R01-6.100.0006-5

***Alternative Liquid Fuel Effects on Cooled Silicon Nitride Marine Gas
Turbine Airfoils***

Final Report

**Prepared for:
Office of Naval Research
Arlington, VA 22217-5660**

Under Contract No. N00014-99-C-0386

John Holowczak

February 2002

DOE Patent Clearance Granted

Mark P. Dvorscak

5.29.03

Mark P. Dvorscak
(630) 252-2393

Date

E-mail: mark.dvorscak@ch.doe.gov
Office of Intellectual Property Law
DOE Chicago Operations Office

R01-6.100-0006-5

Alternative Liquid Fuel Effects on Cooled Silicon Nitride Marine Gas Turbine Airfoils

Reported by:

John E. Holowczak

Approved by:

Kay V. Adams

February 2002

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1205, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. RESTRICTIVE DATE February 2002	3. REPORT TYPE AND DATES COVERED 11/17/990-02/15/2002
4. TITLE AND SUBTITLE ALTERNATIVE LIQUID FUEL EFFECTS ON COOLED SILICON NITRIDE MARINE GAS TURBINE AIRFOILS		5. FUNDING NUMBERS N00014-99-C-0386
6. AUTHOR(S) John Holowczak AND Jun Shi		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(S) United Technologies Corporation Research Center Silver Lane Hartford, CT 06108		8. PERFORMING ORGANIZATION REPORT NUMBER R01-6.1000.0006-5
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research Arlington, VA 22217-5660		10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT	12b. DISTRIBUTION CODE
--	------------------------

13. ABSTRACT (Maximum 200 words)

Cooled all ceramic turbine vanes, with and without environmental barrier coating (EBC), were tested in a cascade based on an FT8 engine combustor sector. A total of 31 hours were accumulated, which gas temperatures exceeding 1380 C, and pressures of 18 atmospheres in a combustion environment. Various environmental barrier coatings were developed and evaluated under the subject effort, and one BSAS based system was used on one of the sector tested vanes. Progress in manufacturing complex all ceramic cooled airfoils was made via gel-casting. The uncoated hot spot vane exhibited a concentration of rare earth oxide sintering aide, while the EBC coated vane exhibited surface smoothing in high velocity regions.

14. SUBJECT TERMS Cooled all ceramic turbine vane silicon nitride marine gas turbine environmental barrier coating engine testing			15. NUMBER OF PAGES
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT SAR

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
209-102

TABLE OF CONTENTS

ABSTRACT..... 4

INTRODUCTION..... 4

RESULTS AND DISCUSSION 7

 Task 1 — Ceramic Vane Fabrication Development and Rig Hardware Acquisition..... 7

 Task 2 – Coating Development for Protection of Silicon Nitride Components under
Liquid Fuel Turbine Hot Section Environments 10

 Task 3 Sector Rig Combustor Cascade Testing of Ceramic Vanes..... 12

 Task 4 — Ceramic and Metallic Vane Characterization 19

SUMMARY AND FUTURE WORK 25

ACKNOWLEDGEMENTS 26

APPENDIX A – STEVENS INSTITUTE OF TECHNOLOGY CVD EBC
DEVELOPMENT 27

APPENDIX B – HONEYWELL CERAMIC COMPONENTS VANE PROTOTYPE
DEVELOPMENT 57

Alternative Liquid Fuel Effects on Cooled Silicon Nitride Marine Gas Turbine Airfoils

ABSTRACT

With prior support from the Office of Naval Research, DARPA, and U.S. Dept of Energy, United Technologies is developing and engine environment testing what we believe to be the first *internally cooled* silicon nitride ceramic turbine vane in the United States. The vanes are being developed for the FT8, an aeroderivative stationary/marine gas turbine. The current effort resulted in further manufacturing development and prototyping by two U.S. based gas turbine grade silicon nitride component manufacturers, preliminary development of both alumina, and yttria based environmental barrier coatings (EBCs), and testing of ceramic vanes, with an EBC coating, in a high pressure combustor/vane cascade rig.

INTRODUCTION

Modern marine and stationary gas turbine engines derived from aero engine powerplants operate at continuous average combustor exit temperatures of 1200°C (2200 °F) or higher. Due to the radial and circumferential pattern and profile combustion gas temperature differences common in larger turbines, it is not unusual to have gases immediately adjacent to "hot spot" HPT vanes significantly in excess of 1370°C (2500°F). These high gas temperatures require superalloy vanes to be extensively cooled for long term durability. Reductions in the cooling air requirements for vanes and other hot section structures can allow the air to be put to use elsewhere in the engine. For example, the air can be mixed with additional fuel and used to increase the power output of the engine.

Substitution of monolithic ceramics for thermal barrier coated superalloys has long been viewed as an approach to allowing significantly higher component operating temperatures. They have enjoyed an increasing level of success in small, low-pressure ratio turbine engines, including vehicular, expendable, and small stationary turbine engines. As these engines currently operate with uncooled metallic components, substitution of ceramic components allows considerably higher turbine inlet temperatures, resulting in significant increases in specific power output and efficiency.

Large aeroderivative stationary or marine powerplants already have high pressure turbine components that benefit extensively from advanced air cooling systems. Uncooled ceramic vanes operating in hot spot locations would have unacceptably high operating temperatures to meet long term durability requirements. In order to harness the higher material operating temperatures of silicon based ceramics, these types of components require internal cooling systems.

Under a DARPA Advanced Materials Partnership program entitled "Reduced Cost, Improved FOD Resistance, and Improved Attachments for Insertion of Silicon Nitride Turbomachinery Components," led by Sundstrand Power Systems¹, Pratt & Whitney (P&W) and its central R&D

¹ Administered by Office of Naval Research, Contract No. N00014-96-2-0014, Dr. Steven Fishman, monitor.

facility, United Technologies Research Center (UTRC), have developed an impingement cooled and vented first stage turbine vane in silicon nitride ceramic. The vane application is the P&W/Turbo Power and Marine FT8 aeroderivative engine. The FT8, which entered service in 1992, is an industrial/marine derivative of the P&W JT8D aircraft engine. The FT8, which has an output of 25 MW with an efficiency of 38.2% in electrical power generation applications (including generator losses) and has a 39% shaft efficiency, is currently in use for peak power, natural gas pumping, and marine applications worldwide. The FT8 engine has recently completed successful testing on a Japanese-built, high-speed transport ship prototype.

The FT8 engine is very similar to the GE LM2500 engine, as depicted in Table 1 below. Turbine inlet temperatures, operating pressure ratio (OPR), and power output are very similar. The GE LM2500 engines are in use on U.S. Navy destroyers, cruisers, frigates and fast supply ships.

Table 1. Comparison of the P&W FT8 and GE LM2500 Engines

Property/Engine	P&W FT8-1	GE LM2500
Rotor Inlet Temperature	2120 °F	2240 °F
Combustor Exit Temperature	2220 °F	2340 °F
Overall Pressure Ratio	20	19
Power Output (simple cycle)	25.5 MW	25 MW

Assuming that silicon nitride ceramic hot section components are successful, improvements to the existing LM2500 propulsion systems could be retrofitted. For future gas turbine powered Naval vessels, the FT8 powerplant could be considered as an alternative to the existing powerplants. The Pratt & Whitney/Turbo Power & Marine FT4, an older aeroderivative marine engine derived from the JT4 flight engine, is in use by the U.S. Coast Guard in icebreakers, and could benefit from developments of the project as well.

The potential improvements of utilizing monolithic silicon nitride in marine gas turbine hot section components include efficiency gains as a result of reducing or eliminating cooling on various components, as well as the potential for operation on lower grade "merchant marine" liquid fuels. Gas turbine powered ships utilize NATO F-76 light distillate fuels as their low level of alkali and vanadium sulfates yield longer turbine hot section life for the metallic components used. Use of lower grade, less expensive fuels can provide the Navy with considerable cost savings.

Although the melting point and use temperatures of silicon nitride ceramics are somewhat higher than those of TBC coated superalloys, there are two concerns that make the proposed applications of these materials high risk in nature. Both silicon nitride, and CVI SiC/SiC composites suffer from oxidation problems at high operating pressures and temperatures. Although silicon nitride appears more resistant to this phenomena, the pressures in the HPT of aeroderivative turbines such as the LM2500 and FT8 exceed 250 psi at full power. These pressures are considerably higher than those found in cruise missile, auxiliary power unit, small stationary, and vehicular ceramic turbine engines, as these small engines operate at relatively low pressure ratios compared to the larger marine main propulsion turbines. No testing of these materials at pressures over 150 psi (10 atmospheres) has been performed to date.

The second potential benefit lies in the ability to withstand lower quality fuels, which are higher in alkali sulfates. One school of thought holds that these sulfates must first condense on HPT component surfaces in order for corrosion phenomena to begin to occur. Here the higher surface temperatures of silicon nitride may be a benefit in helping to prevent corrosion. A second school of thought indicates that alkali sulfate corrosion occurs due to impingement of these gas species on the airfoils. As there are considerable unknowns here, we have proposed a task that will take a "first look" at two potential environmental barrier/thermal barrier type coating systems for silicon nitride.

The DARPA funded program for the cooled ceramic vane resulted in a design which reduced the cooling air requirement of the first stage vane by approximately 5% of total core flow. The design limits surface material temperatures of the silicon nitride vanes to a level that enables rig testing for periods of 10 to 200 hours. A separate Dept. of Energy funded effort, administered through ONR, resulted in prototype vane fabrication and low temperature heat transfer testing to validate the cooling approach and component integrity.

The FT8 vanes tested within this program was the first true test of *cooled* silicon nitride components to be designed and tested at full gas turbine conditions, in the United States. Figure 1 shows an exploded view of the FT8 vane design. The silicon nitride portion includes the ID platform, all airfoil surfaces, and a transition section that mates with a superalloy outer platform. The vane is hollow, and a perforated metal baffle (shown) is fitted inside the vane to direct cooling air flow in a specific pattern over the inside surface of the hollow silicon nitride vane. The cooling gases are then expelled through the trailing edge vents and assist in film cooling the trailing edge. As part of the DARPA AMP program, extensive iterations on cooling design were required to minimize thermal gradient stresses on the vane wall, with final tensile stresses below 40 ksi realized for the design.

Figure 1. Silicon Nitride Vane Design

The silicon nitride airfoil is pocketed into the superalloy outer platform, which is in turn capped by an outer spring plate (shown in blue). An Incoloy 909 bolt sandwiches the silicon nitride airfoil between the outer and inner (also blue) spring plates. This feature helps soak up radial thermal expansion mismatch between the metal superstructure and the silicon nitride vane. All

metal surfaces are zirconia TBC coated at the silicon nitride/metal interface points, and alumina fiber cloth is inserted at the interfaces to help prevent reactions between the metal and the ceramic (fiber cloth not shown). The fiber cloth helps to assist in sliding caused by differential thermal expansion, and in some locations is used as a gaspath seal (outer platform/vane interface). While use of alumina fiber cloth as a gaspath seal has long term durability issues, it is sufficient for the 100 hour test duration proposed herein.

The vane is attached to a slightly modified outer vane support, and a Bill of Materials inner support [referred to as tangential on board air injection to the first blade (TOBI)]. The rails on the silicon nitride ID platform bottom are further sandwiched in a spring mechanism to soak up axial thermal expansion.

RESULTS AND DISCUSSION

Task 1 — Ceramic Vane Fabrication Development and Rig Hardware Acquisition

The purpose of this Task was to utilize the design for the cooled ceramic vane previously developed under ONR N00014-96-C-0014 (see Figure 1). Under the program originally proposed, both Honeywell (AlliedSignal) Ceramic Components, and Kyocera Industrial Ceramics Corp. were to further develop methods for fabricating complex, hollow, vented silicon nitride airfoils. At the inception of the program, a business decision at Kyocera resulted in their inability to continue cost sharing further vane manufacturing development. Their level of technology maturation (under prior programs) was deemed adequate for fabricating vanes with simple, circular cross section vent holes. United Technologies elected to proceed with a parts-buy purchase order agreement with Kyocera to acquire vanes for Environmental Barrier Coating (EBC) development, along with additional vanes for sector rig testing. The simplified Kyocera vanes are depicted in Figure 2 below.

Figure 2 — Kyocera SN282 silicon nitride FT8 vanes with simplified trailing edge geometry

The Kyocera vanes were produced by drain slip casting, followed by bisque machining of the trailing edge geometry. After densification, the SN282 vane inner and outer platforms were diamond ground to facilitate attachment into the engine based mounting system.

A second silicon nitride vane fabrication effort was conducted with Honeywell Ceramic Components (formerly AlliedSignal Ceramic Components Division). Under a cost sharing subcontract, Honeywell continued to develop their shape fabrication capability and diamond grinding capability for the complex vane geometry. Honeywell employed their AS800 silicon nitride, which was fabricated using gel casting around a sacrificial core (the core created the cavity required within the vane. Typical gel cast, hollow FT8 vanes are depicted in Figure 3 below:

Figure 3 – Gel Cast AS800 Silicon nitride vanes from Honeywell (AlliedSignal) Ceramic Components, showing hollow core

Honeywell was able to deliver two sector test candidate vanes, one of which was used in high pressure sector rig testing. Details of Honeywell's development activity are provided in Appendix A, attached.

Rig Hardware Fabrication – at the close of sector testing under preceeding contract ONR N00014-96C-00014, it was found that the gases exiting the FT8 vane cascade were subject to high recirculation rates, which melted some of the rig hardware. Considerable efforts were expended in design of a water cooled turning duct to receive the combustion gases coming through the vane passages, and turn them downstream while keeping the flows subsonic and with minimal recirculation. Use of FT8 HPT blades were first considered for this purpose. However the blades produced an excessive blockage of the vane passages due to their fully stalled (fixed position) versus combustion gases traveling through the vane passages at full power condition.

A complete aerodynamic design was undertaken to determine the dimensions of the water cooled turning duct. Key parameters were to match the Mach number (gas velocity) of the flow through the vanes in the rig to that of the engine. To do so, the duct was carefully contoured using a 2D version of Pratt & Whitney's Y237 aerodynamic design code. The design was iterated until the rig (duct) flows matched those of the engine, see Figure 4 below:

Figure 4 – Gas velocity of FT8 engine at full power (left) and in the FT8 based sector rig (right)

The vane in the rig analysis at the bottom of the figure is a bill of materials cooled cobalt alloy vane, as it bisects the edge of the flow. The high Mach number on this vanes' suction side was not of concern, provided that the flow did not recirculate.

Upon completion of the aerodynamic design, a detailed heat transfer study was performed to determine the cooling water requirements for each wall section of the enclosed duct. This information and the aerodynamic design were used to construct a 3D CAD model of the duct to facilitate manufacturing. A depiction of the CAD model is shown in Figure 5 below.

Figure 5 CAD representation of water cooled turning duct

The duct was constructed of mild steel, with a plasma sprayed zirconia thermal barrier coating on the interior. Over 500 water passages were painstakingly milled or EDM'ed into its various walls. The completed duct was pressure tested to ensure weld integrity. The "blast side" of the duct (shown in blue above in Figure 5) was provided with a separate water cooling system due to its much higher heat load.

Task 2 – Coating Development for Protection of Silicon Nitride Components under Liquid Fuel Turbine Hot Section Environments

Efforts under this Task focused on 3 types of environmental barrier coatings (EBC's) for gas turbine grade silicon nitride;

- 1.) A rare earth oxide coating developed by UTRC/P&W, and applied via electron beam physical vapor deposition (EB-PVD),
- 2.) Aluminum oxide, developed by subcontractor Stevens Institute of Technology, and applied via chemical vapor deposition (CVD), and,
- 3.) A coating based on barium strontium aluminosilicate, as developed by UTRC and others under prior efforts funded by NASA and U.S. DoE for silicon carbide fiber composite, and applied via plasma spraying

Efforts by Stevens Institute to coat Kyocera SN282 gas turbine grade silicon nitride proved to be difficult. Adherence tended to be poor, unless very thin coatings (< 2 microns) were used, and these proved to have incomplete coverage. It was thought that the large thermal expansion mismatch between silicon nitride (3.2 ppm/°C) vs. alumina (7.8 ppm/°C) caused cracking upon post deposition heat treatment to crystallize the coating.

Efforts were then directed towards examining whether UTRC's "DOE-9" coating could be utilized as a base coat with CVD alumina as a top coat. It was anticipated that the outer alumina layer would provide protection from vanadium species present in both NATO grade, and merchant marine liquid fuels. UTRC's "DOE-9" coating is a plasma sprayed multilayer coating that was optimized under prior U.S. Dept. of Energy funded efforts to protect large SiC fiber, SiC/Si matrix composite combustors for stationary gas turbines. However, attempts to coat 1 cm. by 1 cm SN282 silicon nitride test coupons resulted in cracking of the coating. Later in the program, Honeywell AS800 silicon nitride turbine vanes were coated using the DOE-9 process. When used on the higher expansion (4 ppm/°C) silicon nitride, the BSAS system appeared to be crack free. The vanes were cross sectioned, and sections were provided to Stevens Institute for CVD alumina top coating. Further details of efforts under the UTRC subcontract to Stevens are available in Appendix B.

A second concept explored the use of EB-PVD deposited yttrium oxide as an environmental barrier for protection of silicon nitride. The yttrium oxide coating was thought to provide 3 functions – firstly, it is known that yttrium reduces the activity of silica. By providing the surface of the silicon nitride with abundant yttrium oxide, the silica oxidation product should

become supersaturated with yttrium (see Figure 6). A second function is to provide a means to keep the surface of the silicon nitride from being exposed to the high gas velocities intrinsic to turbine vane operation (related testing at NASA has indicated that higher velocities increase water based oxidation of non-oxide ceramics). Thirdly, because the FT8 HPT and similar components (i.e. GE LM2500 Navy/Marine engine HPT vanes) are expected to be cooled, the relatively low thermal conductivity of yttrium (and other rare earth oxides) should lower the surface temperature of a cooled silicon nitride airfoil.

Figure 6 Schematic of EB-PVD EBC concept

Six "as-cast" SN282 turbine vanes were acquired from Kyocera. Yttrium oxide coatings were deposited via EB-PVD, at a substrate temperature of approximately 1000°C. Target coating thicknesses were 50, 100, and 200 microns, respectively. All coatings remained adherent upon rapid cooling from the deposition temperature. Coating coverage/adherence on the platforms appeared poor, while adherence on the main body of the airfoils appeared good.

Three airfoils from the lot, one with each target thickness, were exposed to rapid thermal cycling, using a bottom load furnace set at 1300°C. Every 30 minutes, the bottom was dropped on the furnace and the parts were exposed to a room temperature air quench assisted by a fan. All of the coatings spalled catastrophically after 6 cycles (see Figure 7). It is conjectured that the columnar structure of the EB-PVD yttria allowed the coating to withstand initial rapid cooling from the deposition temperature. However, when heated above the substrate deposition temperature, the columnar cells attempt to expand at a much higher rate than the underlying substrate, resulting in spallation. The thermal expansion of yttrium oxide, and SN282 silicon nitride, are 8 ppm/°C, and 3.2 ppm/°C, respectively. When cooled from the deposition temperature, typical 20 micron EB-PVD yttria columns would be expected to develop maximum

tensile stresses of 2 Mpa (300 psi), well within the intrinsic strength of the material. One suggestion for future work is to raise the substrate deposition temperature to 1300°C to prevent column crowding when heated above the deposition temperature. With the added benefit of a thermal gradient across the coating during cooled vane operation, adherence would be expected to be good.

Figure 7 EB-PVD yttrium oxide deposited directly only SN282 silicon nitride vane, showing effect of 6 rapid thermal cycles to 1300°C.

In order to examine at least one type of environmental barrier coating in the cascade test, UTRC's DOE-9 coating was examined. The coating system was applied to both Kyocera SN-282 silicon nitride and Honeywell AS800 silicon nitride. Coatings applied to SN282 silicon nitride exhibited extensive cracking in the silicon bond coat, and further work on SN282 was abandoned. However, the DOE-9 coating exhibited good adherence to Honeywell AS800 silicon nitride. Coating trials were also performed on full scale vane prototypes supplied under subcontract from Honeywell, and coating thickness distributions were used to change the plasma spray coating procedures to ensure even and complete coverage. Two engine sector candidate vanes were coated, and one EBC coated Honeywell vane was used in sector rig testing (see Task 3 below).

Task 3 Sector Rig Combustor Cascade Testing of Ceramic Vanes

The purpose of this Task was to expose a cascade of FT8 cooled silicon nitride vanes to a combustion environment identical to that experienced by HPT vanes in an operating Navy 25 MW propulsion gas turbine. An existing FT8-1 sector rig (representing a 1/9th slice of the combustor and combustor to vane transition section) was used to provide temperature, temperature distribution, and pressure conditions seen in an actual high pressure turbine. The ceramic vane cascade and its mounting hardware was previously developed, and initially tested under a prior contract (ONR Contract No. N00012-96-2-0014).

The sector rig with cooling duct (depicted in CAD format in Figure 5, above), and the assembled cascade and cooling duct is shown in Figure 8a and 8b. Pressure taps were installed in the duct, immediately downstream of the vane passages, to determine whether any portion of the hot gas flow had become transonic.

Figure 8a Vanes in final assembly of rig (in outer assembly support, and inner TOBI support), from left to right: one cobalt alloy production vane, three Kyocera SN282 vanes, and one Honeywell AS800 vane with BSAS based EBC coating

Figure 8b Closeup of EBC coated AS800 vane prior to test. Chipping of coating on platform occurred during handling. Pressure side is on left, and suction side is on right

Within the cascade, one metal vane, three Kyocera SN282 silicon nitride, and one Honeywell AS800 vane were installed. The Honeywell vane had the BSAS based EBC applied as discussed under Task 2 above. Each vane had an internal pressure tap to determine vane integrity and assess cooling flow. After the vanes were attached to the outer assembly support, inner TOBI support, and baseplate, the cooling duct was installed as shown in Figure 9.

Figure 9 Installation of water cooled turning duct

The combustor can/transition duct/vane/turning duct was then assembled into UTRC's Jet Burner Test Stand, and the turning duct was plumbed for cooling water, as shown below;

Figure 10 Vane cascade, turning duct and combustor assembled to sector housing, with water cooling lines installed

A single FT8-1 combustor can (from the 9 can FT8 engine) was then installed in the rig and shakedown testing was performed by flowing 530°C T3 air through the system without a combustion flame. Various temperature and pressure probes throughout the rig were used to monitor system performance. A view of the rig from the control station, and the computer system used to monitor rig function are shown in Figure 11.

Figure 11 – View of high pressure sector rig from control room (left), and computer monitoring of system pressures and temperatures, and flow controls inside control room (right)

Due to limitations in contract funds, natural gas fuel was substituted for the NATO grade petroleum fuel originally planned for the test. After successful T3 testing, the combustor was lit off and conditions were set to simulate 70% of engine full power conditions. Typical run conditions are shown in the screen shot below:

PERFORMANCE				Natural Gas				Pressures			
PT3	245.2	244.0	0.2	Wf Tot	932	910	0.2	PT3 avg	244.64		
T3avg	794	794	0.0	I/2w	0.0176	0.0175	0.4	Pdiff avg	230.92		
W31	14.74	17.11	13.9					PS4	234.92		
W4b	14.74	14.76	0.2	Duct Parameters				PT4 Calc	234.72		
Bleed	0.00	2.35	100.0								
FPD	2.13	2.135	0.3	DuctP1	223.87	0.95	0.28	Run	7.6		
Diff DP	2.59%			DuctP2	221.24	0.94	0.30	Point	32		
Noz DP	1.63%	2.69%	UNNN	DuctP3	230.35	1.02	UNNN				
EMISSIONS				Vane Parameters							
NOx	0										
COLO	0			FVDP1	235.3	0.9	0.37	set pt (%)	100	25.40	
COFI	0			FVDP2	234.7	0.0	10.01		0.10	0.4	
HC	0.00			FVDP3	245.3	10.6	4.51		0.40	0.4	
	20			FVDP4	233.4	2.13	0.54		1.40	1.13	

Figure 11 Pressure and sensor outputs from FT8 sector rig/vane cascade under 70% power operation

The rig was operated for 8 hours at 70% power condition, in order to generate a hot streak of approximately 1400°C (2550°F) at the hot spot vane, and 1200°C (2200°F) at the EBC coated vane, at total inlet pressure of approximately 16 atmospheres (combustion gas temperatures taken from historical thermocouple rake data). During shutdown, the rig was brought down to minimum conditions that would support combustion, followed by fuel shutoff. Cooling water temperatures for the turning duct remained within expected parameters, except for a small section abutting the air cooled vane at the edge of the sector. Following cool down from this segment, the combustor was removed and the vanes were observed looking through the combustor to vane transition duct, as depicted in Figure 12 below:

Figure 12 - Vanes following first 8 hour test on natural gas. From left to right, the first vane is BOM cobalt alloy, the next 3 vanes are Kyocera SN282 (no coating), and the vane on the right is BSAS EBC coated AS800

As seen in Figure 12, a hairline crack developed in the hot streak vane at the fillet to the inner platform. As the vanes had been designed with backflow margin (excess cooling air in the event of cracking) the decision was made to continue the test.

Two attempts were made to reinitiate testing for an additional 8 to 10 hours. During both attempts, the turning duct cooling zone abutting the cooled vane experienced very high temperatures, triggering two "trip" type, emergency fuel shutoffs from approximately 60% power level. Following the second trip shutdown, the rig underwent a boroscope inspection to determine the potential cause of the phenomena, and the vanes were inspected by boroscope as well (see Figure 13, next page). The problem was traced to a cooling line fitting that had come loose, allowing the high pressure combustion exhaust to backfill the cooling duct jacket and prevent water flow. The rig aft section was removed and the problem was rectified.

Figure 13 Boroscope inspection following 8 hours operation, and 2 emergency trip shutdown. Figure (a.) shows the hot streak vane with crack partially open, as also seen in Figure 12. The EBC coated vane experienced shipout at its vestigial outer platform where it seats in the superalloy pocket (b.). A crack was also observed in the SN282 vane adjacent to the hot streak vane (c.)

Following repairs to a cooling line, the vanes accumulated an additional 15 hours of testing at the 70% power rating described previously, with no further rig issues or vane damage observed. Following another combustor can removal for inspection, the decision was made to attempt to reach as high a temperature as possible. One of the 4 mechanical compressors which fed the FT8 sector was down for repairs, but it was found that sufficient supply of warm T3 air existed to reach 80% power level condition (18 atmosphere inlet pressure, 1450°C (2650 °F) hot streak). This condition was held for one hour, followed by a normal shutdown sequence. The vane cascade was then removed from the sector. A total of 33.5 hours were accumulated under

combustion conditions, with over 31 hours at 70% power level or higher. The vanes shown looking from the combustor are shown in Figure 14.

Figure 14 – Vane cascade following completion of 31 hours at 70% or higher FT8 natural gas engine operation conditions

The chipping observed on the EBC coated vane occurred on initial rig assembly, and was not a result of sector operations. Surprisingly, the EBC coating remained completely intact on the AS800 vane, despite only being optimized for SiC/SiC composite substrates. The EBC coated vane saw combustion gas temperatures of 1230°C (2250°F) at the 80% power condition, based on historical thermocouple rake data. The internal pressure of the EBC coated vane never reached an appropriate delta over P4 observed pressures, indicating that its cooling system may not have functioned properly. For the SN282 (uncoated) vanes, pressure differentials were lower than expected within the design. See post-rig test pressure testing discussion below:

Task 4 — Ceramic and Metallic Vane Characterization

Vane characterization focused on post test (macro) inspection, post test pressure/flow testing, and microscopic examination of environmental degradation. Following completion of the sector test, the rig was disassembled and the condition of the vanes were observed.

The hot streak vane suffered the most substantial damage, as shown in Figure 15 below. All 4 fragments of this vane remained assembled and correctly positioned within the vane cascade and mounting system. Oxidation of the fracture surface was observed in the area first observed to exhibit cracking (after the first 8 hour test segment). The fracture surface is shown optically in Figure 16.

Figure 15 – Hot streak (hot spot) SN282 vane following disassembly.

Figure 16 Optical macrograph of initial fracture surface in hot streak vane

The white powder observed in Figure 17 was later identified by x-ray diffraction as a rare earth disilicate, commensurate with residual grain boundary phase material following oxidation.

The EBC coated AS800 suffered damage to its outer platform as described in Task 2 above. The vane is shown in Figure 17 below. Although some discoloration appeared on the upper 1/3rd of the span, the EBC coating remained intact. Chip outs on the platforms were present prior to vane cascade assembly and test.

Figure 17 Post test inspection of EBC coated AS800 vane

The final vane which saw mechanical distress was the vane located between the hot streak vane and the EBC coated vane. This vane exhibited a crack emanating from a cooling hole which propagated down into one of the inner platform runners (see Figure 18). It is important to recall that the vane's original mechanical design included a complete (not clipped back) trailing edge, which would have stiffened and strengthened this region of the vane. The 4th SN282 vane, located between the hot streak vane and the air cooled vane, did not exhibit any mechanical failure.

Figure 18 – Mechanical failure of “near hot streak” vane, 2 pieces (single crack)

Following preliminary assessment, 2 of the 4 vanes were subjected to post rig test pressure/flow testing. Various source pressures were used, and the pressure drop across the vane was evaluated. This was then compared to the reference cooled ceramic vane design. Only the intact SN282 vane, and the EBC coated AS800 vane were tested. See Figure 19

Figure 19 Post sector rig flow testing of cooled silicon nitride vanes. “Uncoated” refers to an SN282 vane, “Coated” refers to the AS800 vane, and “Calculation” shows the expected cooling flows from the reference cooled ceramic vane design

As shown in Figure 19, the SN282 vane flowed considerably more air than the reference design. This was believed to be caused by leakage at the vane/superalloy platform interface. The EBC coated AS800 vane did not flow as well as the reference design (its superalloy platform to vane seal was different) and this is believed to be caused by EBC coating partially obscuring the vane cooling holes.

After post test visual inspection, and pressure testing, two of the vanes were cross sectioned for detailed microscopy analysis. The hot streak SN282 vane, and the EBC coated AS800 vane were both cross sectioned. In order to best interpret the effects on vane surfaces, it is useful to the reader to understand the local combustion gas velocity at various locations along the turbine airfoil: these velocities can range from less than Mach 0.1 to Mach 0.9. The Mach number maps are shown in detail for the hot streak vane, and the EBC coated vane, in Figure 20. These data are for the 70% power level, for vanes in the rig. The Mach number distributions within the actual FT8 engine HPT vane are very similar. The stagnation point is the area at the leading edge where velocity drops to nearly zero (dark blue in figure). The area where velocities reach Mach 0.8 to 0.95 is referred to as the “suction side” (opposite side from “pressure side”).

EBC Coated Vane (top)

Hot Streak Vane (center)

Figure 20 Combustion gas velocities (predicted) within the EBC coated vane (right) and the hot streak vane (left) within the sector rig, at 70% of full power engine condition.

Figure 21 Electron microprobe evaluation of surface cross section of hot streak SN282 vane (uncoated).

The hot streak SN282 vane was analyzed using optical and SEM microscopy, and by electron microprobe. The reddish hue (see Figure 16) found on the pressure surface only (not at the

stagnation point) was determined to be iron, as shown in the electron microprobe maps in Figure 21. From the coloration shown in Figure 16, iron was not present in regions of the vane expected to reach temperatures in excess of 1280°C. This could indicate that iron bearing particles impinged upon the vanes early in the test initiation, but then evaporated as iron silicates. The silica layer was approximately 10 microns, with some indication of segregation of rare earth oxide (possibly concentrated due to evaporation of silicon nitride via the $-OH$ mechanism).

The stagnation point of the hot streak SN282 airfoil is shown in Figure 22. Here, gas velocity approaches zero, while static pressures are very high. This leads to the highest material temperatures in most turbine airfoil designs. As noted, no iron was seen. Areas with high levels of rare earth were observed (bright areas in back scattered electron images). The high rare

Figure 22 Backscattered and secondary electron images of the stagnation point on the hot streak vane.

earth oxide areas may be commensurate with known issues currently affecting the SN282 silicon nitride material. Segregation during processing into regions with very high, and very low, concentrations of rare earth oxide appear to be affecting the ultimate tensile strength of these materials.

The EBC coated AS800 vane was extensively characterized, as this was the first test known to have occurred with EBCs at high Mach number. Testing of EBC coatings on combustors typically involve gas velocities on the order of Mach 0.1, while most turbine vanes easily see velocities in excess of Mach 0.8. Areas of the EBC coated vane, and their cross sectioned secondary electron images are shown in Figure 25.

Figure 23 Effect of engine environment on EBC in various regions of the vane. The top 2 pictures represent the stagnation point, while the bottom 2 pictures show the suction surface. Suction (high velocity) region shows surface smoothing (bottom).

As can be seen in Figure 23, the suction side of the airfoil exhibited surface smoothing of the EBC top layer. The stagnation point appeared unchanged from the as-deposited coating, and the occurrence and spacing of cracks in the silicon bond coat has not increased. There appeared to be an effect of the turbine engine combustion environment on the "as-processed" surface of the AS800 silicon nitride. This region tends to be somewhat porous, even if heat treated in air at temperatures of 1250°C, as shown in Figure 24.

In comparison, an absence of porosity was evident on the tested vane protected by the BSAS based 3 layer EBC, as seen in Figure 25. One suggestion is that the high water vapor/high temperature environment, in combination with the EBC constituents, somehow caused the as-processed layer to sinter and densify.

Figure 24 Optical micrograph showing porosity typically found in the as-processed surface of AS800 silicon nitride

Figure 25 Secondary electron images showing reduced porosity in tested silicon nitride vane surface layer, protected by EBC

SUMMARY AND FUTURE WORK

The highlight of the subject program constituted the first test of an actively cooled silicon nitride vane within the United States. The test also broke new ground in the combination of high temperature and high pressures achieved, and was the first proof of concept test of EBC coated ceramic articles in high mach number environments. Considerable effort was expended in the design and construction of a water cooled turning duct to allow the cascade to more closely mimic actual HPT vane gas velocities and temperature distributions, as seen in the engine. Vanes without EBC protection exhibited segregation of sintering additives at the surface. EBC coated vanes showed surface smoothing in high Mach number regions.

Due to limitations in funding, the sector testing had to be performed under natural gas fuel conditions. Future tests should examine liquid fuel effects on both coated and uncoated silicon nitride vanes. The EB-PVD based EBCs should be revisited using higher substrate temperatures.

Within ONR N00014-01-0XXX, UTRC will apply a rainbow of EBC coatings to the FT8 cooled vanes and operate them in another natural gas fueled sector test, as proof of concept for the EBCs being developed under that contract. As part of this effort, some continuation in Stevens Institute's efforts in CVD alumina EBC coatings has been performed.

ACKNOWLEDGEMENTS

This work and the efforts leading to it would not have been possible without Dr. Steven Fishman's guidance, and financial support of ONR, DARPA, and Dept. of Energy Power Technologies (Steven Waslo, Deborah Haught). The cost sharing provided by United Technologies, Kyocera Industrial Ceramics and Honeywell Ceramic Components Division is gratefully acknowledged. In addition, I would like to thank the many UT-Research Center and UT-Pratt & Whitney personnel who helped make this project a success over the years as listed below:

Konstatin Kouris -	Mech. Design	P&W
Mike Blair	Aerothermal Design	UTRC
Andrea Karalus	Rig Design	UTRC (now at P&W)
Luca Bertuccoili	Rig Aero	UTRC
Mike Weber	Rig Testing	UTRC JBTS
Scott Kearney	Rig Testing	UTRC JBTS
Dave Eigner	Rig Fab	UTRC (now at P&W)
Rich Ferraro	Rig Fab.	UTRC
Tony Fernandes	Baffle fab.	UTRC (now at P&W)
Harry Eaton	EBCs for Vane	UTRC-Components
Tom Lawton	EBC's for Vanes	UTRC-Components
Ellen Sun	Post test characterization	YTRC-Components
Phil Malinoski	Baffle fab	P&W
Ron Carubba	Supplier Coord.	UTRC Purchasing
Joel Wagner	Thermal Validation	UTRC (now at P&W)
Debroah Hass	Thermal Validation	UTRC

Guidance, encouragement and help provided by Bill Day (P&W-PS), Vince Nardone (UTRC-PW Programs) Mark Zelesky (P&W-PS), Dan Pfau (UTRC JBTS) Hannes Alholm (P&W-Combustors), Frank Goppel (FT8 TurbineMC) and a variety of other P&W personnel

APPENDIX A – Stevens Institute of Technology CVD EBC Development

CVD- Al_2O_3 and CVD-Si Development for Next Generation Environmental Barrier Coatings for Si_3N_4 Turbine Components

I. Tsarenko, H. Du, and W. Y. Lee
Department of Chemical, Biochemical, and Materials Engineering
Stevens Institute of Technology
Hoboken, NJ 07030

I. Abstract

We have discovered a novel procedure for preparing a dense, homogenous layer of $\kappa\text{-Al}_2\text{O}_3$ on silicon nitride (SN282) without microcracks by chemical vapor deposition (CVD) using AlCl_3 , H_2 , and CO_2 as precursors. Although it was not the thermodynamically stable $\alpha\text{-Al}_2\text{O}_3$ phase that we initially intended to prepare, the $\kappa\text{-Al}_2\text{O}_3$ layer significantly improved the oxidation resistance of SN282 at 1400°C . Uncoated SN282 exhibited classical features of severe oxidation degradation such as formation of blisters in the TGO and extensive cracking and spallation of the TGO. In contrast, the TGO formed on the coated SN282 was amorphous and smooth without the appearance of blister formation and extensive microcracking. Also, the TGO growth rate was reduced by a factor of five. These results were consistent with our earlier investigation of the beneficial effect of Al implantation on the oxidation behavior of silicon nitride under the influence of Na impurity.

A dense, polycrystalline Si layer was also deposited on SN282 by CVD using SiCl_4 and H_2 as precursors. When SN282 was coated with the CVD Si layer, the TGO growth rate was reduced by a factor of three upon isothermal exposure in air at 1200°C . The reduced oxidation rate was attributed to the ability of the CVD Si layer to act as a diffusion barrier to mitigate the incorporation of impurity and additive cations such as Na and Mg from SN282 to the TGO. However, at 1400°C , the beneficial effect of the CVD Si layer was not evident, as the oxidation temperature was near the melting point of Si and consequently it was no longer an effective diffusion barrier.

These experimental results, while preliminary, provided strong evidence to suggest that the CVD Al_2O_3 and Si layers, upon further improvements, could be utilized as key building blocks for designing and making next generation environmental barrier coatings (EBCs) for silicon nitride turbine components.

II. Technical Background

Monolithic silicon nitride has considerable potential for being used for hot section components for aircraft engines and power generation turbines. Both silicon nitride turbine vanes and rotating blades show promise for significantly increasing both the fuel efficiency and low grade fuel

tolerance of gas turbines for power generation and aircraft propulsion. The key to using these types of materials over long service life times, with low grade and less expensive fuel, lies in the ability to develop environmental barrier coatings similar in behavior to the MCrAlY coatings used to protect single crystal Ni-based superalloys.

Figure 1 shows two state-of-the-art EBCs that have been developed by the ORNL and NASA/GE/UTRC research teams with promising characteristics in water vapor and molten salt environments. The beneficial features of the thin mullite layer produced by chemical vapor deposition (CVD) are: (1) resistance to molten salt attack¹ and (2) slow scale growth.² As shown in Figure 1(c), the CVD mullite layer reduces the thickness of thermally grown oxide scale (TGO) on the SiC surface by two orders of magnitude. However, due to its high silica activity, mullite ($3\text{Al}_2\text{O}_3 \bullet 2\text{SiO}_2$) is expected to be susceptible to attack by high-velocity water vapor, although CVD mullite has not yet been tested in such an environment.

The advantages of the BaO-SrO- Al_2O_3 - SiO_2 (BSAS)-based EBC produced by air plasma spray (APS) are: (1) resistance to water vapor, (2) slow TGO growth; and (3) improved coating adhesion due to the Si layer.³ However, major problems associated with this EBC design are: (1) the coating, which contributes significant non-load bearing weight to the turbine component, is too thick for some small turbine components; (2) infiltrating the coating into the intricate surface contours of small vanes and integrated turbine rotors in microturbines is not possible due to the line of sight nature of the APS technique; and (3) the APS process requires roughening of the initial substrate surface by grit-blasting to promote mechanical interlocking between the coating and substrate. This type of surface roughening can result in considerable strength reduction of the surface damage sensitive Si_3N_4 .⁴

Fig. 1. State-of-the-art EBC designs: CVD mullite and APS BSAS-based coatings. The performance of these coatings has been assessed mainly for protecting SiC/SiC ceramic matrix composites, which suffer from water vapor-related environmental problems similar to Si_3N_4 .

Furthermore, the APS layers are intrinsically porous as they contain splats and microcracks produced during the spray process, and therefore do not serve as "diffusion barriers" to mitigate

the incorporation of oxidants and impurities during the TGO growth. Also, the APS-Si is a very brittle layer, and therefore should not be too thick for the EBC application. However, the APS-Si layer cannot be made thinner since starting powder size for conventional APS is typically limited to about 30 to 40 μm .

The ultimate motivation behind this research was to evaluate and demonstrate a multifunctional interface design approach as the enabling concept for producing reliable and durable EBC-coated Si_3N_4 components, as schematically illustrated in Figure 2. The design concept involves the integration of four distinct layers with each layer providing its specific function(s) while tailoring their interfaces for thermochemical and thermomechanical stabilities:

- (1) Plasma-sprayed $\text{BaO-SrO-Al}_2\text{O}_3\text{-SiO}_2$ (BSAS) for thermal insulation and water vapor resistance. Its primary function is an environmental barrier ($\sim 75 \mu\text{m}$) although for air-cooled Si_3N_4 vanes in aeroderivative turbines it also acts as a thermal barrier ($2 \text{ W/}^\circ\text{K}$).
- (2) CVD $\alpha\text{-Al}_2\text{O}_3$ for enhanced water vapor and hot corrosion resistance. This layer is expected to be very thin, likely in the sub-micron range, to mitigate micro-cracking and spallation caused by thermal expansion mismatch with adjacent layers. This layer was also designed to protect small Si_3N_4 components where the thick BSAS layer may not be accommodated.
- (3) CVD mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) for interfacial stability and as an oxidant diffusion barrier ($\sim 1 \mu\text{m}$).
- (4) CVD Si as the preferred surface, instead of the Si_3N_4 vane surface, for the formation of high-quality thermally grown oxide (TGO) during oxidation. This layer ($1\text{-}5 \mu\text{m}$) is designed to increase the cyclic oxidation life of EBC-coated components since the thickness and quality of the TGO is expected to be predominant life-limiting factors.

Fig. 2. Multifunctional interface design concept for next generation EBC architecture.

III. Approach

While the full exploitation of the concept was beyond the scope of this project, the specific objectives of the project were to assess: (1) the feasibility of synthesizing CVD-Si and CVD- α - Al_2O_3 layers, as the key building blocks of the multifunctional interface design approach that have not been previously developed and (2) the oxidative stability of the CVD-Si and CVD- α - Al_2O_3 layers deposited on sintered Si_3N_4 and single crystal Si substrates.

In the BSAS-based EBC, we suspected that Si plays an important role in gettering oxidants from the environment through its sacrificial oxidation. Oxidation of Si takes place without the adverse effects of (1) evolution of a gaseous byproduct (N_2), which could induce interfacial bubble formation and even spallation in the TGO layer, and (2) segregation of additive and impurity cations from Si_3N_4 , which could markedly accelerate the oxide growth and crystallization.⁵ The role of Si in enhancing the coating adhesion can be interpreted in terms of: (1) the chemical and thermochemical nature of the modified Si- Si_3N_4 and Si-mullite interfaces due to native oxide and/or TGO and (2) the closer CTE match between Si_3N_4 ($3.2 \times 10^{-6}/^\circ\text{C}$) and Si ($4.7 \times 10^{-6}/^\circ\text{C}$).

We expected that CVD-Si possesses a denser morphology and a smoother interface than what can be made with the APS method. The denser morphology and smoother interface were expected to increase the quality of TGO and therefore its adhesion to the Si surface.

The second objective of this project was to prepare a thin CVD α - Al_2O_3 layer (0.050 to 1 μm) using metalorganic and chloride precursors of Al. High-purity α - Al_2O_3 exhibits excellent stability in molten salts and water vapor.⁶ It is a superior diffusion barrier because of extremely slow ionic diffusion in polycrystalline α - Al_2O_3 with grain boundary diffusion of oxygen anions as the predominant diffusion mode of oxidant transport.⁷

A properly designed thickness, likely in the submicron range, was expected to provide significant crack and spallation resistance in α - Al_2O_3 , despite its mismatch in coefficient of thermal expansion (CTE) with the overlying BSAS and the underlying mullite layers (α - Al_2O_3 : $8 \times 10^{-6}/^\circ\text{C}$, BSAS: $>5 \times 10^{-6}/^\circ\text{C}$, mullite: $5.6 \times 10^{-6}/^\circ\text{C}$). The remarkable resistance of thin films, compared to their thick counterparts, to stress-induced cracking or spallation is well recognized.⁸

Our experimental work on amorphous MOCVD Al_2O_3 layers of a wide thickness range on single crystal Si (CTE of Si: $4.7 \times 10^{-6}/^\circ\text{C}$) and their subsequent exposure to oxygen (1 atm, 1100°C, 20 hours) revealed a clear correlation between damage and thickness of the Al_2O_3 layers. As shown in Figure 3, the 2.55 μm Al_2O_3 layer spalled off the Si substrate, whereas the 290 nm layer was still adherent, but with the presence of microcracks. In contrast, the 40 nm layer was free of microcracks. Polycrystalline α - Al_2O_3 was expected to exhibit a similar damage-thickness correlation, but with superior resistance to cracking and spallation compared with its amorphous counterpart. The physical basis for the reduction in stored strain energy density with decreasing the thickness of thin films, which is the driving force for nucleation and propagation of cracks, has been documented by Lange et al.⁹

Fig. 3. SEM micrographs of Si coated with amorphous MOCVD Al_2O_3 films: (a) 2,550 nm, (b) 290 nm, and (c) 40 nm after exposure in 1 atm O_2 at 1100°C for 20 h. The thick coating layer in (a) has experienced significant spallation, whereas the thinner layers in (b) and (c) showed considerable resistance to cracking and spallation.

IV. Experimental Results and Discussion

Substrate Preparation and Characterization and Oxidation Techniques

Two substrate materials were used: (1) single crystal p-type Si wafer produced by MEMC Electronic Materials Inc. ($1\text{ cm} \times 1\text{ cm} \times 0.05\text{ cm}$) and (2) cold isostatically pressed Si_3N_4 (SN282) containing Lu_2O_3 (5.35%), Yb_2O_3 (0.058%), Al_2O_3 (0.045%), Na_2O (0.053%), CaO (0.016%), and MgO (0.002%) specifically produced for this project by Kyocera Industrial Ceramics Corporation ($1\text{ cm} \times 1\text{ cm} \times 0.5\text{ cm}$ coupons with a 0.2 cm diameter hole). Unpolished and polished SN282 samples were investigated to study the effect of surface conditioning on the oxidation behavior of SN282 as well as on the surface morphology of the CVD-Si layer. The samples were polished by the tribochemical polishing method.¹⁰ A CrO_3 water solution was used with a contact load of 4 N at a rate of disk rotation of 20 mm/s for 40 hours at room temperature. The surface roughness (Ra) of the polished SN282 surface was measured to be 10 nm.

A field emission scanning electron microscope (SEM, LEO 982, LEO Electron Microscopy Inc., Thornwood, NY) equipped with an energy dispersive spectrometer (EDS) was used for morphological and compositional analyses. In order to minimize the charging problem associated with the nonconductive specimens, an Au-Pd layer was sputtered on the sample surface along with the use of carbon tape and silver paste. A Siemens D 5000 X-ray diffractometer (XRD) was used for phase characterization.

Luminescence spectroscopy was also used to determine the presence of $\alpha\text{-Al}_2\text{O}_3$ in the coating layer as well to infer the average hydrostatic stress status of the $\alpha\text{-Al}_2\text{O}_3$ phase. $\alpha\text{-Al}_2\text{O}_3$ has trigonal symmetry with rhombohedral Bravais centering¹¹ and can possess trace amounts Cr^{3+} cation impurities.^{12,13} The Cr^{3+} , having the same valency as Al^{3+} , substitute for them in the

alumina crystal lattice easily. The reason for the fluorescence, as described by Gregori et al.,¹² is that the electronic environment of the Cr^{3+} , as influenced by the surrounding O^{2-} in the lattice. When excited by a laser, the electrons of the Cr^{3+} emit photons. The two characteristic photon energies for the $\alpha\text{-Al}_2\text{O}_3$ phase are: 14402 (R1) and 14432 cm^{-1} (R2). In contrast, most of the other metastable alumina phases, with the exception of $\theta\text{-Al}_2\text{O}_3$ and $\kappa\text{-Al}_2\text{O}_3$, do not exhibit fluorescence peaks. When there is a stress in the $\alpha\text{-Al}_2\text{O}_3$ phase, there is a physical shifting of the lattice as a whole and the relative positions of the oxygen and chromium ions in particular. This shifting changes the electronic environment of the chromium, and there is a corresponding shift in the R1 and R2 lines.^{12,13} In this work, a Dilor XY 800 triple stage Raman microprobe and a coherent Innova 308C Argon ion laser operating at 514.5 nm with a 100 mW output power were used in Oak Ridge National Laboratory in collaboration with Dr. Michael Lance. The laser was focused onto areas of interest with an optical objective providing a spatial resolution of 2 or 10 μm , depending on the objective used.

SN282 uncoated and coated with CVD Si and CVD Al_2O_3 were first oxidized under various conditions. Single crystal Si was also oxidized simultaneously for comparison. Oxidation experiments were carried out in horizontal and vertical Al_2O_3 -tube furnaces (CM Furnaces, Bloomfield, NJ). The temperature in the furnace was measured using a Pt -10% Rh thermocouple. The temperature fluctuation in the hot zone of either furnace was $\pm 5^\circ\text{C}$. The thickness of the oxide layer was estimated by weight method and cross-sectional SEM. The oxidized samples were characterized using XRD and SEM in conjunction with elemental mapping using EDS analysis.

CVD-Si Experiments

CVD-Si experiments were performed using SiCl_4 and H_2 in a hot-wall reactor at Stevens. The schematic diagram of the reactor is shown in Figure 4. The overall reaction for the CVD process is:

The SiCl_4+H_2 precursor chemistry has been previously used for epitaxial and polycrystalline Si growth in the microelectronic industry.¹⁴ Substrates were placed along the direction of gas flow using a quartz substrate holder.

Fig. 4. Schematic diagram of the CVD reactor used for CVD-Si experiments.

Table I. Processing conditions for CVD-Si experiments

Exp No.	Sample		Processing parameters					
	No.	Substrate	T (°C)	P (Torr)	Time (h)	Flow rate (cm ³ /min)		Deposition rate (nm/min)
						SiCl ₄	H ₂	
1	1 ¹ , 2 ² , 3 ³	Si	1050	30	2	2	200	4.1
2	4 ⁴ , 5 ² 4n ⁴ , 5n ²	Si Si ₃ N ₄	1050	5	2	5	200	83.2
3	6 ⁴ , 7 ² 7n ²	Si Si ₃ N ₄	1100	1.5	1	2	200	28.0
4	8 ⁴ , 9 ² 8n ⁴ , 9n ²	Si Si ₃ N ₄	1100	1.5	1	10	200	58.8
5 [#]	10 ⁴ , 11 ² 10n ⁴ , 11n ²	Si Si ₃ N ₄	1120	1.5	2	0.5	200	6.5

Sample location measured from the entrance of the reaction chamber: ¹ –22.5 cm, ² –25 cm, ³ –27.5 cm, ⁴ –17 cm.

[#] - For this experiment, substrate was pre-treated with H₂ for 20 min at 1120°C prior to the CVD step.

The process parameters used for five deposition experiments are listed in Table I. The experiments were not designed to be parametric in nature. The process conditions were adjusted heuristically after every experiment to make the surface morphology of the Si layer "denser", as the first three experiments produced relatively "poor" surface morphologies (Figures 5 and 6). The process adjustments were largely based on our prior experience with controlling the nucleation and growth behavior of CVD materials (e.g., CVD morphology becomes more crystalline, denser, and large-grained with simultaneously increasing temperature and lowering pressure.¹⁵⁻¹⁸

As summarized in Table II and Figure 7, the SEM results showed that we were able to improve the surface morphology of the Si layer. The surface grain packing density, which is defined as the percentage of the surface area covered by the grains to that by the pores, increased from ~36-40% for Experiment #1 to ~73-99% for Experiment #5, due to the increased deposition temperature and the decreased pressure. Based on these observations and in order to further improve microstructural features of the Si coating, we recommend that the next series of CVD Si experiments should utilize the following conditions: deposition temperature higher than 1120°C, pressure less than 1.5 Torr, SiCl₄ flow rate of about 5 cm³/min, hydrogen flow rate of about 200 cm³/min.

Fig.5. SEM micrographs of CVD-Si on Si wafer: the micrographs show that the surface morphology became denser from Exp. 1 to Exp. 5.

Fig. 6. SEM micrographs of CVD Si on SN282.

Table II. Characterization of surface morphology of Si-CVD

Exp No	Samp. No	x^1 (μm)	Avg. grain size (μm)	Avg. pore size (μm)	Grain packaging density D^2 (%)
1	1	0.16	0.7	> 2	40
	2	0.64	0.65	> 2	38
	3	0.69	0.6	> 2	36
2	4	12.3	0.1	0.35	54
	4n	8.5	0.11	0.3	48
	5	11.9	0.027	0.135	62
	5n	7.22	0.045	0.225	57
3	6	1.99	0.07	0.35	68
	7	1.54	0.06	0.25	73
	7n	1.52	0.19	0.03	88
4	8	3.4	0.15	0.21	87
	8n	3.62	0.2	0.27	80
	9	3.7	0.1	0.1	98
	9n	3.4	0.21	0.13	78
5	10	0.87	0.17	0.75	73
	10n	0.80	0.11	0.125	82
	11	0.75	0.09	0.17	99
	11n	0.71	0.1	0.1	86

¹ Estimated coating thickness based on weight gain² D (grain packaging density) is defined as the percentage of the surface area covered by the grains to that by the pores.

Fig. 7. Effects of deposition temperature and pressure on grain packing density.

Figure 8 shows that (111), (220) and (311) reflections were the dominant XRD peaks for the CVD-Si deposited on Si wafer and SN282. As expected, the XRD data showed that the CVD-Si coating was polycrystalline. No impurity phases as well as impurity elements were measured within the detection limits of the EDS technique. Figures 5 and 6 show morphological differences and similarities between the CVD-Si layers deposited on the Si wafer and SN282 surfaces. The CVD-Si layer on the Si wafer was generally denser and had smaller grains. The difference in the surface packing density might be related to the smoothness of the Si wafer surface, while the initial roughness of the SN282 surface became accentuated as the CVD layer grew. The coarser grains observed on the SN282 surface could not be explained with the available data.

Fig. 8. XRD of CVD Si on (a) SN282 and (b) Si substrates.

Oxidation Evaluation of Single Crystal Si and SN282

Ten hours of oxidation of single crystal Si at 1200° and 1400°C resulted in formation of 0.9 and 3.0 μm -thick TGOs, respectively. Illustrated in Figure 9 are the SEM micrographs of the oxidized samples. Oxidation of Si at temperatures below 1200°C typically results in amorphous TGO in an environment free from moisture and impurities. According to Figures 9 (a) and (b), the 1200°C-oxidation exposure led to significant crystallization in the amorphous silica matrix. The spherulitic nature of the crystallized regions is characteristic of formation of cristobalite. Ready crystallization in the 1200°C-TGO was not surprising in that specific measures were neither taken nor necessary to ensure a high-degree of purity of the oxidation environment - our primary material of interest, SN282, already contains a substantial amount of impurities and additives. At 1400°C, TGO formed was fully crystallized, as shown in Figures 9 (c) and (d). Other than crystallization and cracking, there was no other obvious sign of morphological degradation (such as spallation) in the TGOs.

Fig. 9. SEM micrographs of Si oxidized for 10 hours at 1200°C (a and b) and at 1400°C (c and d). The spherulites are cristobalite form of SiO_2 .

In contrast, as-received SN282 underwent dramatic oxidation degradation in the entire temperature range we investigated. After oxidation at 1200°C for 10 hours, the thickness of TGO formed at SN282 was 2.6 times as high as one on single crystal Si (Figure 10(b)). The morphological degradation of the TGO was severe in form of cracking and spallation. The TGO heterogeneity in phase and composition is evident in Figures 10(a) and (c).

Fig. 10. SEM micrographs of SN282 oxidized at 1200°C for 10 hours.

The classical features of oxidation degradation become more pronounced with increasing temperature and time. Shown in Figure 11 are a series of SEM micrographs of a sample after oxidation in air at 1400°C for 24 hours. The size of “blisters” increased significantly compared with 1200°C oxidation. TGO thickness fluctuation from 2 to 10 μm , spallation and bubble formation, which took place in peak regions in general, were commonly observed.

Such drastic differences in the morphology of TGO formed on Si and SN282 can be explained in terms of impurities effects. As shown in the EDS spectra in Figure 12 obtained from the valley ($\sim 2 \mu\text{m}$) and the peak ($\sim 10 \mu\text{m}$) regions (seen in Figure 11 (d)) of the TGO layer, compositional heterogeneity of the TGO on SN282 was evident. The valley peak region was basically SiO_2 in nature whereas the peak area was enriched with Lu, Na, Mg and Ca cations. XRD analysis of the oxidized SN282 revealed the presence of cristobalite/tridymite and crystalline $\text{Lu}_2\text{Si}_2\text{O}_7$, as shown in Figure 13. It can be stated, according to our experimental observations, that (1) outward grain boundary diffusion of the additive and impurity cations from the bulk of SN282 to the TGO took place during high-temperature oxidation and (2) phase separation occurred in the TGO layer that resulted in formation of regions of relative pure crystalline SiO_2 and regions of multi-component silicates of low eutectic temperature and low viscosity. The peak features were in fact blisters resulting from the pressure build-up of N_2 gas in liquid silicates. Excessive pressure, relative to that of the environment (1 atm) eventually leads to bursting and spallation of the blisters. Formation of crystalline SiO_2 in the TGO made it highly susceptible to cracking and spallation. The severity of oxidation degradation of SN282 was clearly exacerbated by the presence of alkali and alkaline earth network modifying impurity elements in the ceramic.^{5,19} In fact, surface polish, which removes the presumably impurity-laden surface skin of SN282, notably reduced the extent of its oxidation by $\sim 20\%$ at 1200°C and $\sim 30\%$ at 1400°C (See III).

Fig. 11. SEM micrographs of SN282 oxidized at 1400°C for 24 hours. Blister formation, cracking, and spallation of the TGO are a classical sign of severe oxidation degradation of SN282.

Fig. 12. EDS spectra from the valley (a) and peak (b) regions of the TGO on SN282.

Fig. 13. XRD pattern of SN282 oxidized at 1400°C for 24 hours.

Table III. Results from oxidation experiments with and without CVD-Si.

Substrate	TGO thickness								
	1400 °C					1200 °C			
	Uncoated	Uncoated polished	Si5	Si7	Si11	Uncoated	Uncoated polished	Si4	Si11
Si ₃ N ₄	3.0	2.4	2.5	4.4	-	2.3	1.6	0.6	0.8
Si	3.0	-	2.5	3.7	2.2	0.9	-	0.9	0.9

Oxidation Evaluation of Single Crystal Si and SN282 Coated with CVD-Si

At 1200 °C Oxidation of single crystal Si was not affected by the presence of the CVD Si coating. For instance, both TGOs on uncoated and coated Si substrates were about 0.9 μm thick after oxidation at 1200°C for 10 hours, indicating that single crystal Si and CVD Si behaved similarly in oxidation. However, the CVD Si had a significant effect on oxidation of SN282. TGO grew on the CVD Si surface rather than in SN282. The thickness of the TGO on the Si coated SN282 was only about one third of that on uncoated, nonpolished SN282 after oxidation at 1200°C for 10 hours. It appeared that the thickness of CVD Si did not play a significant role in determining the thickness of TGO, as long as the CVD Si was not fully consumed by oxidation.

Illustrated in Figures 14 and 15 are the surface morphology of CVD-Si coated SN282 after oxidation at 1200°C. As shown, the morphological characteristics of the coated samples were much improved compared to those of the uncoated ones. The TGOs on CVD-Si coated SN282 did not spall and were bubble free. The extent of TGO cracking was also reduced for these samples.

EDS analysis of TGOs on CVD-Si coated SN282 suggested the presence of impurity elements. But, their contents were much less than in the TGOs on uncoated SN282. The EDS results are summarized in Figure 16. Our data suggested that CVD Si acted as an effective diffusion barrier to diffusion of impurity species from SN282 to TGO, which was responsible for the reduced rate of TGO formation and improved TGO morphology observed for the CVD Si-coated SN282.

Fig. 14. SEM micrographs of SN282 coated with CVD Si (# 4) after oxidation at 1200°C for 10 hours.

Fig. 15. SEM morphologies of SN282 coated by CVD Si (# 11) after oxidation at 1200°C for 10 hours.

Fig. 16. Impurity type and amount in the TGOs formed on as received SN282 and CVD-Si coated SN282 based on the analysis of relative EDS peak intensity ratios.

At 1400 °C There was no apparent benefit of the CVD Si layer in the oxidation resistance of SN282 at this temperature. This could be attributed to the fact that the oxidation temperature was near the melting point of Si (~1417°C for single crystal Si), and it was no longer an effective diffusion barrier to impurity diffusion. The lack of beneficial effects of the Si layer was also expected since our comparative studies of oxidation of single crystal Si and as-received SN282 showed similar TGO growth rate at 1400°C (Table III).

CVD Al₂O₃ Preparation at SECO

CVD-Al₂O₃ was initially prepared on SN282 at SECO Tools, Sweden, using a chloride-based CVD process commercially used for the cutting tool industry.^{20,21} The non-line of sight, atomistic growth technique is attractive for manufacturing, since engineering components with intricate shapes and complex surface features can be readily coated. The CVD process is the only technique currently capable of commercially producing α -Al₂O₃ in the form of coherent and dense coatings. PVD methods such as sputtering,²² reactive sputtering,^{23,24} reactive evaporation,²⁵ ion-assisted deposition,^{26,27} and cathodic arc plasma deposition²⁸ are generally known to produce metastable or amorphous Al₂O₃, unless post-deposition annealing above 1000°C is applied. However, the annealing of metastable and amorphous phases causes extensive microcracking, due to volume shrinkage during their transformations to the thermodynamically stable α -Al₂O₃ phase. Therefore, the annealing approach is thought to be undesirable as a method for producing a high-quality α -Al₂O₃ coating.

In the cutting tool industry, WC/Co substrates are deposited with Ti(C,N) and Ti₂O₃ interlayers prior to the α -Al₂O₃ growth step. The Ti(C,N) interlayer is used as a diffusion barrier, since some of substrate elements and impurities (particularly Co) are found to cause the formation of metastable phases or undesired morphological features such as whiskers during the coating growth.²⁹ It has been postulated that the role of the Ti₂O₃ layer is to promote the preferential nucleation of α -Al₂O₃.³⁰ Another important processing feature is that air leaks into the CVD process must be tightly controlled in order to avoid the development of "cauliflower" growth morphology and powder formation in the gas phase. Despite these difficulties, remarkable engineering progress has been made with controlling the nucleation and growth behavior of Al₂O₃ on the cutting tool surface. For example, the selective growth of α -Al₂O₃ or κ -Al₂O₃ (even α -Al₂O₃/ κ -Al₂O₃ multilayers) is possible by adding a small concentration (0.1%) of TiCl₄ or ZrCl₄ as a dopant to the gas phase during the initial period of coating growth.^{29,30}

In this CVD process, AlCl₃ is generated by passing HCl over Al pellets:

A CO₂ and H₂ gas mixture is fed into the reactor to form water vapor inside the reactor chamber utilizing the reverse water-gas shift reaction:

Subsequently AlCl₃ and H₂O react at the coating surface to deposit Al₂O₃:

The overall reaction for the CVD-Al₂O₃ process is:

The in situ generation of the H_2O vapor (Eq. 2) is preferred because the H_2/CO_2 gas mixture is relatively stable at high temperature environments, and therefore can act as a water reservoir.²⁹ This effect can be used to increase the deposition zone, allowing for more uniform coating deposition over larger substrate geometries. Additionally, as the rate-determining step of the overall reaction (Eq. 4), the reverse water-shift reaction (Eq. 2) serves as a mechanism of controlling the growth rate of alumina. For example, if H_2O were directly introduced into the reaction system, there would be homogeneous nucleation in the vapor phase near the gas inlet, resulting in alumina powder formation and incomplete reaction products (e.g. AlO_xCl_y).³¹

In this investigation, coating specimens were prepared at a deposition temperature of $\sim 1000^\circ\text{C}$ and a reactor pressure of ~ 10 kPa at SECO Tools. The CVD- Al_2O_3 layer deposited on SN282 was ~ 3.5 μm thick. As shown in Figure 17, the coating layer contained larger crystallites of ~ 2 - 4 μm which were dispersed in a matrix of needle-like crystallites. The coating did not contain voids or porosity detectable by SEM, but was microcracked. From the XRD pattern of the coating (Figure 18), the presence of α - Al_2O_3 as a major phase was detected. Elemental EDS maps, as shown in Figure 19, indicated that the larger crystallites were rich in Al and O.

Fig. 17. Micrographs of CVD- Al_2O_3 deposited on SN282 (a) before and (b) after oxidation.

Fig. 18 X-ray diffraction pattern of SECO alpha alumina coating

Fig. 19. SEM/EDS elemental maps of CVD- Al_2O_3 deposited on SN282

During luminescence spectroscopy characterization, the large crystallites emitted stronger R1 and R2 luminescence peaks (Figure 20), suggesting that the large crystallites were α - Al_2O_3 . The R1 and R2 peaks did not shift, and therefore the anticipated tensile stress of the α - Al_2O_3 phase in the coating layer appeared to be relieved by microcracking of the coating layer.

One of the CVD- Al_2O_3 coated SN282 specimens was subjected to oxidation at 1200°C for 8 hours while flowing pure oxygen. Interestingly, no weight change was detected after the oxidation treatment while uncoated SN282 specimens exhibited reasonable weight gains for TGO formation. Although the weight gain was insignificant, some morphological changes were observed for the coated specimen as evident from its grazing incidence XRD pattern and surface micrograph (Figures 21 and 17 (b), respectively). From the GIXRD analysis, the formation of SiO_2 was evident. Also, the coating surface upon oxidation showed smoothing of the faceted surface features.

Fig. 20. Luminescence spectrum of CVD- Al_2O_3 deposited on SN282.

Fig. 21. XRD of CVD- Al_2O_3 on Si_3N_4 after oxidation.

In summary, the experimental observations with the commercial chloride-based CVD process suggested that the formation of a fully continuous and microcrack-free layer of $\alpha\text{-Al}_2\text{O}_3$ on the sintered Si_3N_4 surface would be difficult unless the processing procedure could be further tailored. The coating, although not fully $\alpha\text{-Al}_2\text{O}_3$ and continuous, appeared to reduce the kinetics of TGO formation.

CVD- Al_2O_3 Preparation at Stevens

A laboratory scale reactor was used for a few initial coating experiments at Stevens. As schematically shown in Figure 22, the hot-wall CVD reactor utilized the same precursors used for the CVD process at SECO Tools. The reactor was interfaced with a sample loading chamber was used to conduct a series of short-time deposition experiments (i.e., 10 minutes). The basic design of this reactor was similar to that of another reactor used in our prior work³² except for the following features. An IN600 alloy reactor chamber (6-cm diameter x 36-cm length), welded to two IN600 flanges and an IN600 sample holder, were used in this work. The reactor chamber and the sample holder were pre-aluminized by pack cementation at Chromalloy prior to coating experiments. The sample loading chamber, along with a magnetic transporter, was used for rapid insertion and retrieval of the substrate holder from the hot reactor chamber. The ability to rapidly quench coating specimens was important, particularly for the short-time deposition experiments, so that the samples would not be subjected to slow furnace cooling which might cause phase transformations of the alumina coating layer. It was estimated by heat conduction calculations that the surface temperature of the disc substrates could be cooled to $\sim 200^\circ\text{C}$ in several minutes during the retrieval of the sample holder from the reactor chamber to the sample loading chamber.

Fig. 22. Schematic diagram of the CVD reactor used at Stevens.

With this experimental configuration, coating experiments were performed using the following procedure. The reactor chamber was heated to 1050°C ($\pm 5^{\circ}\text{C}$) in flowing H_2 . Prior to inserting the sample holder into the hot reactor chamber, both the reactor and sample loading chambers were evacuated to ~ 13 Pa. Substrates were placed on the substrate holder, and the substrate holder was inserted into the chamber. Subsequently, the reactor pressure was increased to a desired level using an Ar stream, H_2 , CO_2 and AlCl_3 were then fed into the reactor to start the coating process.

The $\text{H}_2 + \text{CO}_2$ mixture was introduced into the chamber for 1 min (Step #1 in Table IV) with the intent of oxidizing the surface of SN282. The AlCl_3 was subsequently added to the $\text{H}_2 + \text{CO}_2$ stream for a 1 min to form Al_2O_3 nuclei (Step #2). Phase transformation of the Al_2O_3 nuclei to the alpha- Al_2O_3 phase was intended by exposing the nuclei in the pure H_2 stream (Step #3). This nucleation procedure was followed by a 10 min deposition step by flowing AlCl_3 , H_2 , and CO_2 (step #4). After the deposition step, the AlCl_3 , CO_2 , and H_2 flows were stopped, the reactor chamber was evacuated and the substrate holder was retrieved from the hot reactor chamber. The reactor and sample loading chambers were pressurized with Ar to the atmospheric pressure, and the two chambers were then isolated by closing the gate valve. The coating specimens were removed from the loading chamber through the removable window shown in Figure 22.

Table IV. Experimental conditions for CVD- Al_2O_3 processing.

N, step	T, °C	P, Torr	τ , min	Flow rate, Cm^3/min		
				HCl*	CO_2	H_2
1	1050	10	1	0	250	240
2	»	»	1	20	250	»
3	»	»	30	0	0	»
4	»	»	10	20	250	»

A homogeneous and dense Al_2O_3 coating was deposited on silicon nitride substrate. Figure 23 shows that coating characteristics depend much on the substrate treatment. The coating deposited on the unpolished SN282 substrate was about 400 nm thick with highly faceted 100 - 200 nm grains. On the other hand, the coating on the polished SN282 was about 200 nm with grains of 50 - 100 nm. Dependence of CVD Al_2O_3 coating morphology and composition on both substrate material and surface treatments have been studied in another research project and described elsewhere.^{33,34} In comparison with the SECO's coating (Figure 17), the Al_2O_3 coating at Stevens was more homogeneous without microcracking. The XRD data in Figure 24 indicated that the CVD coating made at Stevens was $\kappa\text{-Al}_2\text{O}_3$. Interestingly, phase composition of the coatings formed on unpolished and polished substrates was differed only by lutetium silicate modifications. The coating on unpolished SN282 contained Lu_2SiO_5 only whereas that on polished substrate has both Lu_2SiO_5 and $\text{Lu}_2\text{Si}_2\text{O}_7$ with the latter as the dominant phase. The absence of $\alpha\text{-Al}_2\text{O}_3$ phase in both the coating specimens was confirmed by the absence of the R1 and R2 peaks during luminescence spectroscopy.

Fig. 23. Surface morphology of CVD- Al_2O_3 deposited on SN282 unpolished (a) and polished (b) at Stevens.

Fig. 24. XRD pattern of CVD- Al_2O_3 deposited on the polished SN282 at Stevens.

Oxidation Evaluation of SN282 coated by CVD Al_2O_3

The effectiveness of the CVD Al_2O_3 layer as an oxidation barrier coating was demonstrated in our oxidation investigation of SN282 coated with the $0.4\text{ }\mu\text{m}$ -thick CVD Al_2O_3 in air at 1400°C for 24 hours. Shown in Figure 25 are SEM micrographs of the coated sample after oxidation. The surface morphology of the oxidized sample was a sharp contrast to that of the oxidized, uncoated SN282 (Figure 11). The sample surface was remarkably smooth. There was no visible sign of spallation and crack formation. In contrast, the TGO on the uncoated SN282 sample exhibited classical features of severe oxidation degradation - formation of blisters, extensive cracking and spallation of oxide (Figure 11).

Fig. 25. SEM micrographs of CVD- Al_2O_3 coated SN282 (a) unpolished and (b) polished after oxidation at 1400°C for 24 hours.

Illustrated in Figure 26 are cross-sectional SEM micrographs of coated and as-received SN282 samples after oxidation. The overall thickness of the "TGO" was only $\sim 1.3 \mu\text{m}$, after discounting the thickness of the initial CVD layer, on the coated sample. On the other hand, the TGO on the as-received sample was $\sim 8.5 \mu\text{m}$.

Figure 27 revealed the fact that solid state reaction took place between the Al_2O_3 layer and the TGO during oxidation. As a result of the reaction, a significant amount of Al was incorporated into the TGO structure. Additional X-ray diffraction analyses (Figure 28) have suggested that this outer Al-rich oxide layer on the coated SN282 was largely amorphous (a striking result that needs to be further confirmed). The process of Al-rich layer formation in TGO structure was in fact highly beneficial in promoting homogeneity and amorphous phase stability of the TGO in light of the presence of bulk impurities such as Na and Mg. These results were consistent with our earlier investigation of the beneficial effect of Al implantation on the oxidation behavior of silicon nitride under the influence of Na.^{19,35}

Fig. 26. SEM micrographs: (a) SN282 coated with a CVD Al_2O_3 layer and (b) as-received SN 282 after oxidation in air at 1400°C for 24 h.

Fig. 27. Cross-sectional SEM and EDS elemental mapping of SN282 coated by CVD Al_2O_3 after oxidation.

Fig. 28. XRD pattern of SN282 coated by CVD Al_2O_3 after oxidation.

Acknowledgements

This research was sponsored by the Office of Naval Research (ONR) N00014-99-C-0386 as a subcontract project to United Technology Research Center (UTRC). We are grateful to Mr. J. E. Holowczak at UTRC and to Dr. Steve Fishman at ONR for their support and encouragement. Mr. Ray Bratton, Kyocera, prepared SN282 coupons especially for this study. Dr. Sakari Ruppi at SECO Tools (Sweden) prepared the industrial CVD Al_2O_3 coating specimens on SN282 for our evaluation. Dr. Michael Lance performed the luminescence study at Oak Ridge National Laboratory (ORNL), and Dr. Ellen Y. Sun at UTRC helped us with the XRD analysis. We also acknowledge the help from some members of Prof. Lee's CVD Group: Mr. Y.-F. Su for his assistance in sample characterization and interpretation by SEM and XRD, Mr. Jinil Lee for the CVD-Si coating samples, Mr. Justin Daniel Meyer and Mr. Limin He for the CVD- Al_2O_3 coating samples.

References

1. W.Y. Lee, K.L. More, D.P. Stinton, and Y.W. Bae, J. Am. Ceram. Soc., **79** [9], 2489 (1996).
2. J.A. Haynes, K.M. Cooley, D.P. Stinton, R.A. Lowden, and W.Y. Lee, Ceram. Eng. Sci. Proc., **20**, 355 (1999).
3. K.N. Lee, H. Fritze, and Y. Ogura, "Effects of Impurities and Coating Design on the Durability of EBC for Silicon-Base Ceramics, Proceedings of Perkofstad Memorial Symposium, Electrochem. Soc. (in-press).
4. Private Communication with T. Strangman, Honeywell International, Phoenix, Arizona.
5. N.S. Jacobson, J. Am. Ceram. Soc., **76**, 3 (1993).
6. M.G. Lawson, F.S. Pettit, and J.R. Blachere, J. Mater. Res., **8**, 1964 (1993).
7. W.D. Kingery, H.K. Bowen, and D.R. Uhlmann, Introduction to Ceramics, 2nd ed., John Wiley, NY, NY (1976).
8. C.J. Brinker and G.W. Scherer, Sol Gel Science, Academic Press, San Diego, CA (1990).
9. F.F. Lange, Science, **273**, 903 (1996).
10. Fischer T.E., "Tribiochemistry of Ceramics: Science and Applications", in I.M. Hutchings (ed.), New Directions in Tribology, London, MEP, 211-215 (1997).
11. I. Levin and D. Brandon, "Metastable Alumina Polymorphs: Crystal Structures and Transition Sequences," J. Am. Ceram. Soc., **81** [8], pp. 1995-2012 (1998).
12. G. Gregori, W. Burger, and V. Sergo, "Piezo-spectroscopic Analysis of the Residual Stresses in Zirconia-toughened Alumina Ceramics: the Influence of the Tetragonal-to-Monoclinic Transformation," Mat. Sci. Eng. A, **271**, pp. 401-406 (1999).
13. D.R. Clarke, R.J. Christensen, and V.T. Tolpygo, "The Evolution of Oxidation Stresses in Zirconia Thermal Barrier Coated Superalloy Leading to Spalling Failure," Surf. Coat. Technol., **94-95**, pp. 89-93 (1997).
14. S.M. Sze, "VLSI Technology," p.60, McGraw-Hill, NY, NY, 1988
15. J.-J. Hajjar, R. Reif and D. Adler, "Structural and Electrical Properties of Polycrystalline Silicon Films Deposited by Low Pressure Chemical Vapor Deposition with and without Plasma Enhancement", J. Electronic Materials, **15** [5] 279-285 (1986)
16. B. N. Beckloff, W.J. Lackey and E. M. Pickering, "Large Grain Polycrystalline Silicon via Chemical Vapor Deposition", J. Mater. Res., **14** [3] 672-681 (1999)

17. T.L.Chu, H.C.Mollenkopf and S.C.Chu, J.Electrochem.Soc. **123** [1], 106 –110 (1976)
18. R.Bisaro, J.Magarino, N.Proust and K.Zellama, J.Appl.Phys., **59** [4],1167-1178
19. Y.S. Cheong, P. Mukundhan, H.Du and S.P. Withrow, "Improved Oxidation Resistance of Silicon Nitride by Aluminum Implantation II: Analysis and Optimization", J. Am. Ceram. Soc., **83** [1] 161-165 (2000).
20. S. Vuorinen and J. Skogsmo, "Characterization of α -Al₂O₃, κ -Al₂O₃, and α - κ multioxide Coatings on Cemented Carbides," Thin Solid Films, 193/194, pp. 536-546 (1990).
21. M. Halvarsson, V. Langer, and S. Vuorinen, "Determination of the Thermal Expansion Coefficients of α -Al₂O₃ by High Temperature XRD," Surf. Coat. Technol., **76-77**, pp. 358-362 (1995).
22. M. K. Smit, G. A. Acekt, and C. J. van de Lann, Thin Solid Films, **138**, 171 (1986).
23. H. K. Pulker, W. Haag, M. Buhler, and E. Moll, J. Vac. Sci. Technol. A., **3**, 2700 (1985).
24. T.C. Chou, D. Adamson, J. Mardinly, and T.G. Nieh, "Microstructural Evolution and Properties of Nanocrystalline Alumina Made by Reactive Sputtering Deposition," Thin Solid Film, **205**, 131 (1991).
25. A. Feldman, E. N. Farbaugh, and Y. N. Sun, Optical Society of America Technical Digest Series 6, pp. 14-17 (1988).
26. R. S. Bhattacharya, A. K. Rai, and A. W. McCormick, Surf. Coat. Technol., **46**, 155 (1991).
27. M. S. Al-Robae, M. G. Krishna, G. N. Subanna, K. N. Rao, and S. Mohan, J. Mater. Res., **9**, 2668 (1994).
28. T. D. Schlemmel, R. L. Cunningham, and H. Randhawa, Thin Solid Films, **181**, 597 (1989).
29. E. Fredriksson and J.-O. Carlsson, "Chemical Vapor Deposition of Aluminum Oxides from Various Gas Mixtures," J. Chem. Vapor Dep., **1**, 333-417 (1993).
30. M. Halvarsson, and S. Vuorinen, "The influence of the Nucleation Surface on the Growth of CVD α -Al₂O₃ and κ -Al₂O₃," Surf. Coat. Technol., **76/77**, 287 (1995).
31. P. Wong and M. Robinson, "Chemical Vapor Deposition of Polycrystalline Al₂O₃," J. Am. Ceram. Soc., **53**, [11] 617-21 (1970).
32. W. Y. Lee, Y. Zhang, I. G. Wright, B. A. Pint, and P. K. Liaw, "Effects of Sulfur Impurity on the Scale Adhesion Behavior of a Desulfurized Ni-based Superalloy Aluminized by chemical Vapor Deposition," Metall. Trans. A, **29A**, 833 (1998).
33. Y.-F. Su, M.A. Torzilli, J.D. Meyer, C.J. Rawn, M.J. Lance, S. Ruppi, W.Y. Lee, "Effect of Electroplated Pt Interlayer on Morphology and Phases of Chemically Vapor Deposited Alumina on Single Crystal Ni-Based Superalloy Substrates" (manuscript in preparation)
34. Y.-F. Su, M. Torzilli, J.D. Meyer, W. Y.Lee, C. Rawn, M. Lance, and S. Ruppi, "Synthesis of alpha-Al₂O₃ Template on Ni Superalloy Surface by Chemical Vapor Deposition," pp. 15-28 in Elevated Temperature Coatings: Science and Technology IV, Edited by N.B. Dahotre, J.M. Hampikian, and J.E. Morral, The Minerals, Metals, and Materials Society, Warrendale, PA (2001).
35. P. Mukundhan and H. Du, "Oxidation Behavior of Norton NBD 200 Silicon Nitride," J. Am. Ceram. Soc. **82**, 2260-2262 (1999).

APPENDIX B – Honeywell Ceramic Components Vane Prototype Development

Final Report

Prepared for United Technologies Research Center

Contract. Number 2600041

“FT-8 Cooled Vane Development, Phase II”

March 8, 2001

Summary

United Technologies Research Center (UTRC) conducted this program, jointly funded by the Office of Naval Research and the Department of Energy, to increase their engine operating temperatures above current capabilities by designing air-cooled ceramic components. The program supported UTRC plans to commercialize the cooled ceramic vane technology through the Flexible Mid-Size Gas Turbine, along with other, proprietary initiatives.

Under Phase I of this program, Honeywell Ceramic Components (CC) delivered a prototype AS800 silicon nitride FT-8 vane to UTRC to demonstrate the feasibility of gelcasting hollow vanes with complex-shaped (non-pullable) cores. In Phase II, test hardware was fabricated. A series of simple-shaped cooling channels were substituted for the UTRC designed trailing edge cooling channels. The blanks were thermally processed to full density, and the platforms were machined by diamond grinding as required to fit the test rig. Two FT-8 vanes were delivered to UTRC for rig testing. The rig tests simulate engine conditions to verify UTRC's heat transfer models.

Task 1 Prototype FT8 Cooled Vane Development

The prototype FT-8 vane delivered under Phase I had platforms of a simplified design and there were no cooling channels from the airfoil's hollow core to its trailing edge. The goal of Phase II is to fabricate FT-8 vanes with the cooling channels and machined platforms for rig testing. The prototype FT-8 vane gelcasting mold tool from Phase I was evaluated, and it was determined that rework of the original mold would not be cost effective. A new mold tool was designed and purchased, in order to provide sufficient stock for final grinding of the platforms. In addition, fixtures for bisque machining of the cooling passages and final grinding of the platforms were designed and purchased.

The mold tool for near-net shape gelcasting was received and its performance was excellent, e.g., no leaks were observed and disassembly appeared smooth. The overall quality of the gelcast vane blanks was also very good; however, minor defects in the castings were observed, such as small air bubbles. A representative casting is shown in Figure 1.

Figure 1. The near net shape gelcast FT-8 vane blank required green machining prior to thermal processing and finish grinding.

The airfoil's trailing edge was machined to a flat surface approximately 0.120" wide, and thirty-six holes of $\varnothing$ 0.042" were drilled into the central cooling channel at approximately 0.078" between centers. The first vanes cast in the new mold tool, shown in Figure 2, were processed through bisque firing, or pre-sintering, before machining the trailing edge.

Figure 2. Four vanes with trailing edge clipped and holes drilled into the central cooling channel.

While work continued on producing a machined, fully dense vane for engine rig testing, a defect was detected by fluid penetrant inspection in several of the vanes. Cracks were observed at the trailing edge of the central cooling channel on either end. The cause of this crack was attributed to the gelcast mold tool design.

The mold tool consists of two halves with a parting line along the leading and trailing edges of the airfoil. The core is clamped into place between the two halves for casting. After gelcasting the blank and removing the core, one half of the mold is removed, exposing the gelled part on one surface of the airfoil and the adjoining halves of the vane platforms. The gelled part must then be removed from the other half of the mold, which is when the cracks described above

occurred. The vane platforms tend to adhere to the mold surfaces, and when excessive force is required to remove the gelled part from the mold, cracks tend to form, extending from the trailing edge of the airfoil. The mold tool was reworked to facilitate removal of the vane blanks with a minimum of stress, which markedly improved the yield of castings with no cracks.

However, the sintering results of FT-8 vane blanks remained unacceptable. Vanes were processed in modified binder burnout and sintering cycles to improve density results, but no vane blanks were sintered to full density. Prior experience had shown that gelcast AS800 sinters to full density more readily with no presintering, so it was suspected that presintering was the most probable cause. This was confirmed using several prototype FT-8 vanes that had been cast during Phase I. Those vanes had not been presintered, and every one reached full density upon sintering. Therefore, the presintering step was eliminated. In the revised process, the trailing edge cooling channels were drilled into green blanks, and all grinding on the platforms was done after sintering.

One vane had been cast with an experimental, higher-solids loading formulation prior to the elimination of presintering. This vane sintered to full density; however, the sintering shrinkage was reduced by the higher solids loading, resulting in an oversized vane that could not be ground to the proper final dimensions. The next two vanes were cast with standard gel slurry and were sintered to full density. One of these was destroyed during the machining process due to a CNC program malfunction, but the second vane was properly fully machined. The first fully machined prototype FT-8 AS800 vane is shown in Figure 3, alongside a SLA model. The oversized vane (higher solids loading) also was fully machined. UTRC agreed to accept thinner platforms on the oversized vane, such that it would fit into the engine test rig. Both fully machined vanes were delivered to UTRC for environmental barrier coating application and engine rig testing thus completing the program on schedule and within funding available.

Figure 3. The first fully machined AS800 FT-8 vane (right) is shown next to a plastic model (SLA) for comparison. Plastic model shroud sections are attached to the vanes' outer platforms.