SUPERALLOYS - THE UTILITY GAS TURBINE PERSPECTIVE

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Abstract

The growing market for large utility gas turbines (UGTs) in recent years has rekindled competition for high efficiency, costeffective large units. This, in turn, has accelerated the introduction of advanced superalloys and coatings narrowing the temperature gap with aeroturbines. The significant differences between aeroturbines and UGTs in size, operating environment and duty requirements create superalloy challenges that are unique to UGTs.

The superalloy related development needs for UGT blades, vanes and discs are discussed with reference to alloy composition, manufacturing processes, corrosion/oxidation, coatings, inspection, rejuvenation and repair. Minimum life cycle cost, the key market driver, dictates the need for advances in each of these fields. The current status and the approaches for achieving these advances are reviewed.

Background

Growth of Utility Gas Turbine Industry

Electric power consumption per capita has grown (Figure 1)⁽¹⁾ steadily in the USA and is projected to grow even more in future. Industrialization, electrical appliances, heating/air conditioning and more recently computerization have each been contributing factors. Worldwide growth in per capita consumption and population have increased the demand for electric power. Considering that several population intense countries such as China and India are still at the low end of per capita power consumption and advanced technologies are being introduced at a phenomenal pace, it is expected that the need for additional power generation will accelerate rapidly.



Figure 1: Growth of per capita power consumption in USA⁽¹⁾

This power demand has been met through several different resources. Fossil fuel has dominated (Figure 2) and is expected to do so for the foreseeable future. Some growth is expected in hydro power worldwide, but the growth of nuclear power is expected to continue to be limited to a few countries. Solar and wind power, although politically popular, are not significant sources and their role is not expected to change.



Figure 2: Sources of world power generation

Historically, steam turbines have dominated fossil power production with gas turbines filling only peak power needs because of their rapid start-up capability. Pollution concerns with coal, coupled with the abundant cost effective supply of gas and emergence of combined cycle technology, have, however, propelled gas turbines to the forefront as the major source of new base load capacity. The near 60% efficiency of combined cycle plants far exceeds that achieved by either steam turbine or gas turbine plants alone. Consequently, new gas turbine capacity is expected to grow rapidly (Figure 3) throughout the world with USA and Asia clearly dominating.



Figure 3: UGT growth by region

Superalloys 2000 Edited by T.M. Pollock, R.D. Kissinger, R.R. Bowman, K.A. Green, M. McLean, S. Olson, and J.J. Schirra TMS (The Minerals, Metals & Materials Society), 2000 The size of combined cycle plants is steadily increasing (Figure 4), approaching that of medium sized steam turbine plants. Also, gas turbine temperature (Rotor Inlet Temperature) and efficiency have almost doubled over the last forty years (Figure 5) primarily as a result of better high temperature materials, more effective cooling designs and aerodynamically more efficient airfoils. This growth in size and efficiency are expected to continue.



Figure 4: Evolution of UGT plant size



Figure 5: Historical increase in UGT efficiency and R.I.T.

The amount of superalloys used in UGT units has steadily increased (Figure 6) with the increase in unit size. This, combined with the increased demand for UGTs, has created a dramatic surge in the total quantity of superalloys consumed by UGTs. UGT sales^(1a) and share of the total gas turbine market rose sharply in 1999 over the previous year. Sales increased from \$8.5B to \$13.0B and market share from 30% to 38%. By contrast, aeroengine market share^(1a) actually declined (65% to 59%) despite a growth in the absolute value of sales (\$18.0B to \$20.0B). UGTs are expected to dominate the gas turbine market in the coming years. The focus of the superalloy industry, which historically has been only on aeroengines, must now shift towards UGTs. This shaft has already begun and it is significantly changing the outlook of superalloy manufacturers.



Figure 6: Increase in superalloy consumption per UGT

Customer Needs, Market Drivers and Materials Requirements for Utility Gas Turbines

Surplus new unit manufacturing capacity, despite greater demand for power production, has kept the market highly competitive. Competition is fierce due to deregulation and globalization. To succeed in this highly competitive market, engine manufacturers must have a clear understanding of customer needs, the associated critical market drivers and the resulting critical materials requirements. Needs and market drivers vary from customer to customer and country to country. The needs, market drivers and critical materials requirements common to most customers are summarized in Table I and discussed in this section.

Table I – Customer Needs, Market Drivers and Critical Materials Requirements for UGTs

Customer	Market	Critical Materials	
Need	Driver	Requirements	
Regulations	Emission Levels	HT Materials to In-	
Compliance		crease Efficiency and	
		Reduce Cooling Air	
Low Plant	Size	Manufacturability of	
Cost		Blades Vanes, Discs	
Low Fuel	Efficiency, Fuel	HT Materials, Corro-	
Cost	Flexibility	sion Control	
Low Main-	Reliability,	Inspections, Life Exten-	
tenance Cost	Maintenance	sion	
Short Project	Cycle Time	Material, Process and	
Time	-	Component Behavior	
		Modeling	

<u>Regulations Compliance</u> - A critical regulation that customers must meet to obtain an operating permit concerns emission limits. While the percentage of emissions is controlled through the combustion process, improved engine efficiency reduces the amount of fuel needed per MW of power thereby reducing their total amount. Emissions can also be lowered if the materials allow the amount of cooling air to be reduced. The net result is a need for better higher temperature materials.

Low Plant Cost - Plant cost is affected by unit size. Generally, plant cost/MW decreases with increase in engine size, but increase in engine size means bigger components. The manufac-

ture of large blades, vanes and discs from nickel based superalloys, particularly directionally solidified (DS, SC) blades and vanes, pose serious challenges of cost and quality.

Low Fuel Cost - With deregulation of the power industry, power producers will no longer be able to transfer fuel cost directly to consumers. The lowest fuel cost is achieved by the most efficient engines capable of operating with a wide variety of fuels. The implication of higher efficiency is the need for new materials of higher temperature capability. Fuel flexibility requires understanding the corrosion phenomenon and developing corrosion resistant coatings.

Low Maintenance Cost - Initial plant and fuel costs are very important, but to achieve the lowest life cycle cost, the equipment must be reliable and easy to maintain. In-service inspection, rejuvenation and repair are all critical elements of low maintenance cost.

<u>Short Project Time</u> - There is greater and greater emphasis on reducing the total project time for new plants. Return on investment begins only after the project is complete and commercialization has begun. While concurrent engineering has helped reduce project time, computer modeling of new alloys, their processing and component behavior will shorten the development cycle of new materials and lower costs by eliminating a large number of trial and error experiments.

The Use of Aerotechnology for Utility Gas Turbines

Since the aeroindustry has traditionally been the major user of superalloys, especially advanced superalloys, it has been the primary focus of the superalloy industry. The cold war drove new technologies for high performance military aeroengines and major advances were made in new superalloy compositions, processing technologies and solidification structures. The logical question that arises is, "Can the technology needs of UGTs be met through the advances already made in the aeroindustry?" The answer is not a simple "yes" or "no". The answer cannot be categorical because of the differing requirements of aeroengines and utility gas turbines. The key differences are summarized in Table II and discussed briefly below.

Table II – Key Differences Between the Requirements of Aeroturbines and Utility Gas Turbines

Parameter	Aeroengine	UGT
Weight	Very Important	Not Significant
Operating Time, Hours Steady State Peak Temperature	25,000 < 1000	> 100,000 > 100,000
Cyclic Duty	Severe	Severe
Environment	Non Corrosive	Corrosive
Size	Small	Large

<u>Weight</u> - Weight is a critical parameter in aeroengines. The development and selection of aeromaterials is constrained by the need to consider alloy density, coating thickness and dimensional tolerances. Since weight is not of prime importance in UGTs, aeromaterials developed solely for weight considerations are of no direct relevance.

<u>Operating Time</u> - The highest temperature experienced by aeroturbines is during the brief take-off period and the total time at peak temperature over the life of the engine is less than 1,000 hours. During cruise, the aeroturbine actually operates at temperatures significantly lower than those during the steady state operation of UGTs. Cruise time over the life of the aeroengine is expected to total about 25,000 hours contrasting with the 100,000 + hours of steady state operation by UGTs. Thus, long term alloy stability, extrapolation of properties and interaction of creep and fatigue are much more critical for UGTs than for aeroengines.

Cyclic Duty - Both UGTs and aeroturbines must have adequate cyclic capability. While maximum temperature and strain are high, the hold period (take-off time) for aeroengines is very short (minutes). In contrast, UGTs operate at higher strain for days and weeks, especially for base load operation, making the interaction of creep and fatigue a much more severe damage mechanism.

<u>Environment</u> - Fuel quality in aeroengines is generally high and relatively free of corrosive elements such as vanadium, sulphur etc. Fuel quality in UGTs, however, varies considerably from plant to plant, region to region and country to country. These variations must be considered during design and operation in order to minimize corrosion and improve reliability.

<u>Size</u> - The most significant difference between aeroturbines and UGTs is size. Typical first stage blades for aeroturbines and UGTs are compared in Figure 7. All UGT dimensions are generally 2-3 times larger so that blades are 20-30 times heavier. Similarly, disc sizes (diameter and thickness) are also much bigger. This size/weight difference has an immense impact on component manufacturability and cost.



Figure 7: Comparison of typical Row 1 blades

Superalloy Challenges for Utility Gas Turbines

The UGT materials requirements discussed above pose major challenges to the superalloy industry. These include high temperature capability, processing SC materials for large blades and vanes, processing large disc materials, corrosion resistance, advanced thermal barrier coatings, advanced inspection techniques, life extension and computer modeling. The current status and implications of each of these challenges for the industry is discussed.

High Temperature Capability

The high-temperature oxidation resistance of Ni-Cr alloys was recognized in the early 1900's and the superalloy containing about 20% Cr has been a principal material for electrical heating elements ever since⁽²⁾. The discovery that these Ni-Cr alloys could be strengthened by the coherent precipitation of Ni₃ (Al, Ti) led to the development of the modern gamma prime (γ') strengthened superalloys. Increasing the volume fraction of γ' required the reduction of chromium. Although higher creep resistance could be achieved with reduced chromium levels, this resulted in both a loss of solid solution strengthening and oxidation resistance. The addition of molybdenum for solid solution strengthening and aluminum for oxidation resistance initially compensated for the reduced chromium, but it was quickly recognized that chromium levels around 15% were needed⁽²⁾ to avoid the onset of hot corrosion. Molybdenum levels above approximately 3.5wt% were also found to be harmful to hot corrosion resistance, leading to the substitution of some molybdenum by other refractory metals such as tungsten, tantalum and niobium⁽³⁾. Grain boundary carbides play a major role in the control of creep and fracture behavior and can be modified by heat treatment and by the addition of minor constituents such as boron and zirconium. Hafnium is also a strong carbide former and is added to polycrystalline alloys to improve grain-boundary ductility(4).

Until recently, UGT hot section components where type II corrosion dominates, were made of superalloys containing high chromium (chromia formers). The lower chromium, higher aluminum containing alloys (alumina formers) were developed for aeroturbines, where gas stream temperatures are higher and oxidation concerns dominant. As firing temperatures of UGTs continued to increase, the emphasis shifted from modifying the composition of equiaxed alloys to controlling grain structure (Figure 8), as in the case of aeroturbines some twenty five years ago⁽⁵⁾.



Figure 8: Increase in temperature capability of superalloys in UGTs

Directionally solidified (DS) and single crystal (SC) superalloys for blades and vanes are being introduced (Figure 9). Single crystals derive their beneficial properties from the absence of grain boundaries and, in directionally solidified nickel base superalloys, their preferred low elastic modulus in [100] orientation. The absence of grain boundaries eliminates preferred sites for crack nucleation under fatigue and thermomechanical fatigue conditions. Under creep conditions, the absence of grain boundaries not only removes the preferred sites for fracture initiation but also removes a potential mechanism of high temperature deformation, specifically grain boundary sliding.



Figure 9: Evolution of grain structures in UGT blades

The first generation single crystals were without any rhenium additions. Since then, second and third generation single crystals have been developed containing 3% and 6% Re respectively. Although single crystals find widespread applications in aeroturbines, the castability of large single crystal blades and vanes (discussed later) poses some unique challenges for UGTs.

Processing Single Crystal Materials for Blades and Vanes

The directionally solidified (DS & SC) structures deliver excellent properties but their processing is not without challenges. This is particularly true for the large blades and vanes used for UGTs. Because of these challenges efforts are ongoing to improve conventional SC casting processes and develop alternate processes.

This section discusses the conventional SC manufacturing process, its limitations, ways to overcome some of these limitations, and alternate processes for producing cost effective defect-free blades and vanes.

<u>Conventional SC Manufacturing Process</u> - The conventional Bridgman process for manufacturing single crystal blades and vanes has been used extensively for applications in aeroturbines. When used for large UGT parts, the result is very low yield due to distortion and cracking of the core, shell rupture, mold-metal reaction and numerous crystal defects. Figure 10 shows a large single crystal UGT blade with various defects. Continued improvement of the efficiency necessary for reducing emissions and lowering fuel costs depends on finding cost effective ways to manufacture these large blades and vanes in directionally solidified structures. Some of the approaches are discussed below:



Figure 10: Casting defects in a large single crystal UGT blade

<u>Better Core and Shell Materials</u> - Since a much larger volume of molten metal is required, there is a significant increase in the hydrostatic pressure on molds. Also, the longer solidification time increases mold-metal reactions and causes creep deformation of cores. To overcome these problems, it is necessary to develop shell systems and core materials that have greater high temperature strength and dimensional stability. The high shell strength has to be carefully balanced against the increased strain and corresponding propensity for recrystallized grains in castings.

<u>Thermal Management</u> - The crystal structure during directional solidification is controlled by growth rate and temperature gradient. Successful casting of single crystals therefore depends on proper thermal management during solidification. Historically this has been achieved through trial and error based on prior experience. The solidification modeling of the system allows optimization of the numerous parameters that control the growth rate and temperature gradient. Section size, mold clusters, mold wall thickness and conductivity, baffle design, withdrawal rates etc. all play an important role and the optimum combination of parameters for a given blade/vane geometry must be established.

<u>Defect Tolerance</u> - In producing real parts for engines there must be a trade-off between the need to accept only defect-free parts for optimum material performance and the need to allow some level of defects for realistic commercial production. Many different types of defects can be formed in a cast and heat treated single crystal part. Figure 11 illustrates typical defects that are found in such single crystal castings. Just as the preferred orientation and absence of grain boundaries enhance single crystal properties, the misorientation and presence of grain boundaries degrade them.



Figure 11: Typical defects in single crystal castings

In casting large single crystals, it is impossible to maintain perfect [001] crystal orientation. Mold geometry and the difficulty in controlling furnace baffling mean that [001] crystal growth cannot be maintained parallel to the desired axis at all locations within a part. Thus, parts must be accepted with orientations that lie close to but not exactly parallel to the preferred [001] axis.

High angle grain boundaries and multiple boundaries such as recrystallized regions and freckle chains, are obvious sources of weakness. These defects are particularly pernicious since the single crystal formulations do not contain the grain boundary strengtheners found in conventional alloys. In such cases the supposedly single crystal alloys will be even weaker than their conventionally cast counter-parts and the property deficit relative to expected single crystal properties can be catastrophic.

Considered less deleterious are the low angle grain boundaries (LABs) that form between essentially parallel single crystals. LABs are very difficult to avoid in large castings and for the sake of commercial viability some levels of LABs are always accepted. Their impact on properties is significant, although difficult to quantify precisely. Traditionally, the acceptance of LABs has been based on a philosophy similar to the effect of misorientation, the deleterious effects of LABs being related to the severity of the misorientation across the boundary.

The aeroindustry has established acceptance limits for various defects. Since minimum property requirements for UGTs differ from those for aeroturbines and critical property requirements vary from location to location within large UGT components, it seems prudent to reassess and indeed customize the prevailing aeroengine acceptance standards.

<u>Alloy Optimization</u> - The evolution of DS and SC alloys has been governed by their high temperature strength without much consideration for the manufacturability of large UGT blades/vanes. Alloys that are less susceptible to casting defects and less sensitive to grain defects need to be developed. The absence of any grain boundary strengtheners in SC alloys make them particularly sensitive to grain defects. Additions of small amounts of grain boundary strengtheners may provide a better alloy balance. Cannon Muskegon have developed^(6,7) a second generation DS alloy called CM186. They have manufactured SC components from this alloy which contains C, B, Zr and Hf and found it to be less sensitive to heat treatment and low angle boundaries. However, under such conditions, the ability to fully solution heat treat has to be sacrificed. Effectively, a further trade-off between performance and yield has to be made.

<u>Alternate SC Manufacturing Processes</u> – Alternate manufacturing processes are being developed because advances in the conventional SC manufacturing process may not fully meet the quality and size demands of advanced UGTs. Two of these alternate processes, liquid metal cooling and transient liquid phase bonding, are reviewed.

Liquid Metal Cooling - Since many of the SC yield detractors in the conventional process result from low thermal gradient, slow growth rate and long solidification time, the use of liquid metal (Al, Sn) as a cooling medium holds great promise for casting large SC components. Figure 12 shows⁽⁸⁾ a schematic comparison of the conventional Bridgman process and the liquid metal cooling (LMC) process. LMC has numerous advantages, the main one being increased thermal transfer due to conductive rather than radiative cooling. It has been shown (9) that heat transfer rates for LMC are three times faster than those obtained with radiation cooling in the Bridgman process. Also, since the liquid metal is in equal contact with every individual mold, view factor effects are minimized and greater part to part consistency is expected. The increased withdrawal rate due to the higher thermal gradient decreases the time for mold-metal reaction and increases the rate of production. Minimum mold spacing allows more pieces to be cast at one time, further improving the economics.



Figure 12: Conventional and liquid metal cooling processes⁽⁸⁾

Compared with parts cast by the Bridgman process, parts cast by LMC have⁽¹⁰⁾ a much finer dendrite arm spacing (less than half). The benefits of finer arm spacing are reduced heat treatment time, a more uniform microstructure and improved mechanical properties due to less $\gamma - \gamma'$ eutectic.

<u>Transient Liquid Phase Bonding</u> - In this approach, small, easily castable segments of the blade/vane are produced as separate single crystal pieces and joined together to form the complete structure ⁽¹¹⁾. For this purpose, a very high quality joining process that can regenerate the optimum single crystal structure and properties across the bondline is required.

Transient Liquid Phase bonding is a high quality precision bonding technology that has been shown⁽¹²⁾ to be capable of bonding Nickel-based superalloy single crystals for turbine applications. This process uses a bonding medium that is compositionally matched to the material to be bonded but containing a small amount of a melting point depressant element such as Boron. It is also critical that the melting point depressant exhibit high solid state diffusivity in the alloy. By using only a very thin layer of bonding medium, a bond region can be formed by isothermal solidification which exhibits not only the same chemistry as the substrate, but also the same crystallography and fine scale microstructure. The principle of this process is shown in Figure 13⁽¹³⁾. Figure 14 illustrates ⁽¹²⁾ how well matched bond zone and base material chemistries can be achieved when the Transient Liquid Phase bonding process is controlled.



Figure 13: Principle of transient liquid phase bonding⁽¹³⁾



Figure 14: Microprobe analysis across the transient liquid phase bonded CMSX-4 single crystal bond region

For a bond region to demonstrate the same high level of mechanical properties as the original single crystal, not only must the bond region chemistry match that of the rest of the single crystal but the component must also be properly heat treated to produce the optimum $\gamma - \gamma'$ morphology. Specifically, for the second generation single crystal alloys the morphology of the γ' should consist of cuboidal particles of about 0.5 microns on edge and a secondary dispersion of finer spheroidal particles. Figure 15 demonstrates ⁽¹²⁾ that the appropriate post bonding solution heat treatment and subsequent precipitation aging treatment can create a bond line microstructure indistinguishable from the interior regions of the unbonded single crystals. Thus, proper bonding chemistry, bonding cycle and post bonding heat treatment not only generate the optimum microstructure in bonded materials but also produces mechanical properties close to those of the base material.⁽¹²⁾



Figure 15: Gamma-prime morphology of a) bond zone and b) base material in bonded CMSX-4 single crystal

While high levels of mechanical properties can be achieved in transient liquid phase bonded materials including single crystals, such properties are not always needed in real components. Most often, the full capabilities of advanced materials are needed at only a few critical locations in a blade or vane. At many other locations the imposed temperatures and stresses allow material properties to be well below those needed for critical locations. Thus, judicious placement of the bond in a low stress region will provide considerable margin in using transient liquid phase bonding.

Finally, process engineering practices for handling the large components used in UGTs are required. In contrast to aircraft gas turbines, the blade and vanes of UGTs can be over thirty inches in length and weigh several tens of pounds. Handling such parts for bonding is not a trivial task.

Processing Turbine Discs

Although superalloy discs are common in aeroengines, they are less frequently used in UGTs for a number of reasons⁽³⁾. First, rotating blades have a long shank between the platform and the root, keeping the dove-tailed root setion of the disc away from the hot gas path and enabling it to operate at significantly lower temperatures than those observed in aircraft engines. Second, although the utility turbine discs can have very large diameters, weight is not a consideration. Increased section size can therefore be used to reduce stress levels. Third, the difficulty of manufacturing large superalloy ingots lowers yield and increases cost.

The higher firing temperatures and pressure ratios of the latest generation UGTs have led some engine manufacturers to use superalloy discs. Alloy 718 is the most widely used superalloy for aerospace disc applications, but high niobium levels create 'freckle' problems (regions of positive macrosegregation) in the large diameter ingots required for UGT discs. Alloy 706 has been developed to allow the production of ingots larger than those of alloy 718 without segregation problems. Ingots with diameters as large as 1,016mm (40 inches) have been successfully cast in alloy 706⁽¹⁴⁾.

Corrosion Resistance

Although most gas turbines operate with clean gas fuel, variable oil quality and diverse ambient environments create potential for severe corrosion damage in hot parts. The corrosion concern is much more severe in UGTs than aeroturbines since the latter use high quality fuels. Also, the potential use of steam as a cooling medium in advanced UGTs requires thorough evaluation of its impact on oxidation and the effect of steam borne impurities. Details of steam cooling, corrosion resistant materials and oxidation/corrosion resistant coatings are discussed in this section.

<u>Steam Cooling</u> - The advanced UGT engines are expected to use closed-loop steam cooling for transitions and the early stages of vanes. Closed-loop steam cooling increases plant efficiency by eliminating the need for cooling air injection into the turbine flow path. Steam is a more effective cooling medium and the heat removed while cooling the components is recovered in the combined cycle steam turbine.

There are challenges to the successful use of closed-loop steam cooling. These include preventing corrosion and spalling of corrosion products over long periods of time, blockage of closed-loop cooling channels due to corrosion product outward growth, and loss of mechanical properties due to thickness loss. Also, common impurities in steam such as NaC1, Na₂SO₄, Na₃PO₄, SiO₂ and metal oxides may deposit inside the cooling holes leading to component failure from corrosion and / or blockage.

Steam passes through pipes, flanges, valves, blade ring and manifolds before being introduced into the vanes and transition cooling channels. Spallation of corrosion and oxidation products in these components carried by the steam may lead to cooling channel blockage in vanes and transitions. Therefore, in addition to vane and transition materials, the balance of plant materials need to be evaluated in high-temperature steam as well as in the presence of salt impurities.

<u>Corrosion Resistant Materials</u> - Until recently, high chromium alloys were commonly used to combat hot corrosion in UGTs. To meet the high temperature strength requirements of increased firing temperatures, the chromium contents have been gradually decreased and the inherent loss in corrosion resistance compensated by application of oxidation/corrosion resistant coatings. There are isolated cases of some high chromium single crystal alloys such as AF56 and PWA1483. More recently, Cannon Muskegon have developed⁽¹⁵⁾ two new SC alloys CMSX11B and CMSX11C containing 12% and 14% chromium respectively. To the author's knowledge, these alloys have not yet been used.

Oxidation/Corrosion Resistant Coatings - In the early years of superalloy development, a majority of the coatings that provided oxidation and corrosion resistance were diffusion aluminide coatings. These were initially obtained by a pack cementation $process^{(16)}$ and more recently, by chemical vapor deposition processes⁽¹⁷⁾. The diffusion aluminide coatings possess excellent isothermal high temperature oxidation resistance but moderate to poor cyclic oxidation resistance, hot corrosion resistance and thermal fatigue resistance. To overcome the limitations of the diffusion aluminide coatings, overlay coatings were developed which were sprayed on to the part either by plasma spray processes or by physical vapor deposition. The overlay coatings provided a much larger aluminum reservoir for the oxidation resistance and also had superior mechanical properties (18,19). The overlay coatings are denoted as MCrAlY, in which M represents a base metal of Ni, Co, Fe or some combination of these elements and Y represents a rare earth element, such as yttrium. In these alloys, A1 provides the oxidation resistance, Cr increases the chemical activity of A1, Y improves adherence of the oxide scale to the bond coat and M provides compatibility with the substrate alloy. A typical microstructure of an MCrAIY coating on a superalloy substrate is shown in Figure 16. The outer surface consists of an oxide scale which, ideally, is slow growing and dense to prevent direct reaction of gases and deposits with the coating alloy. Since the protective scale on an MCrAlY coating is achieved by selective oxidation of A1 in the alloy, the materials immediately beneath the scale will be depleted in A1 content. A similar depletion zone is expected at the substrate/coating interface due to diffusion of A1 into the substrate. Based on superior fatigue and oxidation data across several substrate-bond coat systems, these coatings are used in most hot section components in utility gas turbines.



Figure 16: Typical MCrAly coating after thermal exposure

Advanced Thermal Barrier Coatings

As discussed earlier, significant increase in superalloy temperature capabilities has been achieved over the years through compositional modifications, process changes and structural controls. The third generation SC alloys are approaching the practical upper limit of temperature. Considering that manufacturing large UGT SC parts even with simpler alloys is a major challenge, the second and third generation alloys become virtually impossible to produce. It is therefore unlikely that additional advances in superalloy temperature capability can be realized by further modifications of superalloy compositions and structures. The next materials system for improved temperature capability is ceramic or ceramic matrix composites (CMCs). Despite many years of effort on ceramic systems, considerable research and development is still required before CMCs are commonly used in UGTs. The temperature capability gap between superalloys and CMCs has to be filled and the only viable means for doing so is the use of thermal barrier coatings (TBCs).



The thermal barrier coating system consists of a metallic bond coat and a ceramic thermal barrier coating (Figure 17). The bond coat provides oxidation and corrosion resistance by forming a slow growing adherent protective aluminum oxide scale, whereas the ceramic top layer reduces the substrate alloy temperature.

Figure 17: A thermal barrier coating system

Depending on the ceramic thickness and cooling effectiveness, substrate temperatures can be reduced by 100° - 300°F allowing a significant reduction in cooling air, and consequent increase in engine efficiency. The ceramic top coats are deposited on to the MCrAlY coatings, which function as a physical and chemical bond between the thermal barrier coating and the substrate (Figures 18-19). The current industrial standard for a ceramic thermal barrier coating is 8wt% yttria stabilized zirconia (8YSZ) deposited by air plasma spraying (APS) and electron beam physical vapor deposition (EB-PVD). Although, both coatings act as thermal insulators, their microstructures are fundamentally different from each other and so are their performances and application temperatures. APS coatings obtain their strain tolerance from gaps between the intersplat boundaries and vertical microcracks within the ceramic splats (Figure 18). A coating more tolerant to strains induced from thermal cycling can be obtained by EB-PVD. EB-PVD coatings have a columnar microstructure with intercolumnar gaps (Figure 19), which lend themselves to superior strain tolerance at temperatures higher than those of APS coatings. The higher performance of the EB-PVD coatings is, however, available only at an increased cost.



Figure 18: Air plasma sprayed thermal barrier coating



Figure 19: EB-PVD thermal barrier coating

With an increase in bond coat temperature, oxidation induced failure of the TBC system is expected to occur more rapidly. Depletion of aluminum in the bond coat is more rapid because of the increased growth kinetics of the aluminum oxide and interdiffusion with the substrate alloy. This severely degrades the ability of the MCrAIY coating to function as an oxidation resistant coating. The increased thickness of the thermally grown oxide (TGO) also results in the spallation of the TBC.

The thermal barrier coating, 8YSZ, is also vulnerable to the increased operational temperatures due to sintering of the intersplat boundaries and the microcracks within the splats. The sintering of the coating results in densification and loss in strain tolerance leading to spallation of the TBC. This failure occurs prior to spallation from bond coat oxidation - contrary to the previously observed failure modes. EB-PVD coatings are also expected to be susceptible to sintering resulting in a reduced time to spallation. In addition, at operating temperatures above 1200°C, the as-deposited non-transformable teteragonal phase destabilizes upon exposure (greater than 100h) ⁽²⁰⁻²¹⁾, possibly leading to a loss of the mechanical integrity of the coating.

It is evident that future coating systems should overcome the limitations of both bond coat oxidation and poor sintering resistance of ceramic coatings. At expected higher temperatures, these new bond coats should form a slow growing adherent oxide scale. New TBC materials should possess a sintering resistance superior to that of 8YSZ and also maintain their phase stability at high temperatures. In addition, it is critical to understand that development of new bond coats for higher temperature capability is limited by superalloy design temperatures. Therefore, future benefits can be significant only if new TBC materials can simultaneously withstand higher surface temperatures and provide larger thermal gradients. These new TBC systems are required to reduce cooling air, increase reliability and extend component life.

Advanced Inspection Techniques

Deregulation is leading the power industry to push for the lowest operating costs, a key element of which is the lowest life cycle cost of parts. As more and more DS and SC components are used, component costs will rise significantly. To minimize costs, it is essential to rejuvenate and repair parts rather than replace them. To optimize rejuvenation and repair frequencies and minimize unit shutdowns it is necessary to develop inspection techniques to determine the amount of life consumed and on-line monitoring to detect the initiation and propagation of cracks.

Currently, the remaining life of components is assessed using analytical methods and destructive tests. These approaches have inherent limitations. Analytical methods must use worst case assumptions about stresses, material properties and operation so that results tend to be conservative. In the case of destructive tests, testing material from the most severely damaged location may not always be possible and there is usually insufficient time to test long term properties and insufficient material to test all the relevant properties.

Life Assessment Using NDE - It would be highly advantageous if components could be examined non destructively to determine the percent life consumed. Advanced NDE techniques are being explored for this purpose. Chou and Earthman⁽²²⁾ have demonstrated the feasibility of using laser light scanning to characterize low cycle fatigue damage in IN718. Goldfine and Clark⁽²³⁾ have reported an excellent correlation between the meandering winding magnetometer conductivity measurements and percent of total fatigue life of St. 304. Jeong K. Na, et al⁽²⁴⁾ have studied the accoustic properties of longitudinal velocity and non-linearity parameters and observed a linear correlation with log cycles in high cycle fatigue tests on St. 410 Cb material. The results from these NDE techniques are shown in Figure 20. These and any other promising approaches should be pursued further with the objective of developing practical tools for inservice applications.



Figure 20: Fatigue damage detection by various NDE techniques⁽²²⁻²⁴⁾

On-line Monitoring - It would be even more advantageous if the above measurements could be taken while the turbine is running. Unit availability would significantly increase by eliminating the need for frequent shutdowns and openings. This may at first seem impossible since combustion turbines typically operate at 3000 or 3600 rpm with the blades moving at about 1200 miles per hour and completely encased in a pressure vessel. Further, the components of interest operate up to 1000°C with the gas temperatures up to 1540°C. Review of current sensor capabilities, however, reveals that the task is not impossible. Many of the sensors are based on electromagnetic or optical principles which have very fast measurement and response times. Relative to the speed of these sensors, the running turbine might as well be standing still. The real limiting factor becomes the ability to manage the data. Fortunately, the newest generations of personal computers have adequate capability.

Optical sensors could play an important role in real time materials measurements. The information content of the light scattering spectrum included in Raleigh, Brillouin and Raman scattering parameters is quite impressive. They are capable of measuring important properties like chemical composition, phase information, acoustic velocity, moduli, and thermal diffusivity. The measurements can be taken at light speed from a distant vantage point of milder conditions. Adding to the optimism, the most critical rotating components move past the sensor to create a self-scanned measurement map of the component, thus greatly reducing the number of sensors required to monitor many parts. Infrared imaging arrays could examine rapidly moving components in real time for thermal properties. Components with thermal barrier coating could also be examined to detect the formation and growth of defects.

Electromagnetic sensors could measure conductivity, permeability, or dielectric properties. The sensors must be used in close proximity to the component limiting measurements on rotating components. However, many useful measurements could be made on critical stationary components without these concerns.

Life Extension

It is important to distinguish between rejuvenation and repair although both are processes undertaken to extend the useful life of a component. Repairs can be thought of as 'external' processes that return the component to its original size and shape, or replace the protective coating. Rejuvenation can be defined as the regeneration of a microstructure leading to the restoration of mechanical properties equivalent to those of the original component prior to initial service.

<u>Rejuvenation</u> - The primary types of internal degradation observed in superalloys experiencing prolonged elevated temperatures are: gamma prime precipitate coarsening or overaging; changes in grain boundary carbides; cavity or void formation and the generation of Topologically Close Packed (TCP) phases. A conventional heat treatment involving complete solutioning, controlled cooling and subsequent aging should generally be sufficient to regenerate the original microstructure. It reverses the deleterious effects of gamma prime precipitate coarsening and changes in grain boundary carbides, and also sinters^(25,26) cavities below a certain critical size.

The creep properties of relatively simple superalloys (such as Nimonic 80A) containing low volume fractions of gamma prime can be restored by merely annealing at temperatures below the γ' solvus temperature⁽²⁷⁾. In this type of alloy where the degradation is caused by the formation of cavities, annealing at the creep temperatures without any stress is sufficient to sinter the cavities. The time required to sinter a cavity will obviously depend upon its size and the sintering temperature. Cavities formed during tertiary creep may not be amenable to healing by heat treatment alone.

The creep properties of the more complex alloys containing higher volume fraction of γ' are controlled by microstructural changes such as overaging of γ' and carbide degeneration. Rejuvenation of this type of alloy can be achieved only by heat treatments which dissolve and reprecipitate the γ' in a distribution and size similar to those of the original microstructure⁽²⁸⁾.

Proper timing of a rejuvenation treatment is imperative if the maximum economic benefit is to be gained. It is generally agreed that to ensure the regeneration of creep properties the rejuvenation treatment should be applied at the end of the secondary or beginning of the tertiary state of creep. Creep strength can be recovered⁽²⁹⁾ after up to 1% creep deformation by heat treatment alone. Economical rejuvenation at later stages of creep may be possible if an HIP cycle is incorporated.

Conventional cast parts can be routinely rejuvenated using HIP and resolution heat treatment cycles to restore the microstructure and properties. The rejuvenation of directionally solidified (DS) and single crystal (SC) parts pose a greater challenge. Recrystallization is a major concern for DS and SC parts. Exposure to fatigue and creep loading in service may induce damage that can manifest itself as recrystallization during rejuvenation treatments at temperatures near to or above the γ ' solvus. However, it is not only service exposure that can lead to recrystallization. Prior handling damage or machining induced strains at the manufacturing stage may also result in recrystallization during rejuvenation.

Recrystallization may be present on the surface or in the interior cooling channels. The conventional back reflection laue technique used in the aeroindustry could, in theory, detect surface recrystallization, but it is totally inadequate for detecting internal recrystallization. For this reason, a patented method⁽³⁰⁾ of through transmission diffraction (Figure 21) has been developed to detect small secondary crystals, as well as the orientation of the primary and secondary crystals relative to the component axis. A high flux, low energy, x-ray generator is used to provide the necessary photons for diffraction imaging of internal recrystallized grains. Figure 22 shows the diffraction pattern of a secondary internal crystal in a single crystal specimen, using this technique.



Figure 21: Schematic of SC through-transmission imaging





<u>Repair</u> - Repair of today's advanced superalloys poses significant challenges. As the industry developed new nickel based superalloys with higher temperature capabilities, the volume percent of γ' increased from 30-40% in the earlier forged and cast alloys, to 60-70% in some of today's DS and SC alloys. The high γ' content and the directional solidification of these latest alloys make repairs especially difficult. However, the high cost of these components dictates the need for developing cost effective repair procedures.

Earlier researchers have published⁽³¹⁾ formulae (Figure 23) which correlate the blade material composition with its weldability. The high volume percent of γ' gives these alloys high strength at elevated temperatures, but very low ductility, which, combined with the residual stresses from welding, frequently results in cracking.



Figure 23: Weldability diagram for a number of nickel-base superalloys and related materials⁽³¹⁾

Currently weld repair is generally limited to the low stress tip regions of the components. Typically, welding is performed using manual Gas Tungsten Arc Welding (GTAW), and the weld filler material has been a low strength, solid solution strengthened nickel base alloy, such as Inconel 625. This high ductility filler material absorbs some of the welding stresses by yielding, and thereby reducing cracking. Still, some minor cracking is inevitable in the higher γ' alloys. The addition of braze filler to mend microfissuring is usually inadequate to meet engineered part life. Repairs that use higher strength or more oxidation resistant weld filler materials have been developed, but these repairs are also limited to the tip and platform areas. To minimize cracking when welding high γ' alloys, the weld parameters must be carefully controlled. A highly concentrated heat source, lower heat input, automation and judicious application of preheat and controlled cooling are critical. Processes that provide a concentrated heat source include Laser Beam Welding - LBW (with powder or wire filler material), Electron Beam Welding - EBW, and Plasma Transferred Arc - PTAW (with

The challenge is to improve the repair techniques for DS and SC alloys and to extend the repair envelope to higher stress regions elsewhere on the component. New and improved repair techniques must be developed. Some of these techniques are discussed briefly below.

powder or wire filler material).

<u>Material Conditioning</u> - Pre-weld heat treatments have been found⁽³²⁾ to improve the ductility and hence weldability of some alloys. These heat treatments usually overage the material, raising ductility and lowering strength. <u>High Preheat Welding</u> - Crack-free welds were achieved by high preheat welding using the EBW process⁽³³⁾. In high preheat welding, the component is heated to temperatures near the solution temperature during welding.

<u>Blade Alloy and Filler Material Composition</u> - Careful control of some of the elements that form low melting point compounds at the grain boundaries can improve weldability with little compromise in mechanical properties.

<u>Transient Liquid Phase Bonding</u> - The transient liquid phase bonding process discussed earlier⁽¹²⁾ in connection with manufacturing large SC blades and vanes, yields excellent properties and can be used for repairs.

Liquid Phase Diffusion Sintering (LPDS) - LPDS uses a combination of a high melting point powder (typically a composition similar to the superalloy being joined) and a low melting point powder (typically a braze with boron as the melting point depressant). The powders are applied to the area to be repaired in the form of a paste, putty, or sintered preform. The repair is subsequently sintered in vacuum furnace below the melting point of the base metal substrate.

DS and SC alloys are among the most difficult materials to join. The challenge is to develop economical joining processes that achieve required strength. In the past, many of these alloys were considered unweldable, but today, some limited repairs are already possible. No one best process has yet been found, but success will be achieved by optimizing today's processes, selecting the best process for each specific application, and continuing the search for the new processes of tomorrow.

Material, Process and Component Behavior Modeling

The development of new alloys, their manufacturing process and evaluation of component behavior is an expensive and time consuming undertaking. It can take up to ten years and tens of millions of dollars to complete this cycle for a new alloy. To reduce cycle time, the experience-based trial and error approach of the past has to be replaced with a much shorter computer based modeling approach. An overall vision for modeling is shown in Figure 24. The conceptual materials model shown in Figure 25 is discussed below.



Figure 24: An overall vision for computer modeling

Successful modeling of advanced materials requires the ability to predict changes in the phase constitution as a function of composition, temperature and time, and translate this information into properties targeted by the design engineer, such as creep strength, fatigue, oxidation and corrosion resistance.



Figure 25: A conceptual material model

Several investigators⁽³⁴⁻³⁶⁾ have reviewed the progress in modeling the phase stability of complex materials systems, especially multi-component alloys. They have focussed on predicting phase stability in thermodynamic equilibrium, a situation expected only upon long term exposure to high temperatures. Materials engineers, however, seek a heat treatment schedule which will optimize a specific mechanical property. To address such realistic aspects of materials processing, the models will require incorporation of kinetic aspects such as phase transformation and interdiffusion of components across several phases. Upon successful prediction of the phase compositions with temperature and time, it is necessary to correlate properties with composition, based on fundamental and empirical models.

In addition to predicting materials properties, it is important to evaluate susceptibility of advanced materials to the aggressive environments of the gas turbine, such as high temperature oxidation and corrosion. These may be modeled by using combined thermodynamic and kinetic models which include calculations for the activity and mass transport of the various components in the alloy, its oxides and surrounding environment. For reliable predictions, it is also imperative to know the correct physical and thermo-physical properties, such as elastic modulus, density, heat capacity, thermal conductivity etc. for each component. Predicting the behavior of the system (material and its environment) is definitely an important step for materials modeling and key to early identification of superalloy degradation during service.

Considering the progress already made on phase stability, composition-property correlations and environmental interactions, future efforts to combine these aspects in a unified model is no longer an unrealistic vision. This is especially true given the recent tremendous progress in efficient interfacing of software databases. A unified model will minimize the advanced materials development cycle and facilitate introducing new technology into the utility gas turbine industry.

Summary 5

1. The growing demand for utility gas turbines and increased use of superalloys in them have created a dramatic surge in the market for superalloys. 2. The need to minimize the cost of electricity drives the need for increasing engine efficiency and reducing the life cycle cost of parts.

3. UGTs present unique challenges for transferring aeroturbine materials technologies and developing new UGT targeted materials. The key issues include longer life requirements, operation in hostile environments, cost effective manufacture of large components, inspection, rejuvenation and repair.

4. The cycle time for materials and process development for UGTs must be shortened by using knowledge-based systems and advanced computer modeling instead of trial and error.

5. The market for advanced superalloys with directional structures (DS and SC) will continue to flourish so long as the superalloy industry meets the power producers' need for high quality large components at low cost, short processing cycles, and rejuvenation and repair techniques applicable to the advanced superalloys used in UGTs.

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