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GAS TURBINE LOW CONDUCTIVITY THERMAL BARRIER COATING VALIDATION AND DEMONSTRATION

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ABSTRACT

As gas turbine (GT) temperatures have increased, thermal barrier coatings (TBCs) have become a critically important element in hot section component durability. Ceramic thermal barrier coatings permit significantly increased gas temperatures, reduced cooling requirements, and improve engine fuel efficiency and reliability. Next generation TBCs are now being introduced into select engine applications to provide additional high temperature capability.

The Electric Power Research Institute (EPRI) and Cincinnati Thermal Spray (CTS) have teamed together in two joint programs to commercialize a NASA developed 10Mol% YbGd-YSZ TBC low k coating system for gas turbine combustion hardware with a goal of extending to hot section airfoils. The approach taken was to benchmark conventional YSZ TBCs and to validate key properties of the YbGd-YSZ TBC for each application followed by component engine testing. Based on extensive property testing, a dual layer YSZ/YbGd-YSZ TBC designated CT1702 was selected and applied to three F-class transition pieces and three baskets. These components have successfully completed 7,846 equivalent operating hours (EOH) of field service operation. The microstructure of the coating applied to the production components and the results of post engine test inspections are presented.

For airfoil applications, a three layer YSZ/YbGd-YSZ multilayer TBC is being benchmarked against a porous and vertically cracked 7YSZ TBC. As with the combustion hardware program, the project will conduct spray trials, coat property test specimens and scrap airfoils, and perform material property testing. Component qualifications on scrap F-class airfoils will verify conformance to the EPRI TBC coating specifications for the multilayer TBC. The objective is to demonstrate readiness to coat F-class Stage 1 blades for potential rainbow rotor engine testing in 2017.

INTRODUCTION

While the industry standard 6-9 wt.% Yttria Stabilized Zirconia (7YSZ) has been the preferred ceramic composition for the past 30+ years, efforts have been underway to develop improved TBCs. The principal development goals have been to lower thermal conductivity, increase sintering resistance and create a more stable crystalline phase structure allowing use above 1200° C. In certain applications (aero in particular) the resistance to CMAS (Calcium-Magnesium Alumino-Silicate) mineral dust deposits has also been of concern and is an additional screening criterion.

Many new TBC compositions have been studied and a search of the patent literature shows well over 580 patents or patent application filed in the past 20 years describing alternatives to 7YSZ. Many of the gas turbine OEMs have been active in developing and patenting their own unique compositions that are typically zirconia based with different rare earth oxide dopants, although hafnia and scandia based systems are also reported. Figure 1 highlights some of the elements being evaluated for the next generation of TBCs, most of which are found in the Lanthanide series on the periodic table of the elements. A listing of the broad range of compositions and crystal structures being evaluated is listed in Table 1. Another trend that has been noted is the increased use of multilayer TBCs where the structure and composition of each TBC layer is designed to improve overall system performance and durability. (Zhu and Miller 2007, Wigren 2007, Vassen et al 2009, Sampath et al 2012, Lee 2013, Sansom 2013 and Viswanathan et al 2014 & 2015)

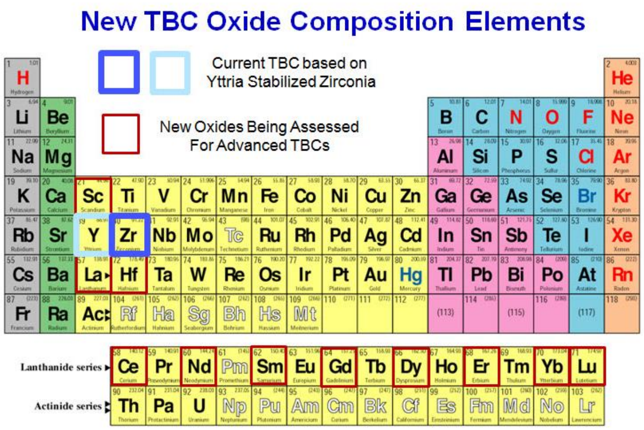

Figure 1 Periodic Table of the Elements Highlighting New Oxide Composition Elements Being Evaluated for Low k TBCs.

TBC Crystal Structure	TBC Compositions	References
Tetragonal-t'	(6-8 wt% YSZ; 12 wt% YbSZ; YbGd-YSZ; YbGdTiTa-YSZ; YbSm Stabilized Zirconia; ZrO2-HfO2-YbO1.5-TiO2-TaO2.5; YTaO4- ZrO2)	Stecura 1984, 1985; Zhu & Miller 2007 & 2010; Torigoe 2011; Fu et al 2010; Witz et al 2011
Cubic	(Er-YSZ; YbGd-YSZ; Nd-ZrO2; Ln3NbO7, Ln3TaO7)	Rickerby et al 2000; Zhu & Miller 2004; Liu & Howard 2010; Liu and Lawton 2004 & 2006; Nagano et al 2013
Pryrochlores	(e.g. La2Zr2O7, Gd2Zr2O7, Nd2Zr2O7, Sm2Zr2O7, Gd2Hf2O7)	Maloney 2000, 2001a&b; Kaiser et al 2011; Ulion et al 2008; Subramanian 2001 & 2012;
Perovskite structure	(e.g. SrZrO3, CaZrO3, LaAlO3 ; BNT{ BaNd2Ti3O10 }; BaCeO3 or SrCeO3)	Birkner & Stamm 2004; Sambasivan & Steiner 2010; Witz et al 2011
Rhombohedral	(e.g Yb3Zr2O12, Lu3Zr2O12 or Er3Zr2O12, Yb3Hf2O12; Yb4Zr3O12; Yb4Hf3O12)	Boutwell et al 2009a&b; Krichanmurthy et al 2014
Hexagonal	(Zr3Sc4O12)	Bowker et al 2001
Spinels	(BaY2O4 or SrY2O4)	Witz et al 2011
YAG	(Y3Al5-xFexO12)	Gell et al 2013
Magnetoplumbite Structure	(LaMgAl11O19)	Feist & Nicholls 2011
Tungsten Bronze Structure	(e.g. BaO—RE2O3-xTiO2 {BaNd2Ti4O12}; Ba(Nd1.2Sm0.4Gd0.4) Ti4O12)	Kulkarni et al 2013; Allen et al 2014
Monazite	(LaPO4)[xxxiii],	Witz et al 2011; Feist & Nicholls 2011

Table 1 Listing of advanced TBC crystal structures types and compositions found in the patent literature. *Note (Ln or RE = Rare Earth Lanthanide).* (Smith 2015)

While the standard 7YSZ coating composition is still by far the predominant coating in use today, PWA (Cowles 2008), Siemens (McGraw 2006, Kiesow 2013), MHI (Ito 2010) and GE (Schaefer 2015) have announced the introduction of new low k, phase stable, sinter resistant TBCs as bill of material in production for select engine applications. The development of next-generation TBCs with higher temperature capability and improved thermal stability has become a necessity for advancing the ultra-efficient and low emission gas turbine engine technology.

Zhu and Miller at NASA developed a series of coatings with multiple stabilizing rare earth oxides that show excellent sintering resistance, phase stability and low thermal conductivity (Zhu and Miller 2004 a&b, 2007 a&b and 2010). Their coatings are based on the incorporation of rare earth dopant oxides in various proportions into the ceramic coating matrix stabilizing the TBC against sintering via a defect clustering effect. In addition, it has been found that certain combinations of dopant oxides also impart a greater stability against thermal cycling to the TBC.

One of the coating systems NASA developed is based on Ytterbia, Gadolinia and Yttria additions to ZrO_2. The NASA 10 Mol. % YbGd-YSZ develops a cubic crystal structure that is more stable to higher temperature than the tetragonal 7YSZ. In addition to approximately 20-50% lower thermal conductivity than 7YSZ depending on density, it has demonstrated thermal stability and sintering resistance to 1650° C (3000° F). This advanced low conductivity (low k) TBC was developed for combustion hardware applications and has demonstrated substantially greater durability than the conventional 7YSZ TBCs in rig testing and in advanced aero engine combustion hardware component testing by NASA and aero engine manufacturers.

EPRI/CTS Low Conductivity TBC program

Given the attractive properties that NASA demonstrated in advanced aero engine combustion hardware applications, EPRI and Cincinnati Thermal Spray, Inc (CTS) have collaborated on joint programs to commercialize the YbGd-YSZ TBC for IGT combustion hardware and more recently to extend this to IGT airfoil applications. CTS obtained a license for the commercialization of the NASA advanced rare earth oxide, defect cluster TBCs and has substantial production experience with TBC coating of various IGT combustion hardware components and airfoils for OEM and repair customers.

NOMENCLATURE,

7YSZ	6-9 wt.% Yttria Stabilized Zirconia
APS	Air Plasma Spray
BC	Bond Coat
°F	Temperature – degrees Fahrenheit
°C	Temperature - degrees Celsius
CMAS	Calcium-Magnesium Alumino-Silicate
CPI	Cracks per Inch
CTS	Cincinnati Thermal Spray, Inc.
EPRI	Electric Power Research Institute
FCT	Furnace Cycle Test
GZO	Gadonium Zirconate ($Gd_2Zr_2O_7$)
IGT	Industrial Gas Turbine
k	Thermal Conductivity
NASA	National Aeronautics and Space Administration
OEM	Original Equipment Manufacturer

PSI	Pounds per Square Inch
Mil	0.001 inch/ 25.4 µm
Mol. %	Molar Percent Composition
SPE	Solid Particle Erosion
TBC	Thermal Barrier Coating
TP	Transition Piece
VCC	Vertically Cracked Coating
Wt. %	Weight Percent Composition
YbGd-YSZ	10 Mol% Ytterbia, Gadolinia, Yttria Stabilized Zirconia

THE EPRI/CTS LOW CONDUCTIVITY TBC COMBUSTION HARDWARE PROGRAM

The EPRI /CTS Low-K TBC program consists of four tasks:

Task 1: Property Validation Testing of Low k Coating System

Task 2: Develop EPRI YbGd-YSZ TBC Specification

Task 3: Qualify Low k Coating on Selected Combustor Hardware

Task 4: IGT Combustor Hardware Engine Testing

Tasks 1 and 2 were completed in 2014 and the details of the test results were presented at the ASME Gas Turbine Conference held in Dusseldorf, Germany and published in in the Journal of Engineering for Gas Turbines and Power (Smith et al 2014 & 2015).

Highlights of the property validation and dual layer low k TBC coating specification will be summarize in the next section.

Combustion Hardware Coating Summary

<u>Property Validation Test Specimens</u>

Test specimens for this program were all coated in a similar configuration to that used for coating combustion TPs and baskets. Figure 2 shows the thermal spraying of an IGT TP and an example of a combustion basket.

Figure 2 Transition Duct being Plasma Sprayed with a TBC (Left) and a TBC Coated Combustion Basket (right). (Courtesy of CTS)

In order to generate property data for each of the property validations tests to be measured, Figure 3 shows the configuration of the over forty test coupons that were attached to the ID of 30.5 cm diameter by 94 cm tall cans used for each spray trial.

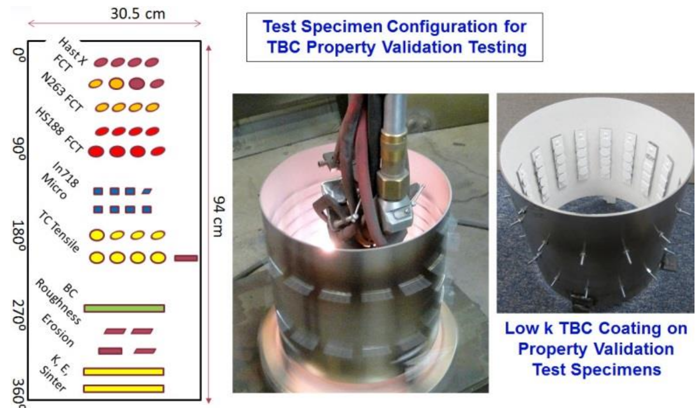

Figure 3 Thermal Spray Configuration for Combustion Hardware Property Validation Test Specimens.

<u>Property Validation Tests</u>

In order to validate the dual layer YbGd-YSZ TBC system, CTS sprayed over thirty coating trials to develop and define appropriate processing for the low k TBC system and to generate baseline 7YSZ TBCs representing three porosity levels (~10%, ~ 20% and <5% with vertical segmentation cracking). The bulleted listing below are the key characteristics evaluated.

- Metallographic Coating Thickness and Structure
- Bond Coat Surface Roughness
- Tensile Bond Strength (Bond Coat to Substrate and Ceramic Top Coat to Bond Coat)
- Solid Particle Erosion
- Thermal Conductivity and Sintering Resistance (As Coated and after 1400° C/100hr Sinter Cycle)
- Furnace Cycle Testing (1093° C / ~ 1.25 hr. cycle)

The CT1702 YbGd-YSZ TBC system is shown in Figure 4 below. The MCrAlY bond coat is nominally 8 mils thick, the 7YSZ layer is 7 mils with a porosity level of 10-20% and the top YbGd-YSZ outer layer is targeted at 15 mils with a 10-15% predominant porosity level.

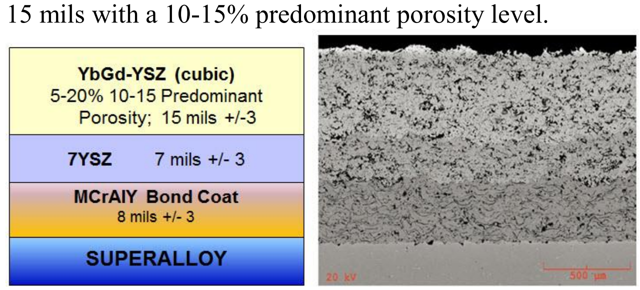

Figure 4 CTS CT1702 low k dual ceramic layer 7YSZ/YbGd-YSZ TBC coating system

The CT1702 TBC out performed all of the baseline 7YSZ TBCs regardless of structure in the Furnace Cycle Test (FCT) with an average life of 900+ cycles compared to 788, 540 and 780 for the 10 %, 20% , <5% VCC porosity TBCs respectively. The elevated temperature solid particle erosion (SPE) resistance is about 60% of the baseline 7YSZ with the same structure (Zhu and Miller 2007b & 2010; Shin and Hamed 2016) and is typical of alternative TBCs with lower conductivity than the 7YSZ. The YbGd-YSZ has been shown to be ~ 1.6 x better than the GZO low k TBC in recent testing (Shin and Hamed 2016). One of the more remarkable characteristics observed with the CT1702 coating was its resistance to sintering during high temperature exposure compared to the baseline 7YSZ TBCs. Dinwiddie (1996) reported that 7YSZ plasma sprayed TBCs can sinter at temperatures above 1000 C with an associated increase in thermal conductivity. Following a 1400 C / 100 hour sintering cycle the 20% porosity TBC the thermal conductivity increased ~ 75% from the as coated condition, the VCC TBC increased ~ 55% during the thermal exposure, while the YbGd-YSZ increased only ~ 20% demonstrating its resistance to sintering and ability to maintain lower thermal conductivity during engine service.

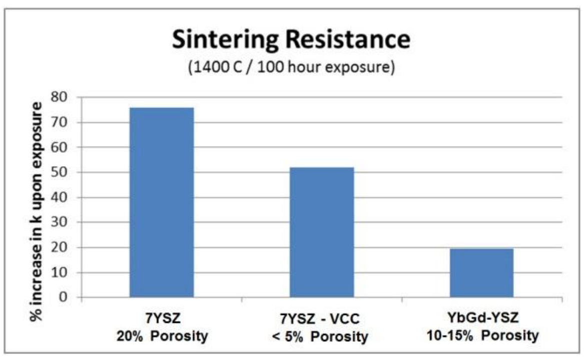

Figure 5 Increase in Thermal Conductivity for 7YSZ compared to YbGd-YSZ TBCs following a 1400 C / 100 hour thermal exposure

Qualification Results For CT1702 on Combustion Hardware

Three combustor baskets (S/N 209, 210 & 211) and three transition pieces (S/N 177, 178 & 179) that had previously run ~ 8000 hrs in an F-class gas turbine served as the engine demonstration of the CT1702 low k TBC coating system. An additional scrap basket and TP was also made available for coating set up and qualification trials.

CTS performed approximately seven development runs each on the scrap basket and TP in order to optimize the robotic programing and validate coating characteristics such as metallurgical thickness of the bond coat and top coat, metallurgical structure for the TBC and tensile bond strength of the top coat. Figure 6 shows the test coupons locations inside the scrap components used to qualify the baseline coating process prior to coating the production components. Results of these trials demonstrated process capability and CTS was released to coat the production hardware. The composition of the CoNiCrAlY bond coat is shown in Table 2 and the compositions for the 7YSZ and YbGd-YSZ powder lots used to coat the production hardware is listed in Table 3.

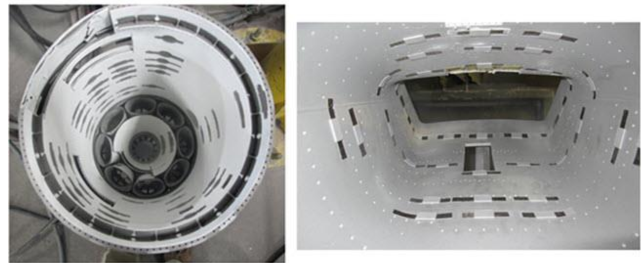

Figure 6 Test Tab locations used to qualify the CT1702 Coating Process on a Scrap Combustor Basket (left) and Transition Piece (right)

Coating Type	Element Range (Wt. %)							
	Ni	Co	Cr	Al	Y	O_2	N_2	Other
CoNiCrAlY	31.0	Bal.	22.0	8.0	0.41	0.03	0.01	Fe 0.06 C 0.01

Table 2 Bond Coating Material Composition Powder Certification

Coating Designation	Coating Type	Element Range (Wt. %) Balance ZrO_2									
		ZrO_2	Y_2O_3	Yb_2O_3	Gd_2O_3	SiO_2	TiO_2	Al_2O_3	Fe oxides	HfO_2	Others
7 YSZ	YSZ	Bal.	7.1	0	0	0.22	0.069	0.093	0.021	1.63	< 0.21
YbGd-YSZ	Low k (Cubic)	77.9	9.5	5.7	5.2	0.01	<0.01	< 0.01	0.01	1.6	0

Table 3 Ceramic Material Compositions Powder Certification

Combustor Basket QC Results

The three MHI 501F production combustion baskets coated for engine test are shown in Figure 7. Coating thickness results are listed in Table 4. Coating thickness for the bond coat, and the ceramic layers were measured metallographically and the ceramic layers were also verified by eddy current measurements. It should be noted that the eddy current measurements are in good agreement with the metallographic results. Microstructures for each basket are shown in Figure 8.

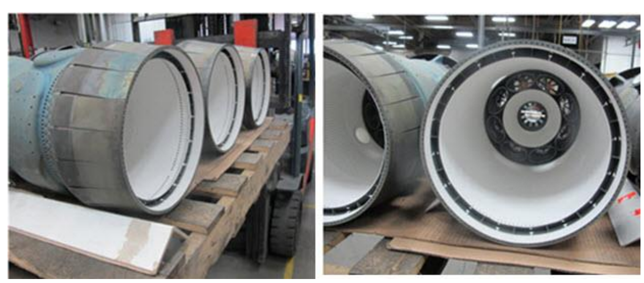

Figure 7 Combustion Baskets – As Coated

Panel #	Bond Coat (mils)	Intermediate Coat (mils)	Top Coat (mils)	Total TBC Ceramic (mils)	Eddy Current results (mils)
Production #1 S/N 209	3.0	7.5	19.5	27.0	21.9 +/- 3.5
Production #2 S/N 210	4.5	10.0	22.5	32.5	25.1 +/- 5.1
Production #3 S/N 211	4.5	7.5	20-30	27.5 - 37.5	29.0 +/- 4.3

Table 4 As Coated QC Results for Engine Test Baskets

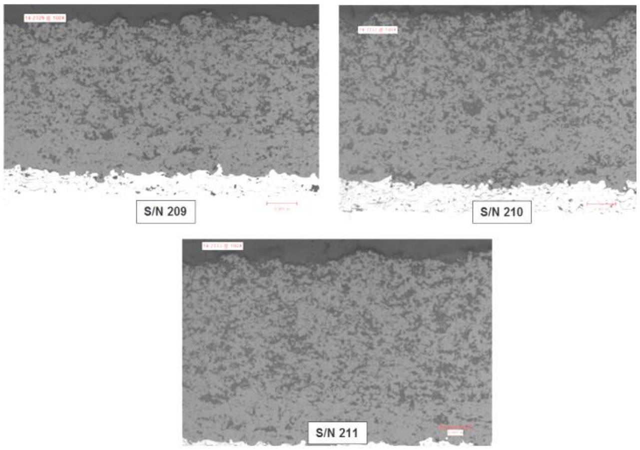

Figure 8 Task 3 QC results for Combustion Baskets – As Coated Microstructures

Transition Piece QC Results

The three production combustion transition pieces coated for engine test are shown in Figure 9. Coating thickness results are listed in Table 5. Coating thickness for the bond coat, and the ceramic layers were measured metallographically and the ceramic layers were also verified by eddy current measurements. As with the baskets, it should be noted that the eddy current measurements are in good agreement with the metallographic results. Microstructures for each basket are shown in Figure 10.

Figure 9 Combustion Transition Pieces– As Coated

Panel #	Bond Coat (mils)	Intermediate Coat (mils)	Top Coat (mils)	Total TBC Ceramic (mils)	Eddy Current results - Duct (mils)
Production #1 S/N 179	5.0	5.5	16.0	21.5	20.8 +/- 6.0
Production #2 S/N 178	5.0	5.5	15.5	21.0	21.9 +/- 3.0
Production #3 S/N 0177	5.0	5.5	15.5	21.0	19.0 +/- 4.1

Table 5 As Coated QC Results for Engine Test Transition Pieces

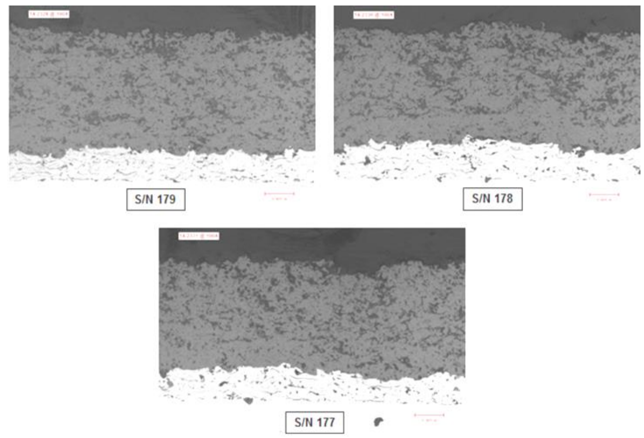

Figure 10 QC results for Combustion Baskets – As Coated Microstructures

Figure 11 Combustion Transition Pieces and Baskets coated with CT 1702 low k TBC system Ready for Shipment

Inspection Results following Engine Testing for CT1702 TBC on GT Combustion Hardware

The 3 baskets (S/N 209, 210 & 211) and 3 transition pieces (S/N 177, 178 & 179) coated with the CT 1702 Low K TBC system in March 2014 were run as part of a set with OEM coated hardware with the baseline 7YSZ TBC. The set consists of a total of 16 baskets and 16 TPs. The components were run 7,846 EOH in the second interval with the low k TBCs (Jul. 2014 - Sep. 2015). Onsite visual and eddy current inspection of the engine run hardware was performed in December, 2015

Visual Inspection

Visual inspection was performed on all baskets and TPs and representative photos of the TBC condition are shown in Figures 12 and 13. The TBCs were characterized as being in "pristine" condition and no evidence of coating distress was observed. Close inspection of the coatings around the cooling holes appeared identical to the as shipped condition with no evidence of erosion.

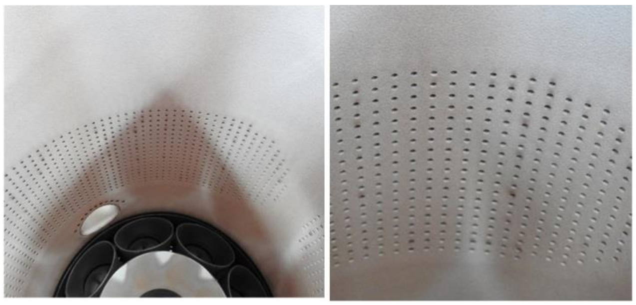

Figure 12 Basket Visual Appearance of TBC after engine test

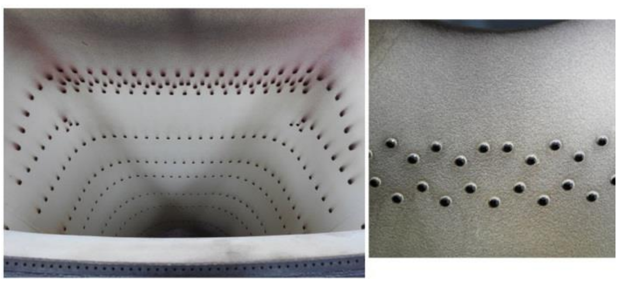

Figure 13 Transition Piece S/N 178 Visual Appearance of TBC after engine test

Eddy Current Inspection

Eddy Current TBC thickness readings were performed on all CTS coated components as well as select components coated by the OEM. Summary of the eddy current TBC thickness readings are shown in Tables 6 and 7 comparing reading taken in the as coated condition and following engine service. There is no evidence of loss of coating thickness during operation. On the non-CTS coated TP's there was substantial thickness variation noted likely due to issues with optimization of the robotic TBC coating program used.

	CTS Coated S/N			OEM Coated S/N	
	209	**210**	**211**	**214**	**212**
As Coated					
Average Thickness	**21.9**	**25.1**	**29.0**	*na*	*na*
max	24.5	28.7	32.5	*na*	*na*
min	17.5	18.6	24	*na*	*na*
Plus/Minus	3.5	4.85	3.7	*na*	*na*
After Engine Operation					
Average Thickness	**23.2**	**27.8**	**28.1**	**17.3**	**17.4**
Max	18.5	21.3	21.3	12.4	12.0
Max	29.1	33.8	33.7	19.5	20.0
Plus/Minus	5.3	6.3	6.2	3.6	4.0

Table 6 Comparison of Eddy Current Readings Taken As Coated and Following Engine Service for Baskets. *Thickness readings in Mils*.

	CTS Coated S/N			OEM Coated S/N	
	177	178	179	TP7	TP12
As Coated					
Average	**19.0**	**21.9**	**20.8**		
Max	24.4	25.0	27.0		
Min	16.2	19.1	15.1		
Plus/Minus	4.1	3.0	6.0		
After Engine Operation					
Average	**21.0**	**23.8**	**22.8**	**18.8**	**15.5**
Max	24.2	29.3	25.4	30.0	40.9
Min	17.3	16.1	19.7	9.2	2.6
Plus/Minus	3.5	6.6	2.8	10.4	19.2

Table 7 Comparison of Eddy Current Readings Taken As Coated and Following Engine Service for Transition Pieces. *Thickness readings in Mils*.

Summary

All tasks in the EPRI advanced TBC program have been successfully completed. Three F-class transition pieces and three combustion baskets coated with CT 1702 YbGd-YSZ TBCs were successfully engine tested at an EPRI member utility's site. The components completed 7,846 EOH. Visual inspection and eddy current testing of the TBC indicated that they could be returned to service for another 8000 hr interval.

EPRI / CTS Low K TBC Airfoil Program

Based on the success of the low k combustion hardware coating program, EPRI and CTS are extending the YbGd-YSZ coating system to airfoil applications. The approach is similar to that used in developing and validating the CT1702 coating on combustion components.

Task 1: EPRI Property Validation Testing of Low k Coating System for airfoil applications
Task 2: Develop EPRI YbGd-YSZ TBC airfoil Specification
Task 3: Qualify Low k Coating on F Class Stg 1 Blades
Task 4: IGT Airfoil Rainbow Rotor Engine Testing

Property Validation Testing

The test panel configuration that will be used to generate TBC validation property data is shown in Figure 14. It is a flat panel 5" x 12" with 35 coupons mounted on it. The panel geometry emulates the general geometry of an F-class stage 1 blade, coated with a vertical "ladder" thermal spray program. The list of properties to be evaluated are shown below.

- Metallographic Coating Thickness and Structure
- Bond Coat Surface Roughness
- Tensile Bond Strength (Bond Coat to Substrate and Ceramic Top Coat to Bond Coat)
- Solid Particle Erosion
- Thermal Conductivity and Sintering Resistance (As Coated and after 1400° C/100hr Sinter Cycle)
- Furnace Cycle Testing (1093° C / ~ 1.25 hr. cycle)

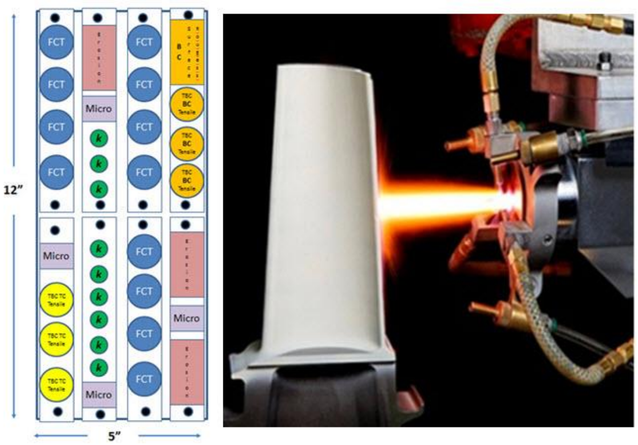

Figure 14 Airfoil TBC Program Thermal Spray Specimen Layout (left), IGT Airfoil being Coated with a TBC (right)

Figure 15 shows the two baseline 7YSZ TBC structures commonly used on IGT airfoil applications. The target coating thickness is 8 mils for the MCrAlY HVOF bond coating and a ceramic layer thickness of 27.5 mils. The baseline porous coating will have a nominal 10-15 % porosity level and the vertically cracked TBC will have < 5% porosity, > 65 cracks per inch and > 5000 psi tensile bond strength.

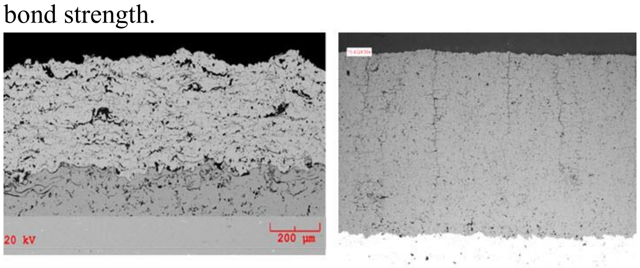

Figure 15 Photomicrograph of Baseline 7YSZ Porous TBC 10-15% porosity (left) and Baseline 7YSZ VCC TBC

Figure 16 shows a schematic of the multilayer architecture for the low k TBC and a photomicrograph of the targeted three layer system. Recent work by the Center for Thermal Spray Research at Stony Brook University has demonstrated advantages of using a three layer system to optimize erosion resistance in the outer layer (VCC structure), low conductivity, porous middle ceramic low k layer, and a thin high fracture toughness inner 7YSZ layer to maximize thermal fatigue resistance (Sampath 2012 and Viswanathan 2014 & 2015). By changing the TBC structure from 10-15% porosity TBC to < 5% porosity VCC TBC the elevated temperature erosion resistance has been shown to increase by over 10 x (Shin and Hamed 2016).

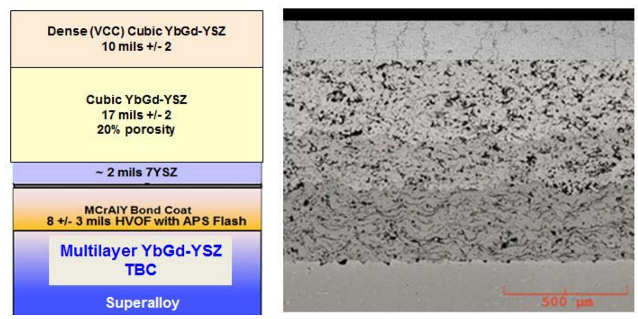

Figure 16 Schematic of Multilayer YbGd-YSZ TBC and Photomicrograph of Multilayer YbGd-YSZ TBC

Coating Qualification on Components

In order to qualify the baseline and low k multilayer TBCs for F-class production blades, test coupons will be affixed to scrap components and microstructure and tensile bond strength characteristics will be compared to those evaluated on the flat panels in Task 1. Figure 17 shows the blade sectioning plan that will be used in order to qualify the baseline porous, VCC and multilayer TBCs on actual components prior to coating production hardware for a rainbow rotor engine test in 2017.

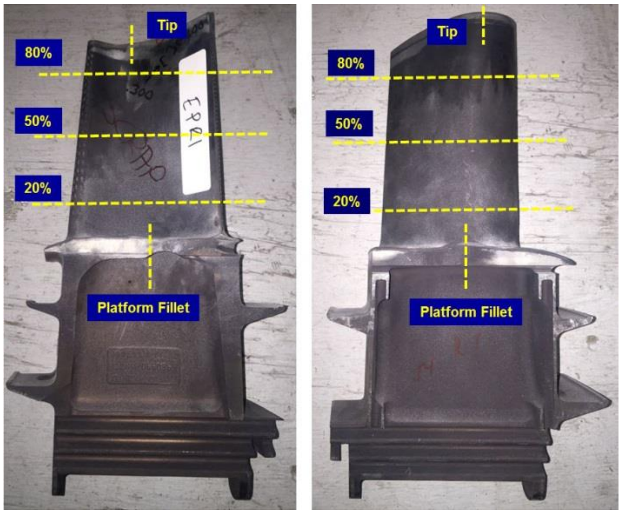

Figure 17 Metallographic Sectioning Plan for Qualifying Baseline and Low Multilayer TBCs on F Class Stage 1 turbine Blades

Summary

Coating of the property test specimens and initial coating trials on Stage 1 scrap blades is underway. Property testing on panel mounted coupons and witness coupons on scrap airfoils are expected to be completed by the end of 2016. It is anticipated that F Class stage 1 production blades will be coated for a rainbow engine test during 2017.

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