



Thermal Barrier Coatings Issues in Advanced Land-Based Gas Turbines

W.P. Parks, E.E. Hoffman, W.Y. Lee, and I.G. Wright

The Department of Energy's Advanced Turbine Systems (ATS) program is aimed at fostering the development of a new generation of land-based gas turbine systems with overall efficiencies significantly beyond those of current state-of-the-art machines, as well as greatly increased times between inspection and refurbishment, improved environmental impact, and decreased cost. The proposed duty cycle of ATS machines will emphasize different criteria in the selection of materials for the critical components. In particular, thermal barrier coatings (TBCs) will be an essential feature of the hot gas path components in these machines. The goals of the ATS will require significant improvements in TBC technology, since these turbines will be totally reliant on TBCs, which will be required to function on critical components such as the first-stage vanes and blades for times considerably longer than those experienced in current applications. Important issues include the mechanical and chemical stability of the ceramic layer and the metallic bond coat, the thermal expansion characteristics and compliance of the ceramic layer, and the thermal conductivity across the thickness of the ceramic layer.

Keywords advanced turbine systems, bond coatings, combustion turbines, land-based turbines, thermal barrier coatings

1. Introduction

THE PREDICTED worldwide need for new electricity generation capacity in the 1990s is 600 GW. In the United States, energy consumption is expected to increase by 46% in the next 10 years or so (Ref 1), which suggests a market in the U.S. alone for new base-load electricity generation capacity of 20 GW per year. Approximately 44% of the current electricity-generating capacity in the U.S. will be more than 40 years old by the year 2010 (Ref 1), and its replacement will be necessary to meet stringent emissions standards. The technology required by conventional fossil fuel-fired steam boilers to meet these demands is ready and available; however, substantial reductions in CO₂ emissions will probably necessitate some fuel switching, since approximately 40% of all the carbon emissions in the U.S. currently are produced by the electric utilities (Ref 2). The projected efficiency of the best available coal-fired steam boiler technology, represented by the Electric Power Research Institute's State-of-the-Art Power Plant (SOAPP) (Ref 3), is 42% (8100 Btu/kW-h net at full load, based on the higher heating value [HHV] of the fuel) when an advanced supercritical steam cycle is employed, which compares with approximately 38% for the best coal-fired plants currently in operation in the U.S.

Gas-fired gas turbine combined-cycle systems are expected to account for a significant fraction of the projected new capacity. Such plants are available in a range of sizes, up to more than 200 MW(e) per turbine, which allows the concept of modular buildup of new capacity to meet growth needs. Also, gas turbine power generation equipment offers a low-risk, low-capital-cost,

quick-return option. Current combined-cycle plants have claimed cycle efficiencies on the order of 49% (7000 Btu/kW-h, based on the HHV) and can achieve environmental compliance for SO₂ and NO_x with minimal effluent or byproduct streams. Further, they can be installed in a short time frame (possibly fewer than 12 months) as a turnkey operation. Given that gas turbines will likely account for an increasing fraction of the base-load generating capacity, improvements in their efficiency and environmental compatibility would have a significant positive effect on the economics of the power industry.

2. Overview of the ATS Program

The overall goals of the ATS program are to develop advanced gas turbine systems to serve both utility and industrial power generation markets. The systems intended for utility application will have an efficiency rating of at least 60% (based on the lower heating value; better than 54%, based on the HHV), whereas the industrial power generation systems will be at least 15% more efficient than current gas turbines. The baseline fuel is natural gas. The ATS machines will have superior environmental compliance, with NO_x levels of less than 8 ppm, and CO and hydrocarbon emissions of less than 2 ppm. The goal of these systems is to reduce the cost of electricity by at least 10%. The systems developed also must be adaptable to coal and biomass firing; this assumes that gasification processes will be developed (Ref 4) to allow a smooth transition from natural gas to coal when that is economical and strategically necessary.

3. Approaches to Achieving the ATS Program Goals

The approaches available for achieving the program goals were analyzed in an initial phase, in which systems studies were conducted by Allison Engines; ABB Power Generation, Inc.; General Electric Company; Solar Turbines, Inc.; United Technologies; and Westinghouse Electric Corporation. Several ma-

W.P. Parks, Department of Energy, Office of Industrial Technologies, Washington, DC 20585, USA; **E.E. Hoffman**, Department of Energy, Oak Ridge Operations Office, Oak Ridge, TN 37831, USA; **W.Y. Lee** and **I.G. Wright**, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.

major areas were identified where improvements could be made and where significant investment would be required:

- Recuperation to preheat the air entering the combustor
- Advanced combustors/catalytic combustion to achieve significant reduction in NO_x levels
- Methods for increasing the rotor inlet temperature (RIT). An increase of 55 °C (100 °F) can provide an 8 to 13% increase in power output and a 1 to 4% increase in simple cycle efficiency. Suggested approaches include introduction of single-crystal alloys; introduction of low-sulfur alloys; adaptation of advanced cooling designs; development of closed-circuit cooling with steam; development of new alloys and advanced cooling designs, which could require ceramic core and mold development; use of thermal barrier coatings (TBCs; a TBC is essentially a materials system consisting of a thermally insulating ceramic bonded to an oxidation-resistant metal coating that is integral with the substrate); and development of ceramic vanes and blades.
- Increased aerodynamic efficiency from the use of improved sealing and advanced airfoil designs. This area of improvement also applies to steam turbines.
- Improved steam cycles by the generation of higher-temperature steam—from 10 MPa/538 °C with reheat to 538 °C (1450 psi/1000 °F/1000 °F) to 12.4 MPa/593 °C/593 °C (1800 psi/1100 °F/1100 °F), or 10 MPa/816 °C (1500 psi/1500 °F) once-through.
- Thermodynamic recuperation by the use of exhaust heat in a methane reforming process to produce fuel gas that would augment the normal fuel.

Table 1 indicates the potential gains associated with some of these approaches.

4. Materials Development Needs

Some of the materials developments required to realize the goals of the ATS program will be based in part on technology already in use in modern aircraft engines. These engines emphasize maximization of specific thrust—especially peak thrust in the case of military applications, which is achieved largely through increased turbine inlet temperatures and increased pressure ratios. The pressure ratios of military engines may be as high as 40 to 1, with the gas temperature at the first-stage blade (RIT) above 1500 °C (2732 °F). Compact engine dimensions are

Table 1 Estimated efficiency gains for advanced turbine systems from improved technology

Approach	Potential efficiency gain, %
Advanced materials, TBCs	3-4(a)
Thermodynamic recuperation	2(b)
Advanced air cooling	1-2(c)
Reduced leakage (clearance)	0.5-0.6(a)
Improved aerodynamics (gas turbines and steam turbines)	0.2-0.4(a)

(a) Ref 5. (b) Ref 6. (c) Ref 7

obtained through the use of multispool designs to achieve high pressure ratios and high individual high-pressure turbine-stage loadings. Therefore, a premium has been placed on the development of alloys with appropriate strength at extreme temperatures, and the improvements in aircraft engine performance with time can be accurately tracked by developments in alloy design and processing. Current single-crystal alloys experience bulk metal temperatures of up to 1000 °C (1832 °F) in aircraft engine service, reaching 1075 to 1100 °C (1967 to 2012 °F) at hot spots, but the useful lifetime under these conditions (in the absence of a TBC) is usually less than 5000 h. It is considered that alloying technology will allow one more generation of single-crystal alloys (which are now in the third generation), which may give a further 28 °C (50 °F) increase in temperature capability. Additional increases in the temperature capability of metallic blade and vanes will probably have to rely on advances in cooling techniques and TBCs, in the absence of further alloy technology breakthroughs (Ref 8).

Since superalloys begin to melt at approximately 1260 to 1290 °C (2300 to 2350 °F), it has been necessary to use advanced cooling of the critical components, such as combustors, transition ducts, and the first-stage vanes and blades. This is currently accomplished by a combination of air cooling and the use of TBCs. The air for turbine cooling is bled from the compressor and can be as much as 20% of the compressor capacity. This air bypasses the combustion process, resulting in a significant efficiency penalty. The need for more efficient use of this cooling air has led to more complicated cooling passage designs, and hence more complicated blade and vane castings. Thermal barrier coatings are used routinely in the combustors of aircraft engines, and have been used for approximately ten years on airfoil platforms, and, in some cases, the airfoil surfaces of first-stage vanes and blades. As applied to airfoils, the TBC is viewed as an added benefit since it helps to extend the blade life by reducing the effects of hot spots; however, no credit is taken for the presence of the TBC since the cooling airflow is not reduced compared to uncoated components.

The design of heavy-frame turbines has been typically conservative, with greater emphasis on long service life and minimized maintenance requirements than on higher performance and efficiency. However, the performance of these turbines has gradually improved without much sacrifice of service life and reliability as new materials and designs incorporating aircraft engine experience have evolved. As a result, the RIT of a state-of-the-art heavy-frame engine is on the order of 1300 °C (2370 °F), and pressure ratios range up to 16 to 1. It is expected that the application of advanced air-cooling techniques as well as TBCs will allow an increase in the RIT to 1427 °C (2600 °F), together with a lifetime in excess of 25,000 h. Further increases in the RIT probably would require the use of newer cooling technologies, such as closed-loop cooling with air or steam.

The transfer of aircraft engine technology for the ATS application must be made with the recognition that the different duty cycle envisioned for these engines will impose different requirements on the critical components and associated materials. In particular, ATS engines will run for a large fraction of their operating lives at close to full power, in contrast to the use of close to full power by aircraft engines only during takeoff and landing (and in combat conditions for military aircraft). In addition, the

required time between overhauls and refurbishment is 25,000 h, which is some five times that required for aircraft engines. The inherently longer time at temperature suggests that time-dependent processes such as creep, corrosion, and sintering (of ceramic TBCs) will play an increased role in the degradation processes experienced by ATS engine components. Since the bulk metal temperature must be commensurate with the creep allowances, blade temperatures may have to be somewhat lower than those tolerated in aircraft engines, or more creep-resistant alloys must be introduced.

The short-term and long-term materials needs for developing advanced land-based turbines were recently identified using input from gas turbine manufacturers, materials suppliers, universities, and government laboratories (Ref 9). The key technical areas were considered to be (1) coatings and process development, (2) directional solidification and single-crystal airfoils manufacturing technology, (3) turbine airfoil and ceramics development, (4) materials characterization, (5) catalytic combustor materials, and (6) efficient technology information exchange to fully use parallel efforts.

Materials issues inherent in coatings and airfoil development are corrosion, fouling, uniformity of cooling, the impact of steam cooling, leakage, and operation on coal or coal-derived fuels. The development of TBCs with improved bond coats was rated by many respondents as *the most important element* for advanced land-based turbine applications.

5. TBC Development Needs

Thermal barrier coatings are currently used on combustors and on vane and blade platforms (as well as on airfoil surfaces, but usually as patches) of aircraft engines as a means of increasing the component life, rather than as life-dependent coatings. Coating thicknesses of 500 to 1000 μm (20 to 40 mils) are used routinely on combustors and 250 to 500 μm (10 to 20 mils) on first-stage vanes; on rotating parts, the thickness is limited by weight and aerodynamic considerations to approximately 125 to 250 μm (5 to 10 mils), or possibly 380 μm (15 mils). Given that ATS machines will operate for significantly longer times at close to full power than aircraft engines, to minimize creep it may be necessary to reduce the average bulk metal temperature of the first-stage blades below that permitted for aircraft engines. Even without such a requirement, the relatively thin TBC layer currently applicable to the blade surfaces suggests that substantial cooling of the blade will be necessary.

Based on these considerations, it appears that developments are needed to increase the effectiveness of the TBC that can be applied to blade surfaces. The necessary improvements may involve developments to allow the use of increased coating thickness or coatings with decreased density or decreased thermal conductivity. A further approach to minimize the efficiency penalty associated with cooling requirements may involve cooling the air before it enters the blades or introducing steam cooling for the first-stage vanes to provide more air for the blades. Therefore, these key technical issues must be addressed in the development of current TBCs for use on the hot-section components of ATS machines: the mechanical and chemical stability of the yttria-stabilized zirconia (YSZ) ceramic layer and of the bond coat, the thermal expansion characteristics and compli-

ance of the YSZ layer, and the thermal conductivity across the thickness of the ceramic layer.

6. Proposed Effort on TBCs in the ATS Program

6.1 TBC Materials and Process Development

In order to hold the turbine blade temperatures to the limits required for $\geq 25,000$ h, several materials issues must be considered in the design and manufacture of TBCs. These issues include sintering, phase changes, damage due to high-angle impact of ingested particles, corrosion and destabilization of the YSZ layer, and long-term thermal and oxidation stability at the bond coat interface.

Mechanical integrity and compatibility with the substrate depend on control of the TBC microstructure. For rotating components, a columnar grain microstructure (grain boundaries oriented perpendicular to the surface) as produced by electron-beam-assisted physical vapor deposition (EB-PVD) is preferred. The segmented microstructure allows some relief of the stresses resulting from differential thermal expansion with the substrate, and from temperature gradients across the coating thickness, and thus significantly improves spallation resistance. The ability to control this columnar orientation along with coating uniformity, while accommodating cooling holes and maintaining the desired aerodynamic airfoil surfaces, is a major consideration in the development of processes for coating large airfoils.

Thermal barrier coatings are also deposited by plasma spraying. This often results in a more porous structure (desirable in terms of decreased thermal conductivity) consisting of an agglomeration of solidified splats oriented parallel to the substrate surface. Plasma spraying is less expensive than EB-PVD and is better suited to coating large components.

Sintering and phase changes of the TBCs have been shown to occur at turbine operating temperatures. Sintering increases spallation tendency and thermal conductivity, both of which result in increased temperature of the metal substrate. The longer-term exposure to high temperatures projected for ATS machines will accentuate this problem. Characterization of the thermal and physical properties of the TBC as a function of exposure conditions and of its mechanical performance at rated heat fluxes is thus an essential part of any process development.

The adverse influence of deposited corrodents on the chemical and mechanical integrity of the TBC layer is a potentially serious threat for coal- and biomass-based fuels. For example, the Y_2O_3 phase in the YSZ system is known to be susceptible to fluxing in the presence of molten salts containing sodium and vanadium (Ref 10). Also, infiltration of the TBC surface by deposited salts that are molten at operating temperature could promote spalling of the YSZ when they solidify upon cooldown.

Current coating processes, especially plasma spraying, can result in plugging of cooling holes in turbine airfoils and necessitate secondary processing for removal of the coating in the holes. In advanced turbine airfoils, shaped holes are used to enhance film cooling; a coating that distorts the hole shape, and hence the cooling airflow, could negate the benefits of the TBC. The surface finish of the coating is also important to maintain

aerodynamic performance. Secondary processing that uses coolants that could contaminate the relatively porous TBC would be highly undesirable.

Manufacturing process developments will be required that improve the reliability and reproducibility of TBCs. Intelligent processing techniques may be a useful approach.

6.2 Bond Coat and Metallic Coating Development

Two general types of bond coats have been used: overlaid MCrAlY, where M is typically nickel or NiCo, and diffusion aluminate (or platinum-aluminide). These are shown schematically in Fig. 1. The first coating is formed by plasma spraying directly onto the component, whereas the second is formed by the diffusion of aluminum into the alloy substrate.

A major concern associated with the longer design life for advanced land-based gas turbines is the stability of the bond coat. The ease of transport of oxygen through YSZ ensures that the bond coat will be subject to continued oxidation, as well as hot corrosion if deposited salts can penetrate to the bond-coat region. The ability of the bond coat to continue to support the growth of an alumina scale depends on the total amount of aluminum available; the effective reservoir of aluminum in the bond coat is depleted not only by consumption due to the formation and growth of the alumina scale, but also by diffusion into the alloy substrate. If a point is reached where the aluminum level of the bond coat falls below that at which alumina can be formed preferentially, faster-growing oxides of the other constituents of the bond coat will form, and the adherence of the TBC could be significantly degraded. Another factor is that the

continuing growth of the otherwise protective Al_2O_3 at the bond coat/YSZ interface is a source of increasing strain, which may affect the adherence of the external ceramic layer.

Spallation of the YSZ layer induced by oxidation of the bond coat is considered to be the ultimate failure mode for EB-PVD TBCs. Failure usually occurs at the interface between the bond coat and its oxide scale, whether the bond coat is diffusion aluminate or overlaid MCrAlY. This observation suggests that the life of these TBCs is largely controlled by the factors that govern the bonding at the scale/bond coat interface. For air-plasma-sprayed TBCs, spallation usually occurs within the ceramic layer, but very near to the bond coat/YSZ interface. The major sources of stress leading to degradation of TBCs appear to be thermal mismatch with the bond coat, temperature gradient through the TBC, stress at the YSZ/bond coat interface from oxide growth, and transformation in the YSZ—especially tetragonal to monoclinic, which results in a 3 to 5% volume change (Ref 11).

A recent discovery is that trace amounts (≈ 1 ppm) of sulfur impurity in airfoil alloys can degrade the integrity of the bonding at the scale/alloy interface (Ref 12). This sulfur effect can be minimized by reducing the inherent sulfur impurity level in the alloy through in-melt or postsolidification processing, or through the incorporation of reactive elements additions (such as yttrium). The use of yttrium-containing alloys requires the use of alumina for cores and molds, with inherent difficulties of handling and core extraction. The alternative is modification of current melt practices, as well as bond coating processes. Therefore, definitive microstructural studies are needed to determine the effectiveness of approaches to minimize the sulfur effect on the rate of scale growth on bond-coat alloys, and on the adhesion of TBCs to such alloys, as a function of exposure time and temperature. These issues are shown schematically in Fig. 2.

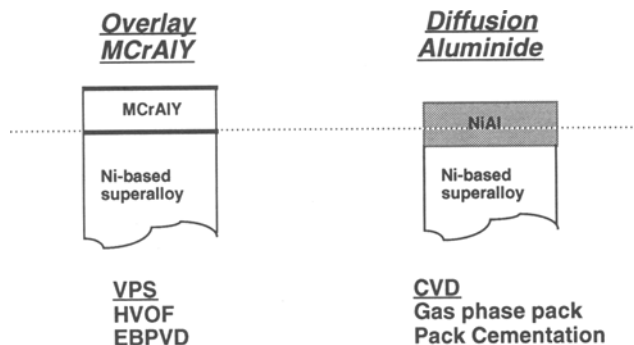


Fig. 1 Major types of bond coating

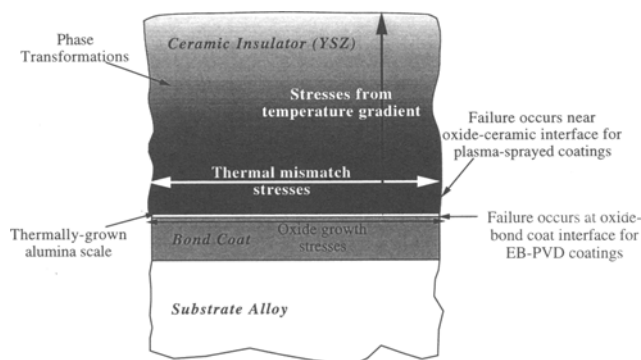


Fig. 2 Factors affecting the cyclic oxidation life of the bond coating

6.3 TBC Analytical Modeling, Life Prediction, and Maintenance and Repair

The development of an analytical model that could predict TBC performance and life based on key TBC parameters and operating conditions could be a major step toward enhanced TBC reliability in an application that is totally dependent on the TBC to reduce airfoil temperature as well as increase airfoil life. The model should address interrelationships among geometric factors (thickness and surface curvature); thermomechanical considerations (gas temperature, cooling characteristics, mechanical stresses, and mechanisms for damage accumulation); and material parameters (conductivity and coefficient of expansion, coating strength, bond strength, long-term creep properties, oxidation resistance, corrosion resistance, and microstructural stability). These issues are summarized in Fig. 3.

It may be necessary to incorporate several different but related models into the overall model, such as heat-transfer models (prediction of temperature and gradients); materials models (prediction of thermal conductivity and stress-strain response); and mechanistic models (prediction of thermal and mechanical stress fields in the coating, substrate, and interface as a function of configuration, temperature, environment, and time). Experimental validation of the interrelationships in these models is key to the implementation and use of the overall model in the TBC manufacturing process. In this manner, such a model and its ex-

perimental verification could aid in establishing system trade-offs and synergistic improvements.

The time-temperature exposures and projected thermal gradients in TBCs to meet ATS needs are beyond the current TBC experience base. Laboratory test facilities will be required that can measure properties needed for modeling as described. In addition, rig test facilities are required that can simulate the temperatures and high thermal gradients, gas velocities, and pressure on the TBCs.

Given the critical role of TBCs, reliable inspection procedures will be needed to determine coating section thicknesses and to detect defects. Built-in sensors capable of predicting imminent TBC failure in the field would reduce the risk associated with applications where the higher inlet temperature and reduced cooling air are dependent on the TBCs. A methodology must also be established for the repair of components, either on-site or at a designated depot. Techniques that can establish non-destructively the remaining life of turbine airfoils are actively being sought for aircraft turbines. Such techniques will become even more critical for land-based gas turbines, where time-dependent properties such as creep assume greater importance.

6.4 Revolutionary TBC Concepts

Thermal barrier coatings with better thermal properties than achievable by current concepts (YSZ) may be needed to reach

the target operating temperature of the ATS hot gas path components. Simply increasing the thickness of a given monolithic coating does not necessarily produce a corresponding increase in thermal resistance, since radiation contributes significantly to the overall heat-transfer process at the ATS design temperature.

The goal of radically new concepts for TBCs would be to maximize thermal resistance while minimizing coating thickness; thinner coatings might be expected to exhibit improved mechanical properties. There are several approaches for increasing the thermal resistance of a TBC; examples include: (1) controlled increase in the population of microstructural discontinuities (grain boundaries, voids) in currently used ceramic materials to increase thermal resistance; (2) multiple layers of precisely controlled ceramic thickness to provide light-refracting interfaces for selected wavelengths; and (3) compositionally graded structures to provide a transition in thermal, as well as mechanical properties (such as coefficient of expansion) across the bond coat/TBC interface; and, less revolutionary.

7. Summary

The ATS program has the goal of developing gas turbine systems for both utility and industrial power generation applications that will have efficiency ratings significantly higher than current gas turbine systems, that will operate for significantly

Improving TBC performance requires a systems approach

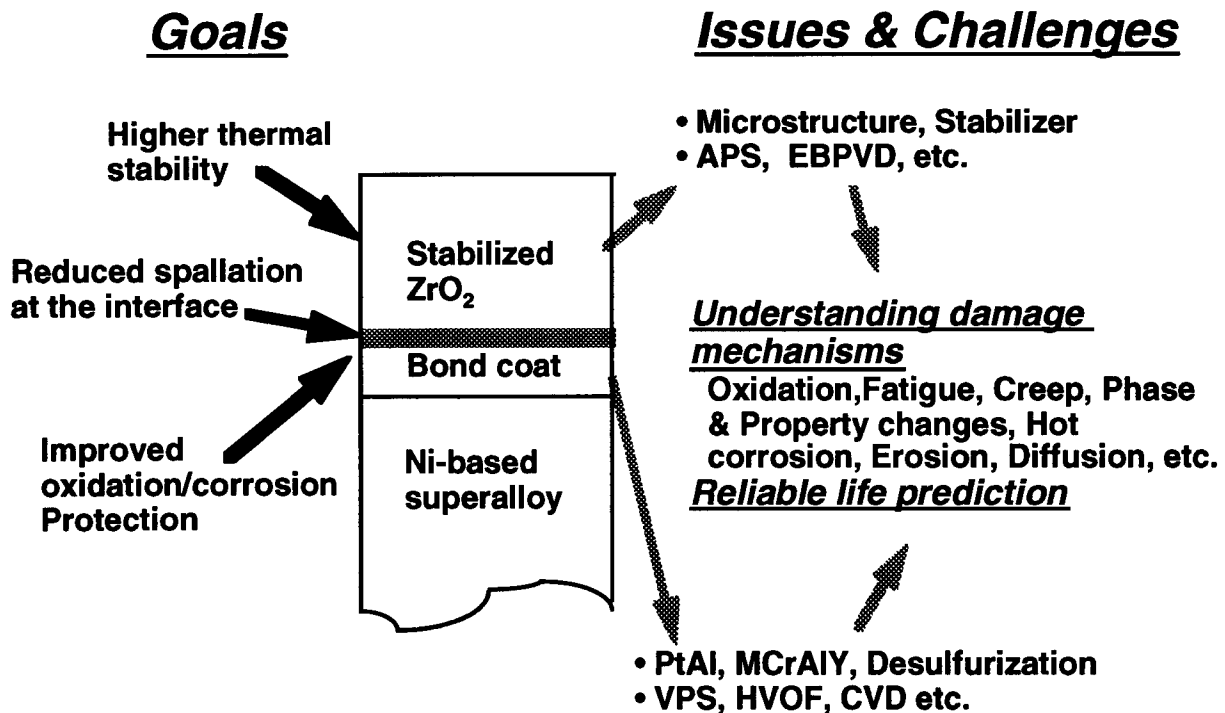


Fig. 3 Approaches for improving TBC performance

longer periods between scheduled maintenance outages, and that will have superior emissions performance. Realization of these goals will require the use of hot gas path component technologies developed for aircraft engines, but adapted to the quite different duty cycle of ATS machines, which will operate mostly at close to full power rating and exhibit significantly longer lifetimes. A major difference will be that the ATS machines will *depend* on TBCs to allow a reduction in the cooling air requirements and to realize extended component lifetimes. In aircraft engines, TBCs are used on blades and vanes only to gain added service life benefits, and no reliance is placed on them so that cooling air flow can be reduced.

A significant TBC development effort thus is planned in the ATS program that will address the following issues: (1) improvement of the performance of TBC materials, including the ceramic insulator and the metallic bond coating; (2) development of processes for applying TBCs to large, complex structures with good control of the coating thickness and structure; (3) analytical modeling of the coating degradation processes to allow life prediction, maintenance, and repair; and (4) exploration of revolutionary TBC concepts that have potential for increased thermal resistance and thinner coatings.

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References

1. C.A. Ervin, "The Role of Advanced Turbine Systems in Energy Efficiency and Renewable Energy's Mission," keynote talk presented at Ad-

- vanced Turbine Systems 2nd Annual Program Review Meeting (Arlington, VA), 9 Nov 1994
2. P. Godley, "The Role of Gas Turbines in Utility Research and Development," keynote talk presented at Advanced Turbine Systems 2nd Annual Program Review Meeting (Arlington, VA), 9 Nov 1994
3. S. Pace, "State of the Art Power Plant (SOAPP)," paper presented at Sargent and Lundy Engineering Conf. (Chicago), Spring 1992
4. N.A.H. Holt, Advanced Gas Turbines Ready to Produce Coal-Based Power, *Private Power Exec.*, Vol 2 (No. 2), 1994, p 36-41
5. H.E. Miller, "Technologies for Next Generation Power Systems," program element overview presented at Advanced Turbine Systems 2nd Annual Program Review Meeting (Arlington, VA), 9 Nov 1994
6. R.L. Bannister, Overview of Westinghouse's Advanced Turbine Systems Program, *Proc. Advanced Turbine Systems Annual Program Review Meeting*, DOE/OR-2025, Office of Industrial Technologies, U.S. Department of Energy, Nov 1994, p 21-26
7. J.C. Corman, "Gas Turbine Power Generation Evolution Advances the Future," paper presented at Advanced Turbine Systems 2nd Annual Program Review Meeting (Arlington, VA), 9 Nov 1994
8. R.V. Hillery, "Coatings for High-Temperature Structural Materials," paper presented at Advanced Turbine Systems 2nd Annual Program Review Meeting (Arlington, VA), 9 Nov 1994; see also "National Materials Advisory Board Report," National Academy Press, 1996
9. E.E. Hoffman, M.A. Karnitz, J.H. DeVan, R.S. Holcomb, D. Anson, R.W. Harrison, and R.P. Allen, "Materials/Manufacturing Plan for Advanced Turbine Systems Program," Report No. DOE/OR-2007, Office of Industrial Technologies, U.S. Department of Energy, April 1994
10. R.L. Jones and D. Mess, Indium as a Hot Corrosion-Resistant Stabilizer for Zirconia, *J. Am. Ceram. Soc.*, Vol 75 (No. 7), 1992, p 1818-1821
11. E.Y. Lee, R.R. Biederman, and R.D. Sisson, Jr., Diffusional Interactions and Reactions between a Partially Stabilized Zirconia Thermal Barrier Coating and the NiCrAlY Bond Coat, *Mater. Sci. Eng.*, Vol A121, 1989, p 467-473
12. A.W. Funkenbusch, J.G. Smeggil, and N.S. Bornstein, Reactive Element-Sulfur Interaction and Oxide Scale Adherence, *Metall. Trans.*, Vol 16A, 1985, p 1164-1166