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Thermal-Barrier Coatings for Utility Gas Turbines

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Prepared by

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ABSTRACT

Ceramic coatings on the external surfaces of cooled turbine blades or vanes provide an effective barrier to heat transfer. Such thermal barrier coatings offer significant potential benefits through increased efficiency or component life. The purpose of this work was to assess the potential of thermal barrier coatings for use in utility gas turbines. The primary research effort was carried out by Westinghouse under contract to the National Aeronautics and Space Administration - Lewis Research Center with the Electric Power Research Institute sponsoring the Westinghouse work.

Pressurized passage and ambient pressure doped fuel burner rig tests revealed that thermal barrier coatings are not resistant to dirty combustion environments. However, present thermal barrier coatings, such as duplex partially stabilized zirconia and duplex Ca_2SiO_4 have ample resistance to the thermo-mechanical stress and temperature levels anticipated for heavy duty gas turbines firing clean fuel as revealed by clean fuel pressurized passage and ambient pressure burner rig tests. Thus, it is appropriate to evaluate such coatings on blades, vanes and combustors in the field. However, such field tests should be backed up with adequate effort in the areas of coating application technology and design analysis so that the field tests yield unequivocal results.

EPRI PERSPECTIVE

PROJECT DESCRIPTION

The purpose of thermal barrier coatings is to provide insulation for the cooled metal components of the combustion-turbine hot gas path. The coatings are composed of outer ceramic and inner metallic layers either continuously merged to form a graded coating or sharply divided to form a duplex coating. This thermal insulation has the potential advantage of allowing about 150°F higher gas temperature at the same metal temperature for improved performance or about 150°F lower metal temperature at the same gas temperature for improved durability or a combination of these benefits compared to uninsulated surfaces. The major developmental issues are the durability and reliability of the coatings themselves.

Ceramic thermal barrier coatings have been developed by NASA, coating specialist organizations, and the aircraft jet engine manufacturers since the mid-1950s. By the late 1970s thermal barrier-coated combustion liners were being installed in commercial jet engines. With this favorable background a joint DOE-EPRI program was developed, using NASA as the coordinator and detailed project director. Memos of understanding (MOU) were signed between EPRI and NASA and between DOE and NASA. RP1039 was contracted under the EPRI-NASA MOU. Virtually all of the funding was used in a subcontract, NASA-21377, between NASA and the Westinghouse Electric Corporation Research and Development Center, which did the actual testing and evaluation work. The DOE-NASA MOU, DE-A1-773T1-350, provided for in-house NASA work and for extensive outside contracting. This work had the aim of developing improved thermal barrier coatings and processes. While the MOU negotiations were proceeding, preliminary evaluation of the durability of ceramic coatings when using contaminated fuel was incorporated in a previous EPRI project, RP421-1, which is presented in a four-part series entitled Ceramic Turbine Components Research and Development (EPRI Summary Report AP-1539-SY and EPRI Final Reports AP-1539, Parts 1, 2, and 3). Spalling of the coatings was observed. These results were utilized in formulating the work schedule for RP1039 to include a range of tests using fuels containing various ash constituents.

The RP1039 work concentrated on laboratory testing of currently available thermal barrier coatings on small (0.25-inch-diameter and 0.50-inch-diameter) hollow cylinders with cooling air flowing down the center. The coatings were either duplex coatings with a discrete interface between the metallic inner layer and the ceramic outer layer or blended coatings where the metallic inner layer material gradually transits into the ceramic outer layer. The ceramic outer layers tested were made of (1) zirconia (containing various proportions of yttria), (2) calcium silicate, and (3) zirconia-magnesium oxide. The inner layers were made of the MCrAlY type: M = metal (either nickel or cobalt), Cr = chrome, Al = aluminum, and Y = yttrium. The coated cylinders were tested in combustion tunnels to establish laboratory data on the effects of gas and metal temperatures, fuel impurities, water washing, cycling, and pressure on coating durability. One-atmosphere tests were used to screen out the unfavorable coatings. High-pressure tests were used to confirm these choices. Finally, long-term ($\sim$4000-hour) one-atmosphere tests were used to confirm the durability potential of the coatings.

PROJECT OBJECTIVE

The objective was to obtain laboratory data to help determine the durability potential of currently available thermal barriers for coating utility gas turbine components. Emphasis was to be placed on the compatibility with the ash constituents commonly found in residual petroleum fuel oils. The laboratory combustion tests were to sort out the more promising coating types. These were to be tested for specific fuel and combustion conditions to indicate whether there was enough durability potential so that further in-engine tests would be advised.

PROJECT RESULTS

All coatings were found to have premature failure in combustion gases containing alkali and vanadium impurities. Vanadium was particularly virulent. Magnesium additive showed no capability of easing the vanadium attack on the ceramic coatings. Graded coatings were found to be less vulnerable to the impurities than the duplex coatings of the same type, but that is academic information, since none were acceptable.

With clean fuels, on the contrary, a number of coatings were found to be acceptably durable based on the laboratory tests. The duplex coatings were found to be superior to the graded coatings, since the metallic layer is kept cooler in the former type. The best-performing coatings were the duplex coatings with either calcium silicate or zirconia-8% yttria stabilized ceramic outer layers on MCrAlY metallic inner layers. These coatings performed favorably enough to indicate that they are ready for coating on blades and vanes for in-engine field evaluation at a utility site which burns clean distillate or gaseous fuel.

Arthur Cohn, Project Manager
Advanced Power Systems Division

CONTENTS

ILLUSTRATIONS

TABLES

SUMMARY

Ceramic coatings on the external surfaces of cooled turbine blades or vanes provide an effective barrier to heat transfer. Such thermal barrier coatings offer significant potential benefits through increased efficiency or component life. The purpose of this work was to assess the potential of thermal barrier coatings for use in utility gas turbines. The primary research effort was carried out by Westinghouse under contract to the National Aeronautics and Space Administration - Lewis Research Center with the Electric Power Research Institute sponsoring the Westinghouse work.

The coatings investigated by Westinghouse included the duplex coating concept and the graded coating concept. In the former the coating consists of an inner metallic bond coat layer (NiCrAlY) and an outer ceramic layer. In the graded coating concept, the transition from metal to ceramic is made gradually. The ceramic layers were either zirconia with various levels of yttria stabilizer, zirconia - 24 percent magnesia or calcium silicate.

Early tests, carried out in ambient pressure burner rigs with clean GT No. 2 fuel confirmed that the partially stabilized ZrO_2 - 8 w/o Y_2O_3 coating was superior to fully stabilized ZrO_2. These tests also revealed that the graded coatings degraded rapidly as a result of oxidation of the metal grading layer particles at metal temperatures as low as 1550°F.

The results of initial tests carried out at only 1475°F metal temperature in GT No. 2 fuel doped to simulate a water washed and treated residual oil (1 ppm

Na, 50 ppm V, 2 ppm P, 0.5 ppm Ca, 2ppm Fe, 150 ppm V), revealed that the graded ZrO_2 - 8 w/o Y_2O_3 coating could withstand up to 500 hours of cyclic exposure. In contrast, a duplex ZrO_2 - $8Y_2O_3$ coating failed in less than 100 hours. In a less severe test, (1 ppm Na, 2 ppm V, 2 ppm P, 0.5 ppm Ca, 2 ppm Fe, 6 ppm Mg), graded coatings ZrO_2 - $8Y_2O_3$ and ZrO_2 - 24 MgO exhibited an advantage over their duplex counterparts. The only duplex coating exhibiting good durability in doped fuel tests was the NASA Ca_2SiO_4 coating. It performed as well as the graded ZrO_2 - $8Y_2O_3$ coating in the last mentioned test (500 hours with no failure) as well as in a test run with a fuel doped to 9 ppm Na, 180 ppm V, 18 ppm P, 4.5 ppm Ca, 2 ppm Fe, 594 ppm Mg. Further details of the latter test will be given later.

Water washing tests were carried out to assess the effect of a normal utility cleaning practice on thermal barrier coatings. The tests had no significant effect on coating durability.

The key tests in this program were run at 9 atm in a pressurized passage with either clean GT No. 2 fuel or a simulated water washed and treated residual oil (1 ppm Na, 20 ppm V, 2 ppm P, 0.5 ppm Ca, 2 ppm Fe, 66 ppm Mg). Two cycles were run. The initial cycle involved insertion of cold specimens into the passage which was running with the gas stream held at 1950^oF. This cycle is far more severe in thermal stress generation than the gradual ramp-up and ramp-down cycle used in practice. The second type of cycle run simulated the actual cycle used in practice. Both cycles were run with the clean fuel and dirty fuel described previously. The coatings tested were duplex and graded ZrO_2 - $8Y_2O_3$ and duplex Ca_2SiO_4.

With the dirty fuel, all coatings failed in less than 20 cycles regardless of whether a ramped or stepped cycle was used. With the clean fuel, all coatings survived 20 cycles of either type. Finally, all coatings survived a 50 ramped cycle test in which the fuel was an SRC-II blend (2.9 middle distillate/1 heavy distillate).

In conjunction with the 9 atm dirty fuel test, a test was run at ambient pressure at 9 times the dopant level used in the pressurized passage. This test, alluded to earlier, induced failures at ambient pressure in graded and duplex ZrO_2 - $8Y_2O_3$, duplex Ca_2SiO_4 and graded ZrO_2 - 24MgO in 100 cycles or less. Therefore, it was concluded that the high flux of impurities in the pressurized passage was responsible for the rapid failures seen with doped fuel. The mechanism of failure of ceramic coatings in dirty fuel is related to infiltration of coating porosity by molten salts.

The final test was a 4000 hour endurance test run at ambient pressure with clean fuel. Metal temperature was 1475^{o}F and gas temperature was 2100^{o}F. Under these conditions, the graded ZrO_2 - $8Y_2O_3$ coating showed the problem of grading layer oxidation in about 2000 hours or less. Duplex ZrO_2 - $8Y_2O_3$ and Ca_2SiO_4 coatings survived in good condition.

From this program it was concluded that thermal barrier coatings are not resistant to dirty combustion environments. However, present thermal barrier coatings such as duplex partially stabilized zirconia and duplex Ca_2SiO_4, have ample resistance to the thermo-mechanical stress levels anticipated for heavy duty gas turbines firing clean fuel. Thus, it is appropriate to evaluate such coatings on blades, vanes and combustors in the field. However, such field tests should be backed up with adequate effort in the areas of coating application technology and design analysis so that the field tests yield unequivocal results.

Section 1

INTRODUCTION

BACKGROUND

The concept of applying an aerodynamically smooth insultating coating to cooled components of gas turbines has long been of interest for improving performance (1).* Performance improvements could be achieved with such coatings by either allowing higher turbine inlet temperatures or by reducing cooling air consumption at fixed inlet temperatures. Alternatively, component durability could be improved by a reduction of metal temperature at fixed coolant flow. In addition, since such thermal barrier coatings (TBC) are based on ceramic layers, they also may have potential to provide increased protection of metallic components against erosion and fuel impurity hot corrosion. The TBC concept is illustrated in Figure 1-1 (2). The benefits

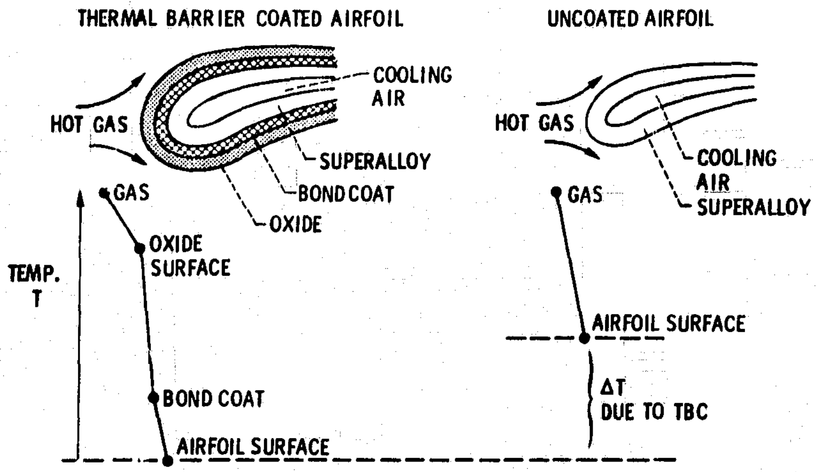

Figure 1-1 - Thermal Barrier Coatings (TBC): The Concept

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*Numbers in parentheses are references.

result from the large temperature drop (ΔT) developed across the ceramic layer. The magnitude of this ΔT is a function of ceramic thickness and thermal properties as well as of the heat transfer conditions such as pressure and flow regime. Early analytical studies showed that a NASA Lewis ZrO_2-12w/oY_2O_3/NiCrAlY coating, only 12-20 mils thick, lowered metal temperatures of air-cooled blades 150°F or more (1). These results have been confirmed in laboratory tests (3) and in short time research aircraft turbine engine tests of a full set of first stage rotor blades (4). In both cases, the coatings adhered and performed the thermal barrier role. Coating ability to withstand high heat flux conditions (as in advanced gas turbine engines) or combustion environments other than from clean aircraft fuels and coating durability have yet to be fully demonstrated. The compatability of ZrO_2-12w/oY_2O_3 duplex thermal barrier coatings with various fuel impurities was investigated by Westinghouse under Electric Power Research Institute (EPRI) sponsorship (5) and by NASA (6). These laboratory burner tests disclosed spalling of the oxide by combustion products of usual petroleum fuel impurities. However, the results were limited in terms of the impurities and test conditions and to basically a single coating structure and ceramic composition.

To further assess the potential of thermal barrier coatings for utility gas turbines, the project Thermal Barrier Coatings for Heavy Oil Gas Turbines was initiated with NASA Lewis via an EPRI/NASA Memorandum of Understanding dated October 19, 1977 (RP 1039-1). Under this agreement, NASA Lewis has performed a contract management and program coordination function for EPRI. All EPRI funds (with the exception of a small contract auditing fee) have been applied to the contract "Evaluation of Present Thermal Barrier Coatings for Potential Service in Electric Utility Gas Turbines" (NAS 3-21377) with the Westinghouse

Research and Development Center. NASA funding covered NASA manpower costs. The contract was initiated in August 1978 via a NASA competitive procurement. The NASA Contract Manager was Dr. Robert A. Miller while the Westinghouse Program Manager was Dr. R. J. Bratton. Drs. S. K. Lau and S. Y. Lee were the Westinghouse Investigators. The results of this contract are reported in NASA CR-165545 (7).* The purpose of this report is to provide additional background and perspective to the Westinghouse results. This is needed because of parallel programs being carried out under NASA and Department of Energy sponsorship. These programs are covered technically and referenced in the Appendix.

The bulk of the DOE funded research contemporary with the EPRI sponsored program was carried out at NASA or under contract to NASA via interagency agreements. In-house research was primarily sponsored by DOE/NASA Interagency Agreement DE-AI01-77 ET - 10350 -- Gas Turbine Critical Research and Advanced Technology Support Project. Contract research was primarily supported by DOE/NASA Interagency Agreement DE-AI01-77 ET - 1311 -- Advanced Conversion Technology. The object of the in-house research was to further the understanding of thermal barrier coating behavior in dirty fuels and to improve coating durability in dirty fuels. The object of the contract research was to carry out a preliminary design of a thermal barrier coated utility turbine component and to improve coating durability in dirty fuels. In contrast, the EPRI funded program examined the potential of current TBC for use in heavy-oil gas turbines.

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* The cited report is available from the EPRI Project Manager or from the National Technical Information Service, Springfield, VA 22166

CONCLUSIONS AND RECOMMENDATIONS

Based on the results of the work carried out by Westinghouse under EPRI sponsorship, as summarized in this report and in greater detail in reference 7, and parallel efforts carried out under NASA and Department of Energy sponsorship, as described briefly in the Appendix, the following conclusions and recommendations have been obtained.

1. Present thermal barrier coatings, such as duplex partially stabilized zirconia and duplex Ca_2SiO_4, have ample resistance to the thermo-mechanical stress levels anticipated for heavy duty gas turbines firing clean fuel. Thus, it is appropriate to evaluate such coatings on blades, vanes and combustors in the field. However, such field tests should be backed up with adequate effort in the areas of coating application technology and design analysis so that the field tests yield unequivocal results.

2. It has been amply demonstrated by the results of the EPRI funded contract and parallel efforts that present thermal barrier coatings are not resistant to dirty combustion environments.

Section 2

EVALUATION OF PRESENT THERMAL BARRIER COATINGS FOR POTENTIAL SERVICE IN ELECTRIC UTILITY GAS TURBINES

The purpose of the contract with Westinghouse was to evaluate the sensitivity of present thermal barrier coatings to conditions simulating utility gas turbine service. The tasks along with their purposes and scope are outlined below.

TASK I - THERMAL BARRIER COATINGS SENSITIVITY TESTS

Purpose

To evaluate a variety of presently available coatings at ambient pressure under a range of temperature, contaminant and clean-up conditions simulating utility gas turbine service.

Scope

This task consisted of three subtasks. The plasma spray deposited coatings involved, as listed in Table 2-1, were relatively mature at the inception of the contract. Two coating structures were investigated: duplex and graded. The duplex coating systems consist of an outer ceramic layer over an NiCrAlY bond coat. This approach was brought to the forefront by NASA (3,4). The microstructure of a duplex coating is shown in Figure 2-1. Note the porosity present in the ceramic layer. In the graded coatings the transition from the metallic bond coat to the ceramic is made gradually to minimize the abrupt transition in thermal expansion associated with duplex coatings. The microstructure of a graded coating is shown in Figure 2-2. Prior experience with early graded coatings had indicated that oxidation of isolated bond coat particles in the graded zone tended to be a primary failure mechanism.

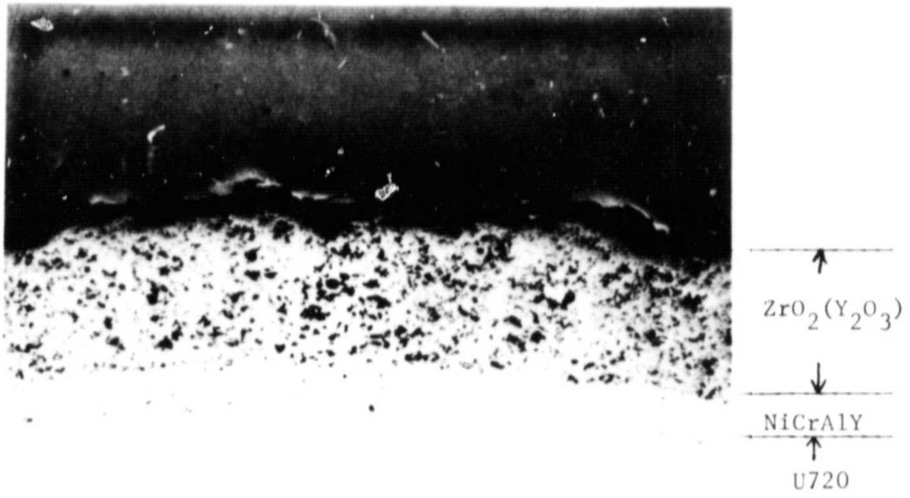
Table 2-1

THERMAL BARRIER COATING SYSTEMS

Oxide* Thermal Barrier	Coating** Description	Oxide Phase
1. ZrO_2 - $8Y_2O_3$	Duplex - Two Layers: 5 mil NiCrAlY Bond Coat 15 mil Oxide Overcoat	95 Tetragonal/cubic 5 monoclinic
2. ZrO_2 - $15Y_2O_3$		Tetragonal/cubic
3. ZrO_2 - $20Y_2O_3$		Tetragonal/cubic
4. ZrO_2 - 24.65MgO		82 Tetragonal/cubic 18 monoclinic and Free MgO
5. Ca_2SiO_4		Ca_2SiO_4
	* * * * * * * * * * * * * * *	
1. ZrO_2 - $8Y_2O_3$	Graded - Three Layers: 4 mil NiCrAlY 8 mil Graded Zone 8 mil Oxide Overcoat	Tetragonal/cubic monoclinic
2. ZrO_2 - $15Y_2O_3$		Tetragonal/cubic
3. ZrO_2 - $20Y_2O_3$		Tetragonal/cubic
4. ZrO_2 - 24.65MgO		82 Tetragonal/cubic 18 Monoclinic and Free MgO

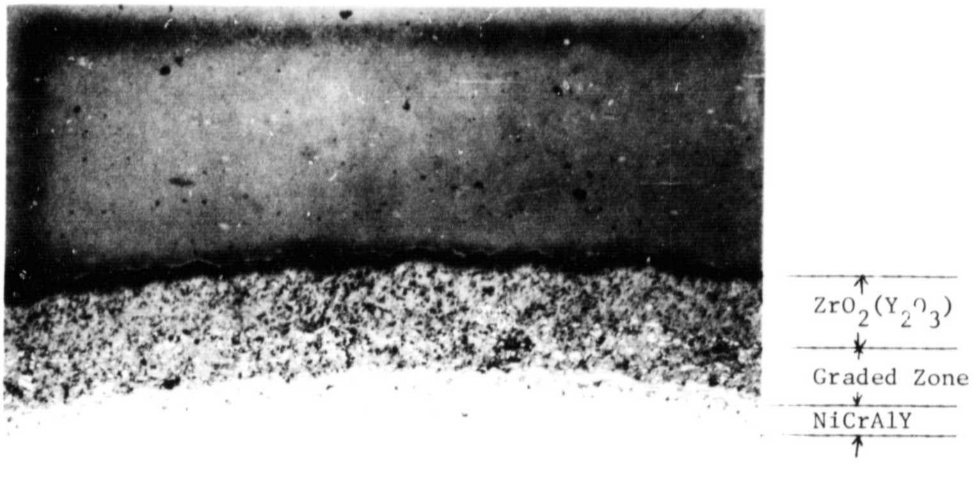
* Nominal oxide composition in weight percent

** Nominal NiCrAlY composition (weight percent): Ni-20Cr-11Al-0.4Y



(50X)

Figure 2-1 - Typical metallographic cross-section of a duplex ZrO_2 - Y_2O_3 coating.*



(50X)

Figure 2-2 - Typical metallographic cross-section of a graded ZrO_2 - Y_2O_3 coating.*

*Please note that the illustration(s) on this page has been reduced 10% in printing.

However, with the relatively low bond coat operating temperatures anticipated for utility gas turbine components with a TBC, and with the highly oxidation resistant bond coat composition selected (Ni-20Cr-11Al-0.4Y), the graded coating approach was deemed worthy of investigation.

The ceramics selected were ZrO_2-24 w/o MgO and ZrO_2 fully stabilized with Y_2O_3 at the 12, 15 and 20 weight percent levels. Based on NASA results available at the inception of the contract, ZrO_2-12 w/o Y_2O_3 was dropped in favor of partially stabilized ZrO_2-$8Y_2O_3$ (6,8). Also, based on NASA results, Ca_2SiO_4 was added early in the contract (6). While all coatings were relatively mature at the inception of the contract, they are all still of current interest with particular emphasis being directed at the present time toward partially stabilized ZrO_2-Y_2O_3 (6 to 8 w/o Y_2O_3) as a result of the research of Stecura (8). Thus, while the coating systems were selected about three years ago, the results of this effort, as the reader will see, are quite contemporary.

TASK IA - CLEAN FUEL TESTS

Purpose

To evaluate the effect of temperature on TBC durability.

Scope

This test, as well as the other Task I tests and the Task III endurance test were conducted at ambient pressure in a low-velocity (12 ft/sec) oil burner. Specimens were 0.5 in. diameter air-cooled hollow pins. The reference fuel for the clean fuel tests was GT No. 2 fuel (ASTM 2880-76), Table 2-2. Three tests were run in Task IA to evaluate the effect of substrate composition and substrate temperature on TBC durability. The tests were run at 2100°F gas temperature with the substrate cooled to either 1475, 1550, or 1650°F for

500 one-hour cycles. The substrates were Udimet 720, a nickel-base blade alloy (Ni-15Co-18Cr-2.5Al-5Ti-3Mo-1.5W-0.04B-0.04Zr-0.04C), and ECY 768, a Co-base vane alloy (Co-10Ni-24Cr-7W-3.5Ta-0.2Ti-0.05Zr).

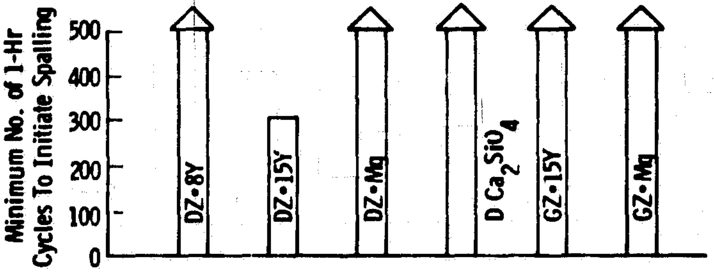
Table 2-2

TYPICAL CHEMICAL ANALYSIS OF NO. GT-2 FUEL OIL

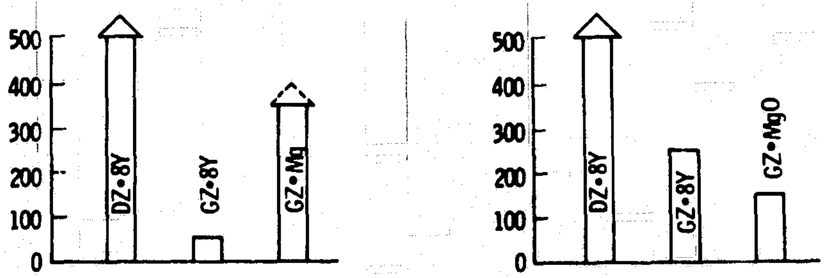
Element	Concentration (ppm)
Fe	2.0
Cu	0.8
Si	0.8
Mn	0.6
Pb	0.5
Al	0.3
Mg	0.3
Na and K	0.3
P	0.3
Ca	0.2
Cr	0.2
V	0.07
S	0.242 (wt percent)

Results

The results of Task IA are summarized in Figure 2-3. Early on it was demonstrated that there was not a significant difference between the performance of the coatings on the two substrates, so no distinction between substrates is given in the results. The 1475°F test, Figure 2-3a revealed a durability problem for the only fully stabilized coating available at the time-duplex ZrO_2-15 w/o Y_2O_3 (denoted DZ-15Y) whereas the graded version (GZ-15Y) lasted the full 500 hours. However, the graded coatings lacked durability at the higher substrate temperatures of 1550 and 1650°F. Although not shown in Figure 2-3, a duplex Ca_2SiO_4 coating ran successfully for 500 hours at 1550°F. Ca_2SiO_4 coated specimens were not available for the 1650°F test.



(a) Clean fuel tests IA2 and IA2R run at 2100°F gas/1475°F metal



(b) Clean fuel test IA1 run at 2100°F gas/1650°F metal

(c) Clean fuel test IAX run at 2100°F gas/1550°F metal

Figure 2-3 - Cycles to failure in 500-hour cycle burner rig tests using clean fuel (GT No. 2).

The duplex coatings failed by cracking in the ceramic close to the ceramic/bond coat interface as illustrated in Figure 2-4. The failure mechanism for the graded coatings was bond coat oxidation as can be seen in Figure 2-5. Note that the failure location is similar to that of duplex coatings in clean fuel. Post-test evaluations of the ZrO_2-MgO coatings revealed almost complete destabilization with the cubic phase (ZrO_2-24 MgO) decomposing to monoclinic zirconia plus MgO in 500 hours. Also, substantial MgO sulfation and hydration was noted as indicated by the detection of $MgSO_4 - 6\ H_2O$ by XRD.

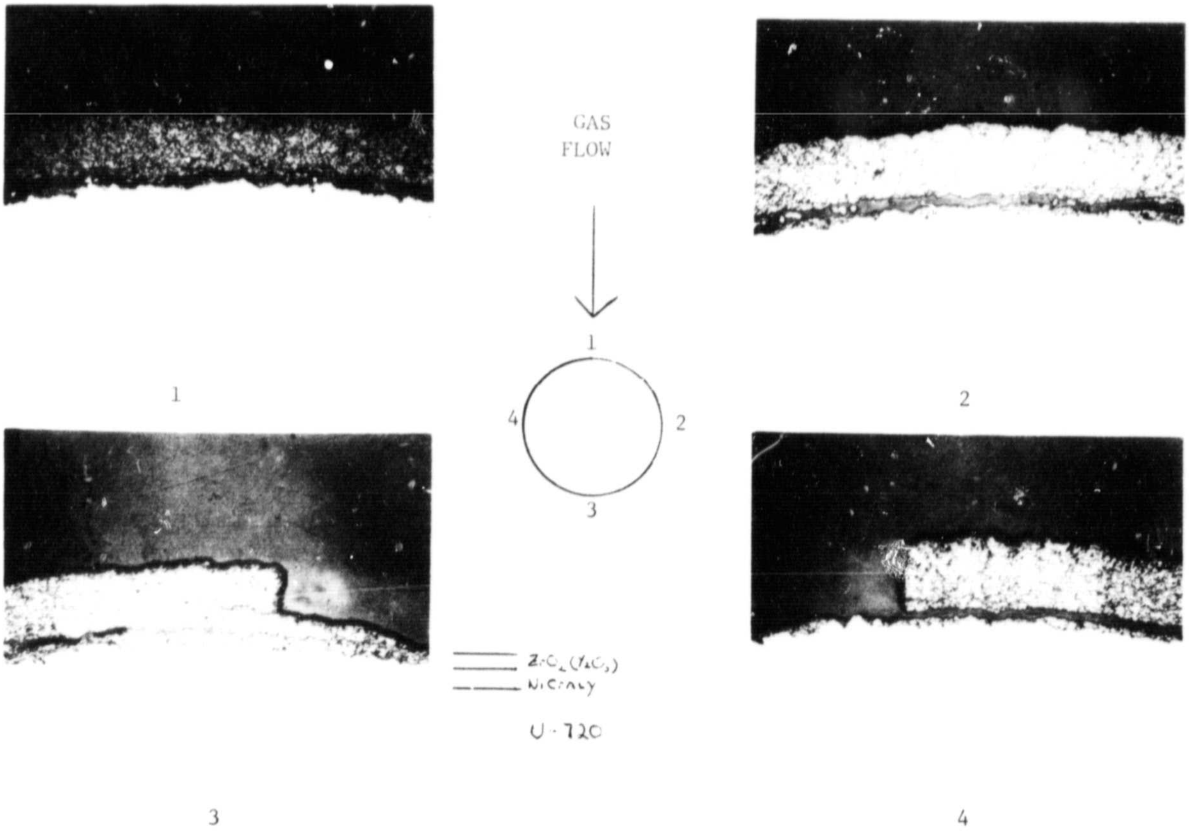


Figure 2-4 - Metallographic cross-sections from four different locations of specimen B-3 (ZrO_2 - $15Y_2O_3$) after 350 hours of exposure in clean fuel. (30x)*

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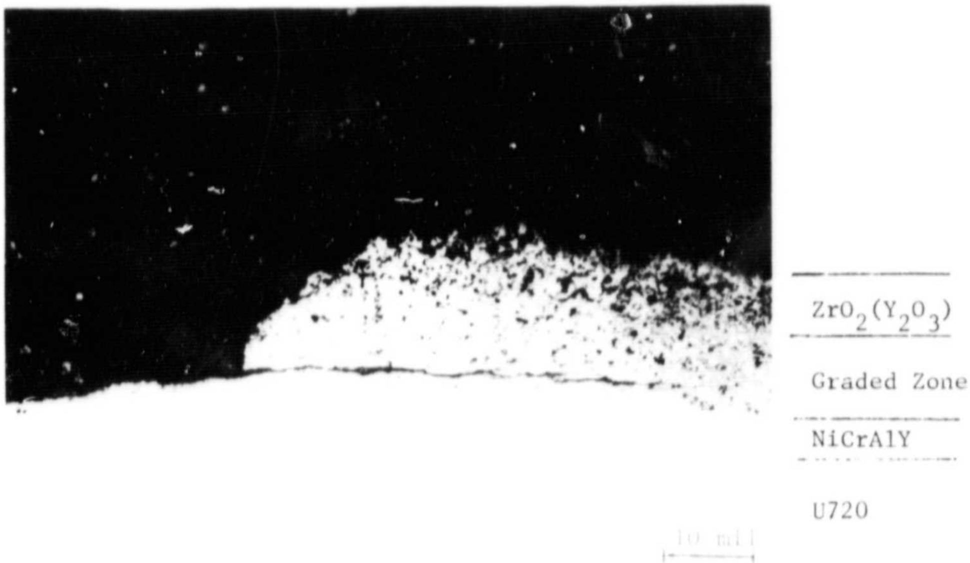


Figure 2-5 - Graded ZrO_2 - $8Y_2O_3$ after 133 cycles in clean fuel.

TASK IB - FUEL SENSITIVITY TESTS

Purpose

To determine the sensitivity of TBCs to fuel impurities.

Scope

The emphasis of these tests was placed on simulated water washed and treated residual oil - a fuel of considerable interest at the time these tests were run. Tests were run at 2, 50 and 180 ppm vanadium with an Mg fuel additive in the ratio of 3 Mg: 1 V by weight. The test conditions are summarized in Table 2-3. In test IBX the impurity levels used in the Task II, 9 atm pressurized passage test were multiplied by 9 to arrive at 180 ppm V and additional Mg additive was used to cope with phosphorous. The 9x factor adjusts for pressure, but no attempt was made to correct for mass flux. Test IB6, an accelerated clean fuel-simulated heavy sea salt ingestion test, was run with two metal temperature levels achieved by adjusting the air cooling.

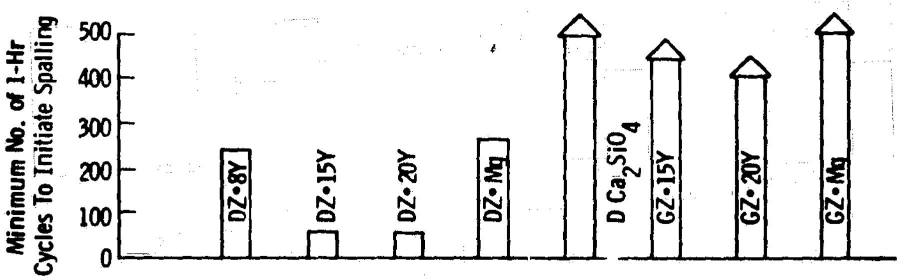
Table 2-3

SUMMARY OF FUEL SENSITIVITY TEST CONDITIONS

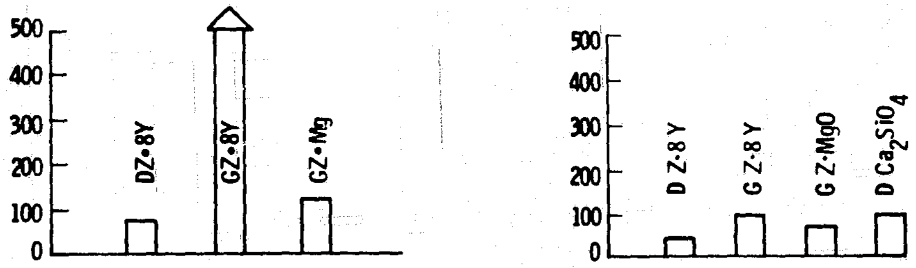
Test No.	Gas/Metal Temp.(^{o}F)	Fuel
IB4	2100/1475	GT No. 2 doped to 1 ppm Na, 2 ppm V, 2 ppm P, 0.5 ppm Ca, 2 ppm Fe, 6 ppm Mg
IB4R	2100/1475	GT No. 2 doped to 1 ppm Na, 2 ppm V, 2 ppm P, 0.5 ppm Ca, 2 ppm Fe, 6 ppm Mg
IB5	2100/1475	GT No. 2 doped to 1 ppm Na,. 50 ppm V, 2 ppm P, 0.5 ppm Ca, 2 ppm Fe, 150 ppm Mg
IBX	2100/1475	GT No. 2 doped to 9 ppm Na, 180 ppm V, 18 ppm P, 4.5 ppm Ca, 2 ppm Fe, 594 ppm Mg, and 2.25 wt percent S
IB6	2100/1475 and 2100/1650	GT No. 2 doped to 100 ppm Na, 180 ppm Cl, 13 ppm Mg, 4 ppm Ca, 4 ppm K and 2 wt percent S

Results

The results for the simulated water washed and treated residual oil tests, all run at 2100°F gas/1475°F metal, are summarized in Figure 2-6. These low temperature tests indicated a clear advantage for graded coatings and for partially stabilized rather than fully stabilized zirconia. The latter result is in agreement with reference 6. Of all coatings tested, duplex Ca_2SiO_4 performed the best. However, no coating displayed a time to first failure in excess of 100 hours in the 180 ppm V test. A NiCrAlY-only coated specimen showed no signs of distress after 500 hours of exposure in this test. Metallographic evaluation of specimens revealed that failure occurred in the duplex coatings in the usual location - in the ceramic layer very close to the bond coat. The failure location in graded coatings shifted from the graded zone - NiCrAlY region observed with clean fuels to the ceramic zone - graded zone region as illustrated in Figure 2-7.



(a) Tests IB4 and IB4R
Fuel: GT No. 2 doped to (ppm) 1-Na, 2-V, 2-P, 0.5, Ca,
2-Fe, 6-Mg



(b) Test IB5
Fuel: GT No. 2 doped to (ppm)
1-Na, 50-V, 2-P, 0.5-Ca
2-Fe, 150-Mg

(c) Test IBX
Fuel: GT No. 2 doped to (ppm)
9-Na, 180-V, 18-P,
4.5 Ca, 2-Fe, 594-Mg

Figure 2-6 - Cycles to failure in 500-hour cycle burner rig tests using doped fuel (2100°F gas/1475°F metal).

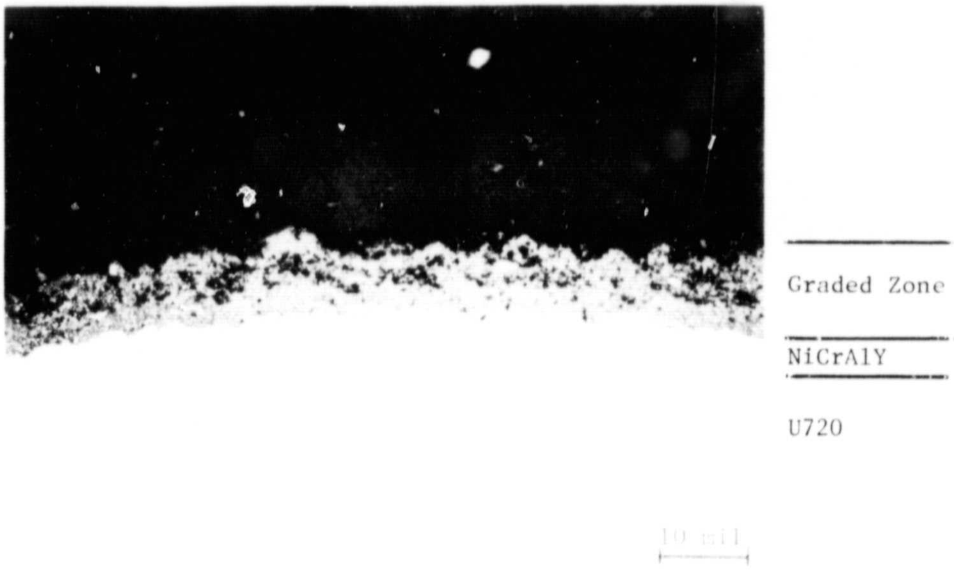


Figure 2-7 - Graded ZrO_2 - 24.65 MgO after 150 cycles in doped fuel (Test IB5).

Post-test XRD analysis of the ZrO_2-Y_2O_3 coatings revealed that destabilization of the zirconia to the monoclinic phase occurred near the surface of the coatings as a result of reaction with combustion gas condensates. Failure was attributed to cracks initiated by the disruptive volume expansion associated with yttrium leaching from zirconia and resultant monoclinic phase formation. However, no reaction products involving yttrium and condensates were detected. An alternative explanation consistent with the analysis of Miller (9) is that the combustion gas condensates filled in the 10 to 15 percent porosity found in the as-sprayed coating. As a result, the ability of the coating to accommodate thermal cycling was compromised. In fact, both mechanisms may have contributed to coating failure.

XRD analysis of the tested ZrO_2-24 MgO and Ca_2SiO_4 coating systems revealed a strong tendency for $MgSO_4$ and $CaSO_4$ formation, respectively, as a result of reaction with SO_x. In addition, Ca_2SiO_4 apparently reacted with $Mg_3V_2O_8$ and $MgSO_4$ as suggested by overlapping of Mg, Si, and Ca in electron microprobe elemental maps of metallographic cross sections.

Bare and NiCrAlY coated alloys were included in the tests just described. The Mg additive effectively inhibited hot corrosion attack in all of the vanadium-doped fuel tests.

The results of the accelerated sea salt corrosion test are illustrated in Figure 2-8. Among the 1475°F metal temperature specimens, the graded ZrO_2-$8Y_2O_3$ system was the most durable, but failed in less than 200 hours. The duplex Ca_2SiO_4 coating performed almost as well as the graded zirconia-based system, but at 1650°F, Ca_2SiO_4 coating life decreased markedly.

The most likely cause of coating failure in the accelerated sea salt corrosion test was penetration of the ceramic with molten sulfates and mechanical

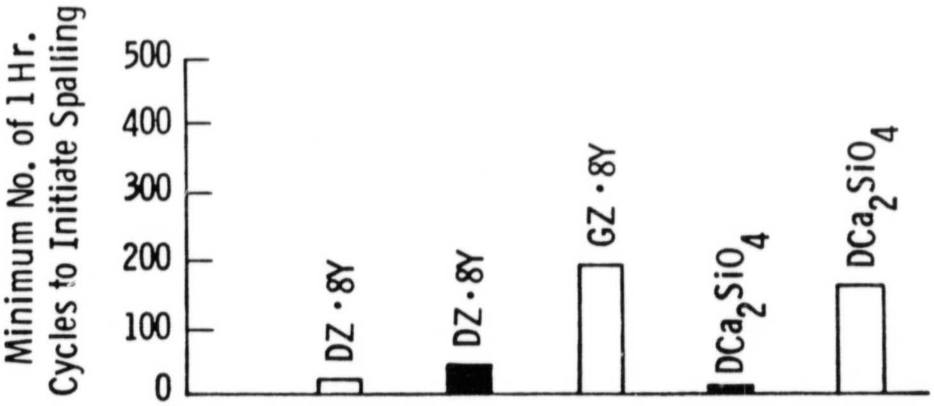


Figure 2-8 - Cycles to failure in a 300-hour cycle burner rig test simulating high levels of sea salt intake (Test IB6).

Temperature: ☐ 2100°F gas/1475°F metal
■ 2100°F gas/1650°F metal

Fuel: GT No. 2 doped to (ppm): 100-Na, 180-Cl, 13-Mg, 4-Ca, 4-K, 2 wt percent S disruption as a result of cyclic freezing and thawing. As with the prior tests, Ca_2SiO_4 and ZrO_2-MgO reactivity toward sulfur were noted. With these coatings, these reactions may have contributed to failure. Phase instability of ZrO_2-MgO may have been an additional contributor.

The NiCrAlY coated specimen exposed in the accelerated sea salt corrosion test exhibited severe hot corrosion attack with penetration of the 1/8" thick substrate wall occurring in some instances. One should note that NiCrAlY deposited by low pressure plasma spraying would not be as susceptible to such attack. An extremely noteworthy observation was that the Linde applied bond coats were not hot corroded in TBC coatings after most of the ceramic layer had spalled. The reasons for the inhibiting effect of the thin and generally discontinuous residual TBC layers in the case of the duplex ZrO_2-$8Y_2O_3$ and graded ZrO_2-MgO coatings are not known. However, this observation is worthy of further investigation. With the NASA applied Ca_2SiO_4/NiCrAlY system, no inhibition of corrosion was noted, possibly due to the higher porosity of the bond coat.

TASK IC - WATER WASHING SENSITIVITY TESTS

Purpose

To determine if the common practice of turbine clean-up by water washing has an effect on thermal barrier coatings.

Scope

The emphasis of these tests was again placed on simulated water-washed and treated residual oils. The use of fuel additives containing Mg to inhibit vanadium induced hot corrosion causes turbine fouling and performance losses. Thus, water washing is commonly used to periodically remove deposits (Nutshelling is also sometimes practiced). Two fuels treated with a Mg additive were run in 500 hour tests each. The first was a 50 ppm V fuel (see

Table 2-3, test IB5). The second fuel had a V level of 20 ppm with the other impurities at the same level as in the first fuel. The second fuel was the same as was run in the Task II pressurized passage dirty fuel tests. Washing by deionized water spray (5 ppm Na + K) was performed at 50, 100, 150, 250, 350, and 450 hours in the 50 ppm V test. This procedure simulated actual turbine washing practice. The amount of deposit was determined before and after washing. Except for the final 450 hour wash, specimens were oven dried at 300°F for 1.5 hours after washing. In the 20 ppm V test, washing was performed at 150 to 200 hour intervals.

Results

The results of the 50 ppm V water washing sensitivity tests are partially summarized in Figure 2-9. The duplex Ca_2SiO_4 coating, for which results are not presented, survived the test. The durability of the graded ZrO_2 - $8Y_2O_3$ coatings were basically unaffected by washing. Exposure of non-dried specimens after the 450 hour washing revealed that intact coatings were unaffected while coatings which had already experienced spalling or cracking were degraded further.

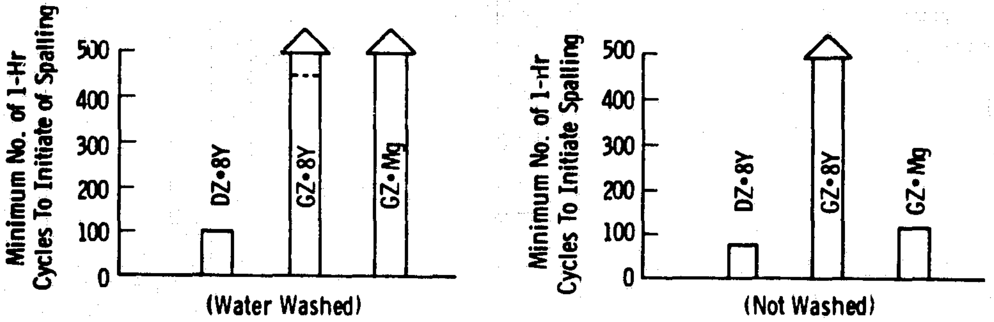


Figure 2-9 - Effect of water washing on number of cycles to failure (Tests IC1 and IB5).
Temperature: (2100°F/1475°F metal)
Fuel: GT No. 2 doped to (ppm): 1-Na, 50-V, 2-P, 0.5 Ca, 2-Fe, 150-Mg

Deposit accumulation was quantitatively followed only for the graded ZrO_2-$8Y_2O_3$ system where a baseline for oxidation could be established from the 500 hour clean fuel test. On this coating, deposits accumulated in a linear manner up to 150 hours. Thereafter, the amount of deposits remained constant. The water washing procedure which involved 3 wash cycles each of ten minutes duration (0.5 gallons/minute) did not totally remove the deposits. Removal ranged from about 25 to 85 percent for the range of coatings tested. The duplex ZrO_2-$8Y_2O_3$ coating was more amenable to washing than the graded versions. Because of the reactivity of the graded ZrO_2-MgO coating and the duplex Ca_2SiO_4 coating and the solubility of $MgSO_4$, it is difficult to draw a conclusion about the ease of deposit removal from these coatings.

The results of the second water washing test at the 20 ppm V level are summarized in Figure 2-10. In this test two of three graded ZrO_2-MgO coatings spalled before the first washing at 150 hours. The third specimen

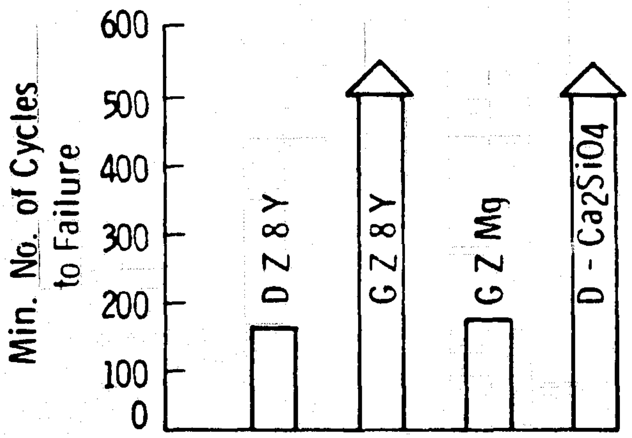


Figure 2-10 - Cycles to failure in burner rig washing sensitivity test (IC2)
Temperature: (2100°F/1475°F metal)
Fuel: GT No. 2 doped to (ppm): 1-Na, 20-V, 2-P, 0.5-Ca, 2-Fe, 66-Mg

survived for 500 hours. Although not visibly failed, metallographic examination revealed large circumferential cracks after 500 hours. The duplex ZrO_2-$8Y_2O_3$ coating survived somewhat longer in this test than in the 50 ppm V test. This may be due to the fact that less monoclinic zirconia formed at the 20 ppm V level.

TASK II - HIGH PRESSURE EFFECTS

Purpose

To evaluate thermal barrier coatings under heat transfer conditions typical of utility gas turbines.

Scope

Clean and doped fuel tests were carried out at 9 atmospheres in a pressurized passage. The specimens were cooled cylinders identical to those used in the ambient pressure tests. The heat flux in the pressurized passage test was about 0.13 MBTU/ft^2-hr whereas row 1 turbine blades would see a maximum of 0.10 MBTU/ft^2-hr. Two cycles were run. The initial cycle, ran initially with dirty fuel (1 ppm Na, 20 ppm V, 2 ppm P, 0.5 ppm Ca, 2 ppm Fe, 66 ppm Mg) involved insertion of the cold specimens into the passage which was running with the gas stream temperature held at 1950^{0}F. After 55 minutes, the specimens were removed and cooled to about 300^{0}F before being reinserted. This cycle is far more severe in thermal stress generation than the gradual ramp-up and ramp-down cycle used in practice. Since all samples failed in less than 20 hours, it was decided to use a cycle which simulates utility practice. This cycle is illustrated in Figure 2-11 along with the severe cycle. In both cycles metal temperature was maintained at 1475^{0}F by air cooling. Steady-state specimen surface temperatures, calculated from heat transfer data, were about 1600 to 1700^{0}F. Thus, the temperature drop

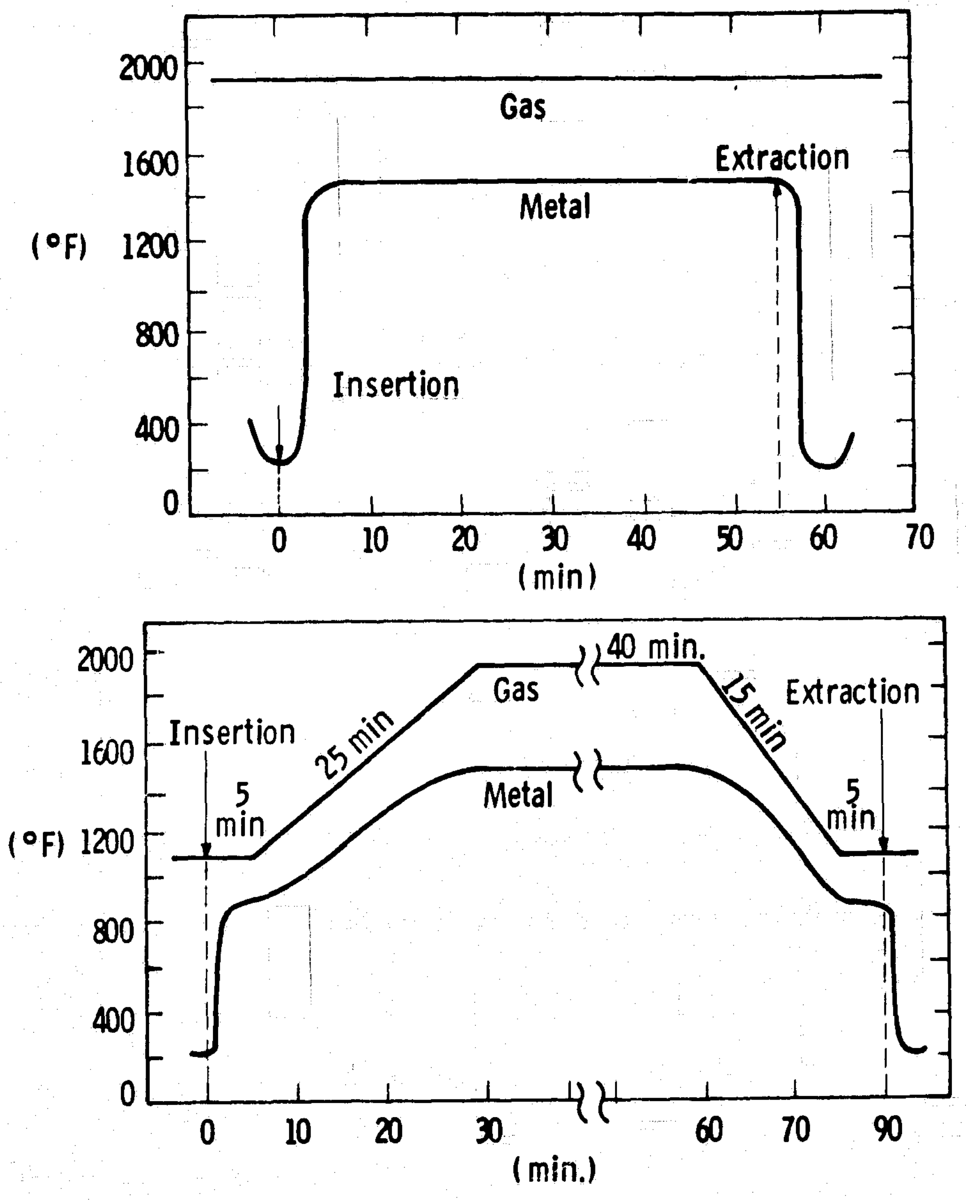
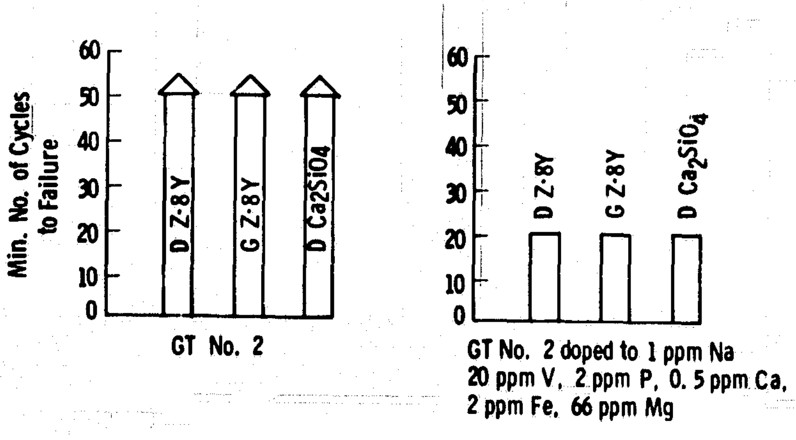


Figure 2-11 - Thermal cycles for test pins in pressurized passage.

through the thermal barrier coatings was 125 to 225°F. Both cycles were run with clean fuel as well as with the dirty fuel described previously. In addition, one test with the ramped cycle was run with SRC-II. Due to the high costs of these tests, no test was run for more than 50 cycles. In all cases two specimens each of duplex and graded ZrO_2-$8Y_2O_3$ and duplex Ca_2SiO_4 were run.

Results

The results of the GT No. 2 and vanadium doped fuel tests are summarized in Figure 2-12. Regardless of the cycle used, all three coating systems lasted for 50 cycles in GT No. 2 whereas they all failed badly in less than 20 cycles in the V doped fuel. In the (2.9 middle distillate/1 heavy distillate) SRC-II test, all three coatings survived for 20 ramped cycles at which time the test was terminated. The impurity levels for the SRC-II fuel were as follows: Ca-1.5 ppm, V - 0.43 ppm, Na - 2 ppm, Pb - 2.7 ppm, Ti - 0.66 ppm, Fe - 17.7 ppm and K- 1.3 ppm. No evidence of corrosion or erosion was detected with SRC-II. However, the specimens were coated with an Fe_2O_3 deposit.



(a) (b)

Figure 2-12 - Cycles to failure in pressurized passage tests
Temperature: 1950°F gas/1475°F metal
Pressure: 135 psig
(a) Clean fuel tests II-2, II-3
(b) Doped fuel tests II-1, II-1B, II-3B,

Based on the visual appearance of graded ZrO_2-$8Y_2O_3$ specimens from the 20 hour, 20 ppm V pressurized passage test and after 350 hours in the 180 ppm V ambient pressure test, it was concluded that the pressurized passage test is more severe. This can be attributed to the higher flux of impurities in the pressurized passage test due to the higher flow rate.

Post test analyses by metallography, XRD and EMP resulted in observations much the same as those made for the ambient pressure test specimens in so far as reactivity of the coatings, phase stability and failure mode. Deposits formed in the pressurized passage were thicker and denser. Ca_2SiO_4 displayed its usual reactivity toward sulfur in the clean fuel tests. Stress relief by radial mud-flat cracking was noted. In the dirty fuel test, evidence of a surface reaction with the deposits to form calcium - magnesium vanadate was detected by EMP.

TASK III - ENDURANCE TEST

Purpose

To evaluate the durability of TBCs in long time exposures.

Scope

Based on the good performance of present day thermal barrier coatings in clean fuel, an undoped GT No. 2 fuel was selected for the 4000 hour endurance test. The test was run using the same burner rigs as in Task I - i.e. ambient pressure, low-velocity. Gas temperature was $2100^{\circ}F$ and the metal temperature was maintained at $1475^{\circ}F$ for the three ceramic coating systems - namely duplex and graded ZrO_2-$8Y_2O_3$ and duplex Ca_2SiO_4. In addition, Linde applied NiCrAlY specimens were tested at $1575^{\circ}F$ metal temperature. The temperature difference between the TBC coated and NiCrAlY only coated specimens is equivalent to the ΔT produced across the ceramic layer.

Thus, if the ceramic were lost, specimen metal temperature would rise to 1575°F in this test.

Results

Results for the thermal barrier coatings are summarized in Figure 2-13. A cooling air shut down during the 2200th cycle precluded running the test as planned. During the cooling air shutdown, metal temperatures reached as high as 2150°F for 15 to 45 minutes. As a result of this temperature excursion, the graded ZrO_2-$8Y_2O_3$ coatings that had been in test for 771 and 2199 cycles failed while a third specimen with this coating which had been in test for 189 cycles survived. The duplex ZrO_2-$8Y_2O_3$ and Ca_2SiO_4 coated specimens survived the excursion. However, the duplex ZrO_2-$8Y_2O_3$ specimen failed after an additional 123 cycles. Thus, this incident supports the conclusion that duplex coatings are more tolerant of elevated temperature oxidation exposure. Referring to Figure 2-13, a graded coating that had not seen the temperature excursion lasted only 2334 cycles. Metallographic examination of all graded ZrO_2-$8Y_2O_3$ coated specimens revealed extensive

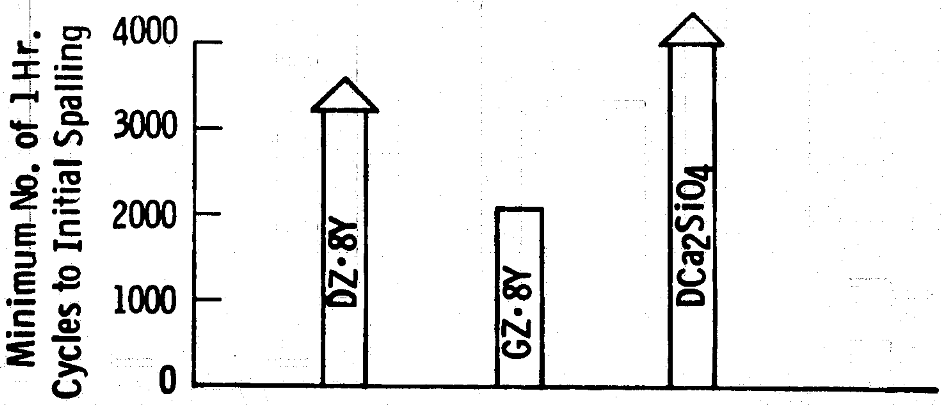


Figure 2-13 - Cycles to failure in the endurance tests
Temperature: 2100°F gas/1475°F metal
Fuel: GT No. 2

oxidation of the graded zone and bond coat. This was true even after only 189 hours of exposure. Thus, oxidation of bond coat particles in the graded zone is the weak link in graded coating performance.

The longest running time on a duplex ZrO_2-$8Y_2O_3$ coated specimen was 3228 cycles. This specimen did not see the temperature excursion since it was removed from test after 1428 cycles and reinstated after 2200 cycles. It showed no evidence of coating failure. Metallographic examination of this specimen revealed excellent coating integrity. Examination of a specimen that had seen the temperature excursion and was left in test for the full 4000 hours also revealed very little bond coat degradation. In both instances a compact Al_2O_3 scale, about 0.2 mils in thickness was formed.

A Ca_2SiO_4 coated specimen which did not see the excursion also lasted 3228 cycles while a second specimen survived for 4000 hours including the temperature excursion. In both cases, some surface microchipping was noted, but no gross coating failure occurred. Metallographic evaluation of the Ca_2SiO_4 coated specimens revealed formation of a $CaSO_4$ surface reaction layer. This layer gave the surface microchipping observed. While this instability of Ca_2SiO_4 is undesirable, it does provide a mechanism whereby the coating may seal itself against penetration of oxygen or condensed salts down interconnected pores (10).

Finally, a NiCrAlY-only coated specimen survived 4000 hours of exposure. Signs of oxidative degradation were evident. Metallographic examination of the NiCrAlY coated specimens revealed some void formation within the NiCrAlY and along the interface with the substrate in addition to the slight surface oxidation attack.

Section 3

TECHNICAL CONCLUSIONS

COATING DEGRADATION MECHANISMS IN CLEAN FUEL

The clean fuel burner rig tests demonstrated the duplex ZrO_2-$8Y_2O_3$ and Ca_2SiO_4 coatings perform well. The clean fuel pressurized passage test, although of limited duration, demonstrated that the duplex coatings can withstand thermal stresses in excess of those encountered during normal start-up and shut down of a utility gas turbine.

The graded coatings, however, are not suitable for utility applications because of their failure as a result of oxidation of the bond coat particles in the graded zone. A limitation to temperatures less than about $1475^{\circ}F$ exists compared to duplex coating where the limit is in excess of $1650^{\circ}F$.

COATING DEGRADATION MECHANISMS IN CONTAMINATED FUELS

This study clearly revealed that present thermal barrier coatings are unsuitable for use in contaminated fuels. Condensed liquid phases infiltrate these porous coatings and are disruptive to coating integrity during thermal cycling. Also, in some cases the impurities react with the ceramic coatings.

This was most clearly revealed by the pressurized passage tests. Up to the time of these tests, results were encouraging with Ca_2SiO_4 and graded ZrO_2-$8Y_2O_3$ coatings surviving 500 hours in exposure to the combustion products of a 50 ppm V simulated water-washed and treated residual oil. However, failures in the pressurized passage in less than 20 hours with a similar, but lower V-content fuel (20 ppm), regardless of whether the cycle was stepped or ramped, clearly showed the deficiency of thermal barrier coatings in dirty fuel. Further acceleration of the ambient pressure tests to 180 ppm V (9 times the 9 atm pressurized passage contaminant level) essentially reproduced the rapid failures seen in the pressurized passage. The effect of V level on cycles to failure for a duplex ZrO_2-$8Y_2O_3$ coating are summarized in Figure 3-1 for both ambient pressure and pressurized passage tests. At the 2 ppm V level, 2 ppm of P was also present and the Mg level was 6 ppm. Thus vanadum plus phosphous were not completely tied up by magnesium. The failure mechanism for vanadium contaminated fuels appeared to be one of YVO_4 formation and zirconia distabilization. However, filling in of porosity and deposit freezing-thawing cycles can not be totally discounted. The destabilization reaction causes a disruptive volume transformation associated with the cubic to monoclinic phase transformation.

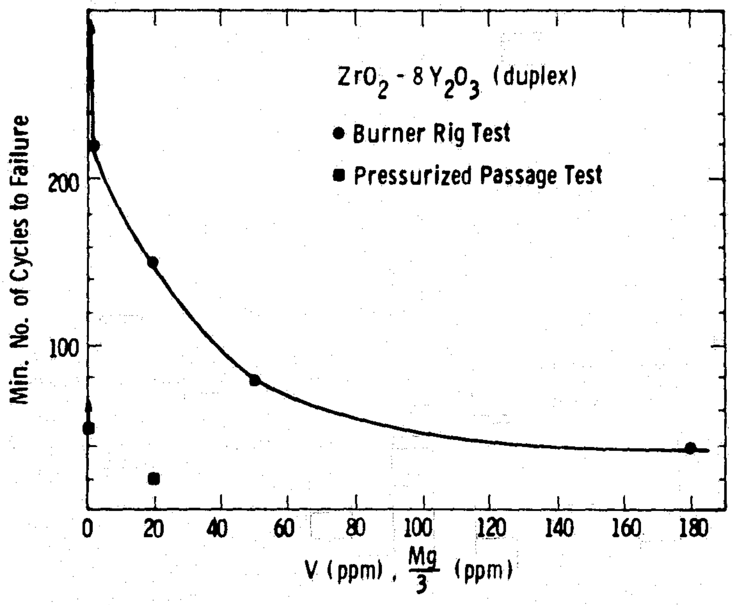


Figure 3-1 - Coating failure as a function of fuel vanadium content

The failure mechanism associated with Na involved formation of a lower melting Na_2O_4-$MgSO_4$ eutectic. The freezing thawing cycle of this pore entrapped salt caused coating failure. It should be noted that this and other molten salts were present in those cases where destabilization of ZrO_2 by V_2O_5 is believed to be the primary cause of failure.

In the case of Ca_2SiO_4 and ZrO_2-24MgO coatings, reaction with SO_3 to form $CaSO_4$ and $MgSO_4$, respectively, were believed to adversely affect these coatings.

An additional significant observation pertaining to the corrosion protection afforded by ceramic coatings in high sodium hot corrosion conditions was made in this study. In these tests the bare alloy and NiCrAlY coated specimens were heavily corroded. In contrast, the ZrO_2 - $8Y_2O_3$ coated specimens were protected from hot corrosion even in areas where most of the ceramic layer had spalled. This protection capability, by whatever mechanism, is worthy of further investigation.

Section 4

CONTRACT CONCLUSIONS AND RECOMMENDATIONS

The conclusions and recommendations of the contract effort "Evaluation of Present Thermal Barrier Coatings for Potential Service in Electric Utility Gas Turbines", as reported in NASA CR-165545 (7)*, are reproduced below. Indented below each conclusion are the NASA comments.

CONTRACT CONCLUSIONS

1. Present-day thermal barrier coatings are viable candidates for utility turbines burning relatively clean fuel such as GT No. 2, but coating improvements are needed for turbines burning lower grade fuel such as residual oil.

> NASA Comment: It is unlikely that the several orders of magnitude improvement required for TBC use with low grade fuels will be attained in the near future.

2. The duplex ZrO_2-$8Y_2O_3$/NiCrAlY coating is ranked highest for clean fuel turbine operation with the duplex Ca_2SiO_4/NiCrAlY ranked second. The present graded ZrO_2-$8Y_2O_3$/NiCrAlY type coating can be operated at temperatures below the oxidation temperature limit of the MCrAlY used for grading from metal to ceramic.

> NASA Comment: The oxidation temperature limit for MCrAlY grading is about 1475°F. This is below the typical 1650°F metal temperature limit for stationary gas turbines. The limit for the bond coat in a duplex coating is in excess of 1650°F.

3. Turbine simulation tests in the pressurized passage, and burner rig endurance tests support the selection of the duplex ZrO_2-$8Y_2O_3$/NiCrAlY

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*The cited report is available from the EPRI Project Manager or from the National Technical Information Service, Springfield, VA 22161.

coating as the primary coating for near term field testing. The duplex Ca_2SiO_4/NiCrAlY coating should also be tested to determine its durability under actual turbine operation.

NASA Comment: The authors concur wholeheartedly .

4. Graded coatings such as ZrO_2-$8Y_2O_3$/MCrAlY show good potential for corrosive turbine operating conditions and therefore warrant further development.

NASA Comment: For an air cooled gas turbine, graded layer oxidation resistance would have to be sufficient for 1650°F operation. This is 175°F above the temperature at which graded coating deficiencies were detected in the endurance test. Thus, it is unlikely that graded layer oxidation resistance can be cost effectively improved to this extent. However, with a TBC present, a 175°F metal temperature reduction can be attained. Thus it may be possible to trade off some temperature reduction to permit use of a graded TBC.

5. In fuels contaminated with vanadium, the present-day zirconia-based coatings are subject to destabilization which leads to failure. The origin of destabilization is reaction of the coating with solid vanadate condensates or gaseous vanadium oxides.

NASA Comment: The filling in of porosity and the presence of Na_2SO_4-$MgSO_4$ eutectics may have also contributed significantly.

6. In fuels contaminated with sodium and magnesium sulfate impurities, the present day zirconia-based coatings are subject to failure due to the large mismatch in thermal expansion coefficients between the condensed Na_2SO_4 or Na_2SO_4-M_gSO_4 phases that deposit in the porous coatings.

NASA Comment: Disruptive freezing-thawing cycles also may play a role.

7. The ZrO_2-MgO/NiCrAlY coating is susceptible to reaction with the SO_3 gas produced from fuels containing sulfur. The reaction product is $MgSO_4$. Accelerated destabilization of the ZrO_2-MgO solid solution occurs as a

result of the SO_3 reaction and leads to failure.

NASA Comment: The filling in of porosity and the presence of Na_2SO_4-$MgSO_4$ eutectics may have been as important as zirconia destabilization.

8. The Ca_2SiO_4/NiCrAlY coating is susceptible to reaction with the SO_3 gas produced from fuels containing sulfur. The reaction product is $CaSO_4$ that does not cause gross spalling but causes microchipping of the coating surface. Ca_2SiO_4 is also reactive toward $MgSO_4$ and $Mg_3V_2O_8$ deposits.

NASA Comment: The positive aspects of Ca_2SiO_4 coating performance should not be forgotten because of this small problem. As a matter of fact, sealing of surface porosity via this reaction could be beneficial in contaminated combustion gases.

CONTRACT RECOMMENDATIONS

This program has identified several promising thermal barrier coatings for use in utility turbines burning GT No. 2 fuel or other clean fuels. The program has further identified the deficiencies of present day thermal barrier coatings in their resistance to lower grade fuels. The following recommendations are made:

1. A field testing program should be initiated using the most promising thermal barrier coating candidates determined from the present study. The coatings should be applied to row 1 turbine blading and the blading installed in a utility turbine engine for long time durability tests. It is recommended that the engine be a W501D in combined cycle, base load operating on a clean fuel.

NASA Comment: Field testing should be backed up with a vigorous design analysis. Testing should be carried out in any of a number of heavy duty, clean-fuel-fired utility gas turbines.

2. A test program for selected present-day thermal barrier coatings should be extended to gas temperatures above 2100°F and at least to 2300°F which is a near term (5-year) turbine inlet temperature objective for utility turbines.

NASA Comment: The technology base for this need is being addressed by the aircraft gas turbine community.

3. A more extensive fuel sensitivity evaluation program should be conducted using available coal derived fuels, and especially those believed to be available in the future for utility turbine operation.

NASA Comment: Field tests should be given higher priority.

4. A more oxidation resistant graded-type thermal barrier coating should be developed and evaluated. The emphasis should be on a broader evaluation of MCrAlY type alloys (M is Ni/Co) for grading purposes. This warrants further effort because of the potential durability of graded coatings for use in turbines burning low grade fuel as well as clean fuel.

NASA Comment: For an air cooled gas turbine, graded layer oxidation resistance would have to be sufficient for 1650°F operation. This is about 175°F above the temperature at which graded coating deficiencies were detected in the endurance test. Thus, it is unlikely that graded layer oxidation resistance can be cost effectively improved. Operation at lower metal temperatures would be possible by giving up some of the temperature drop resulting from the TBC.

5. An effort should be made to develop ceramic coating process specifications for utility turbine components. These include combustors, transition pieces and blading.

NASA Comment: The entire question of coating reproducibility, quality control and NDE methods needs to be addressed in conjunction with any field test program.

6. In the past year, new promising ceramic coatings and processes have been under development by Westinghouse and others. It is recommended that these coatings be continually evaluated for their potential use in utility turbines.

NASA Comment: None of these efforts have yielded the several orders of magnitude improvement required for TBC to be considered for heavy oil fired gas turbines.

Section 5

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Appendix A

REVIEW OF OTHER TBC RESEARCH

The purpose of this section is to discuss the progress that has been made in TBC technology over the past several years and to assess the potential benefits and readiness of such coatings for stationary gas turbines.

POTENTIAL BENEFITS OF TBC FOR UTILITY GAS TURBINES

With their capability to reduce metal temperatures by approximately 100°F in present industrial/utility gas turbines, thermal barrier coatings can offer significant gains in efficiency or durability. Several investigators have examined the potential benefits of thermal barrier coatings for stationary gas turbines (11-15). An example of the gains in efficiency that might be obtained in combined cycle systems is shown in Figure A-1(15). With current systems, efficiency gains are on the order of 1/2 to 1 percent. With more effective cooling systems and higher turbine inlet temperatures, the efficiency gains increase to on the order of 1.5 percent. In so far as durability is concerned, calculations have shown that a 15 mil ceramic coating can yield ten-fold improvements in stress rupture life and low-cycle fatigue life if turbine inlet temperature and coolant flow are maintained constant. However, this approach does incur an efficiency penalty of about 1 percent for a simple cycle system (13). Thus, tradeoffs between improved durability and improved efficiency must be made. For constant turbine inlet temperature, the efficiency vs durability trade tends to balance in a simple cycle whereas in a combined cycle it is possible to get both improved durability and improved efficiency.

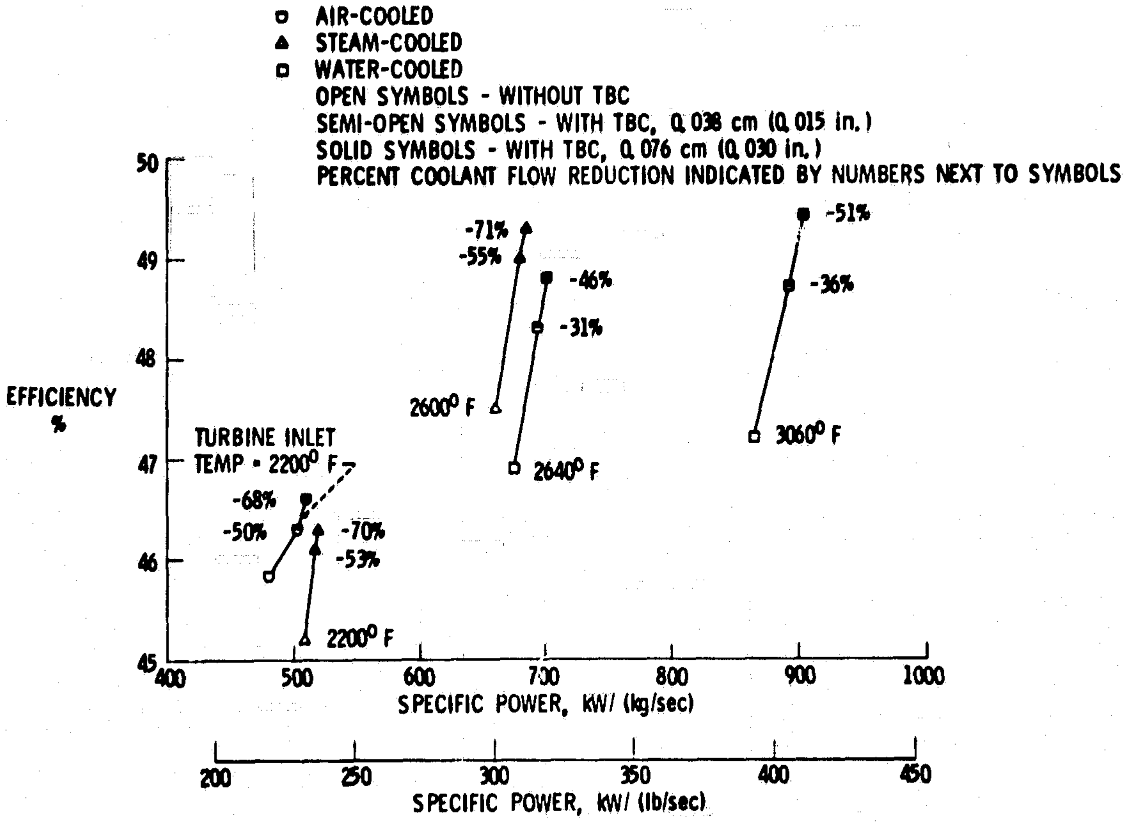

Figure A-1 - Improved performance of combined cycles by reducing coolant flow through the use of thermal barrier coatings (15).

THERMO-MECHANICAL STRESS CONSIDERATIONS

Thermal stress is a primary consideration for monolithic ceramic and metallic heat engine materials. With a composite, such as a two-layer thermal barrier coating on a superalloy, consideration must be given to a thermal expansion mismatch component as well as a thermal gradient induced component in solving a thermal stress problem. In addition, the plasma spray process produces coatings with significant levels of residual stress and these stresses should also be taken into account in the solution of the thermal stress problem. The stress state of the ceramic layer at room temperature may be either compressive or tensile depending on the effective substrate temperature during deposition and the thermal expansion mismatch between the ceramic and substrate. Further-more, the stress state is subject to change due to ceramic sintering, creep and microcracking while the coating is in use. Thus, at present it is not possible to rigorously treat all aspects of the thermal stress problem.

Conventional wisdom with regard to bulk ceramic materials tells us that compressive stresses are favorable. For ceramic coatings, the conventional wisdom does not apply. For example, consider a stabilized zirconia coating on a solid, relatively large diameter, superalloy rod. If this composite is slowly heated to e.g. 2000^{o}F, the zirconia will be put in tension by virtue of the fact that its thermal expansion coefficient is only about 2/3 that of a superalloy. This slow heating results in a thermal expansion mismatch strain which exceeds the reported fracture strain of zirconia (16). Thus, the ceramic should be stress relieved by cracking, but it will still adhere. If the stress relief is incomplete, zirconia or bond coat creep can occur. This will result in compressive stresses on cooling.

However, thermal barrier coatings, when used in applications such as on gas turbine blades, are not slowly heated and cooled. As a matter of fact, heating rates are such that the coatings can be subjected to high compressive stresses during the heat-up transient despite the fact that the thermal expansion coefficient mismatch between zirconia and a typical austenitic superalloy favors development of tensile stresses in the ceramic. Two examples illustrate this point.

In the first, solid 0.5 in diameter Rene' 41 bars were coated with either a Ni-16Cr-6Al - 0.3Y* or Ni-18Cr-12Al-0.3Y bond coating and either a ZrO_2-$8Y_2O_3$* or ZrO_2-12 Y_2O_3 ceramic. Bond and ceramic coating thickness were 5 and 15 mils, respectively. Eight specimens were placed in a rotating

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*Compositions are in weight percent

carousel and rapidly cycled between room temperature and a 1900°F leading edge temperature in a Mach 0.3 atmospheric pressure burner rig firing Jet A fuel. The heating part of the cycle was either 4 minutes in the flame followed by a 3 minute forced air cool or 57 minutes followed by the same forced air cool. Results are presented in Figure A-2 (17). With the less oxidation resistant Ni-16Cr-6Al-0.3Y bond coat, life was governed by the number of thermal cycles since life in terms of cycles to failure was insensitive to cycle heating time. With the more effective Ni-18Cr-12Al-0.3Y bond coat, life is controlled by both time-at-temperature and the number of thermal cycles. One should note that failures occurred not at the leading edge, but at the 100°F hotter trailing edge.

Stress analyses of this experiment indicated that the radial detachment stress was 660 psi. This value is on the order of the reported adhesive/cohesive strength of 930 psi for an as-deposited ZrO_2-12 Y_2O_3 coating (18). Compressive residual stresses which are present in the as-deposited coating are additive to the thermal stress. Such stresses are difficult to measure

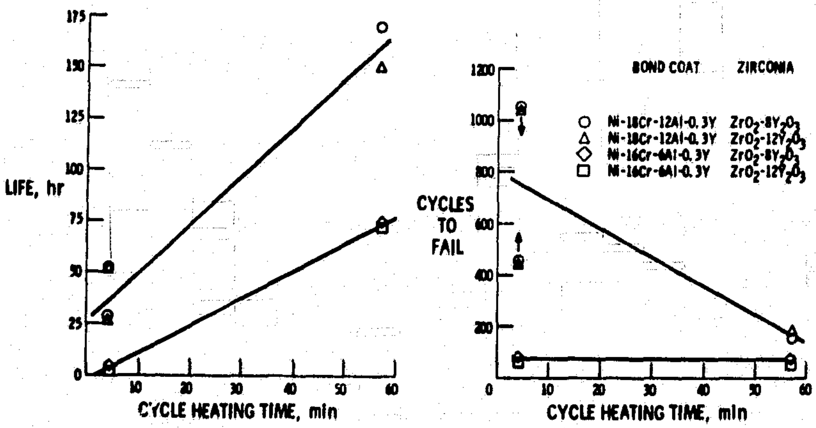

Figure A-2 - Effect of cycling on life of thermal barrier coating Heating-cooling cycle: 4 min heat - 3 min forced cool; 57 min heat - 3 min forced cool. Optical surface temperature, 1900°F and additional work in this area is required. Also, coating bond strength, residual stresses and differential thermal expansion stresses change with thermal exposure.

The second example is a ground based JT9D engine test of the early NASA coating: ZrO_2-12 Y_2O_3/Ni-16Cr-6Al-0.6Y(16). A 7 mil ceramic layer over a 4 mil bond coat was applied to first-stage turbine blades. The engine was run for 264 hours of which 190 hours were cyclic endurance in which 1424 thermal cycles were accumulated. Typical accelerated endurance cycles consisted of 2 minutes at take-off power with maximum turbine inlet temperature reaching about $2600^{o}F$ and 5 minutes at idle power. After 39 hours (327 cycles), coating failure occurred only at the highest temperature locations at the leading edge. At test completion, ceramic spallation was also noted on the blade upper pressure surface near the trailing edge. Heat transfer and structural analyses were carried out (16). The analyses revealed that ceramic failures occurred in regions of combined high temperature and compressive strain.

Figure A-3 illustrates the calculated leading edge ceramic strain during an endurance test cycle. The maximum compressive strain during the acceleration from idle to take-off is about 0.005 in./in. Going back to the thermal stress/detachment stress concepts of the earlier example, the stress in the coating can be calculated and equated to the detachment stress.

$$\varepsilon E_c = \frac{Pd}{2t}$$

With a leading edge diameter of about 0.1 in. and a zirconia modulus of 3.6 X 10^6 psi, P turns out to be about 2100 psi which greatly exceeds the adhesive/cohesive strength of the coating. However, if we consider a large utility gas

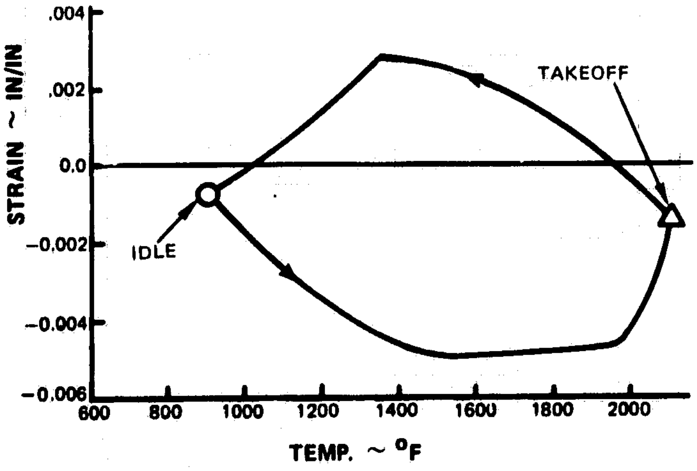

Figure A-3 - Strain in 7 mil ZrO_2 - $12Y_2O_3$/4 mil NiCrAlY TBC at the 70 percent span leading edge of a JT9D first stage blade.

turbine operating at about half the pressure ratio of a JT9D, with slower transients, a more generous leading edge diameter and an appreciably lower turbine inlet temperature during transients, current TBCs might perform quite well.

From the results of the JT9D engine test and analysis, several clear directions for improvement of thermal barrier coatings are apparent. First, the coatings should be deposited so as to minimize residual compressive stress or even make the residual stresses tensile. Second, the coating structure should be segmented to improve compressive stress accommodation. Third, adhesive/cohesive strength should be increased. Fourth, improved bond coatings are needed to eliminate coating disruption as a result of bond coating oxidation. Finally, because of the compressive stress sensitivity of TBCs, attention should be paid to thermal expansion coefficient mismatch optimization.

PERFORMANCE IN NON-CORROSIVE ENVIRONMENTS

Since the JT9D engine test discussed in the previous section, a substantial improvement was made to the durability of the ZrO_2-Y_2O_3/NiCrAlY system (8). This was accomplished by decreasing the Y_2O_3 level from 12 w/o, where the ceramic is essentially single-phase, to the 6 to 8 w/o range, where the zirconia is multiphase. Also, the yttrium level in the NiCrAlY was reduced from 0.6 w/o to the 0.15 to 0.3 w/o range. This modification is believed to enhance the stability of the zirconia/bond coat interface region. These compositional effects are illustrated in Figure A-4 which summarizes the results for coated, solid specimens exposed to a cyclic torch test. In more severe Mach 1.0 burner rig tests, air-cooled turbine blades coated with ZrO_2-8 Y_2O_3/Ni-17Cr-5Al-0.35Y survived 2000 one-hour cycles without failure at a surface temperature of 2650°F and a substrate temperature of 1690°F. The early ZrO_2-12 Y_2O_3 based system failed after 800 hours at somewhat lower temperatures (8).

Two studies of the ZrO_2-8 Y_2O_3 system have been carried out to elucidate its behavior as a TBC. In the first, the constitution of plasma sprayed ZrO_2-$8Y_2O_3$ was investigated as a function of aging time and temperature (19).

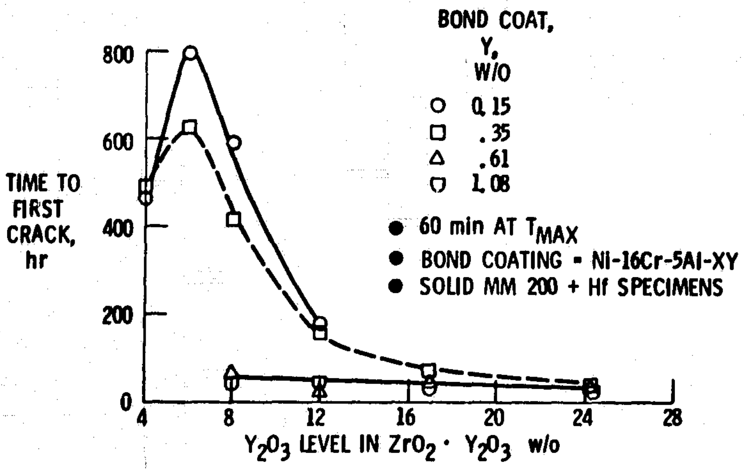

Figure A-4 – Effects of bond coat and zirconia composition on coating life in cyclic natural gas torch tests to 2200°F.

The as-sprayed material was determined to consist of 80 percent of a tetragonal phase which was nontransformable with respect to a martensitic conversion to the low temperature monoclinic phase, but which was diffusionally unstable at high temperatures. Another 12 percent of the as-sprayed material was cubic while the remaining 8 percent was found to be the martensitically transformable tetragonal phase. The latter phase is detected as the monoclinic phase at room temperature. A large and possibly disruptive volume increase is associated with this transformation. The trade-off between this volume transformation and the possible benefits of transformation toughening as we go to very low levels of yttria stabilization (20) remains to be determined. However, the decrease in life at 4 w/o yttria shown in Figure A-4 can be attributed to the volume change associated with the formation of the monoclinic phase (8).

In the second study (21) it was demonstrated that 2730^oF aging of solution annealed bulk ZrO_2-$8Y_2O_3$ results in a gradual increase in hardness with aging time. This hardness is associated with the formation of coherent-tetragonal precipitates. At aging times greater than about 100 hours, hardness drops due to the formation of grain boundary monoclinic precipitates. There was no evidence that transformation toughening, which is observed in very low yttria ZrO_2-Y_2O_3 (20), plays a role in the properties of bulk (21) or as-plasma sprayed (19) ZrO_2-$8Y_2O_3$.

Additional TBC life improvements have been obtained by improving the oxidation resistance of the bond coating. For example life can be doubled either by increasing the bond coat Cr content from 16 to 25 w/o or by increasing the bond coat Al content from 6 to 10 w/o (22). Further improvements can be obtained by increasing the density of the plasma sprayed bond coatings by increasing the power level and adding hydrogen to the arc gas (23, 24).

Further improvements can be expected by going to inert gas shrouding or by going to low pressure plasma spraying (25). Using the latter technique, overlay metallic coatings having environmental resistance equivalent to or better than electron-beam physically-vapor-deposited (EB-PVD) coatings have been obtained (26).

The structure and composition of the zirconia coating also have an effect on the oxidation kinetics of the bond coating. Increasing the density to above about 88 percent of theoretical and decreasing the yttria content reduce the bond coat oxidation rate (27). However, higher zirconia density can adversely affect thermal shock resistance while being beneficial in corrosive environments. Further research is required to explore these trade-offs.

As discussed earlier, the structure and residual stress state of a TBC are important parameters. An investigation of both of these factors has been carried out at Pratt and Whitney as part of the NASA Engine Component Improvement Project. Coating segmentation via the EB-PVD process and residual stress control were most effective as illustrated in Figure A-5 (28).

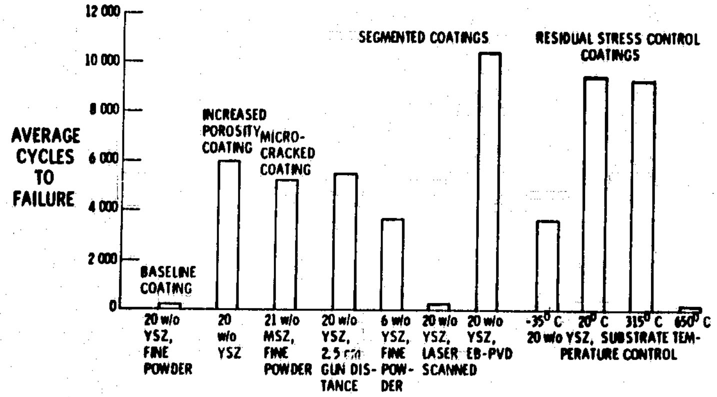

Figure A-5 - Average number of thermal cycles to failure for several thermal barrier coating systems. Thermal cycle: 4 minutes of heating to 1850°F in a Mach 0.3 burner rig followed by 2 minutes of forced air cooling to 500°F or less.

Three coatings were subjected to a JT9D cyclic endurance engine exposure on first stage vane platforms having a cooling system redesigned to take advantage of the TBC. The coatings tested were 15 mil thick ZrO_2-20 Y_2O_3, ZrO_2-6 Y_2O_3, and ZrO_2-21 MgO over a Ni-22Co-18Cr-13Al-0.7Y bond coat. Except for those vanes exposed in a severe hot streak, the coatings survived with no apparent damage. In a current contract effort with Pratt and Whitney (NAS 3-22548) this technology is being extended to turbine blades. It should be noted that the thermal conditions on first-stage vane platforms are about one-third as severe as on first-stage blade leading edges in an aircraft gas turbine and comparable to conditions on first-stage blade leading edges in a typical non-aircraft derivative stationary gas turbine.

PERFORMANCE IN CORROSIVE ENVIRONMENTS

The durability of the ZrO_2-$12Y_2O_3$/NiCrAlY coating system is greatly diminished when trace inorganic contaminants such as Na, V, and S - as found in many industrial/utility gas turbine fuels - are present in the combustion products (5, 6, 29). Impurities may also be ingested with the ambient air. The results of burner rig exposure tests conducted at NASA Lewis with sodium and vanadium additions to the fuel are given in Figure A-6. The observed

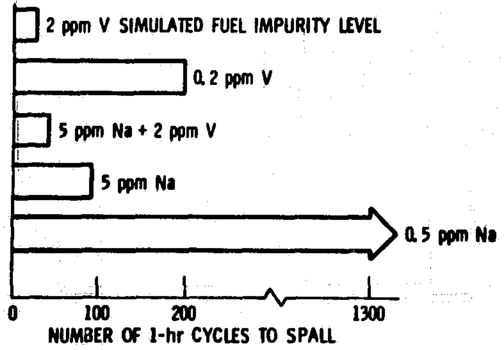

Figure A-6 - Effect of fuel impurities on ZrO_2 - $12Y_2O_3$/Ni-16Cr-6Al-0.6Y thermal barrier coating run in a Mach 0.3 burner rig test at 1800°F surface temperature/1560°F metal temperature.

early failures are thought to be due to the deposition of liquid salts such as Na_2SO_4. These liquid salts are believed to enter the open pores of the coating and permeate parts of the coating where the temperature exceeds the melting point of the salt. Since sodium sulfate does not react with ZrO_2-Y_2O_3 under the conditions of these experiments (30), it is believed that this salt adversely affects the ability of the ceramic to accommodate cyclic thermal stress (9). The mechanism may involve the infiltration of molten salts into the pores and microcracks of the plasma sprayed ceramic coating thereby greatly decreasing its thermal stress resistance. It has been shown that an understanding of the thermochemistry of salt deposition can aid in the interpretation of coating failure induced by impurities derived from the fuel or air. For example, in Figure A-7, the case in which 5 ppm of Na was present in the fuel is considered (9). The sketch shows that the observed location of spalling can be correlated with the dewpoint of Na_2SO_4 for these conditions. It also shows that the observed depth of failure within the ceramic layer can be correlated with the depth in the coating at which the

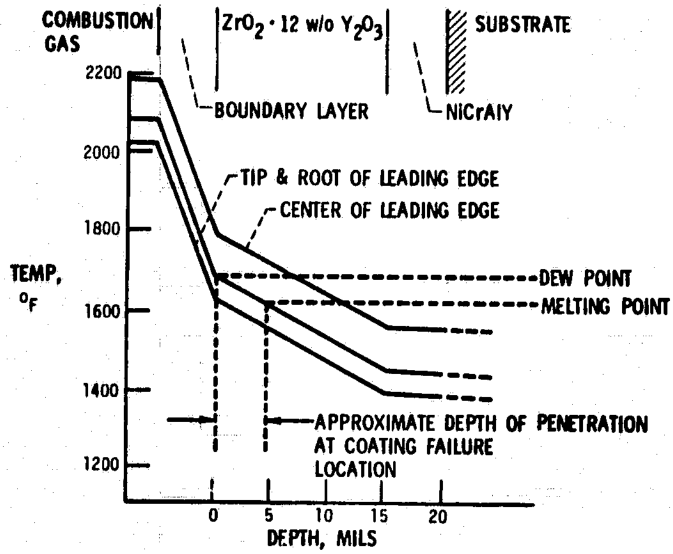

Figure A-7 - Predicted depth of penetration of Na_2SO_4 for 5 ppm Na simulated fuel impurity level.

melting point of Na_2SO_4 is reached. In contrast, in clean fuels failure nearly always occurs in the ceramic very close to the bond coat.

The results of the tests just described, as well as the results of other investigations, indicated a need to identify ceramic coatings having improved resistance to fuel and air impurities (5, 29, 31, 32). An initial step toward this goal was taken when a series of coating systems was tested in a Jet-A fuel-fired Mach 0.3 burner rig with the flame doped to the fuel-equivalent impurity level of 5 ppm Na + 2 ppm V (6). Ceramic coating thickness was maintained at 15 mils, and bond coat thickness was maintained at 5 mils. Results are summarized in Figure A-8. Various thermal and chemical treatments of the ZrO_2-$12Y_2O_3$/Ni-16Cr-6Al-0.6Y system resulted in little or no improvement. A more oxidation/hot corrosion resistant bond coat (Ni-21Co-19Cr-13Al-0.6Y) and a dense Y_2O_3 top-coat with the baseline coating offered some improvement. The ZrO_2-$8Y_2O_3$/Ni-16Cr-5Al-0.15Y coating offered an even greater improvement. The most promising duplex

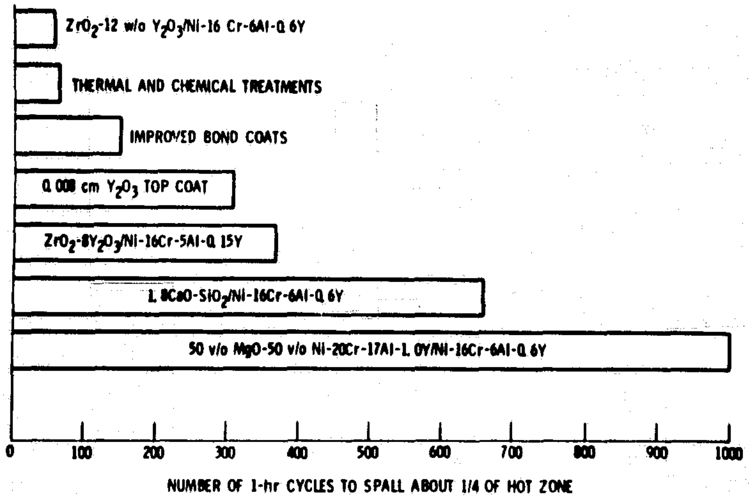

Figure A-8 - Improved thermal barrier coatings. Exposure in a Mach 0.3 burner rig firing fuel doped to 5 ppm Na plus 2 ppm V. Flame temperature, 2500°F; ceramic surface temperature 1800°F; metal temperature, 1550°F.

ceramic coating identified was 1.8 CaO-SiO_2/Ni-16Cr-6Al-0.6Y. A higher thermal conductivity cermet coating consisting of 50 volume percent MgO in Ni-20Cr-17Al-1.0Y over the standard bond coating survived 1000 one-hour cycles without spalling. However, coating thickness was reduced about 50 percent by erosion.

Further studies of the behavior of ZrO_2-Y_2O_3 and Ca_2SiO_4 were carried out using a slightly more severe burner rig test (33). The effects of bond coat and zirconia compositions and ceramic coating thickness were investigated. Results are presented in Figure A-9. In this test ZrO_2-$8Y_2O_3$ was more durable than ZrO_2-$6Y_2O_3$ and ZrO_2-$12Y_2O_3$. Increased bond coat Cr- and Al- content and reduced ceramic coating thickness were both beneficial for ZrO_2-$8Y_2O_3$. With Ca_2SiO_4, increased bond coat Cr and Al were ineffective for nickel-base bond coats, but effective for cobalt-base bond coats. Once again, reduced ceramic thickness was beneficial. The improved durability of the thinner coatings may be attributed in part to the fact that

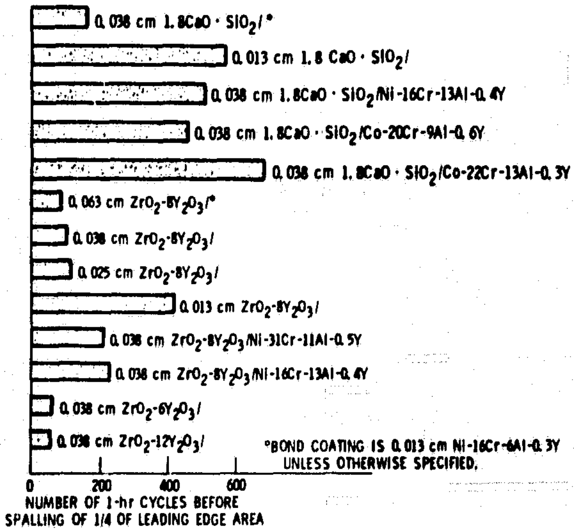

Figure A-9 – Effects of ceramic thickness and bond coat composition on doped fuel Mach 0.3 burner rig lives of thermal barrier coatings. Fuel impurity level: 5 ppm Na plus 2 ppm V. Fuel to air ratio: 0.046. Ceramic surface temperature: 1800°F. Substrate temperature: 1550°F.

they are operating at a higher bond coat temperature and thus condense less salt. Another factor is the reduced detachment stress resulting from the reduced ceramic thickness as discussed earlier.

Analyses of tested specimens by X-ray diffraction and electron microprobe elemental mapping revealed condensation of Na_2SO_4 as can be seen from the coincidence of Na and S in Figure A-10 and formation of YVO_4 in ZrO_2-8Y_2O_3. For Ca_2SiO_4 coatings, Na_2SO_4 and V_2O_5 or $Na_2V_2O_6$ condensation were confirmed and reaction of Ca_2SiO_4 with sulfur to form $CaSO_4$ and $CaSiO_3$ was detected.

In summary, the condensation of combustion gas-borne salts in porous thermal barrier coatings drastically reduces their tolerance to thermal cycling. Exclusion of these salts via a platinum overlay as has been demonstrated by Clarke (34) is one approach that appears to be feasible at low temperatures and flow rates. Other sealants would be required at higher temperatures and gas velocities due to the volatility of platinum oxide. Recently, some

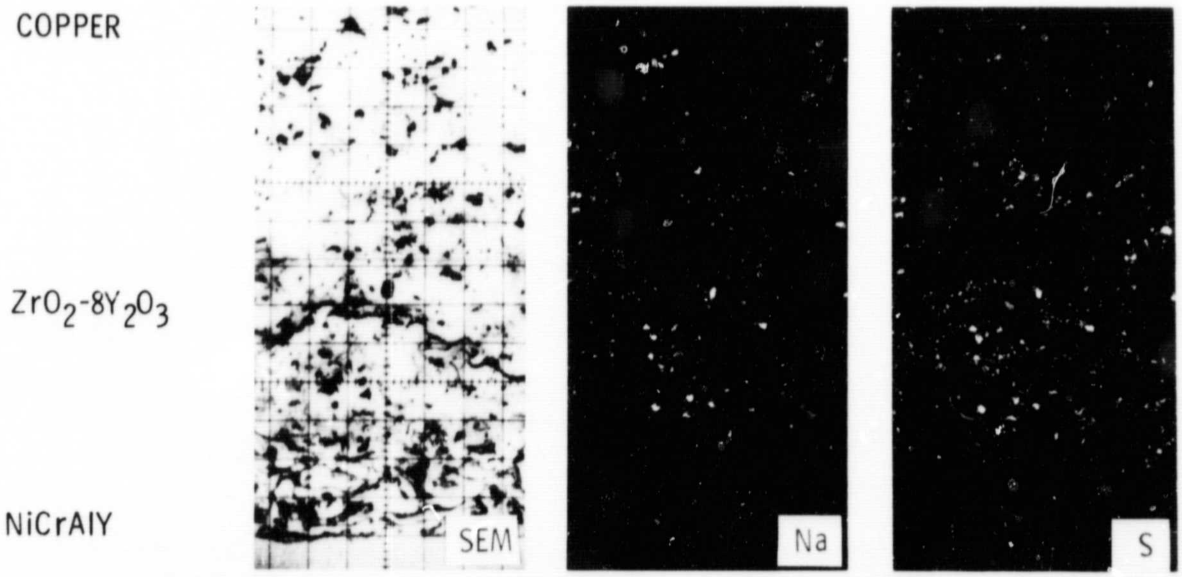

Figure A-10 - Electron microprobe maps for ZrO_2-8Y_2O_3/ Ni-16Cr-6Al-0.3Y after 120 one-hour cycles of expsoure to Mach 0.3 Na plus V doped combustion gases.

success with glass sealers has been obtained by Andersson et al. (13). Laser sealing now appears to be another promising technique (35). In both instances 3 to 4x improvements in life were attained by sealing the surface. The viability of these approaches on erosion prone components is questionable. A preferable approach would involve the development of TBC structures that are immune to mechanical degradation by condensed salts. One step in this direction is to increase coating density. However, trade-offs against thermal stress tolerance are involved.

Finally, it must be noted that severe degradation of TBC life has been observed with levels of combustion gas contamination representative of industrial or marine applications. For aircraft gas turbine applications or gasifier-combined-cycles with cold gas clean-up where the fuels are clean and relatively little sea salt is ingested, thermal barrier coatings appear to have adequate tolerance. For example, the results of Hodge et al. (6) show that at the 0.5 ppm fuel equivalent Na level, the early ZrO_2-$12Y_2O_3$/Ni-16Cr-6Al-0.6Y TBC did not fail after 1300 one-hour cycles (Figure A-8). Also, in furnace corrosion tests at 1650°F (36), precoating of specimens with 5 mg/cm^2 of Na_2SO_4 caused no coating distress in 100 hours. However, distress was observed with as little as 10 percent $NaVO_3$ in the deposit (36).

CONCLUDING REMARKS

The performance of thermal barrier coating systems is governed by many complex and interrelated factors. Coating structure and properties control the ability of the coating to tolerate thermal stress. Compressive thermal stresses which arise on rapid heating are more difficult to accommodate than tensile stresses. The ability of the ceramic to tolerate thermal stress is severely compromised by combustion gas impurities condensed in coating pores.

In addition, factors such as phase stability and bond coat oxidation arise in situations where corrosion and thermal stress are at least initially overcome. Often the obvious direction for coating improvement to cope with one problem aggravates another. For example, increased coating density would limit coating permeation by condensed combustion gas impurities, but thermal stress resistance may be sacrificed. To more effectively make these trade-offs, far more must be learned about coating structure/property/ failure mechanism relationships so that further coating improvements can be made. Such improvements are required for the most stringent gas turbine applications such as aircraft gas turbine airfoils and stationary gas turbines firing dirty fuels. However, for stationary gas turbines firing clean fuels-for example gasifier-combined-cycle systems with cold gas clean-up - thermal barrier coatings are sufficiently developed to warrant field testing. Such an effort would require further coating evaluation to select the currently most promising systems, further development of coating deposition technology (37), generation of coating property data for design analysis and field service testing in the blade durability improvement (rather than the performance improvement) mode. The need for this rigorous approach has been demonstrated by the results of a 500 hour engine test carried out by Solar. ZrO_2-$8Y_2O_3$, $CaTiO_3$, and Ca_2SiO_4 coatings were applied to first stage blades of the Mars engine (14). Thickness control of the bond and ceramic coatings was poor and this poor quality clouded the results. In general, however, the coatings performed reasonably well with some spalling and erosion occurring at blade leading edges and in some instances, elsewhere. Such spalling may have been caused by the thin bond coat application or overly thick ceramic layers.