extensive alloying. In general, iron base alloys are slightly more conductive than cobalt base alloys, and nickel base alloys span the range of each. It would be desirable to have higher thermal conductivity in superalloys to dissipate heat and minimize temperature gradients, thus reducing thermal stresses and the tendency for thermal fatigue failure. In this regard, it is interesting to note that the addition of ThO₂ to pure nickel in TD nickel does not significantly reduce its conductivity.

2.3.4. Oxidation resistance

Within the gas turbine industry, oxidation is defined as the reaction of an alloy with oxygen in the presence of products of combustion of clean fuel, that is, generally free of contaminants such as sodium, sulfur and vanadium. Good oxidation resistance is achieved by formation of a tight continuous surface scale that acts as a diffusion barrier and does not spall off during thermal cycling. In general, nickel-chromium alloys with high aluminium, such as 713C and B-1900, are considered to have excellent resistance to oxidation due to their ability to form the protective oxides Cr₂O₃ and Al₂O₃ [10]. Most cobalt base alloys have somewhat less oxidation resistance than nickel base alloys.

2.3.5. Hot corrosion

In gas turbine industry, hot corrosion (sulfidation) refers to a particularly aggressive attack resulting from the combined effects of normal oxidation and reaction with sulfur and other contaminants ingested with inlet air and these contained in Fuel. Hot corrosion resistance is related to the chromium content in both nickel and cobalt base alloys and is also a function of the sulfide properties of these systems. Cobalt sulfide is far more refractory in nature than nickel sulfide. On the other hand cobalt has a lower diffusivity for sulfur. Further, most cobalt alloys contain a higher proportion of chromium than their nickel counterparts. The net result is that cobalt base alloys as a group have better hot corrosion resistance than the nickel base alloys.

2.4. Strengthening in Ni-based superalloys

The deformation of a polycrystalline material is accommodated both by deformation of the individual grains and by relative movement of the grains within the body of the material, the extents of each of them depend significantly on the homologous temperature and specific composition and/or microstructure. The mechanism of accommodation which predominates depends on the temperature of deformation and the strain rate. Below about $0.6T_M$, most of the deformation occurs within the grains. Above about $0.6T_M$, grain boundary sliding with relative grain movement and rotation can occur. This mechanism accommodates an increasing proportion of the deformation as the temperature increases, as the grain size decreases and the strain rate decreases. The properties of the grain boundaries are determined to a large extent, by the carbides formed in these regions and also the characteristics of the grain boundaries themselves.

Solid-solution strengthening: The requirements for a useful solid-solution strengthening addition are that firstly it should have a wide range of solid solution in the matrix; secondly, it should have the largest possible dissimilarity in atomic size with the matrix atom and thirdly it should have a high melting point. At higher temperatures, where diffusion and dislocation cross-slip are important in determining the strength, then atoms which diffuse slowly such as molybdenum and tungsten would be useful solid-solution additions, as would elements which decrease the stacking fault energy between partial dislocations, such as cobalt.

Precipitation hardening: A majority of nickel base alloys, which are precipitation hardened, rely on the γ' phase for strengthening. The γ' compound is based on the formula $Ni_3(Ti, Al)$ and it can have a range of compositions depending on the titanium and aluminium contents of the alloy. There is further flexibility in the composition since the nickel can be replaced to some extent by cobalt, molybdenum, chromium, and iron, and the aluminium + titanium can be replaced by niobium, tantalum, vanadium, molybdenum, chromium and iron. The important characteristic of γ' in commercial alloys is that it forms as a fine homogeneous precipitate with a spherical or cuboidal morphology.

The effectiveness of the γ' in impeding dislocation movement depends on several factors. To get past a coherent precipitate particle a dislocation, moving on a slip plane can either cut through it loop round it by a mechanism known as Orowan looping [11]. To a first approximation it is the interparticle spacing which decides which by-pass mechanism operates. Dislocation movement occurs on the close-packed (111) crystallographic planes in the [110] directions. When a dislocation enters an ordered phase it creates an anti-phase domain boundary on the slip plane which is a high energy area and which therefore strengthens the alloy [12].

Transformation of γ' : γ' is a metastable form of hexagonal η - phase. The η - phase has a hexagonal crystal structure and is non-coherent with the matrix and generally exists as large platelets which can extend right across grains. In this form, the η -phase confers little benefit on the alloy and therefore the γ' to η transformation is undesirable. Mihalisin and Decker [13] have shown that γ' to η reaction is accelerated by deformation of the alloy and this is because the presence of dislocations at the matrix/precipitate interface facilitates the necessary relative (111) plane shifts.

Carbides: The carbon content of commercial nickel-base alloys ranges from 0.02 % upwards, and metallic carbides can form in these materials both at the grain boundaries and within the grains. There are several types of carbides which can form in nickel base alloys. Mono-carbides of the general formula MC where M is Titanium, Tantalum, Niobium or Tungsten are generally

very stable and form during the melting of the material. They are difficult to dissolve in the solid phase and they play an important part in restricting grain growth during the solution treatment stage. More complex carbides which can be dissolved by a solution treatment in the range 1050 °C to 1200 °C have the general formula $M_{23}C_6$, M_7C_3 or M_6C where M denotes the metallic constituent. In $M_{23}C_6$, M is usually chromium, but this element can be replaced by iron and to a lesser extent nickel, cobalt and molybdenum, depending on the base composition of the alloy. If there is a high super-saturation of carbon then, as Beattie and Versnyder [14] have shown, there is a tendency to form the cellular grain boundary precipitates. Betteridge and Franklin [15] established that a heat treatment at 1080 °C prior to the γ' precipitation at 700 °C gave the best combination of strength and ductility in Nimonic 80A and this type of intermediate heat treatment which optimizes the grain boundary carbide distribution is common for nickel base alloys.

The formation of grain boundary carbides containing chromium can, under certain conditions of heat treatment, leave a region along the boundary which is denuded in chromium. This denudation originally detected by Betteridge and Franklin [15] has been confirmed by Fleetwood [16] using micro-probe analysis. M_7C_3 , where M is mostly chromium is carbide which has been observed in Nimonic 80A and which is stable at high temperatures than $M_{23}C_6$. However during service in the range 600 °C to 800 °C the M_7C_3 transforms to $M_{23}C_6$ and this reaction has been described in detail by Fell [17]. If the molybdenum and tungsten contents of the base material are significant then there is a tendency for the M_6C carbide to form instead of $M_{23}C_6$. Collins and Quigg [18] also examined a range of nickel alloys and established that $M_{23}C_6$ is generally stable up to about 1050 °C, M_6C up to 1150 °C and MC up to at least 1200 °C although in some materials this latter carbide might dissociate into other carbides and γ' at intermediate temperatures.

2.5. Applications of Nickel base Superalloys

Superalloys are generally used in turbine engines (Fig. 2) operating at temperatures above 540 °C, which includes ducts, cases, and liners, as well as the major components: turbine blades, vanes, disks, and combustion cans.

Turbine blades: Turbine blade airfoils generally experience longitudinal stresses to approximately 20,000 psi (138 MPa) and temperatures of 650-980 °C in their airfoil section (Fig. 3). The blade root, which attaches to the disk, is outside the hot gas path and is exposed to a maximum temperature of 760 °C but is subjected to tensile stresses of 40,000 - 80,000 psi (276 – 552 MPa). In addition to these demanding strength requirements, turbine bucket materials must also have adequate ductility to tolerate creep deformation, to resist low-cycle fatigue deformation, and to allow seating of the blade in the disk slot. Since these parts are in contact with high temperature combustion products, good oxidation resistance is mandatory. During cyclic operation, thermal gradients from heating and cooling of turbine sections of varying sizes induce thermal stresses, which subject the blade airfoils to thermal fatigue. Materials with high strength, ductility, high thermal conductivity, and low thermal expansion provide the best resistance to thermal fatigue. In addition to these major requirements, blade materials should be microstructurally stable so that their properties are maintained for long periods of time. They should also have good impact strength, good castability, and low density.

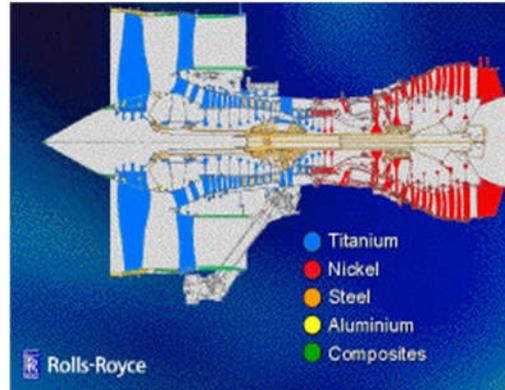


Fig. 3: Materials used in a Rolls-Royce gas turbine engine [9]



Fig. 4: Front view of a directionally solidified gas turbine blade
(Courtesy: CEMILAC, DRDO, India)

Turbine nozzle guide vanes: These are static components, turbine nozzle guide vanes are subjected to relatively low stresses, generally below 10,000 psi (69 MPa). Operating temperatures, however, can be very high as the hot gases entering the turbine section impinge directly upon the first-stage vane. Metal temperatures of approximately 1100 °C are often encountered in advanced turbine vanes. The primary material requirements are creep strength at very high temperatures, thermal fatigue resistance, and resistance to surface degradation by oxidation, hot corrosion, and erosion. As with turbine buckets, secondary requirements are impact strength, castability, microstructural stability, and weldability in some designs.

Turbine discs: Turbine disc operating temperatures are generally around 760 °C (Fig. 4). This temperature is experienced only on the outer rim in the area of blade attachment. In the hub portion, towards the center of the disk, temperatures are much lower. Operating stresses due to centrifugal loads in these rotating components are high at the rim and still higher towards the center, >70,000psi (>483 MPa). Materials, therefore, require very high tensile strength at hub operating temperatures for burst protection and high creep strength at rim operating conditions. Also, good fatigue resistance, both low cycle and high cycle, is the primary disc requirements. For many small gas turbines, such as small air craft engines and vehicular engines, the turbine disc and blades are cast as a single piece, generally known as an integral wheel and are called as BLISKs. Materials for integral wheels must possess the combination of blade and disk properties, in addition to very good castability.

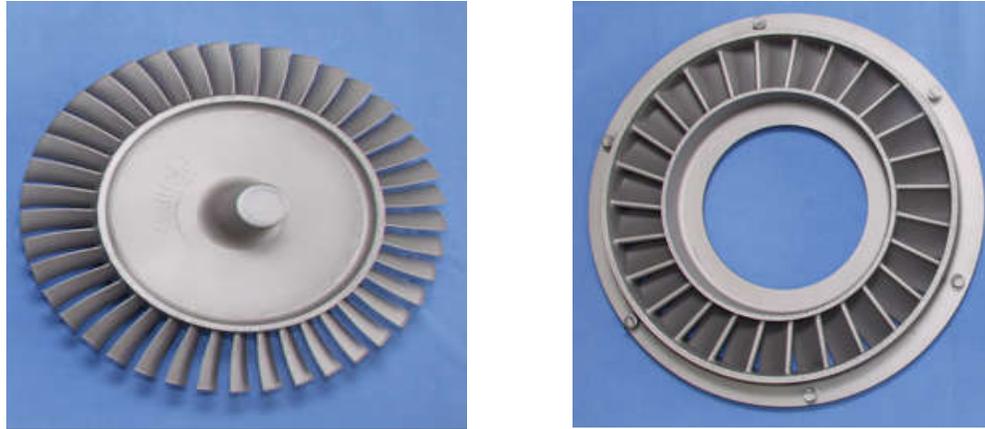


Fig. 5: An assembly of turbine blades on a turbine disc, central portion of the two Photographs. (Courtesy: CEMILAC, DRDO)

Combustion cans: The strength requirements of combustion can (Fig. 6) materials are relatively low, but strength must be maintained to operating temperatures of 1100 °C or greater. Oxidation resistance is the prime requisite, along with resistance to thermal fatigue and buckling. The material must also have good weldability and formability to facilitate fabrication. The great success of superalloy development, primarily an empirical technology, can best be appreciated by noting its effect on engine performance. Early aircraft gas turbines in the United States employed nickel-base and Cobalt-base alloy turbine blades and vanes, iron-base alloy disks, and stainless or nickel-base alloy combustion cans. However, superalloys then accounted for less than 10 % of engine weight, and were limited to use below 815 °C. Now, in modern aircraft engines, superalloys account for as much as 70 % of engine weight. Some of these alloys can withstand temperatures as high as 1040 - 1100 °C. Contemporary engines use nickel base alloys almost entirely for turbine blades, nickel or iron- base alloys for turbine wheels, and nickel or cobalt-base alloys for vanes and combustion cans. Wider use of these improved superalloys has made it possible to increase turbine inlet temperatures from less than 815 °C to well over 1100 °C with the result that engine performance has increased dramatically.



Fig. 6: Combustion cans.

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