

High-Temperature Corrosion Failure of Single Crystal Super alloy Turbine Blades

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Abstract

Two first-stage turbine blades catastrophically failed in operation in Qatar Petroleum Dukhan operation. The Fractured surface indicated that the crack was propagated by high cycle fatigue (HCF). The presence of corrosion products of sulphur, chlorides and oxides on the blades pointed out a possibility of Type 2 high temperature corrosion.

The Manufacturers recommendation was to using a heavy-duty filtration to remove contaminants to eliminate the High temperature corrosion. The alloy used in the blades was a second generation CMSX-4, a product especially developed for high temperature operations for aircraft turbines. This means reason for the failure needed further investigation. The following is the corrosion failure study conducted by the Qatar Petroleum's Corrosion Laboratory of these two first-stage turbine blades in operation.

Super alloys

Super alloys are a group of materials that are used in high temperature applications, for example gas turbines. Gas turbines are most commonly used for power generation, and it is only the very critical components which are exposed to the most severe conditions within the turbine, which are made from super alloy material and are required to operate within extreme conditions of temperature and pressure.

These turbine blades rotate at a typical speed of 10,000 rpm for long periods in an environment of combustion products at working temperatures of 1250 °C and the inlet temperatures of high performance engines can exceed 1650 °C. The blades must be able to withstand impact and erosion from debris drawn in with the air stream. In addition, different parts of the blade may be at different temperatures and they will be subjected to large and rapid temperature changes when the engine is started up and turned off. This significant technical advance was made possible by the development of an alloy with improved properties and the development of a production casting process.

Today these super alloys are classified on the basis on Rhenium alloy concentration (*This is more to the reason of patent requirement of the usage of Rhenium in the design of Single crystal matrix*).

1st Generation Super Alloy- Contains 0% Rhenium (Re). With melting points were lower <612°F (300° C).

nd **2 Generation Super Alloy**

Contains 3% Rhenium (Re)- capable operation of at least 2125°F (1163°C).

Developed in the 1980's by Rolls Royce. (eg: CMSX-4)

rd **3 Generation Super Alloy**

Contains 6% Rhenium (Re)- Capable of operating at temperatures exceeding 2150°F(1180°C). *Used in the Trent 500 engine of Airbus A340-600.(1990)*

After 6% mark of Rhenium small amount of Ruthenium is added to continue the process. It acts as a 'stabilizer' and appears to be recognized in the alloy as another Rhenium atom. Still about 60% of the use-temperature increases have occurred due to advanced cooling concepts; only 40% have resulted from material improvements

Metallurgical and Microstructure stability

Microstructure stability is achieved through precipitation hardening alloys at 970 to 1175°C followed by one-heat treatment at 600 to 815°C. Super alloys microstructure stability depends on the reinforcing Gamma' precipitate. Single crystal alloys large fraction of hardening occurs at temperatures around 900°C producing negative misfits. At $T > 1000^{\circ}\text{C}$ this peculiar microstructure builds up very quickly and will continue practically all the creep life. The mechanical properties of metals can be modified by heat treatment. Blade materials must be resistant to such changes and the microstructure must remain stable at high temperatures.

The density must be low to keep engine weight as low as possible. Metallurgists have developed super-alloys to meet these stringent specifications. Nickel-based super-alloys are able to withstand stresses of over 250 MPa for 30 hours at 850°C with less than 0.1% irreversible creep. The alloy contains 18 constituents and its composition is shown below:

Table 1: Composition of Fatigue/creep-resistant turbine blade super-alloy CMSX4

Element/wt%			Element/wt%		
Nickel	Ni	59	Molybdenum	Mo	0.6
Cobalt	Co	9	Carbon	C	0.0
Tungsten	W	6.0	Silicon	Si	0.0
Chromium	Cr	6.5	Manganese	Mn	0.0
Aluminium	Al	5.6	Copper	Cu	0.0
Tantalum	Ta	6.5	Zirconium	Zr	0.0
Titanium	Ti	1.0	Boron	B	0.0
Hafnium	Hf	0.10	Sulphur	S	<0.008
Rhenium	Re	3.0	Lead	Pb	<0.005

Why the need for so many elements and what does each do?

Alloying elements (re-introducing 'foreign' atoms such as carbon atoms in steel) disturb the regularity of the lattice and by doing so hinder the movement of dislocations. Also dislocations have difficulty in moving across grain boundaries. In super-alloys, obstacles in the form of insoluble precipitates are introduced to hinder dislocation movement. Some elements are also introduced to reinforce grain boundaries. Some elements form a layer of oxide (Cr_2O_3 in this case) on the blade surface which greatly improves resistance to corrosion. Cobalt, tungsten and chromium are all soluble in Nickel (which crystallizes in a cubic closed pack or face centred cube structure). Their atoms are different in size from nickel atoms and they are distributed randomly throughout the nickel matrix – they are in solid solution and they produce irregularities in the crystal.

Any irregularity in the crystal will hinder the progress of a dislocation. Strains set up around substitute atoms impede the movement of dislocations. As the temperature of a metal increases, creep becomes more pronounced. More vacancies are introduced as temperature rises and diffusion of atoms is easier. Additives which made diffusion more difficult, therefore, enhance creep resistance.

Hard precipitates are more resistant to deformation. Their presence in a softer matrix makes it more difficult for planes to slip over one another. We can think of them as acting like boulders thrown into a stream to dam the flow of water. It is also difficult for dislocations to pass through regions with closely spaced hard precipitates. A dislocation passing through such a region has been compared with trying to blow up a balloon in a bird cage. It is difficult for the balloon membrane to pass through the bars. The dislocation is similarly confined by the precipitates in super-alloys.

Cobalt, tungsten and chromium thus act as matrix strengtheners.

Aluminium and titanium react with the Nickel to form stable compounds such as Ni_3Al and Ni_3Ti . The crystal structure of Ni_3Al and Ni_3Ti have a similar packing arrangement to the original (Nickel based) matrix and do not disrupt the regularity of the original matrix to which they are bonded. However, these particles **are extremely hard and are very resistant to sheer deformation**. Metallurgists sometimes call this process the Gamma prime (γ') phase.

[Note: Molybdenum, tantalum, tungsten and titanium also form Carbides MoC , TaC , WC and TiC . These are very hard materials which can also act as obstructions to matrix deformation.]

Other Carbides, mainly based on Chromium (CrC_3) accumulate at the grain boundaries in the matrix. It is believed that **they strengthen these regions by reducing the formation of cracks which lead to failure**. The grain boundaries become the source of weakness following the strengthening of the matrix. If they are filled with hard materials, which are firmly bonded to the grains, it becomes more difficult to shear the grains apart. Grain boundary strengtheners act rather like the cement in crazy paving.

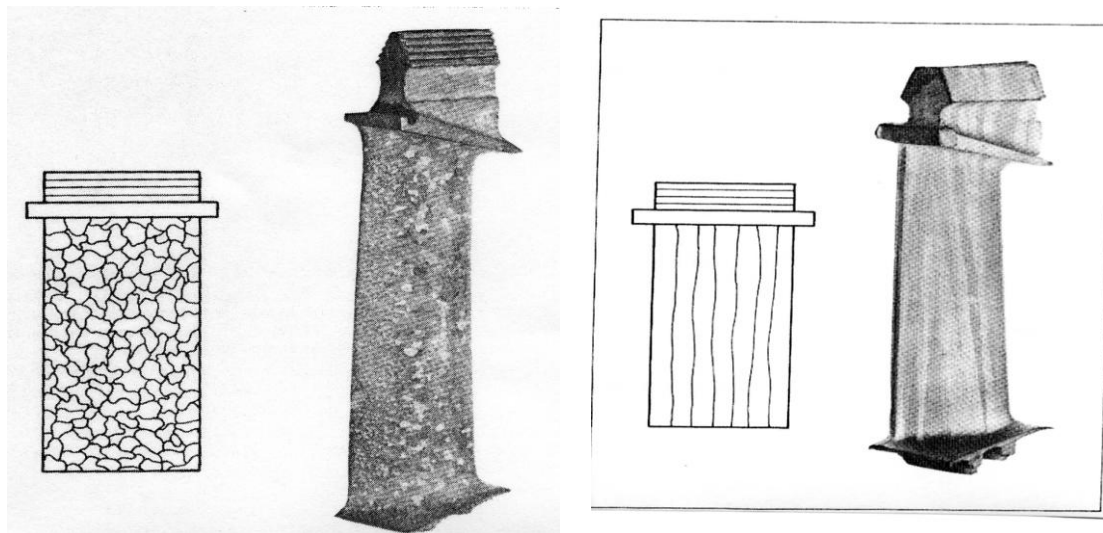
Some elements may have a number of functions in strengthening the alloy. Chromium is a good example. Chromium forms a layer of oxide (Cr_2O_3) on the blade surface which greatly **improves resistance to corrosion**.

Functions of different elements used in super-alloys

Purpose	Cr	Al	Co	Mo	W	Ti	Ta	Nb	Hf	C	B	Zr
Matrix strengtheners	✓		✓									
Gamma prime formers		✓				✓	✓	✓				
Carbide formers	✓			✓	✓	✓	✓	✓	✓			
Oxide scale formers	✓	✓										
Grain boundary strengtheners									✓	✓	✓	✓

Processing developments

Turbine blades were shaped by forging before the introduction of super-alloys, but the new materials were so hard that they could not be forged or easily shaped and so had to be produced by casting into moulds. Conventional (early) casting processes produced blades with a fire grain structure



Conventional as-cast grain structure

Directionally solidified grain structure

The grains were formed during solidification in the casting mould. Each grain had a different orientation of its crystal lattice from its neighbours. The weakest parts of the structure were the grain boundaries and blade failure often occurred at these points due to slippage (under stress and creep). In the 1960s researchers at the jet engine manufacturer Pratt and Whitney set out to eliminate grain boundaries from turbine aerofoils altogether. The first development was to produce blades with all the grains aligned parallel to the stress axis by a process called **directional solidification**.

A mould of molten metal is enclosed in the hot zone of a furnace and the heat is gradually removed from the bottom of the mould. As the mould is gradually removed from the furnace, columnar grains develop along the axis (only) of the blade (fig. 4). The final result is a turbine airfoil composed of columnar crystals or grains running along the length of the blade. For the case of a rotating blade subjected to centripetal forces of the order of 20,000g, the grains are now aligned along the major stress axis. Their alignment strengthens the blade and eliminates inter-granular crack formation in directions normal to the blade span.

The improved creep properties of directional solidification blades allowed engine temperatures to be increased by approximately 50°C with further improvement in efficiency. Building upon directional solidification, Pratt and Whitney reached the goal of eliminating turbine airfoil grain boundaries in the late 1960s. Single crystal blades are grown by incorporating a geometrical construction called a 'pigtail' into the base of the mould. The pigtail is attached to the 'starter' crystal and is helical in construction. It admits only a few columnar crystals from the starter and only allows one crystal to emerge into the blade root, to start the single crystal structure of the airfoil itself.

Strengths and weakness of Single crystal Super alloys turbine blades

Complete elimination of grain boundaries has further advantages. A blade without grain boundaries is a single crystal. Creep resistance is improved and because there are no grain boundaries, the grain boundary strengtheners such as Carbon, Boron, Zirconium and Hafnium used in early super-alloys are not needed. All these elements contributed to the lowering of the melting point of the blade. The development of single crystal blades has increased the melting temperatures of turbine blades by a further 150°C → 200°C. Operating at temperatures above 1800°F (1100 °C), alone make them susceptible to high temperature corrosion attack with air contaminants and reactive alloying elements in its matrix.

(Oxidation at $<950^{\circ}\text{C}$ occur forming surface oxides plus sub-surface penetration of oxides and sulfides)

There are two different types of Hot corrosion can take place in turbine system due to the presence of contaminants found in intake air in the system. There are always contaminants in gas phase in oil and gas operations and they are of a concern if they are released relatively near the gas turbine. Some examples of gas contaminants are ammonia, chlorine, hydrocarbon gases, sulfur in the form of H_2S or SO_2 , and discharge from oil cooler vents or local exhaust stacks. Gas phase contaminants cannot be removed by mechanical filtration. As long as gas contaminants remain in the gas phase, they will not impact the gas turbine. However, if they interact with liquid, they will be partially absorbed and can lead to degradation.

Liquid contaminants are present as aerosols. Aerosols may be generated by condensation of vapor phase mixtures as mentioned above or by liquid agitation. Some common sources of aerosols are cooling tower drift, wave action at coastal sites, condensation of moist exhaust plumes in cold weather, petrochemical discharges, rain, fog, and chiller condensates. The components contained in these contaminants that are detrimental to the gas turbine are chloride salts in water, nitrates, sulfates, and hydrocarbons and they can cause permanent damage to the gas turbine. One of the most important contaminants ingested by the gas turbine, typically in aerosol form, is salt. Salt can be ingested as dry particles, but in this case, the fiber filters can adequately remove it from the airstream. Salt absorbed by liquid aerosols, mainly water, cannot be appropriately stopped. Combination of gas phase contaminants and in the presence of Salts and heat can form many other combination of contaminants such as Na_2SO_4 , Cr_2O_3 , NiSO_4 and $\text{Cr}_2(\text{SO}_4)_3$ etc.

Type I - Hot Corrosion

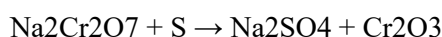
Molten salt induced corrosion happen between $880-950^{\circ}\text{C}$.

- Producing non-protective oxide scales formation;
- Internal sulphidation and depletion of protective scale forming elements such as Al and Cr.

Type II - Hot Corrosion

This molten chloride salt induced corrosion, in the presence of SO_3 . This mechanism happens in the turbines combustion gas area between the temperatures of $650-880^{\circ}\text{C}$. This is a localized pitting form of corrosion attack. In reality the attack starts already at the melting point of Na_2SO_4 and continues to temperatures up to 1150°C . The presence of corrosion products of Co, Cr on the vicinity of the broken blades was identified our corrosion scientists.

NaCl is a solid at room temperature; with a very high melting point (801°C) at its melting point it releases the elements sodium and chlorine. The reverse reaction, combining the elements sodium and chlorine Sodium-sulphate is formed by the fusion of sodium carbonate with sulphur at around $600-900^{\circ}\text{C}$ in the presence of air (source of oxygen):



We carried out microstructural investigation of the Type-II hot corrosion on the same single crystal Ni-based super-alloy (CMSX-4) in a flowing O₂–SO₂–SO₃ atmosphere at 700,800 and 960C. Corrosion occurred by rapid dissolution of the alloy by molten sulfate eutectics, forming an outer layer rich in Co and Ni and an inner layer rich in Cr and Al. The outer layer transformed into mixed oxides of Co and Ni, with concurrent evolution of the continuous S-rich inner layer. A multicomponent analysis provides us the insight into diffusional interactions among Co, Ni, and S.

High temperature corrosion induced cracking behaviour of CMSX 4.

Many Ni-base super-alloys such as CMSX 4 show a time dependent behaviour of crack growth at elevated temperatures above 500°C. The environmental interaction at the crack tip plays an important role on the crack growth rate, and the stress assisted grain boundary oxidation (SAGBO) is the acting mechanism for these alloys cracking in air. In this research, the SAGBO effect on the creep crack growth behaviour of fatigue pre-cracked single edge-notched (SEN) CMSX specimens tested in air and oxygen-free environments is investigated. High temperature moiré interferometry (HTMI) was applied to obtain in-situ crack tip displacement fields of the test specimens at 650°C under constant loading conditions.

The diffusion of oxygen along grain boundaries in front of the crack tip governs the size and degree of environmental damage. The formation of a SAGBO-induced damage zone at the crack tip causes the cracking in a brittle mode as verified by our experimental results. The damage zone induces inter-granular fracture and accelerates the crack growth rate. The coarsening of the damage zone is a linear function with time under given temperatures, oxygen partial pressure, and stress intensity factor.

During casting of CMSX 4 Blades a pre-fabricated seed is used to nucleate the desired orientation. During casting the top portion of the seed is partially melted and this mushy zone could contribute to the origin of defect stray grains. A number of seeds cast at Rolls- Royce CRDF that exhibit extensive defect grain formation in the melt-back region have been analysed using optical and electron microscopy techniques. These defect grains were found to nucleate exclusively at the casting surface where the alloy contacts the mould. Nucleation of the defect grains is a transient behaviour, it occurs only during the preliminary stages of withdrawal. After this time, no further defect grain nucleation was observed. Due to growth propensity effects, non-axially oriented seeds exhibit more prolific defect grains towards one side of the casting.

The benefits of single-crystal, over conventionally cast and directionally-solidified, components critically depends on being able avoid the introduction of casting defects, such as stray grains, freckles or deviations from the required crystal orientation. Otherwise, either the property specifications must be relaxed or an economically unacceptable scrap-rate must be accepted. Two aspects of single-crystal superalloy development have increased the likelihood of solidification defects forming in industrial practice:

The refractory element additions, such as Rhenium, added to Second and Third generation SX super-alloys to enhance the creep performance and alloy stability in service, have had a detrimental effect on their casting characteristics. This has led to difficulties in controlling the single crystal orientation and to an increased occurrence of stray grains and freckle chains. The thermal conditions in producing large castings for industrial gas turbines are quite different from those experienced in the manufacture of turbine blades for aero-engines. In

particular, the critical solidification parameters, temperature gradient and solidification rate are significantly reduced and the solidification front tends to be macroscopically curved, rather than planar. These factors combine to produce conditions where solidification defects are more likely to occur.

Findings

All turbines are subjected to cyclic loading, which give rise to combined creep and fatigue.

Failure will occur if any part is subjected fatigue outside its threshold limit. Mechanical fatigue is predominant at low temperature Low cyclic fatigue (LCF) predominant at elevated temperatures due to creep. Most fatigue induced failures in turbines blades is due to interactions between high temperature oxidation and low cyclic fatigue cracking. If the applied load at this temperature High enough to cause the formation of slip-bands in its matrix, Low cyclic fatigue (LCF), results in crack formation & failure. This failure is inter-granular on the polycrystalline material. To avoid this turbine must be operate at least 0.7% below its fatigue initiation threshold

Conclusion

In conclusion it was derived that the turbine blades failure was due combination of factors given below they are:

- Time to time turbine blades were operating outside their thresh hold limits.
- Uncoated surfaces and poor filtration of airflow was contributing for surface damage due to high temperature corrosion and abrasion.
- Continues operation of the turbines was contributing cumulative strain holding on the blades while freezing stresses in the matrix.

With these findings in the hand the manufacturer was directed to establish the best-fit solution for the present problems.

Creep crack growth behaviour in nickel-base super-alloys has been widely reported to be environmentally sensitive. Creep crack growth rates can be as much as 1000 times faster in air than in vacuum or inert gaseous environment. Additionally, the incubation time for crack growth has been shown to be vastly greater in the inert environment than in air. Two strong interactive mechanisms are responsible for much of the inter-granular cracking, which is the weakest link in IN718 as well as most other nickel-base super-alloys at elevated temperatures. These are slip induced inter-granular cracking and oxidation assisted crack growth.' Some of the original theories behind oxidation assisted crack growth hypothesized that cavitation attributed to the enhanced crack growth. However, upon further research, Gao, et al.,⁴ pointed out that environmentally enhanced cavitation cannot be the dominant mechanism for enhanced creep crack growth, and an alternate mechanism needs to be examined.

A new hypothesis is that the formation of oxides, possibly niobium oxide, forms on the grain boundaries ahead of the crack tip which leads to the brittle inter-granular fracture, i.e. (SAGBO) embrittlement. To verify this theory, one must first explain how an abundance of niobium is present in the grain boundaries. There are several possibilities to elucidate this phenomenon. First, niobium may segregate at grain boundaries of poly-crystals during heat treatment. Research has shown that it is possible to have as much as four times the amount of niobium on the grain boundaries as compared to the bulk percentage after heat treatment.⁵

Also, the possible decomposition of niobium carbide particles may supply excess niobium to the grain boundary. Gao, et. al.,⁴ have shown that some types of niobium carbides do indeed react with the environment as evidenced by the "feathery" appearance of these carbides when

viewed using a scanning electron microscope. Also, preferential formation of δ phase at the grain boundary could occur during aging.

In conclusion it was derived that the turbine blades failure was due combination of factors given below they are:

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What was our recommendations :

- Limit the operational loading limit 15% under the fatigue thresh hold.
- Selecting the right coating for application
- Introduce controlled intervals between maintenance.
- Regular Condition assessment.
- Dynamic Testing and Monitoring.
- Corrosion Control and Environmental Chemistry Monitoring.
- Remaining life prediction – Routine lifetime evaluations based upon condition.

Where do we go from here?

The rationale behind the work is that Ni-based super-alloys (NBSAs) are reaching their temperature limit, and despite improvements with the higher-generation alloys, the improvements are slowing down, and the last 24 years have produced an increase of approximately 100°C¹⁸. There have already been improvements with design, using forced air-cooling, and huge benefits from using coatings, which have an insulating outer layer. Both of these techniques are expensive and can have disastrous effects if they fail, for example, if the coating fails locally. Thus, there has been a push to develop a totally new suite of materials, and platinum-based alloys are one possible solution. Platinum was selected because it has the same FCC structure as Ni, but a higher melting point¹⁹, similar chemistry, and better oxidation and corrosion resistance²⁰. The earlier work has already shown that the same microstructure as the NBSAs could be attained, although the volume of the strengthening precipitate was much less¹⁻⁷, and that the corrosion resistance was much better²¹. The work soon identified Pt-Al as the best system both for beneficial microstructures and for formation of the protecting alumina film and ternary additions were studied. The best ternary alloys were Pt-Al-Cr and Pt-Al-Ru, and these were then combined^{5,22}. The target temperature of the Pt-based alloys is 1300°C, which is about 200°C higher than the currently-used NBSAs, and the optimum composition was Pt-11Al-3Cr-2Ru (at.%). The effect of heat treatment was studied³⁻⁷. However, the problems of the high expense and density remained.

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