SUPERALLOY : PROCESSING AND PERFORMANCE

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ABSTRACT

Superalloy represents a class of high temperature / high performance material, which became available shortly before the Second World War. The concurrent development of gas turbine technology led to a rapid expansion in the use of such alloys. The growing demand for higher temperature capability for the turbine material so as to allow higher operating temperature and higher thrust to improve efficiency has been the main impetus for its development. The initial years were devoted to alloy chemistry whereas the subsequent years have seen more emphasis on process improvement. From a modest beginning of 10 % of the total weight of the engine in 1950's, use of superalloys has now reached a level of around 60 %. This was possible because of simultaneous availability of a variety of newer processes to produce better alloys and defect free products. This includes vacuum melting and refining, investment casting, directional solidification and single crystal technology. The performance of an engineering material to a great extent is determined by the processing technique that is followed. The paper describes how our knowledge on structures of material and its correlation with properties and performance has guided adoption of newer technology in the processing of superalloys.

Key Words : Superalloy, high temperature material, microstructure, directional solodification, creep.

INTRODUCTION

Superalloy is a special class of material developed for elevated temperature applications. This is expected to withstand corrosive environment, exhibit micro-structural phase stability and yet possess sufficient strength to withstand the designed stress and temperature. The development of superalloy and its quick adoption in aero gas turbine has been one of the major technological achievements of the last five decades. 1950 – 1990 is the golden age for superalloy technology. During this period a wide range of processes such as vacuum arc melting, vacuum induction melting, investment casting, directional solidification, single crystal technology and vapour deposition of protective coating became available. These were soon adopted in superalloy technology to improve its performance. During this period the major emphasis has been on new alloy development. The question of superiority Co vs Ni base alloy was soon settled in favour of Ni and Fe-Ni base system. Apparently the cost, availability and performance have been the major consideration. Most of the superalloys currently in use have evolved from binary Ni-Cr system with additional alloy addition to improve its properties. The binary alloy containing 80 Ni 20 Cr known as Nichrome has been in use as heating elements. A look at the phase diagram would reveal that this would fall in the single-phase regime. As a heating element this may not have to withstand stress but it must have excellent oxidation resistance to withstand the environment. Addition of a small amount of Al / Ti to nichrome showed a remarkable increase in its strength. With this started the evolution of superalloy. The increase in strength was associated with drop in ductility. The major challenge in the development of superalloy has been to overcome this problem. Table 1 lists the common alloy additions and the way these are distributed in the microstructure. Table 2 gives the composition of a few of the common Ni base superalloy. 1950-80 was also the period when significant development in our understanding of evolution of microstructure in alloys during solidification and subsequent processing and its correlation with properties took place. There are excellent source books and technical guides on superalloy [1,2]. This paper tries to analyse the role played by the concurrent developments in alloy making technology and our understanding of material behaviour in meeting the growing demand of high performance high temperature material and suggest future direction of research.

Table 1 : Effect of alloy addition on Ni base super alloy [1,2]

Element	*Effect*
Cr	Oxidation resistance
Mo, W	Solid solution strengthening, M_6C
Al, Ti	Forms γ', TiC, Al gives oxidation resistance
Co	Raises γ' solvus temperature
B, Zr, Hf	Improves ductility and rupture strength
C	Forms carbibes MC, M_7C_3, $M_{23}C_6$, M_6C
Nb	Forms γ', Ni_3Nb (hardening phase), d (orthorhombic phase)
Ta	Solid solution strengthening, forms MC, gives oxidation resistance

Table 2 : Typical compositions of a few Ni base superalloy [1-3]

Alloy	Co	Cr	W	Ti	Al	Ta	Others
Nimonic105	20	15		1.2	4.7		5Mo, 0.005 B
Udimet	18.5	15		3.5	4.4		5Mo, 0.025B
Rene 100	15.0	9.5		4.2	5.5		3Mo,0.015 B, 0.06 Zr, 1.0 V
IN738	8.5	16	2.6	3.4	3.4	1.7	1.7Mo, 0.01B,0.1Zr
SRR99	5	8.5	9.5	2.2	5.5	2.8	
CMSX2	4.6	8.5	9.5	2.2	5.5	2.8	
CMSX4	9.5	6.5	6.4	1.0	5.6	6.5	0.5Mo, 3Re, 0.1 Hf

CAST VS. WROUGHT ALLOY

Initial alloys (e.g Nimonics) were made by casting and subsequent forging. This is followed by heat treatment, which often is a multistage process consisting of solution treatment and ageing. In order that the final shape of the product could be made by forging, high ductility was a prime requirement. Studies revealed that poor ductility was due to inter granular fracture. To improve the strength of the grain boundary a large number of alloy-additions were made. The first three alloys in Table 1 are wrought alloys. Clearly the improved performance is due to the presence of a number of grain boundary strengtheners. These alloys derive their strength from precipitates. These are primarily γ' although there may be some amounts of carbides as well. Higher the amount of γ' higher is the strength. Figure 1 gives a schematic phase diagram of Ni base superalloy. The transformation temperatures are plotted as function of γ' forming elements. Initial alloys such as nimonics have 10% γ'. This has a large temperature zone between solvus and liquidus. In this regime it has a single-phase structure and therefore the alloy has a large window for hot working. With increase in volume fraction of γ' this window shrinks. As a result such alloys are more difficult to forge. Alloy IN738 in Table 1 has higher amount γ' forming elements (e.g Al, Ti) and consequently it has a relatively narrow hot working window. This indeed is a cast alloy and it has much superior high temperature properties. Turbine blades have very complex geometry with internal cooling channels. Casting them in final shape is indeed a challenging task. Precision casting techniques such as investment casting are commonly used. This requires close control on the quality of mould material and melting technique. Availability of vacuum melting and casting system proved very handy. Figure 2 shows how significant could be the improvement in ductility if these alloys are made in vacuum.

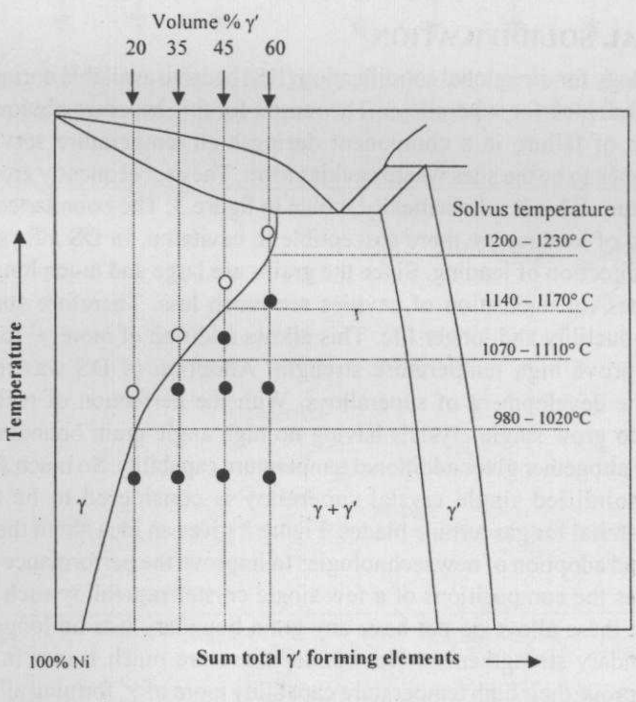
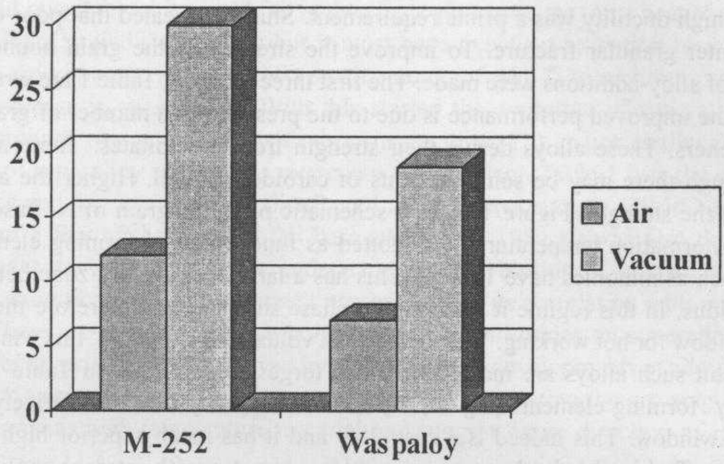


Fig. 1 : A schematic phase diagram showing effect of γ forming elements on solvus line and temperatures for solution treatment (open symbol) and ageing (filled symbol).



Waspaloy: 19.5Cr, 13.5Co, 4.3Mo, 3.0Ti, 1.4Al, 0.006B, 0.06Zr
M-252 : 19Cr, 10Co, 10Mo, 2.6Ti, 1Al, 0.005B

Fig. 2 : Effect of vacuum treatment on the ductility of two commercial Ni base superalloys [2]

DIRECTIONAL SOLIDIFICATION

Technology for directional solidification (DS) became available during the seventies. This was soon adopted for superalloys. The reason for this becomes obvious if we look at the mechanism of failure in a component during high temperature service. The grain boundaries happen to be the sites where cavities form. They subsequently grow and coalesce leading to fracture. This is schematically shown in figure 3. The boundaries perpendicular to the direction of loading are more susceptible to cavitaion. In DS alloys the grains are aligned in the direction of loading. Since the grains are large and much longer the number of potential sites for nucleation of cavities are much less. Therefore such alloys have higher rupture ductility and longer life. This allows addition of more γ' forming alloying element to improve high temperature strength. Adoption of DS was indeed a major milestone in the development of superalloys. With the perfection of technology it was soon possible to grow single crystals having no high angle grain boundary. Removal of grain boundary altogether gives additional temperature capability. So much so that currently directionally solidified single crystal superalloy is considered to be the ideal high temperature material for gas turbine blades. Figure 4 gives an idea about the chronological development and adoption of new technologies to improve the performance of superalloys. Table 1 includes the compositions of a few single crystal superalloy such as SRR99 and CMSX2. Since these alloys do not have any grain boundary it is no longer necessary to add grain boundary strengtheners. No wonder these are much leaner in alloy content. However to improve their high temperature capability more of γ' forming alloying elements are added. In some of the current single crystal superalloy volume fraction of γ' could be as high as 70%. This pushes the solution temperature to very near the liquidus. Apparently there is very little possibility to further enhance the high temperature capability of these alloys. Some attempts are being made to raise the melting point by addition of elements like rhenium (e.g CMSX4). Such addition may also alter the interface structure between γ/γ'. If it were near coherent phase stability would improve and γ' phase will be less likely to grow during service. Nevertheless the scope of playing with chemistry of these alloys is no doubt is very limited.

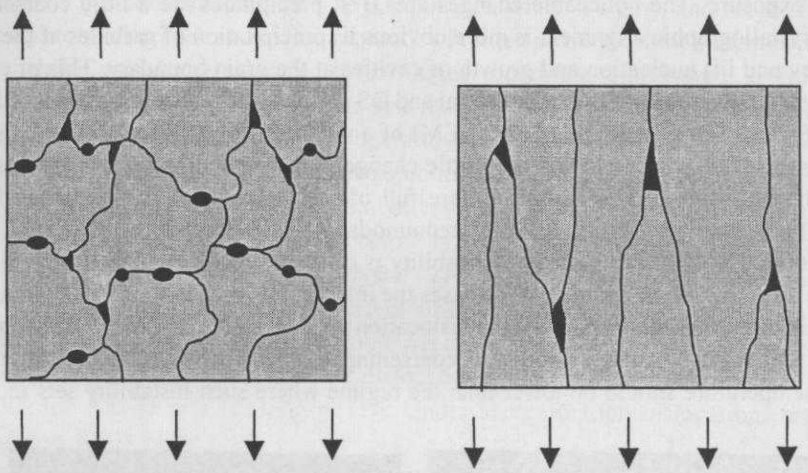


Fig. 3: Schematic diagram showing the likely sites for nucleation and growth of cavities in (a) conventionally cast and (b) directionally solidified alloy.

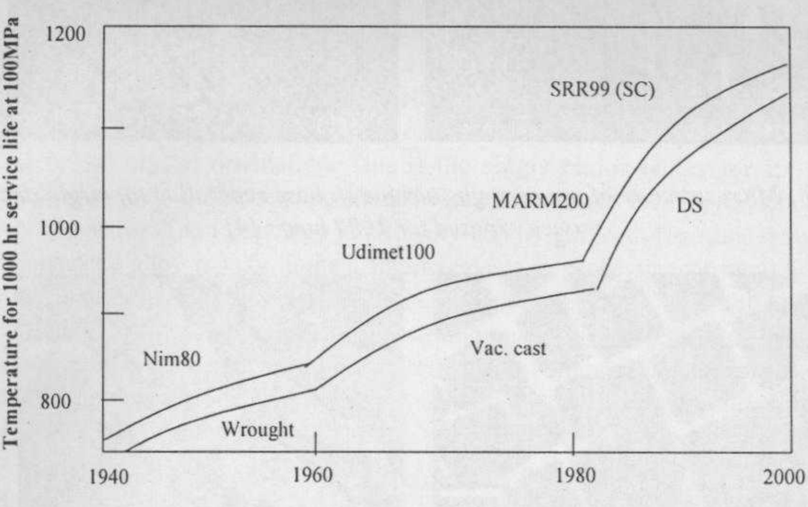


Fig. 4 : Chronological development in the high temperature capabilities of Ni base superalloy with introduction of new technologies and our understanding of structure property correlation.

MICROSTRUCTURAL STABILITY

Microstructural stability is one of the major criteria for selection of material for high temperature application. This superalloy derives its strength from γ' precipitates. Higher the volume fraction of γ' higher is its strength. Although the strength of superalloy is insensitive to the size of γ' there exists a size range over which the alloy exhibits best high temperature capability. Figure 5a gives the microstructure of a turbine blade before it was put into service. Figure 5b shows the change it has undergone after 1000 hours of service exposure. The noticeable changes are: i) γ' precipitates are a little coarser as a result crystallographic alignment is more obvious ii) precipitation of carbides at the grain boundary and iii) nucleation and growth of cavities at the grain boundary. This of course is a polycrystalline alloy. The single crystal and DS varieties have better structural stability. Figure 6 shows electron micrographs (TEM) of a virgin and a crept specimen of a single crystal superalloy (CMSX4). There is little change in the shape and size of γ'. However the g channel after creep deformation are full of dislocations. This shows that during service the entire creep deformation is accommodated within the soft the g channel. Ideal g/g¢ interface having maximum phase stability is coherent. This can be achieved only by suitable alloy additions. In most of the cases the interface is semi-coherent. Depending on the nature of the boundary and interface dislocation present to take care of lattice mismatch, most of these alloys undergo directional coarsening of γ'. This is called rafting. The ideal design temperature should be lower than the regime where such instability sets in.

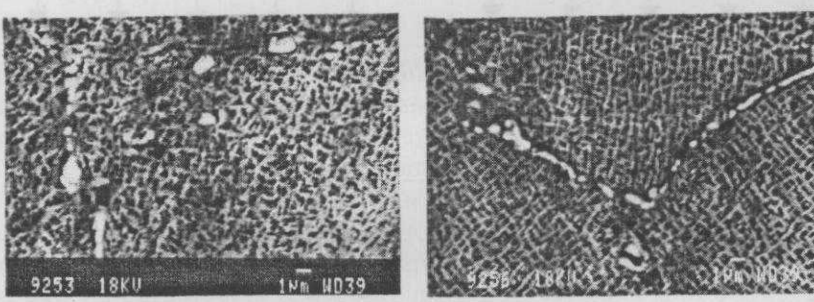


Fig. 5 : Microstructure of an aero-gas turbine Ni base superalloy (a) virgin and (b) service exposed for 1000 hours [4]

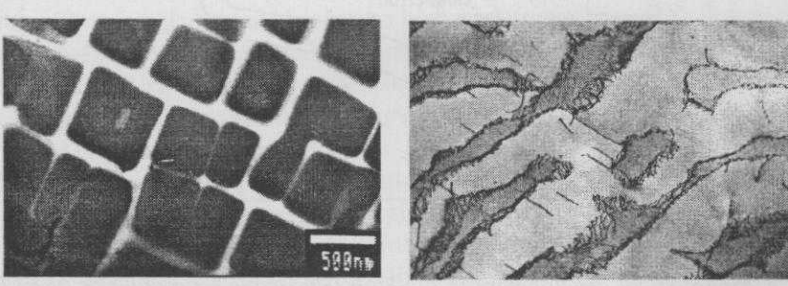


Fig. 6 : transmission electron microstructure of (a) virgin and (b) creep tested specimen 950°C [5]

PERFORMANCE

The development of superalloy is very closely associated with the development in design and fabrication of gas turbine components. Depending on the temperature and stress to which these are subjected, the material must have appropriate combination of strength and toughness. In addition two of the most common properties one would look for are creep and fatigue resistance. Both of these depend on the microstructure of the alloy. Usually a coarse grain structure has better creep resistance where as a fine grain structure has better fatigue life. The components, which are large and subjected to a more complex loading such as the disc, are made of forged polycrystalline superalloy. In contrast the blades, which are subjected to still higher operating temperature, are made of cast superalloy. Clearly in the case of the disc fatigue is the major concern whereas in the case of blade it is creep. Single crystal superalloy is currently considered as the ideal material for blades. However these are anisotropic in nature. Figure 7 gives a comparison of the creep curves for three different crystal directions. It is a mere coincidence that the natural direction of growth of the crystal <001> is also the direction having the highest creep resistance. Ideally in a face centred crystal <111> should be the strongest direction. However in a true sense the alloy in not perfect single crystal. There exists semi-coherent g/γ' interface. The presence of large volume fraction of hard g¢particles, which are difficult to deform, puts severe restrictions on dislocation glide on close packed plane particularly when the tensile axis is along <111>. Under such situation dislocations are forced to glide on {001} plane.

DISCUSSIONS

It now appears that improvement in the performance of superalloy by changing its chemistry is nearing its limit. Solvus temperatures of some of the cast supralloys are very close to their melting point. However the same can not said to be true as regards our ability to exploit its full potential and bring down its manufacturing cost. The castings are so intricate that it is extremely difficult to produce defect free products. The rejection rates are quite high. This may be due to casting defects, imperfect microstructure or unacceptable crystal orientation. This is the single major factor for its exorbitant manufacturing cost. The equipment and facilities required for its production is highly capital intensive. The technology is also very closely guarded. No wonder suppliers for this advanced alloy is very limited. Improvements in processing of moulding material and techniques will allow production of larger defect free parts. This will be very useful in extending the design lives of power generation turbines. In India a major initiative has been taken up by Defence Metallurgical Research Laboratory, Hyderabad to set up such a facility. They have produced a single crystal superalloy having compositions similar to that of CMSX2 [3].

The temperature of the gas as it enters the first stage turbine may be as high as 1400°C or even more. This is close to the melting point of the superalloy. In order to keep the metal wall temperature within the design limit, which is usually in the range 850° - 950°C it is necessary to have and internal cooling system and thermal barrier coatings on blades used in the first two stages. The coating apart from acting as an insulating layer may have to withstand stresses as well. There should be strain compatibility across the interface. Often this consists of several layers. This too is a closely guarded technology. During every overhaul if the coatings on blades of a gas turbine are found to have developed damage these are taken out and sent to the supplier for repair. This is an area where a lot of work is going on to improve quality of coating so that it lasts longer.

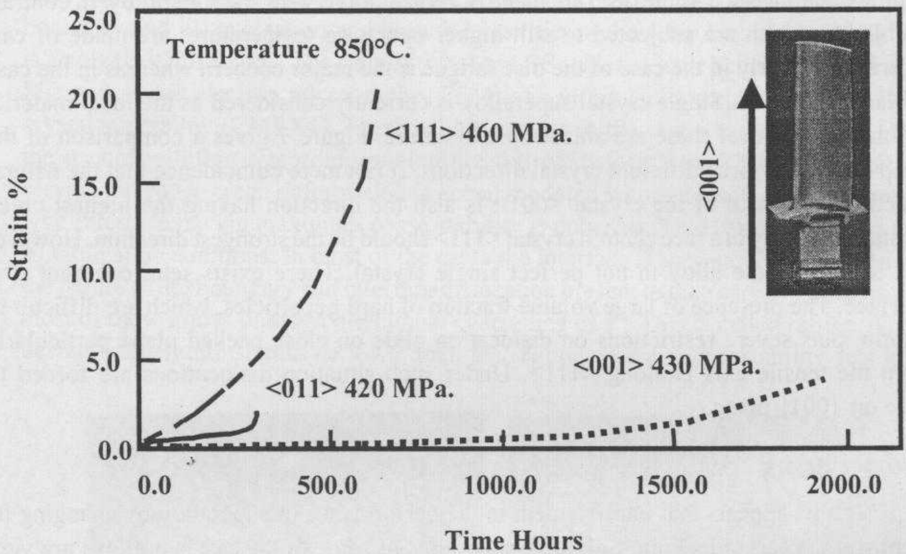
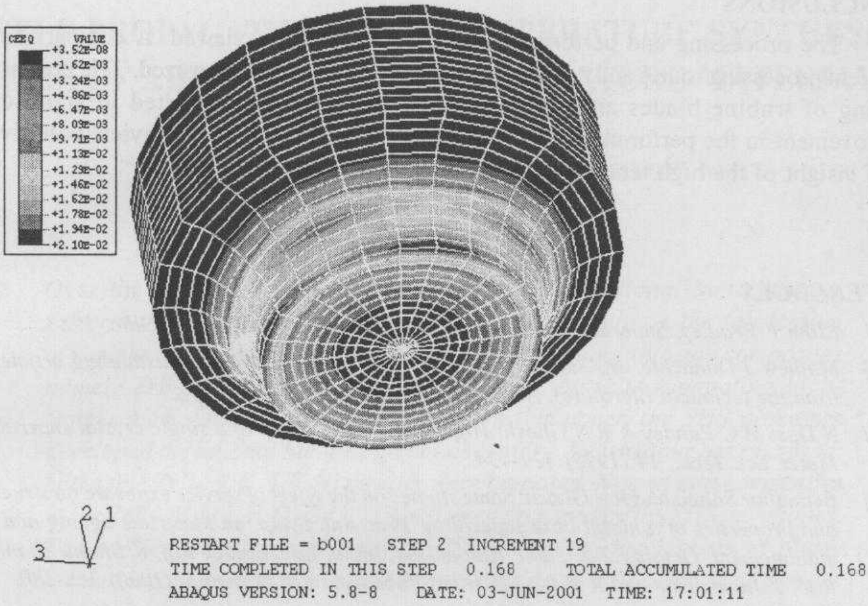


Fig. 7 : A comparison of creep strain time plots of a single crystal super alloy when loaded along different crystallographic directions at 850°C. [6,7]

As far as the temperature capability of the base material is concerned single crystal variety is the best. This is anisotropic. It has superior properties along the natural direction of crystal growth. Creep is an important factor determining stress distribution and design life. None of the existing stress analysis packages can handle crystallographic anisotropy (e.g. ABAQUS, ANSYS etc.). Creep models used in these systems are mostly empirical. It is believed that if creep strain can be described in terms of crystallographic glide on appropriate slip planes and directions it would predict correct stress distribution. Work in this direction is being carried out at our laboratory in collaboration with Professor McLean and his group at Imperial College, London. Incorporating a slip based formalism it is possible to show that the stress distribution around a Bridgman notch specimen reveals four and three fold symmetry depending on the orientation of the tensile axis [6,7]. Further work in this direction is in progress.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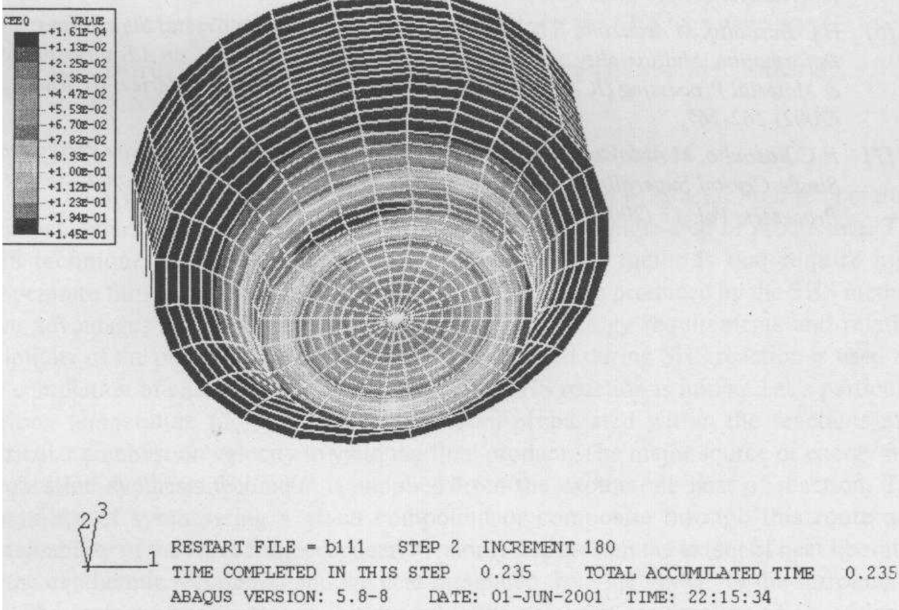
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CONCLUSIONS

The processing and performance of superalloys are reviewed. A comparison of different processing routes and the microstructural stability are emphasized. THe precission casting of trubine blades and directional solodification has resulted in significant improvement in the performance and life of the turbine blades. This review will give a brief insight of the high temperature superalloys.

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