

DOE/OR/22426-96/C0653

CONF- 9510109--6

**Pratt & Whitney Thermal Barrier Coatings**

**Author:**

N. Bornstein  
J. Marcin

RECEIVED  
APR 09 1996  
OSTI

**Contractor:**

Oak Ridge National Laboratory  
P.O. Box 2008  
Oak Ridge, TN 37831-6065

**Contract Number:**

DE-AC05-95OR22426

**Conference Title:**

Advanced Turbine Systems Annual Program Review

**Conference Location:**

Morgantown, West Virginia

**Conference Dates:**

October 17-19, 1995

**Conference Sponsor:**

U.S. Department of Energy, Office of Power Systems Technology,  
Morgantown Energy Technology Center

**Contracting Officer Representative (COR):**

Charles Zeh

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

## **Disclaimer**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, 175 Oak Ridge Turnpike, Oak Ridge, TN 37831; prices available at (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650.

## Pratt & Whitney Thermal Barrier Coatings

N. Bornstein (Bornstns@UTRC.UTC.COM; 860-727-7487)

United Technologies Research Center

Mail Stop 129-22

411 Silver Lane

East Hartford, CT 06108

J. Marcin (860-565-5635)

Pratt & Whitney Aircraft Company

Mail Stop 114-41

400 Main Street

East Hartford, CT 06108

### Introduction

The objective of the Advanced Turbine Systems (ATS) Program is to develop ultra-high efficient, environmentally superior, and cost competitive gas turbine systems. The operating profiles of these industrial gas turbines are long, -less cyclic with fewer transients- compared with those for aircraft gas turbine engines. Therefore, creep rather than thermal fatigue, becomes primary life-limiting for hot section components.

Thermal barrier coatings (TBCs) will be used to achieve the objectives of the program. TBCs allow surface temperatures to increase without compromising the structural properties of the alloy. TBCs typically consist of a ceramic insulating layer, deposited onto the substrate with an intervening metallic layer, which imparts oxidation protection to the substrate and provides a surface to which the ceramic layer can adhere.

### Project Description

The maturation of the iron, nickel, and cobalt base superalloys and the gas turbine engines used in propulsion, transportation, and power generation are intertwined. The increases in power and thermal efficacy is directly related to the increase in turbine inlet temperature. The prevention of structural failures related to melting, creep, oxidation, and thermal fatigue is accomplished in part through compositional and processing changes combined with improved and novel cooling schemes.

The remarkable growth of superalloys and the design of airfoils over the past 30 years is summarized in Figure 1. The early alloys were based on the performance of the Ni-Cr system. In a relatively short period the strength of the alloys was sufficiently increased to transition from wrought to cast. Within two decades, the polycrystalline structure gave way to the columnar grain structure, which within a decade, transitioned to the single crystal technology of today. Thus, within three decades the temperature capability of the alloys increased by more than 200 °F. At the same time significant improvements in casting technology and design further extended the

---

Research sponsored by the U.S. Department of Energy's Oak Ridge Operations Office, under Contract DE-AC05-95OR22426 with Pratt & Whitney Aircraft, 400 Main Street, East Hartford, CT 06118

operational envelope. The design evolution and the associated benefits of advanced cooling concepts are shown in Figure 2.

Further increases in efficiency and power requires additional cooling air and the use of improved thermal barrier coatings. TBCs provide insulation equivalent to about 300 °F (167 °C) from a typical 10 mil (0.254 mm) ceramic layer. The FT-4000 intercooled industrial engine high pressure turbine (HPT) blades are designed to achieve a 25,000-hour life while operating continuously at turbine inlet temperatures of 2700 °F (1480 °C). This is achieved with innovative advanced cooling methods, outstanding coatings and the insulation obtained with the use of TBCs. The morphology of a typical TBC is shown in Figure 2, and the beneficial increase in equivalent metal temperature is shown in Figure 3.

The majority of TBCs currently used on turbine components is based on the yttria stabilized zirconia system. They are applied by plasma spraying or EB-PVD; two distinctly different processes, Figure 4. Plasma deposition is essentially an adaptation of the flame spray process. Particulate matter introduced into the plasma is heated to a semiplastic state and accelerated toward the workpiece. Upon impact, the hot particles deform to produce a complex interlocked structure, which is tightly bonded to the substrate.

The EB-PVD process is an extension of the metallic NiCoCrAlY overlay technique, pioneered and developed by P&W over 3 decades ago. The unique ceramic micro-structure achieved through this process offers a significant improvement in strain tolerance of the ceramic insulating layer, as the failure location for EB-PVD TBCs is distinctly different from that of plasma TBC. In the plasma system, failure generally occurs as a

result of cracking in the ceramic layer parallel and adjacent to, but not coincident with the metallic ceramic interface, Figure 5a. A driving force for failure is the cumulative cyclic mechanical strain superimposed on that induced by oxide growth on the bond coat.

The EB-PVD ceramic system exhibits enhanced durability. It is fundamentally different from that of the plasma sprayed ceramic. Its microstructure confers a high degree of strain tolerance. It is characterized by columnar growth, with little bonding between adjacent columns but strong bonding with the substrate. When failure does occur the location is distinctly different from that of plasma sprayed TBC. It fails by cracking at the thermally grown aluminum oxide layer (TGO) that develops on the bond coat at the ceramic-bond coat interface Figure 5b.

The operational envelope of the industrial gas turbine differs significantly from that of the aircraft engine. The former operates primarily at sea level where the air is often burdened with industrial and agricultural dusts as well as sea salt crystals. The latter are generated at the air sea interface and travel inland more than a hundred miles. The industrial gas turbine utilizes fuels which can contain significantly higher concentrations of known corrodents and can also contain elements and compounds that adversely affect combustion characteristics. Equally important, the industrial gas turbine operates for prolonged durations at baseload conditions whereas the cyclic duration for the aircraft engine is significantly shorter. Lastly, the aircraft gas turbine generally experiences a series of temperature changes during each cycle; a behavior not generally true for the industrial engine. For these and additional reasons, the role of corrosion in the industrial gas turbine presses to the forefront.

The corrosion community has exposed TBCs to the same tests employed to study and rank metallic coatings and aircraft super-alloys, and more often than not the findings from the laboratory are not consistent with field results. We have conducted in-depth analyses of the nature and concentration of deposits from operational industrial gas turbines located worldwide. A model that describes the passage, accumulation, and deposition of industrial oxides and salts, and correlates site location, air and fuel quality with deposition and corrosion behavior has been constructed. For example, it is well established that the principle constituents of the corrosive salts associated with hot corrosion of gas turbine components are the sulfates of sodium, magnesium, and calcium. However, the corrosive salts removed from industrial hardware also contain significant concentrations of potassium. The ratio of potassium to sodium in the deposits is more than an order of magnitude greater than that in sea salt. Analyses of the ratios of potassium to sodium in sea salt, and in deposits removed from compressor and turbine components have shed much light on understanding the deposition mechanism for airborne corrodents. Any deposition mechanism which does not take account of the selective increase in potassium, would not simulate what occurs in practice. The significant differences in composition of sea salt, a primary source of the hot corrosion corrodents and the typical chemistry of the salts associated with hot corrosion, is shown in Figure 6.

Industrial gas turbines are continually subjected not only to sea borne, agricultural, and industrial salts, but also to industrial dusts. The various salts and dusts accumulate onto compressor components and adversely affect

gas turbine efficiency. Equally important the industrial dusts are composed of known oxides that can behave as sintering agents to the TBC ceramics. These oxides are captured on the surfaces of the sophisticated filters specifically developed for industrial and marine gas turbines. However, by their very nature, the filters must pass some of the accumulated matter. The nature of this matter is shown in Figure 7, a typical analyses of filter matter from an industrial site. Based upon the available phase equilibria supported from in-house studies, the oxides of both iron and silicon are active sintering aides.

It is a materials challenge to negate the combination of active sintering aids and corrosive salts. The former can significantly alter both the mechanical and thermal properties of the ceramic, significantly affecting mechanical integrity; allowing the corrosive salts to interact with the metallic substrates. This behavior is illustrated in Figure 8, a view of a ceramic coated combustor component. The salts identified on the surface consist of both the metallic corrosion products and the corrodent.

The corrosive salts on the surface of the TBC can, without physical contact, influence the chemistry of the metallic bond coat. It is well established that many oxides are relatively transparent to the passage of oxygen. Oxygen is readily transported through zirconia. At the salt-ceramic interface, the partial pressures of sulfur and oxygen are established by salt chemistry. The presence of sulfide precipitates are observed in the vicinity of the bond coat ceramic interface without any discernible path for the flow of corrodent. This is shown in Figure 9. Thus, unlike the aircraft environment, the industrial TBC must establish inherent resistance to many fused salts.

## Approach

An overview of the program is shown in Figure 10. The program is divided into the originally suggested four phases. The benchmarking ceramic candidates include (a) air plasma sprayed ceramic on APS bond coat, (b) APS ceramic on LPPS bond coat, and (c) EB-PVD ceramic on LPPS bond coat. Of the benchmarking systems (a) has experienced the most exposure in industrial gas turbines, (b) has accumulated the most time in flight engines, and (c) is the outstanding blade system which has demonstrated excellent performance in revenue service with approximately a 10X increase in durability over plasma sprayed systems.

The compositions of the candidate ceramics were selected based upon the chemical knowledge and experience obtained from the industrial field combined with the thermo-mechanical behavior derived from millions of flight hours. The ceramic systems include enrichment of the yttria level in the ceramic in recognition of the depletion of this element that occurs in the industrial environment. It also includes the evaluation of ceria stabilized ceramic. In addition to the differences in chemical behavior, ceria imparts additional toughness. Further improvements in fracture toughness and chemical stability as well as superior resistance to heat flow are among the benefits to be realized by the interlaying of ceria and yttria stabilized zirconia. Additional systems rely on the chemical inertness of the candidate to dissolution by molten alkali rich salts and the chemical attack by oxides that tend to promote sintering. Lastly, attention is also focused on increasing the strength of the ceramic-bond coat interface and the reduction of the stresses related to the growth of oxide at this critical junction.

The bond coat not only unites the ceramic to the substrate but also imparts oxidation and corrosion resistance. Evidence from the field clearly shows the presence of sulfur-bearing species in the TBC system. The candidate bond systems take advantage of the recent knowledge, first discovered under Government sponsored UTC programs, that relates premature oxide scale spallation to indigenous sulfur present in all superalloys and coatings. The candidate materials include compositions that have inherent resistance to the movement of sulfur that travels inbound through the ceramic or outbound from the substrate alloy. Other candidate materials have inherent resistance to sulfidation corrosion as well as improved mechanical properties, and ease of application.

The approach taken for the TBC Life Model Development is a combination of the analytical studies and empirical/mechanistic investigations previously developed and later expanded under NASA's HOST program. In that study the inelastic behavior of the ceramic was identified as a critical parameter. In the case of the EB-PVD ceramic which behaves predominantly elastic, the critical parameter was identified to be the response of the thermally-grown oxide (TGO) layer. This program focuses upon generic modeling of the TBC failure processes/mechanisms. The intent is to sort out the dominant TBC failure mechanism(s), develop sensitivity relationships, and define a operable TBC life prediction application method.

The Manufacturing Process Development as well as Maintenance, Repair, and Inspection are equally important tasks. Even though many of the processing aspects of TBCs currently in use are proprietary, a

generic approach must be developed to list processing steps. The interchangeability of spray and aluminizing processes as well as EB-PVD to plasma spray need be addressed. An aim, for example, is to transfer TBCs developed for blades to the combustor or vice versa. Other concerns address post ceramic processing such as hole drilling.

With respect to Maintenance, Repair, and Inspection, attention is focused on full ceramic repair which encompasses complete stripping and recoating of both the ceramic and the bond coat. Laser holography and acoustic emission are primary procedures to be evaluated to assess TBC damage. These sensing methods focus on the detection of incipient defects and processing damages long before they become visible to the naked eye.

Lastly, the heart of any corrosion-related undertaking is the test program that generates the necessary information that promotes knowledge and understanding in a meaningful time frame without actually performing full-scale long-term tests. In this program, the gradient test burner rig which

generates surface temperatures in excess of 2600 °F with 300 °F gradients across the TBC coated air cooled test specimens shown schematically in Figure 11, is used in addition to the state-of-the-art burner rigs. Also employed is a unique controlled environment rig in which the partial pressures of oxygen and sulfur are controlled in order to simulate the oxygen and sulfur activities associated with the presence of condensed salts on the surface of industrial TBCs. This data aids in the evaluation and response of the material chemistry with respect to sulfide formation.

## Summary

TBCs will be used to achieve the objectives of the ATS program. They are used in aircraft engines and have accumulated millions upon millions of reliable hours. The differences in the duty cycles of the aircraft and the industrial gas turbine are recognized as is the marked differences in environmental operational envelope. At the completion of this program the TBCs best suited to meet the needs of the ATS program will have been identified, tested, and confirmed.

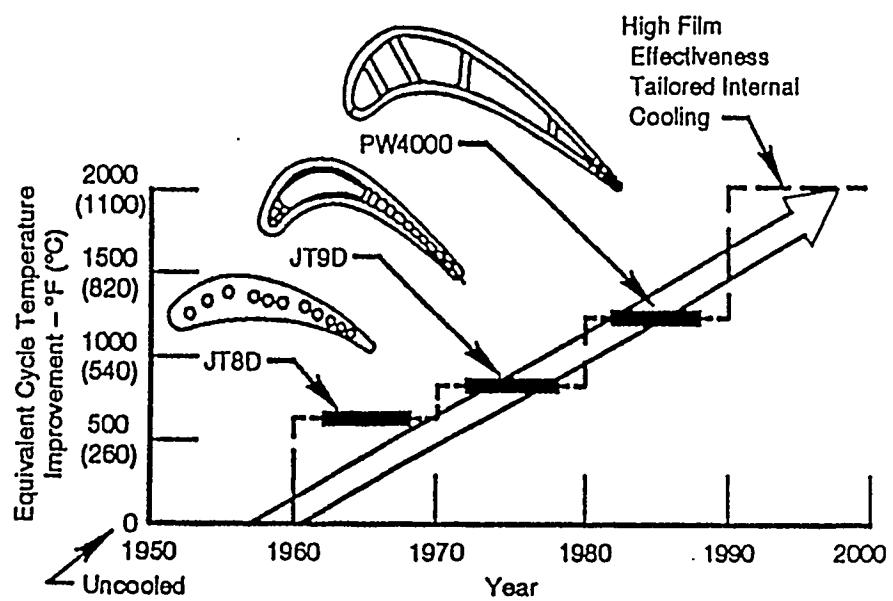
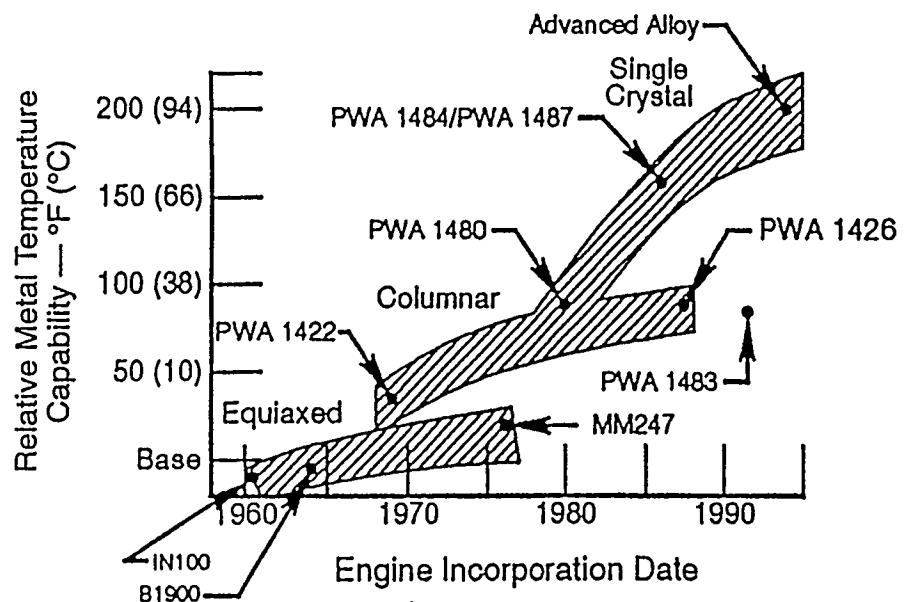
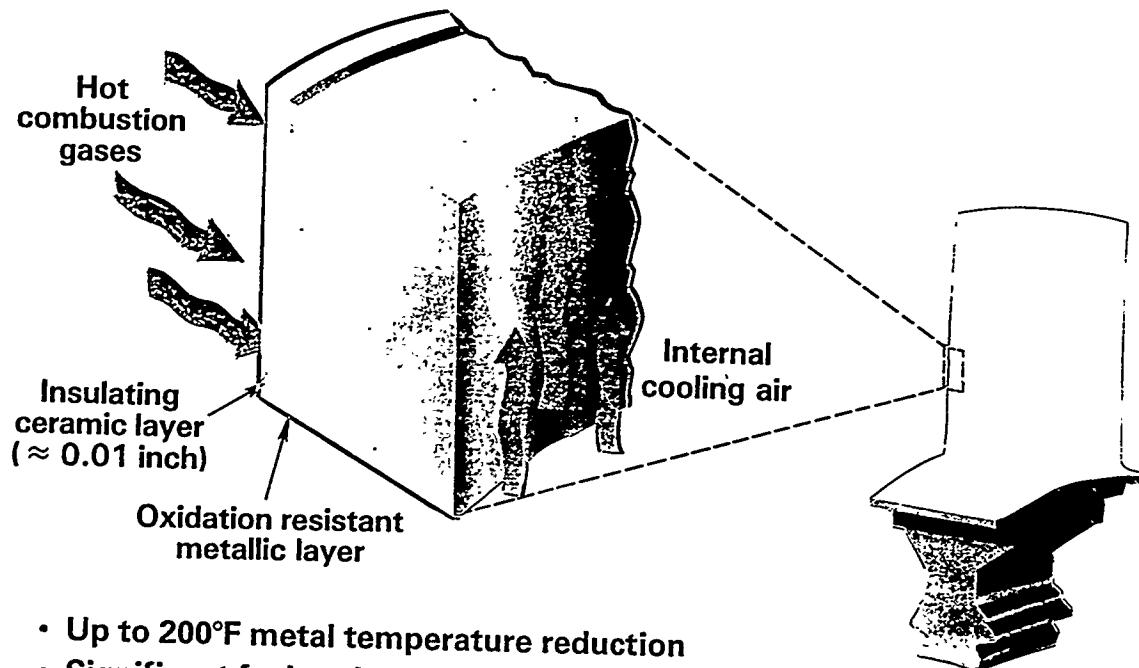


Figure 1. Advances in Turbine Blade Materials and Processes



- Up to 200°F metal temperature reduction
- Significant fuel savings
- Improved durability

Figure 2. Thermal Barrier Coating

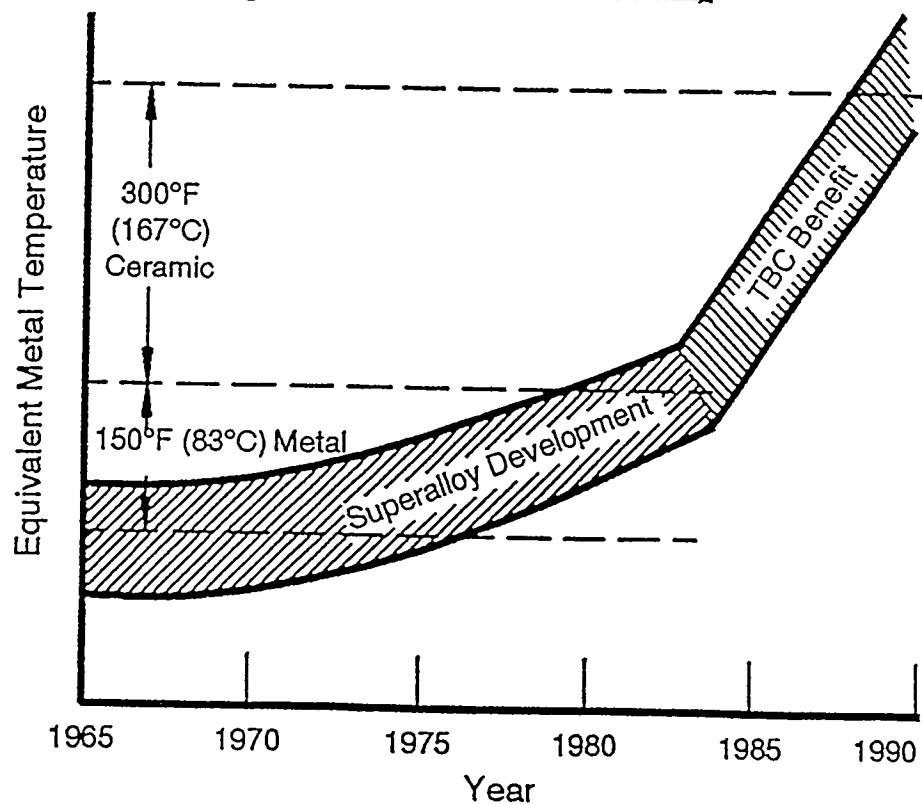


Figure 3. Benefits of Advanced Superalloys and TBCs

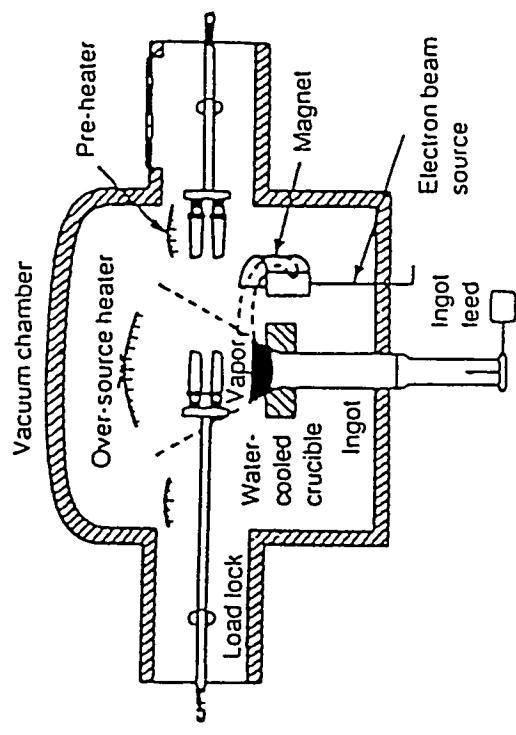
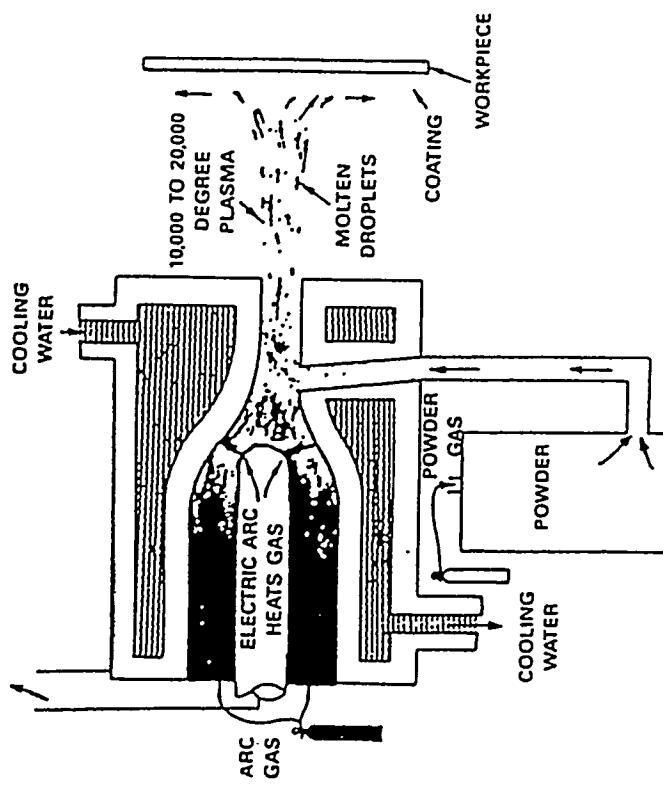
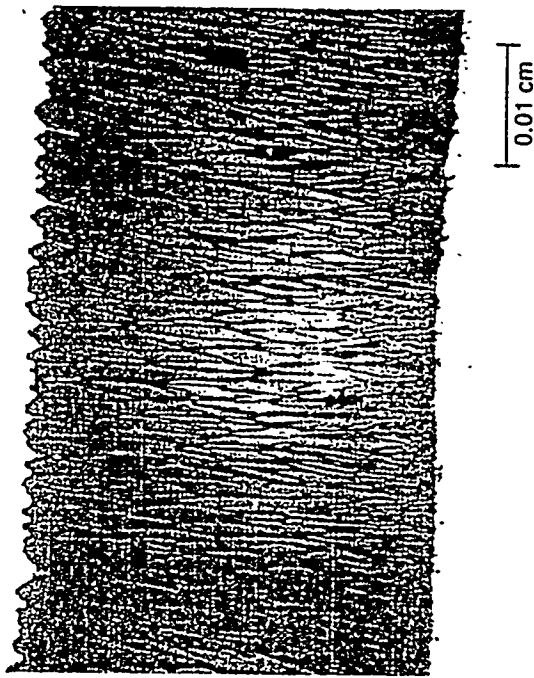
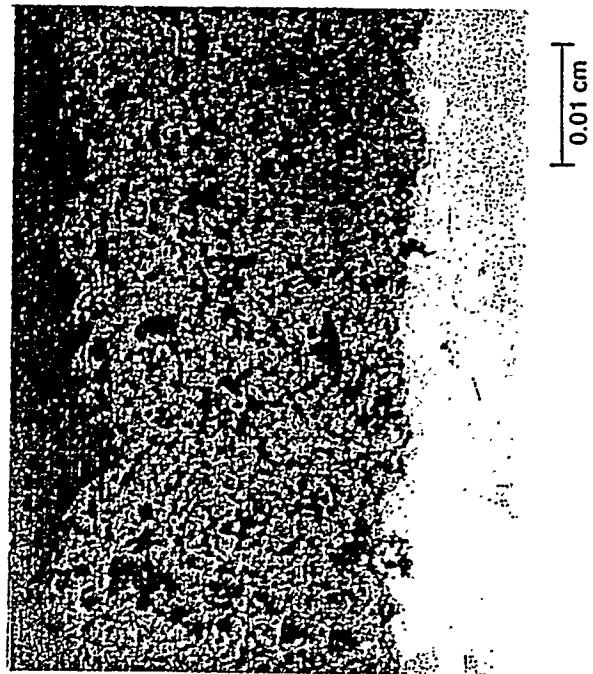
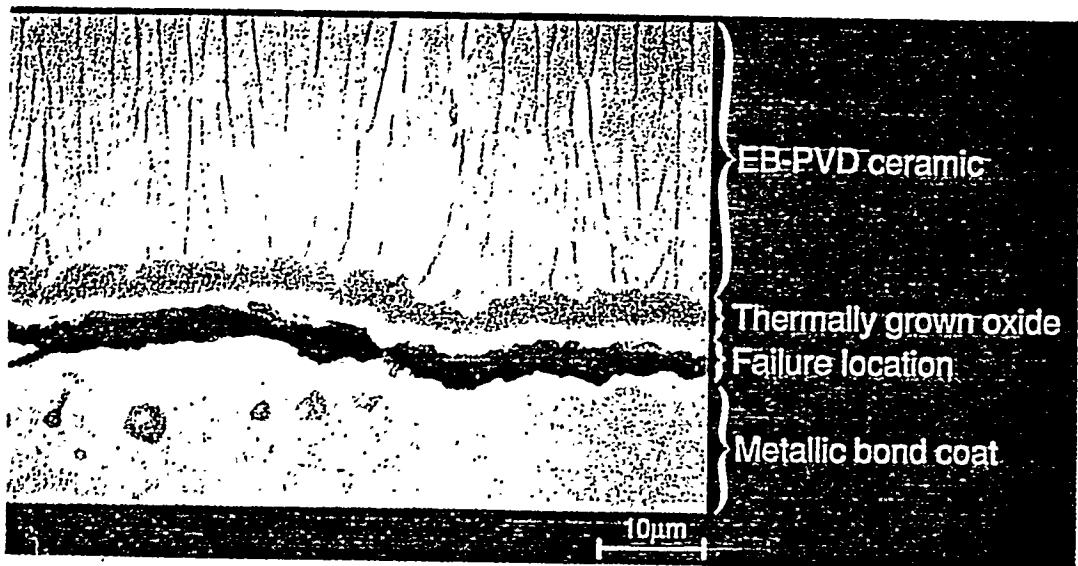


Figure 4. TBC Processes

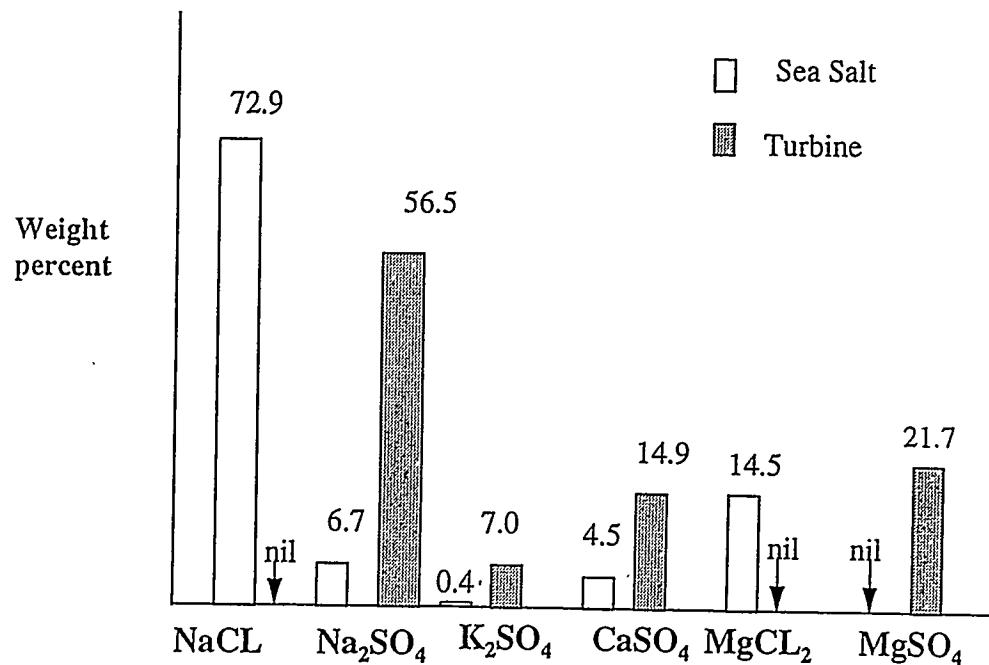


**PWA 264**  
delamination occurs primarily  
within ceramic phase

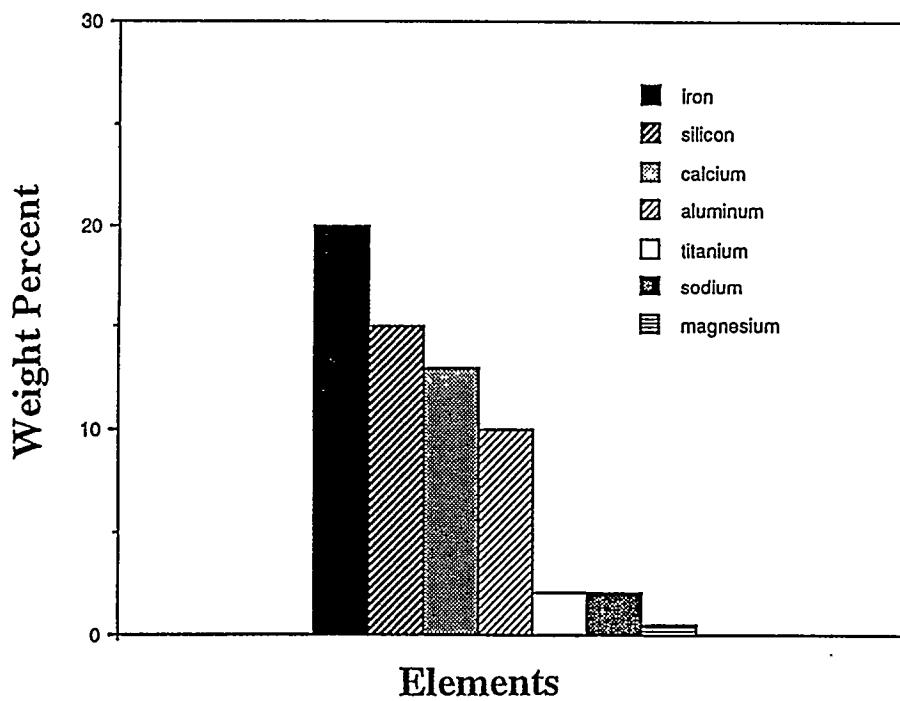


**PWA 266**  
delamination occurs primarily within  
Thermally Grown Oxide

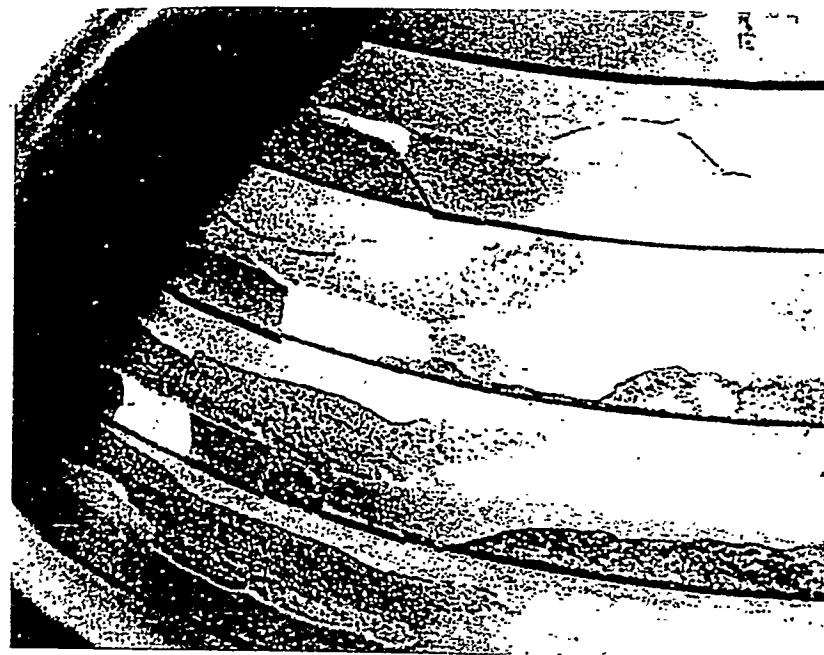
**Figure 5. Failure Modes**



**Figure 6. Comparison of Salt Chemistries**



**Figure 7. Filter Insolubles**



Water soluble salts  
 $\text{CaSO}_4, \text{MgSO}_4$   
 $\text{Na}_2\text{SO}_4, \text{NiSO}_4$   
 $\text{CoSO}_4$

**Figure 8. Industrial and Marine Deposits Acerbate Delamination**



**Figure 9. Sulfides Present at TBC/Bond Coat Interface**

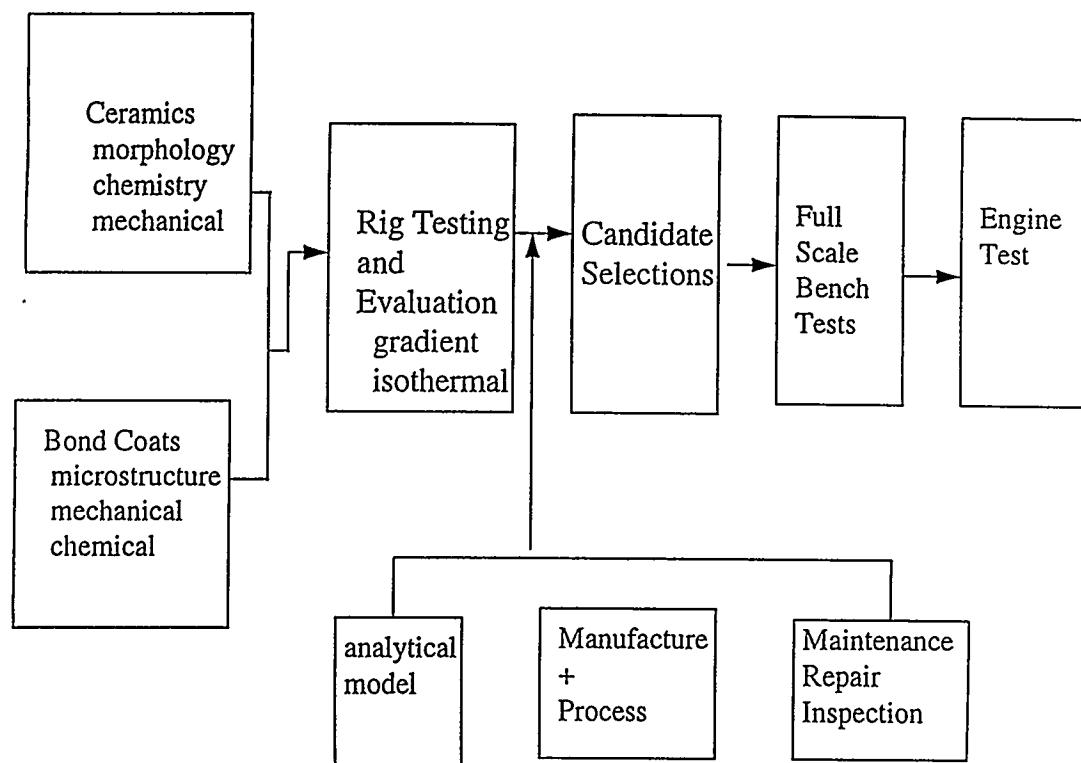


Figure 10. Program Overview

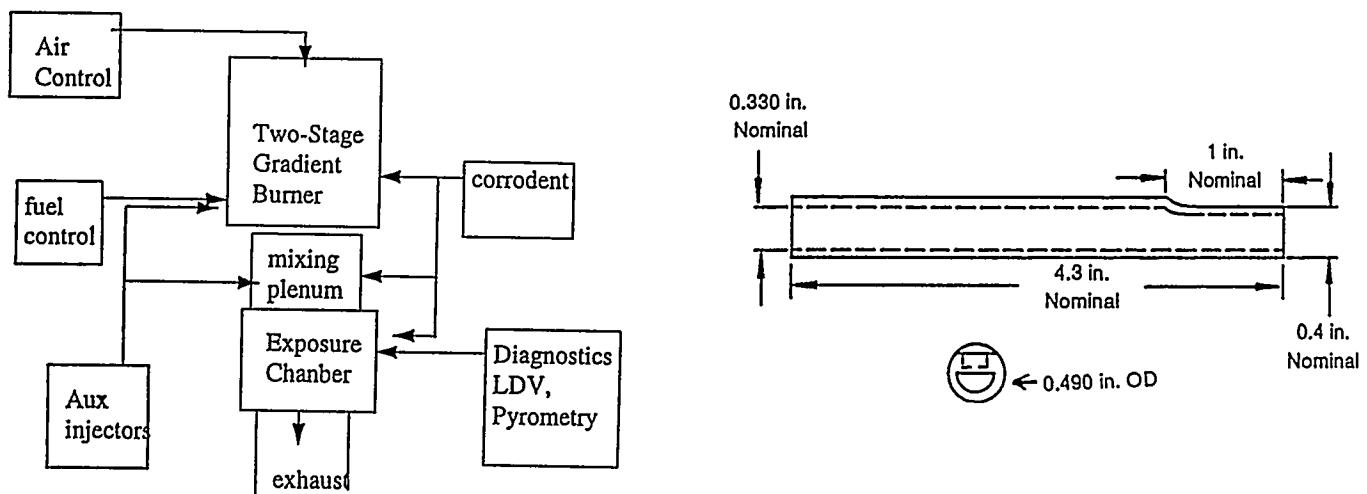


Figure 11. Schematic of Gradient Test Rig and Specimen Configuration