# High temperature materials in energy systems

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*This paper discusses the material selection drivers for industrial gas turbines and reviews several examples of high temperature components and materials. A brief reference to fuel cell materials is included. The main issues associated with high temperature materials in small gas turbines are cost, reliability, NOx, fuel selection, and simplicity of design. The engines run at high speeds and usually modest pressure ratios Uncooled turbines are preferred, so metal temperatures can be quite high. The ability to use alternate as well as low grade fuels means significant consideration must be given to prevent corrosion and coating degradation. Erosion is also a potential problem due to particulate matter. Cycle counts are generally relatively low, but long times at temperature mean we must account for creep damage. Advanced cooling technology, such as Lamilloy® (a registered trademark of Rolls-Royce Corporation), can permit high temperatures with minimal cooling. Another potential solution is to use mechanically alloyed materials or ceramics.*

**Parole chiave: impieghi in temperatura**

## INTRODUCTION

The current world energy generation situation is in a state of rapid change. The maneuverings of OPEC, the increasing energy demands in both developed and developing countries, and efforts to reduce carbon dioxide emissions and prevent further global warming and destabilizing of the "weather machine" combine to make the future uncertain. Add to this the deregulation of the energy business in the U.S., by far the largest energy consumer, and the chaos in California's energy supply, and the future is anything but clear.
What is clear is that the government bodies must agree on the problems and map out a future to meet the burgeoning energy demand in a responsible way that will not destroy our environment. A mix of the cleanest current carbon based systems and renewable energy will be needed.
Table 1 (Ref 1) shows material issues for various energy production systems. There will certainly be a place in this mix for clean, low emission gas turbines and for fuel cell based systems. This paper focuses on these technologies and the material challenges facing designers of such systems.

## GAS TURBINE MATERIALS

Industrial gas turbines use high temperature materials, particularly in the combustor and turbine sections, and increasingly the back of the compressor as pressure ratios and hence temperatures increase.
Surprisingly cost is not the major driver in material selection. Energy distributors are driven by cost per kilowatt hour

*Table 1. Renewable energy technologies and associated materials issues.*

*Tabella 1. Tecnologie di energia rinnovabile e relative questioni legate ai materiali.*

| Energy source | Technology | Materials issues |
|---|---|---|
| Wind | On Shore Wind Turbine | Blade strength/weight ratio, tower strength and compliance, fatigue |
| | Off Shore Wind Turbine | As above plus corrosion, fatigue |
| Hydro Power, Tidal Barrages | Hydro Turbine | Corrosion, erosion, corrosion fatigue, wear resistance, toughness, cavitation corrosion |
| Tidal Stream | Hydro Turbine | Corrosion, erosion |
| Wave Power | Various | Strength/weight ratio, corrosion, erosion, corrosion fatigue |
| Biomass | Combustion or co-combustion plus steam turbine | Boiler corrosion |
| | Combustion plus indirect gas turbine cycles | High temperature materials for heat exchangers |
| | Gasification plus gas turbine or gas engine | Corrosion, gas cleanup systems |
| Waste | Combustion plus steam turbine | Boiler corrosion |
| | Gasification plus gas turbine | Corrosion, gas cleanup systems |
| | Pyrolysis plus reciprocating engine | Corrosion |
| Geothermal | Steam turbine driven by natural, flash purified, or heat exchanged steam | Corrosion |
| Solar Thermal | Collector plus heat exchanger and steam turbine | Corrosion |
| | Concentrator plus Stirling engine | Corrosion, thermal fatigue |

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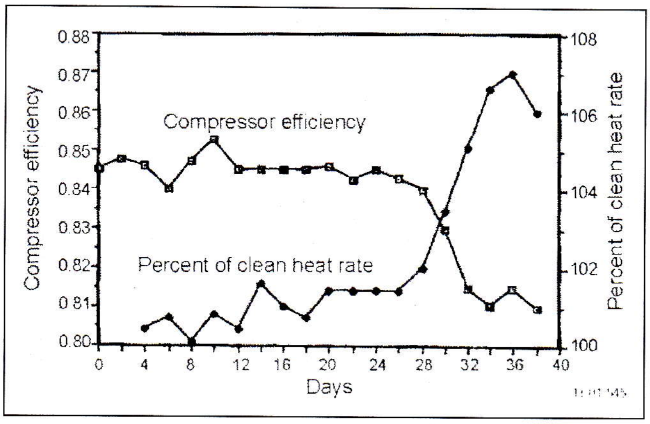


*Fig. 1. Effects of fouling on an industrial gas turbine over time.*

*Fig. 1. Effetti dell'incrostazione su una turbina a gas industriale nel tempo.*

produced, and the lowest cost solutions that meet other design criteria will succeed. Those criteria will include increasingly demanding limits on emissions, particularly $CO_2$ and NOx, which are often imposed by governments or regulatory authorities. Users of gas turbine based systems also demand reliability and simplicity, and these requirements define the design and material selection options.

Operators increasingly like to be able to use alternate fuels, natural gas or oil, and "dirty" fuels, which drive a need for corrosion resistance as an issue in material selections. There is more demand to use biomass fuels, hydrogen fuels, and other damaging fuels. In addition, these turbines frequently operate in atmospheres where particulate matter can damage performance.

A 75 MW unit located in an industrial environment with air loading of 10 ppm will ingest 594 lb of particulates every day (Ref 2). The effects of such fouling on performance are shown in Figure 1.

In addition to performance deterioration, particulate ingestion causes blocking of cooling holes in blades and vanes, which can result in accelerated thermal fatigue. In coastal areas ingestion of salt can cause corrosion, so corrosion-resistant materials and coatings are essential.

In recent years an increased emphasis has been placed on optimization of materials and materials processing technology (melting, casting, forging, fabrication) rather than on the introduction of new materials systems. The days of materials development looking for an application are essentially over. The engine users now drive the innovations for economic reasons. Another distinct trend is using consortia, a group of companies, often comprising the metal producer, fabricator, and user, working together to develop solutions to materials problems.

In Europe the COST 500 series of projects features closely integrated companies working on applied research programs. In the U.S., the Metals Affordability Initiative (MAI) follows similar principles. This U.S. Air Force (USAF) sponsored initiative encompasses the entire supply chain, and frequently competitors work together to reduce the cost of metallic parts. Generic or precompetitive issues are attacked by all consortium members, and competitive processing improvements are dealt with by the individual companies working with the USAF funding agency. Generic issues include business methods and electronic data interchange systems. Interestingly, the selection for funding is made by all the members, ensuring relevance to real world problems.

An example of successful collaborative materials development used by Rolls-Royce and Cannon-Muskegon was the development of the second generation single crystal alloy CMSX 4. In this process, the requirements definition and the practical possibilities were jointly developed and the companies worked together on several iterations before arriving at the optimum solution, as shown in Figure 2.

The U.S. Department of Energy (DOE) also has had a major collaborative program, the Advanced Turbine System (ATS), intended to establish the next generation turbine for industrial and utility machines. This program, which is ending, has been successful in using consortia to move technology forward.

Rather than covering all aspects of high temperature materials development, this paper will focus on combustors and turbines, and coatings that find application in both.

## COMBUSTORS

Combustor demands are being driven by the need for low emissions using dry low emission (DLE) capability. DLE demands highly efficient combustion, low to moderate combustion temperatures, and, for performance and cost reasons, it is preferred not to cool the combustor, or at least to minimize the need for cooling air.

Figure 3 shows the development of materials for combustor applications.

Nickel-based alloys have been the materials of choice for combustors for many years. The materials have to display ease of fabrication by forming and welding. The stronger $\gamma'$ forming alloys are prone to cracking at welds, and have not had widespread applications. The alloy Nimonic 263 was developed for such use and is still widely employed by Rolls-Royce in Europe. In the U.S., the Hastelloy family from

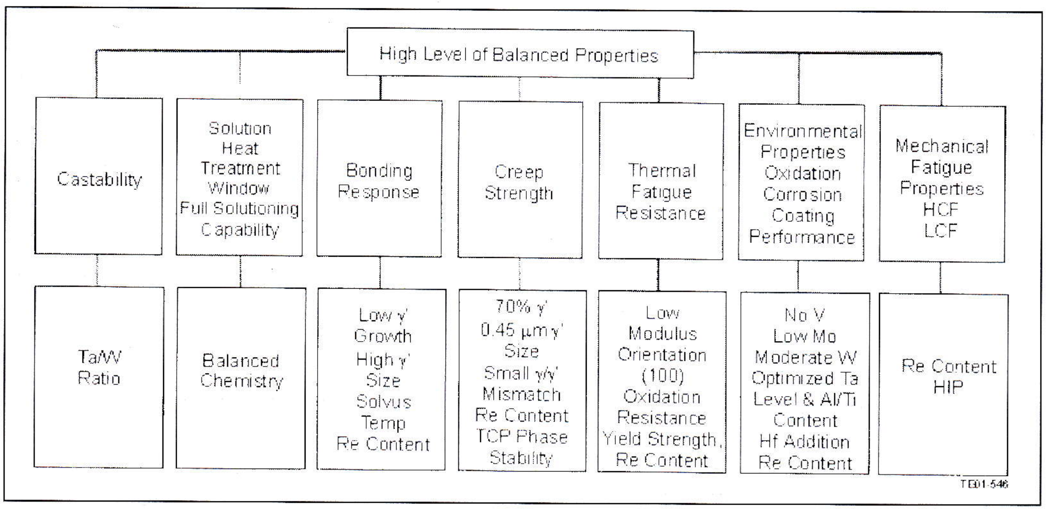


*Fig. 2. CMSX-4 alloy development goal.*

*Fig. 2. Obiettivo di sviluppo della lega CMSX-4.*

| Alloy* | C | Cr | Al | Ti | Co | Mo | Fe | Si | Mn | W | Mg | La | Ce | $Y_2O_3$ | $ThO_2$ | Ni |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Nimonic 75 | 0.10 | 19.5 | -- | 0.4 | -- | -- | 5.0 (max) | 0.30 | 0.30 | -- | -- | -- | -- | – | – | Bal |
| Nimonic 263 | 0.06 | 20.0 | 0.45 | 2.15 | 20.0 | 5.9 | 0.7 | 0.25 | 0.4 | -- | -- | -- | -- | – | – | Bal |
| Hastelloy X | 0.07 | 22.0 | -- | – | 1.5 | 9.0 | 18.5 | 0.4 | 0.6 | 0.6 | -- | -- | -- | – | – | Bal |
| Haynes 188 | 0.10 | 22.0 | -- | – | Bal | -- | 3.0 (max) | 0.35 | 1.25 (max) | 14.0 | -- | 0.05 | -- | – | – | 22 |
| Inconel 617 | 0.07 | 22.0 | 1.0 | – | 12.5 | 9.0 | -- | – | -- | -- | -- | -- | -- | – | – | Bal |
| Nimonic 86 | 0.05 | 25.0 | -- | – | -- | 10.0 | -- | – | -- | -- | 0.015 | -- | 0.03 | – | – | Bal |
| TD Nichrome | -- | 20.0 | -- | – | -- | -- | -- | – | -- | -- | -- | -- | -- | – | 2.0 | Bal |
| Incoloy MA956 | -- | 20.0 | 5.0 | – | -- | -- | Bal | – | -- | -- | -- | -- | -- | 0.5 | -- | -- |
| Haynes 230 | 0.10 | 22.0 | 0.3 | – | 3.0 (max) | 2.0 | 3.0 (max) | 0.4 | 0.6 | 14.0 | -- | 0.05 | -- | – | – | Bal |

*Nimonic, Incoloy, and Inconel are registered trademarks of the Inco family of companies
Haynes and Hastelloy are registered trademarks of Haynes International Inc.

*Table 2. Nominal compositions of some sheet alloys (weight by %).*

*Tabella 2. Composizione nominale di alcune leghe (peso %).*

Haynes International has proven very successful. The newer alloys such as Haynes 230 have improved temperature capability, but pay a penalty in being harder to form.
Haynes 230, a solid solution and carbide strengthened alloy, is the latest in the Haynes family of such alloys. As the quest for better creep and temperature capability continues, other strengthening systems have been evaluated. One with a long gestation period but with increasing application is the mechanically alloyed family of oxide dispersion strengthened (ODS) alloys. The chemistries of several alloys are given in Table 2 (Ref 3).
ODS alloys have excellent thermal stability to temperatures close to their melting points and extend temperature capability beyond conventional alloys.
The primary strengthening mechanism is provided by a fine dispersion of yttria particles, which also inhibit coarsening of the microstructure. The iron-based alloys (MA956, PM2000) provide exceptional oxidation resistance and useful strength to 1320°C, as shown in Figure 4. The nickel-based alloys MA754 and PM1000 provide oxidation resistance to 1093°C and are almost twice as strong as MA956 or PM2000. These alloys are generally less amenable to fabrication, showing lower ductibilities than conventional alloys. The alloys are not amenable to welding since this causes agglomeration of the dispersoid and hence a breakdown in the strengthening mechanism. Joining techniques that have narrow weld beads and minimum melting of the parent metal are preferred. Brazing offers potential but high temperature braze alloys are essential for combustor applications. Rolls-Royce has successfully demonstrated high temperature structural brazing for both MA956 and MA754 in conventional and Lamilloy structures.
In addition to material developments, processing innovations can add significant value in terms of cooling efficiency and temperature capability. Rolls-Royce has been developing and using its patented transpiration multilayered cooling concept Lamilloy in the most demanding applications. Lamilloy construction is shown schematically in Figure 5. This type of construction results in the most efficient use of

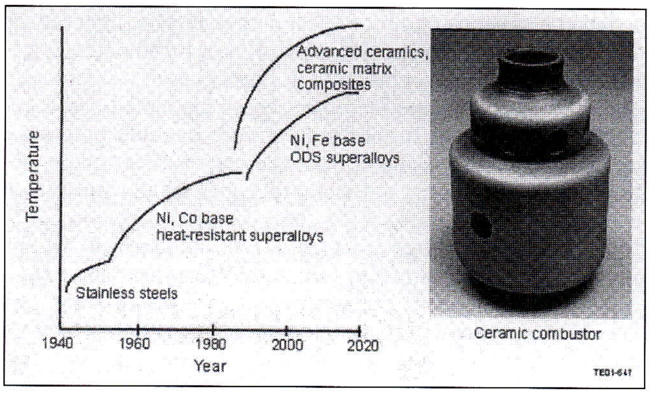


*Fig. 3. Combustor materials development.*

*Fig. 3. Sviluppo di materiali per camera di combustione.*

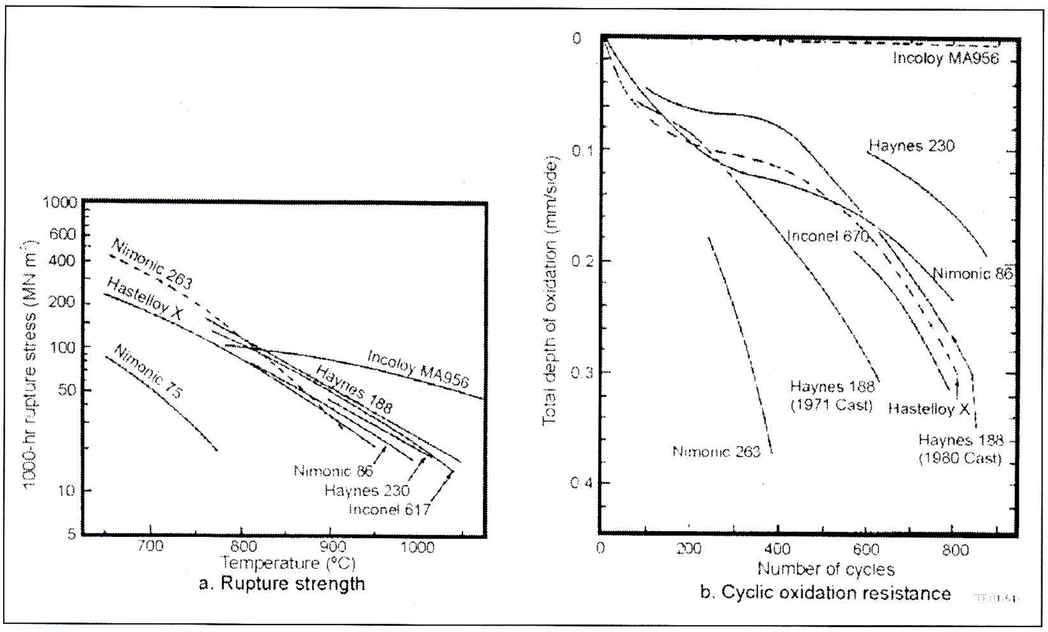


*Fig. 4. Iron-based alloys provide strength and exceptional oxidation resistance.*

*Fig. 4. Le leghe a base di ferro forniscono resistenza eccezionale resistenza all'ossidazione.*

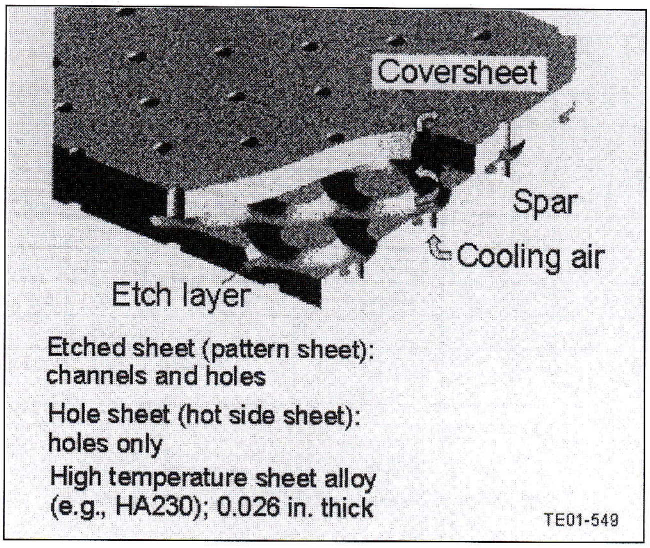


*Fig. 5. Two-ply Lamilloy schematic.*

*Fig. 5. Schema di Lamilloy a due strati.*

cooling air of any metallic system. The multilayer laminate type constructions are manufactured by photo etching a pattern onto the sheet surfaces, putting holes in the sheets, and diffusion bonding the layers together. This gives great design flexibility in terms of hole size and spacing, etched patterns, sheet thickness, etc. Many different combustors have been successfully manufactured and tested using Lamilloy designs.
Metallic combustors often need surface protection from oxidation. Most protection systems depend on the formation of alumina ($Al_2O_3$) or chromia ($Cr_2O3$) surface protective films. The problem is that the presence of aluminum in the alloy can result in weld cracking, and is therefore usually avoided. Thus, chromia formers are more common. The addition of rare earth elements can assist in oxide retention.
As much as 50% of the air entering the combustion chamber is used for cooling, so any improvement in combustion material capability or the more efficient use of this cooling air can improve overall engine efficiency.

## COATINGS

Coatings for metallic components can be simple aluminides or platinum aluminides or overlay coatings of the MCrAlY family. Increasingly thermal barrier coatings (TBCs) are being used to protect the substrate from excessive temperature exposure.
TBCs were launched on their first turbine section applications in the mid-1980s. These coatings were different from previous oxidation-resistant coatings in that the primary goal was to provide insulation to cooled components. The insulation then allowed for significant reductions in component temperatures. While initial commercial coatings were plasma spray deposited partially stabilized zirconia on vane platforms, the eventual coating on airfoils was electronic beam-physical vapor deposited (EB-PVD) yttria stabilized zirconia. There are several advantages of the EB-PVD ceramic coating: smooth as-deposited surface finish, minimal closure of cooling holes, ability to deposit on smooth surfaces, and a reported increased durability. While the last point is the subject of some debate, the other attributes of PVD TBCs are clearly worth pursuing. Since the introduction of PVD TBCs, these coatings have been used on both turbine vane and blade airfoils, and combustors, resulting in component metal temperature reductions as high as 140°C. The potential temperature reduction is even higher, but the use of TBCs to achieve greater temperature reductions is limited by their limited durability. Current research is geared to developing more durable, more reliable coatings for use at higher temperatures. Noting that oxidation of the bond coat is a key factor limiting durability of a TBC, recent advances in TBC durability have been gained by developing more oxidation-resistant bond coats.
Thus further cooling effectivity is possible if the following issues can be addressed:
• Reduced bond coat oxidation
• Increased thermal stability of the ceramic
• Increased process control
• Improved base material/coating system lifing methods
• Increased coating/base metal compatibility.
Coating development is a very active area of research and there are many demands that need to be satisfied.
Advanced TBCs have capability up to 1650°C, thicker adherent coatings with reduced residual stress, lower conductivity, cost effective plasma spray application with EB-PVD durability, and unique coating compositions for specialized applications. Finally, advanced TBCs can predict the behavior of coatings for lifing purposes and to better understand failure mechanisms.
Coatings will truly have come of age when they can be prime reliant and the component life predicted by the life of the coating.

## TURBINE BLADES AND VANES

Turbine blades are exposed to the most rigorous condition in the engine and are often the limiting feature in operating temperature. The requirements for increased efficiency and reduced emissions combine to challenge turbine materials.
The increase in performance capability of turbine blades has been enabled by a combination of technologies. Cooling techniques have become increasingly sophisticated and complex: the advent of higher temperature capable materials, mainly nickel-based alloys, with the use of directionally solidified and single crystal capability and finally the use of coatings.
Industrial gas turbines are generally characterized by few stop-start cycles (compared to aero gas turbines) and extended periods at or near maximum power. This drives selection to creep-resistant materials rather than fatigue-resistant materials, which tend to dominate in aero applications. Smaller industrial engines do have more cyclic content, but time at temperature is still the dominant performance measure.

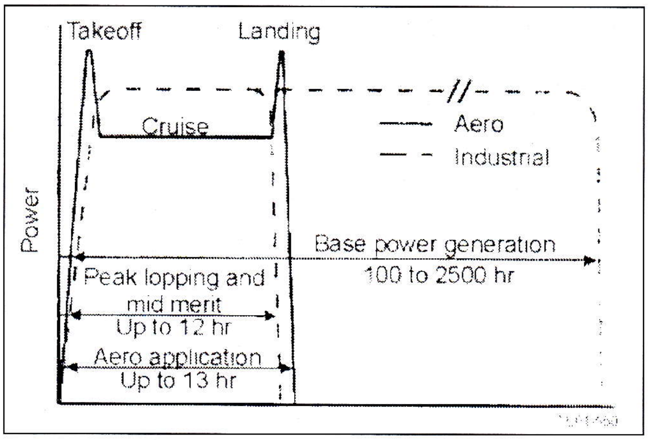


*Fig. 6. Schematic of cycle difference between the aero and industrial products.*

*Fig. 6. Schema della differenza di ciclo fra prodotti per aviazione ed industriali.*

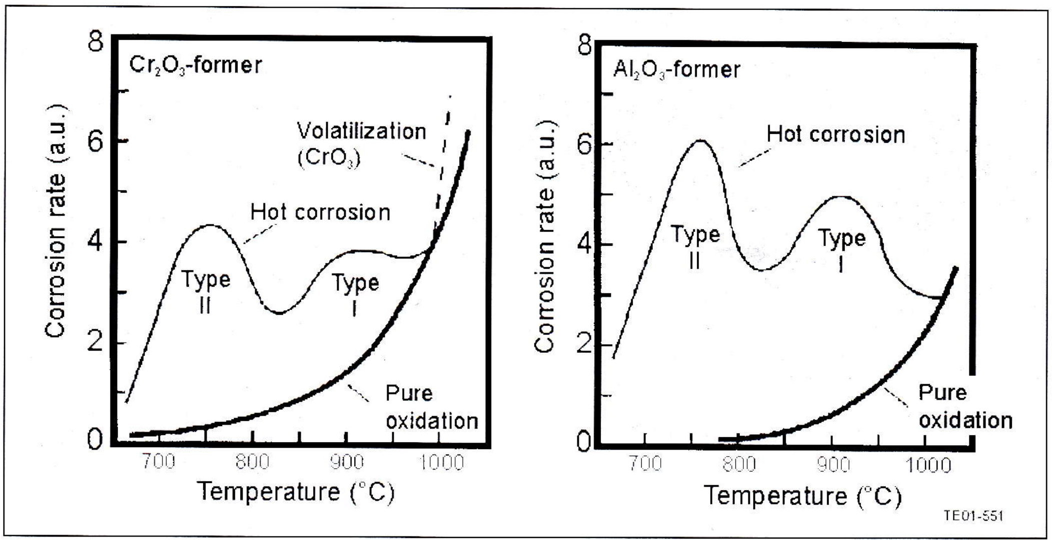


*Fig. 7. Schematic of the various types of high temperature corrosion attack as a function of temperature for (a) chromia-forming and (b) alumina-forming alloys.*

*Fig. 7. Schema dei vari tipi di attacchi di corrosione a temperatura elevata in funzione della temperatura per le leghe (a) chromia - forming e (b) alumina-forming.*

The differences in cycles between aero and industrial engines are shown in Figure 6 (Ref 1). A typical aero engine is dominated by flight cycles (low cycle fatigue); industrial engines operate in generally more aggressive environments, often with low quality fuel. Thus creep and sulfidation are the major life limiting features. Oxidation is a consideration in both aero and energy applications.

Complex cooling designs demand both inspection capability and novel manufacturing techniques. Constructions based on multipart blades, spar shells, and wafer constructions have been used, but there are challenges in manufacturing costs that still must be addressed.

The temperatures at which corrosion and oxidation dominate are shown in Figure 7. Corrosion resistance is enhanced by the presence of chromium in steels and nickel alloys, but chromium increases creep. Aluminum forms an adherent oxide but diffusion of aluminum into the substrate can cause problems.

Single crystal alloys appear to be reaching the limit of their temperature capability. Further advances are unlikely to increase capability by more than a few tens of degrees.

The use of ceramics for turbine blades has been investigated for many years. Advanced ceramics have high melting points and good thermal stability, low coefficients of thermal expansion, and good high temperature strength. Oxidation and corrosion resistance can be attractive for certain systems. Finally, the constituent materials such as alumina, silicon nitrite, and silicon carbide are widely available. Problems inhibiting their use include low toughness and ductility, and hence failure mechanisms that are harder to predict than for metallic systems. Table 3 (Ref 4) gives some properties of common engineering ceramics.

Table 3 shows the fracture toughness levels are less than 10 MPa√m. The main consequence of this is that the critical flaw size is very small, on the order of tens of microns, and these flaws are essentially not detectable by conventional nondestructive testing techniques. This results in a wider scatter in mechanical properties and hence a probabilistic approach to fracture.

The other drawback is that ceramics are expensive. Before they find wide acceptance, low cost processing of raw materials will be needed. Even then toughening of ceramics must be pursued.

Nonetheless, many successful applications have been developed and Rolls-Royce has run many ceramic components in long term endurance tests, particularly for small industrial gas turbine applications. Some of these are shown in Figure 8.

Recently, there has also been increasing interest in refractory metal silicide intermetallics. The most promising systems are based on niobium or molybdenum. These materials have densities of around two-thirds of single crystal alloys, thus reducing the stress on the disks. Also, silicide intermetallics have outstanding oxidation resistance, resulting from the formation of protective silica glass scale. These materials form complex multiphase microstructures that offer a bewildering variety of possibilities for designing to meet specific property goals. Recent work has resulted in learning how to cast ingots, extrude, heat treat and machine these materials.

As with most intermetallic systems, the silicides are brittle. Generally speaking, chemistry changes that improve ductility will reduce oxidation resistance. The other significant

*Table 3. Properties of some engineering ceramics.*

*Tabella 3. Proprietà di alcuni materiali ceramici.*

| Material | Density (g cm$^{-3}$) | Bending strength (MPa) | Toughness (MPa√m) | E (GPa) | Thermal expansion* | Thermal conductivity** |
|---|---|---|---|---|---|---|
| $Al_2O_3$ | 3.97 | 276-1034 | 2.7-4.2 | 380 | 7.2-8.6 | 27.2 |
| Mullite $3Al_2O_3$-$2SiO_2$ | 2.8 | 185 | 2.2 | 145 | 5.7 | 5.2 |
| Partially stabilized $ZrO_2$ | 5.7-5.75 | 600-700 | 8-9 | 205 | 8.9-10.6 | 1.8-2.2 |
| $TiB_2$ | 4.5-4.54 | 700-1000 | 6-8 | 514-574 | 8.1 | 65-120 |
| SiC | 3.21 | 230-825 | 4.6-6.1 | 207-483 | 4.2-5.6 | 63-455 |
| $Si_3N_4$ | 3.19 | 700-1000 | 4.1-6.0 | 304 | 3.0 | 9.30 |

*Thermal conductivity: $10^{-6}$ $K^{-1}$
**Thermal conductivity: W $m^{-1}$ K

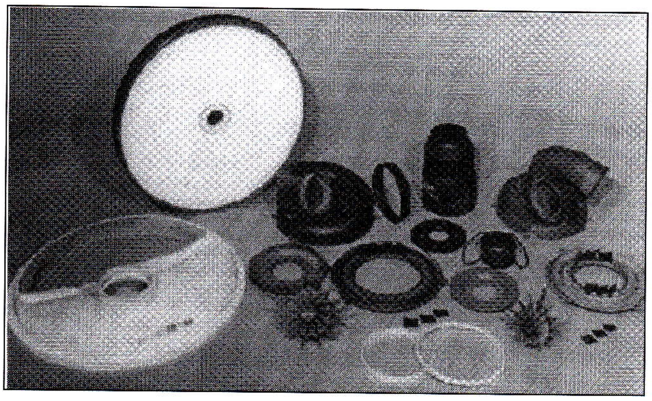

*Fig. 8. AGT 100 engine ceramic components.*

*Fig. 8. Componenti di motore di AGT 100 in ceramica.*

attribute of interest is creep, and there are many programs ongoing in the U.S. to optimize the balance among oxidation, creep, and ductility. These refractory metal silicide intermetallics are the subject of significant work both in the U.S. and elsewhere and will be thoroughly reviewed at the International Symposium on Structural Intermetallics later this year.

The greatest barrier today to the insertion and exploitation of new materials is the disparity between traditional material/process development cycles and shrinking engine development cycles. Using disciplined, computer-aided practices and accurate performance simulation models, designers have reduced the engine development cycle to less than four years. Prevailing materials development cycles are twice as long. This disparity too often results in premature material insertion or decisions rejecting any new material insertion. Thus, interest is lost in the potential benefits of new materials and in investing in new materials technology.

## FUEL CELLS

As a source of clean energy, fuel cells offer a very attractive potential. For small scale energy generation, the most promising system is the ceramic or solid oxide fuel cell. The essential components are shown in Figure 9 (Ref 5), but this simplicity belies many significant materials and other challenges.

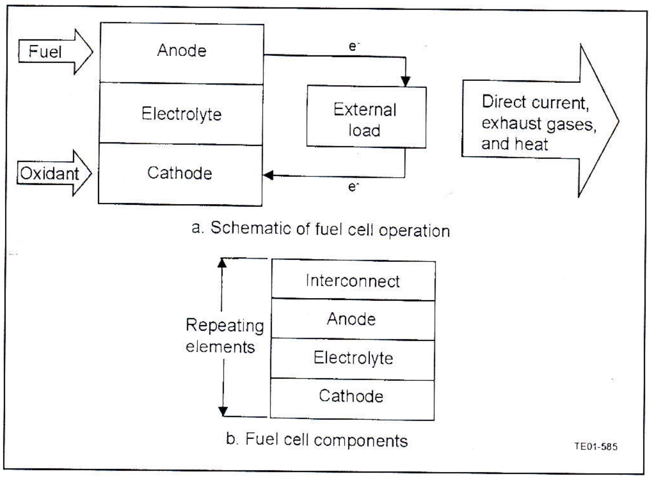


*Fig. 9. Fuel cell operation and essential fuel cell components.*

*Fig. 9. Funzionamento delle celle a combustibile ed i componenti essenziali di celle a combustibile.*

A ceramic fuel cell is a solid state energy conversion device that produces electricity by electrochemically combining fuel and oxidant gases across an ionic conducting oxide (Ref 6). It operates at temperatures higher than 600°C. The most common material selections are $ZrO_2$ electrolyte, $Ni/ZrO_2$ cermet anode, $LaMnO_3$ cathode, and $LaCrO_3$ interconnects. The most common fuel is hydrogen, which is fed to the anode, is oxidized, and has electrons released to the external circuit. Oxidant is fed to the cathode where it is reduced and electrons are accepted from the external circuit. Single cells are connected to a series to form a stack.

Materials demands include thermal stability, thermal expansion compatible with other parts of the system, appropriate porosity and conductivity, high strength and toughness, and low cost. The electrolyte, yttria stabilized zirconia, has to be fully dense and resist cracking since cracks would permit leakage of fuel and oxidant.

The anode performs under reducing conditions and should be porous. The cathode experiences the highest temperatures, and thermal expansion compatibility with other parts of system is crucial. Materials are electron conducting oxides.

Fuel cell output increases with pressure to the integration of a gas turbine, and a solid oxide fuel cell has an attractive potential efficiency as high as 60 to 75%. The future depends on cost effectively solving the technical issues with the fuel cell stack.

## SUMMARY

The current market for industrial gas turbines is very bullish. The major influences on turbine material selection remain cost based, and there is an ever-increasing push for efficiency improvements and reduced emissions. As part of the cost drive, the ability to use lower grade fuels, such as biomass, is increasingly sought.

These drivers demand low cost materials solutions that can cope with corrosive and particulate laden environments and meet long engine running times without significant deterioration.

The maturation of fuel cell technology presents many opportunities for efficient, clean energy generation, but also offers significant materials challenges.

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## ABSTRACT

### MATERIALI PER IMPIEGHI AD ALTE TEMPERATURE NEI SISTEMI ENERGETICI

*Questa memoria discute i principi alla base della selezione dei materiali per turbine a gas industriali e passa in rassegna diversi esempi di componenti e di materiali per prestazioni a temperatura elevata. Comprende inoltre un breve riferimento ai materiali per celle a combustibile.*
*Nelle turbine a gas di piccole dimensioni i punti essenziali associati ai materiali per impiegi a temperatura elevata sono: costo, affidabilità, emissioni di NOx, selezione del combustibile e semplicità di progettazione. Gli impianti operano a velocità elevate e solitamente a modesti rapporti di pressione. Le turbine non raffreddate sono preferibili e pertanto le temperature del metallo possono essere piuttosto elevate.*
*La possibilità di impiego di combustibili alternativi anche di qualità inferiore implica significative considerazioni al fine di impedire la corrosione e il degrado dei rivestimenti. Inoltre anche l'erosione dovuta al particulato rappresenta un problema potenziale.*
*Il numero dei cicli è generalmente basso, ma lunghi periodi in temperatura significa che si debba prendere in considerazione il danneggiamento da creep. Una tecnologia di raffreddamento avanzata, come ad esempio Lamilloy® , può consentire temperature elevate con un raffreddamento minimo. Un' altra soluzione potenziale riguarda l'impiego di leghe MA (Mechanically Alloyed) o ceramiche legate meccanicamente.*
*Nell'attuale mercato delle turbine a gas industriali il fattore principale per la selezione rimane quello dei costi e vi è una crescente spinta verso miglioramenti dell'efficienza e riduzione delle emissioni. Un aspetto della riduzione dei costi investe la capacità di utilizzare combustibili di bassa qualità, come ad esempio la biomassa.*
*Questi criteri di scelta richiedono soluzioni che comportano materiali a basso costo ma resistenti ad ambienti altamente corrosivi e con elevate quantità di polveri, nonché in grado di sopportare lunghi tempi di esercizio senza subire significativi deterioramenti. Lo sviluppo della tecnologia relativa alle celle a combustibile offre molte opportunità in termini di generazione efficiente di energia pulita, ma si presenta con sfide impegnative per quanto riguarda i materiali.*