

**CERAMIC LAYERS IN AERO-ENGINES: ADDING COMPLEXITY TO REACH THE THERMAL LIMITS OF MATERIALS**

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## SUSPENSION PLASMA SPRAY TBC APPLIED ON GAS TURBINE COMPONENTS

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Key Words: Suspension Plasma Spray, Columnar, Thermal Shock, Gas Turbine

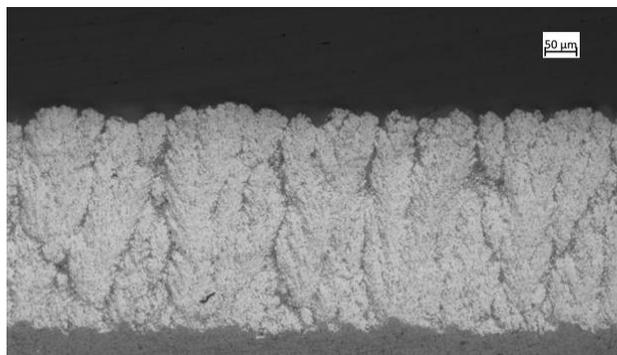
The great industrial interest in improving the performances of thermal barrier coatings (TBC) results in new investigations and insights on Suspension Plasma Spray (SPS) technology.

The main feature of SPS is that powder feedstock is suspended within a solvent such as water or ethanol. The solvent acts as a carrier medium, enabling fine powder to be transported and injected into the plasma stream for processing. The fine scale of the powder particles used in SPS allows for a great range of coating microstructures to be produced.

The aim of the present work was to test and compare different type of microstructures applied by SPS using an ethanol-based suspension. In particular, this investigation focused on micro-porous and columnar TBCs. Spraying parameters have been developed to increase the standoff distance and the process stability, which are the main limits of SPS so far.

SPS TBCs were characterized by means of microstructural investigation, x-ray diffraction, bond strength and thermal cycling test.

This investigation shows a full comparison of new SPS TBCs with the well known porous TBCs and vertically segmented TBCs in terms of coating performances and industrial feasibility. Moreover, the best performing coating was applied on a real gas-turbine blade, scaling-up the parameters from the laboratory to the industrial-scale.



*Figure 1 – Feathery Columnar 8YSZ SPS TBC*

## DEVELOPMENT AND APPLICATION OF THE ADVANCED THERMAL BARRIER COATING FOR HIGH EFFICIENCY GAS TURBINE

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Key Words: Gas turbine, Thermal Barrier Coating, Thermal cycle test, Erosion test

To improve thermal efficiency of GTCC, 1700°C gas turbine is being developed as a Japanese national project. To achieve 1700°C combustion temperature and get high efficiency, researches for each component has been done. As one item of this development project, research and development of advanced Thermal Barrier Coating(TBC) is now ongoing. The surface temperatures of TBC topcoat and bondcoat of 1700°C class gas turbine will be increased to obtain the higher thermal efficiency compared with those of the conventional gas turbine. Therefore, development of the new ceramic topcoat material with low thermal conductivity and the new bondcoat material with high oxidation resistance was carried out. In this paper, the advanced TBC development situation and verification utilizing the MHI's actual power plant are discussed.

For the development of topcoat ceramic materials, material calculation (first principal calculation) was applied to obtain both lower thermal conductivity and better high temperature stability. After first principal calculation, the sintered body of candidate ceramic materials were prepared, physical and thermal properties were evaluated. It was confirmed that advanced ceramic materials have lower thermal conductivities than the conventional YSZ. The new ceramic A and B were sprayed by air-plasma spray (APS) to evaluate coating properties such as thermal conductivity, thermal cycle durability, hot erosion resistance and so on. Thermal cycle durability for New TBC's showed longer cyclic life than the conventional YSZ. In addition, it was confirmed that the new TBC's have superior phase stability, erosion resistance, at high temperature when compared with YSZ.

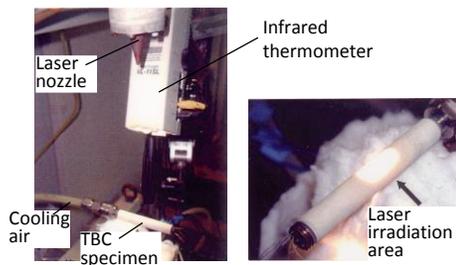


Figure 2 – Thermal cycle test

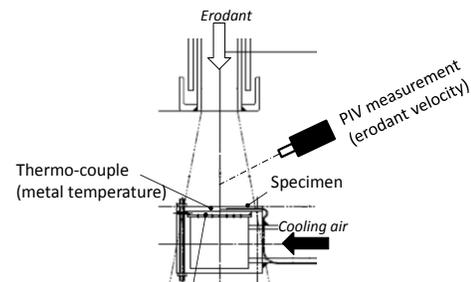


Figure 2 – Hot erosion test rig

For the development of the bondcoat materials with superior oxidation resistance and good ductility, alloy design system which was usually used to develop the superalloys was applied. It was confirmed that the new bondcoat had superior oxidation resistance more than 50°C temperature compared with conventional CoNiCrAlY bondcoat.

The advanced TBCs were installed into the 1,600 °C class gas turbine, M501J in 2011. After the commercial operation period, MHI performed the major inspection in March 2014 to check the mechanical condition of the M501J gas turbine. The hot parts and the other parts were confirmed to be in sound condition. There was not significant TBC crack or spallation about 16,000 hour operation.

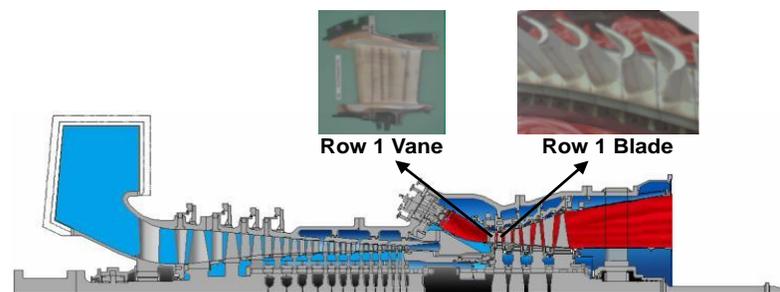


Figure 3 – Inspection result of advanced TBC

## **CURRENT MARKET SITUATION ON AIRCRAFT ENGINES AND INCREASING REQUIREMENTS OF EB-PVD EQUIPMENT**

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Key Words: EB-PVD, Thermal Barrier Coatings, beam deflection control, evaporation

Equipment suppliers use forecast, demands and estimates to determine capacity requirements for coated parts and also coating development.

Fuel efficiencies and longer cycle times of all modern gas turbines, especially for the aviation industry, are the key drivers for the optimization of materials and coatings. In particular EB-PVD coatings designed specifically to accomplish those efficiencies.

Yttria stabilized zirconia coatings applied by EB-PVD achieved standard for the industry over the last decade. In order to produce these coatings in reliable and cost efficient methods, coating equipment design for high throughput and extended campaign times of several days is required.

The challenge for an equipment supplier is to continue to provide equipment and process improvements, realizing, that some of these may require extensive requalification of equipment and process by aviation authorities (e.g. FAA). The equipment and process improvements all take in consideration the safety features for personnel and machinery protection.

As an example of process improvements which also drive equipment design is the application of double layers coatings, which have become a new standard today.

Double layer coatings can be applied sequentially depending on equipment configuration. Today integrated solutions that allow for switching evaporation materials during a deposition run are required. In order to accomplish this several systems are integrated in order to provide a sophisticated and safe beam deflection system with a high flexibility of beam pattern control.

## **OPERATIONAL EXPERIENCE WITH EB-PVD COMMERCIAL EQUIPMENT AND PROCESSES**

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EBPVD TBC on Pt modified diffusion aluminide is the coating of choice for highly stressed airfoils in aero engines. Since 1998 Praxair Surface Technologies, Inc., and now PG Technologies, LLC, provide high quality coating services for EBPVD TBC coating to GE Aviation under a production alliance agreement licensing GE core technology. Beginning with a clean slate, we had the opportunity to set up a coating facility specifically designed for the intended product spectrum. High volume state the art multi-chamber coating machines and the related ancillary equipment were initially implemented in Indianapolis and Singapore. A further expansion to a new coating facility in Ellisville, MS is under way. Over the years, the EBPVD TBC process has been optimized with regard to throughput and yield in a continuous improvement process driven by Six Sigma and lean manufacturing methodology. This presentation will highlight the key factors for product quality, throughput and yield. Selected examples of process and productivity improvements are investigated, such as thermal management for extended coating campaigns and advanced coating fixture design for higher productivity.

# HIGH TEMPERATURE TENSILE PROPERTIES OF $\beta$ - $\gamma$ - $\gamma'$ -MCrAlY And $\beta$ -Ni(Al,Pt) BOND-COATINGS AND INTERDIFFUSION ZONE WITH NI-BASED SINGLE CRYSTAL SUPERALLOYS

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Key Words: bond-coating; ductile-to-brittle transition temperature; high temperature tensile testing; freestanding specimen; interdiffusion.

MCrAlY overlay coatings and Pt-modified aluminide diffusion coatings are commonly used in thermal barrier coating (TBC) systems for turbine blade and vane applications. Purposely designed for oxidation and corrosion protection, MCrAlY and aluminide coatings have a ductile-to-brittle transition temperature (DBTT) of about 600 to 800°C, *i.e.* in the temperature range of service conditions. Therefore, these coatings can be a source of premature crack initiation under thermomechanical loading at low/intermediate temperature. They also creep at high temperature. This drastic change in local mechanical properties significantly impair the structural integrity of such multi-layered materials. Current damage-tolerant design of TBC systems preferentially deals with DBTT than with the effective temperature- and time-dependent mechanical properties of the individual layers constituting the TBC systems. Data on high temperature properties of the bond-coatings and the interdiffusion zone with the substrate are lacking. Indeed, these local properties are particularly difficult to assess up to 1100°C, both using freestanding-layer<sup>[1-4]</sup> or multi-layer specimen approaches<sup>[5]</sup>. Improvements in the prediction of the mechanical behavior and the lifetime of TBC systems require the understanding and the quantification of such local mechanical properties.

In the present study, the tensile properties of thin freestanding MCrAlY overlay coatings and Pt-modified aluminide diffusion coating specimens were investigated in a large range of temperatures, representative of service conditions. Freestanding specimens were both extracted and tensile tested for the bond-coating itself, but also for the interdiffusion zone and the substrate in order to document the gradient of properties within the TBC systems. The ductile-to-brittle transition behavior was shown and a significant ductility was evidenced for both the bond-coatings above the DBTT (*Figure 3*). The interdiffusion zone exhibited intermediate properties between those of the bond-coating and the substrate.

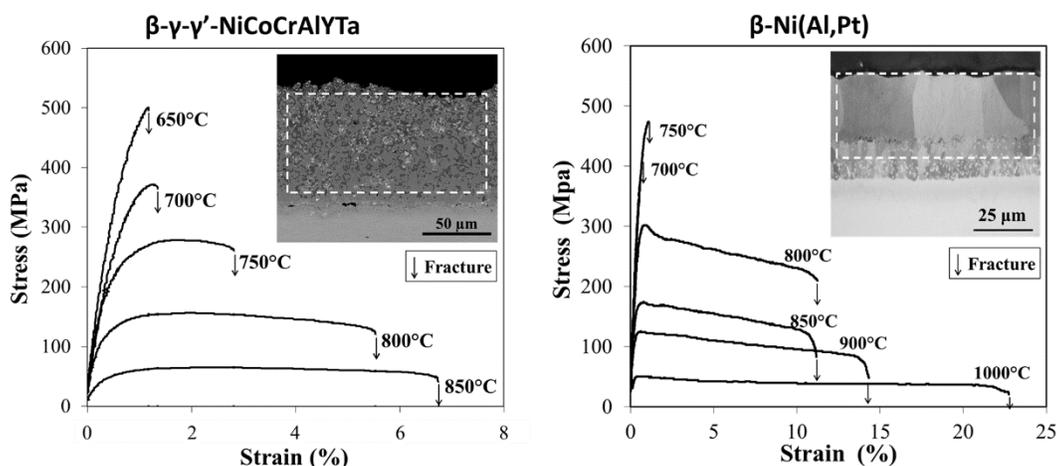


Figure 3 – High temperature tensile properties of freestanding MCrAlY overlay coating and Pt-modified aluminide diffusion coating specimens

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## DEVELOPMENT OF BONDCOATS FOR HIGH LIFETIME SUSPENSION PLASMA SPRAYED THERMAL BARRIER COATINGS

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Key Words: Thermal barrier coatings, suspension plasma spraying, lifetime, bondcoats, surface treatment.

A Thermal Barrier Coating (TBC) system is designed to protect gas turbines from high temperatures and harsh environments. Development of TBCs allowing higher combustion temperatures is of high interest since it results in higher fuel efficiency and lower emissions. It is well known that nano-structured TBCs produced by Suspension Plasma Spraying (SPS) have significantly lower thermal conductivity as compared to conventional systems due to their very fine porous microstructure. Improvement of TBCs manufactured by SPS is of high commercial interest as SPS has been shown capable to produce columnar microstructures similar to the conventionally used Electron Beam – Physical Vapor Deposition (EB-PVD) process. Moreover, SPS is a significantly cheaper process than EB-PVD and can produce coatings with much higher deposition rates than EB-PVD. However, lifetime of SPS coatings needs to be improved further for them to be applicable in commercial applications.

Lifetime of a TBC system is significantly dependent on topcoat-bondcoat interface and bondcoat treatments before spraying topcoat as they influence the growth rate of Thermally Grown Oxide (TGO) layer as well as the mismatch stresses generated in the topcoat during thermal cyclic testing. Grit blasting, shot peening, and controlled atmosphere heat treatment are some of the common methods used to modify the bondcoat surface topography and oxide growth characteristics. The bondcoat microstructure also affects the TBC lifetime significantly. The bondcoat layer in EB-PVD TBCs is typically deposited by Vacuum Plasma Spraying (VPS) in case of NiCoCrAlY bondcoats and Chemical Vapor Deposition (CVD) in case of PtAl bondcoats, while in case of Atmospheric Plasma Sprayed (APS) TBCs, the NiCoCrAlY bondcoats are typically deposited by High Velocity Oxy-Fuel (HVOF) spraying. It is not fully understood yet which bondcoat deposition process and interface topography would be most suitable for SPS TBCs in order to achieve high lifetime.

The objective of this work was to study the effect of different bondcoat treatments and spray processes on bondcoat microstructure, TGO growth rate and lifetime in SPS TBC systems. Commercial NiCoCrAlY bondcoat powder was deposited by high velocity air fuel spraying while axial-SPS was used for yttria stabilized zirconia topcoat deposition using the same spray parameters for all samples. Before spraying the topcoat, the bondcoats were subjected to either grit blasting, shot peening, vacuum heat treatment, or a combination of these three treatments. The lifetime of resultant samples was examined by thermal cyclic fatigue and thermal shock testing. The failure mechanism in each case was investigated. The TGO growth rate was studied by taking out the samples at regular intervals during thermal cyclic fatigue testing before failure. The effect of bondcoat deposition process and interface topography on TGO growth and failure mechanisms in each case will be discussed.

## EFFECT OF SPECIMEN GEOMETRY AND APS FLASH BOND COATING ON TBC LIFETIME

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Key Words: Furnace Cycle Testing, APS flash bond coating, geometry effects

Thermal barrier coatings (TBCs) for land-based gas turbines are primarily thermally sprayed and are unlikely to contain precious metals. For regions of the world where natural gas prices are high, turbine efficiency is a critical issue, however, durability and reliability also are very important for large scale generation. Seeking pathways for improved performance and lifetime model development, a variety of TBC performance parameters have been investigated over the years using furnace cycle testing, including bond coating composition, substrate composition, cycle frequency and environment (i.e. additions of H<sub>2</sub>O, CO<sub>2</sub>, etc.). The baseline system has been superalloy 247 substrates with high velocity oxygen fuel (HVOF) NiCoCrAlYHfSi bond coatings and air plasma sprayed yttria-stabilized zirconia (YSZ) top coatings tested in “wet” air (10%H<sub>2</sub>O) at 900°-1150°C.

Recently, specimen geometry was changed from flat disks to rods. Using similar coating parameters, FCT lifetime in 100-h cycles at 1100°C in air with 10%H<sub>2</sub>O dropped by ~5X for rods compared to disks. Coating architectures that were developed for flat disk specimens did not appear to be effective in improving lifetime in FCT for rod specimens. The addition of an APS “flash” coating resulted in a significant increase in FCT lifetime in rod specimens. The benefit of this additional bond coating layer has generally thought to be due to increased interface roughness compared to a conventional HVOF coating. The most recent testing has returned to 1-h FCT of disk specimens using ~50µm APS flash coatings of both NiCoCrAlYHfSi and NiCoCrAlY flash coatings deposited on HVOF NiCoCrAlYHfSi. A similar set of rod specimens also is being evaluated in 100-h cycles. Both tests are being conducted at 1100°C in air with 10%H<sub>2</sub>O. Both flash coatings show a statistically significant increase in FCT TBC lifetime in 1-h cycles. Surprisingly, the Y only flash coating has significantly outperformed the YHfSi flash coating with some work still in progress. Residual stress in the thermally grown alumina scale has been tracked every 100 1-h cycles and 5, 100-h cycles for one sample of each coating type to quantify the evolution of the reaction product and better understand the FCT results. Failed specimens are being characterized to better understand the benefit of flash coatings on TBC lifetime. Research was sponsored by the U. S. Department of Energy, Office of Fossil Energy, Turbine Program.

## OXIDATION AND INTERDIFFUSION IN MCrAlY-TYPE BONDCOATS AND THE CORRELATION WITH TBC LIFE

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Key Words: MCrAlY-Bondcoats, Oxidation, Interdiffusion, TBC-Lifetime

A pre-requisite for extended and reproducible lifetimes of thermal barrier coating (TBC) systems is the use of oxidation-resistant metallic bondcoats with optimized performance. Whereas in aircraft engines electron-beam physically vapour deposited (EB-PVD) TBCs with Ni-aluminide type bondcoats are used, in land based gas-turbines MCrAlY-type (M=Ni,Co) bondcoats are applied, typically in combination with a ceramic topcoat produced by atmospheric plasma spraying (APS).

Failure mechanisms and parameters, which influence lifetime of the TBC-systems with MCrAlY-bondcoats will be discussed. The performance of MCrAlY-bondcoats will be shown to depend on the contents of the major alloying elements Co, Ni, Cr and Al as well as minor additions of Y and Hf. In addition, the role of manufacturing related properties such as coating thickness, porosity, surface roughness profile and oxygen content in determining TBC-system lifetime will be emphasized.

The requirements of high bondcoat oxidation (corrosion) resistance and good chemical compatibility with the base material are frequently contradictory with respect to the bondcoat chemistry. One of the possible solutions to the latter problem is using multilayered bondcoats with an outer layer optimized for formation of a slowly thickening thermally grown oxide (TGO) and the bottom layer optimized for suitable mechanical properties and reduced interdiffusion with the base material. It will be shown that successful development and application of such complex, multilayer coating systems can be substantially facilitated using thermodynamic/kinetic modeling, the vast potential of which has become apparent in recent years.

## DEVELOPMENT OF BOND COATS FOR EXTENDING LIFETIME OF TBCs

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Key Words: Bond Coat, MCrAlY, oxidation, thermal barrier coatings.

This talk will be focused to study the MCrAlY bond coat for thermal barrier coating applications. First of all, residual stresses in the bond coat have been measured with use of X-ray diffraction, in which effect of temperature and thermal cycling will be studied. Secondly, rumpling phenomena of such bond coat after thermal treatments have been examined to identify factors affecting the stress evolution and rumpling of the bond coat. Thirdly, effect of the bond coat microstructure on early oxidation of the bond coat has been investigated to understand how the grain size in the bond coat affected both oxidation products and oxidation kinetics. Finally, the comparison of MCrAlY bond coat vs the NiPtAl bond coat will be made in terms of residual stress evolution, residual stresses, and oxidation kinetics to illustrate the effect of these factors on failure and lifetime of TBCs.

**HOT CORROSION DEGRADATION OF MARINE GAS TURBINE MATERIALS SUBJECT TO MIXED-MODE  
THERMAL EXPOSURES AND COMPLEX CORROSION ENVIRONMENTS**

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# DEVELOPMENT OF THERMAL BARRIER COATINGS WITH EXCELLENT DELAMINATION RESISTANT PROPERTY BY EXTREME INTERNAL OXIDATION

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Key Words: Thermal barrier coatings, Thermally grown oxide, Delamination, Bond coats, Inward TGO

In Japan, the proportion of thermal power generation has increased since after the Great East Japan Earthquake in 2011, accounting for approximately 85% in 2015. Compared to other power generations, thermal power plants have a large amount of carbon dioxide emissions relative to the amount of power generation. Therefore, it is an urgent task to reduce carbon dioxide emissions by improving the efficiency of thermal power plants.

Increasing the turbine inlet gas temperature improves the efficiency of the gas turbine thermal power plants. However, high-temperature components, such as rotating blades, are close to their maximum service temperature. Therefore, application of the thermal barrier coating (TBC) on the turbine blade substrate is needed to protect a structure. The TBC system usually consists of ceramic top-coating (TC) and intermediate metallic bond-coating (BC) on a Ni-based superalloy substrate. To reduce the effect of the heat flux on the structure, heat resistant material, such as Yttria-Stabilized Zirconia (YSZ), is commonly used for TC layer. While, for BC, MCrAlY (M: Co and/or Ni) alloy is commonly used to protect the substrate from oxidation and corrosion, as well as to improve the bonding strength between the TC and the BC layers. However, delamination of the TBC can occur, because of significant thermal stresses generated when the coating cools down from high to room temperature. Therefore, improvement of TBC delamination resistance is indispensable.

Delamination of the TBC is caused by the Thermally Grown Oxide (TGO) formed at the interface between TC and BC, because of the discrepancy in the thermal expansion coefficient between TGO and TC or BC. Therefore, the TBC formation control is important to improve the delamination resistance of TBC. Previously, authors have succeeded in improving the delamination resistance of TBC by adding cerium (Ce) to the CoNiCrAlY alloy as a BC which assist the formation of the inward TGO. The inward TGO reduces the thermal stress experienced by TBC through the formation of vertical cracks initiated by the inward TGO. However, the inward TGO only forms when the temperature is over 1100°C, which is higher than the substrate temperature during the gas turbine thermal power plants operation temperature. As a result of further research, authors have succeeded in reducing the inward TGO formation temperature to 1000°C close to the actual use environment by adding ceria (CeO<sub>2</sub>) instead of Ce to the BC materials.

In our studies, it was improved that the TBC delamination resistance thanks to the introduction of internal oxidation during BC formation using High Velocity Oxy-Fuel (HVOF) technique. It was showed that internal oxidation introduced during the film formation proceeded sufficient inward oxide at high-temperature exposure (900°C) and exhibited high delamination resistance. Thus, adding CeO<sub>2</sub> to the CoNiCrAlY alloy and introducing internal oxidation during BC formation is efficient to reduce the inward oxide formation temperature. However, when the inward oxide is introduced to BC, the internal oxidation might reduce the oxidation resistance of TBC system. In addition, oxidation and corrosion of the substrate can occur due to direct exposure to the combustion environment through vertical cracks. Therefore, it is needed to develop a new BC combining oxidation resistance and delamination resistance. Two-layer BC is considered. The first layer of the BC, located on the substrate side, has less internal oxidation and helps in the protection of the substrate. The second layer of the BC, located on the TC side, has a lot of internal oxides and improves the coating delamination resistance. Thus, it possible to develop TBC compatible with delamination resistance properties and substrate protection properties.

The aim of our study is to improve the delamination resistance of TBC and develop TBC with reduced inward TGO formation temperature. For this purpose, TBC with CeO<sub>2</sub> and ZrO<sub>2</sub> added to the BC material were prepared. To perform TBC specimens with internal oxide in the BC, BC materials with several particle sizes and several BC spraying methods were used. The internal oxide amount and delamination resistant property of these TBC specimens were evaluated with SEM observation and four-point bending test. And also, the high-temperature oxidation behavior and the delamination resistance of TBC with two layers of BC, aiming to achieve both delamination resistance and substrate protection, were evaluated.

## MULTIFUNCTIONAL THERMAL BARRIER COATINGS ENABLED BY LAYERED MANUFACTURING

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Majority of contemporary TBCs applied either via plasma spray or EB-PVD can typically be described as monolithic single layers, principally based on yttria stabilized zirconia (YSZ). Advent of new ceramic compositions has necessitated to some extent the need for double layers where the interfacial ceramic layer on the bond coat is often made of YSZ to prevent reaction of advanced compositions with TGO. Even in these situation the coating architecture is generally of a single variant. Since TBCs experience location specific performance needs (example interfacial oxidation, sintering resistance in the volume and need for distinct surface characteristics to mitigate against CMAS and erosion) there is an opportunity to engender unique microstructural and material characteristics. In this presentation, we will discuss the coupling of multilayer coating design to meet the disparate coating needs along with advanced layered manufacturing concepts. Plasma spray is uniquely capable of taking advantage of such layered design concepts as the coating itself is built in discrete layers of particle based assembly. Several variants of such multilayer, multifunctional coatings will be presented incorporating guidance from mechanics model, manufacturing advances and performance attributes.

## **AXIAL SUSPENSION PLASMA SPRAYING - MICROSTRUCTURE EFFECT ON THERMAL BARRIER COATINGS PERFORMANCE**

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Key Words: ASPS, microstructure, porosity, thermo-mechanical properties.

Axial Suspension Plasma Spraying (ASPS) is a relatively new thermal spraying technique to produce advanced thermal barrier coatings (TBCs). ASPS has shown to be a very promising technique to produce coatings with lower thermal conductivity as well as higher lifetime than the state-of-art TBCs used today. In addition, ASPS has also shown to have a very wide process window which enables the production of variety of microstructures such as highly dense, highly porous, segmented or columnar. However, tailoring the microstructure of these TBCs for enhanced durability is challenging due to their inherently wide pore size distribution (ranging from few nanometers up to few tens of micrometers).

This work aims to study the effect of feedstock and plasma spray conditions on the various microstructural features and thereby to study the effect of microstructure on coatings functional performance. Various thermo-mechanical properties including thermal conductivity, hardness, E-modulus and toughness along with TBCs lifetime including both the thermal shock as well as thermal cyclic fatigue and sintering behavior is investigated. The effect of various pore sizes at different length scale on various coating properties as well as performance was of specific interest. Based on the detailed experimental investigation conducted in this work, various factors needed for designing an optimized columnar TBC for gas turbine application are discussed. This study reveals that along with the suspension viscosity and surface tension, ceramic top coat total porosity and pore-size distribution at different length scale was found to play varying roles in influencing the TBC performance and were found to be crucial in designing the optimized TBC.

## FABRICATION OF DOUBLE-CERAMIC-LAYER TBCS BY SUSPENSION PLASMA SPRAY

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**Key Words:** Thermal barrier coatings (TBCs), Double-ceramic-layer, Rare-earth zirconate, Suspension plasma spray

Rare-earth zirconates, such as  $\text{La}_2\text{Zr}_2\text{O}_7$  and  $\text{Gd}_2\text{Zr}_2\text{O}_7$ , have been investigated as one of the candidates for replacing conventional yttria-stabilized zirconia (YSZ) for thermal barrier coating (TBC) applications at higher turbine inlet temperatures. Rare-earth zirconate oxides exhibit little phase transformation upon heating up to melting temperature as well as low thermal conductivity, where as their mechanical properties is inferior to those of YSZ TBCs. Double-ceramic-layer (DCL) TBCs have been investigated in order to take advantage of beneficial characteristics of both YSZ and rare-earth zirconate.

In this study, the fabrication of DCL-TBCs with YSZ layer and rare-earth-zirconate top layer by using suspension plasma spray are reported. Microstructure, compositional profile, thermal conductivity, and thermal durability of DCL-TBCs are characterized. The usefulness of these DCL-TBCs is also discussed.

## **MICROSTRUCTURE AND THERMAL CONDUCTIVITIES OF SUSPENSION VACUUM PLASMA SPRAYED YSZ COATINGS**

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**Key Words:** Suspension plasma spraying, vacuum plasma spraying, yttria stabilized zirconia

To increase the efficiency of gas turbine, the turbine inlet temperature should increase. As the turbine inlet temperature increases, the heat load of thermal barrier coating increases. Suspension plasma spraying (SPS) was developed to enhance the performance of thermal barrier coating. Suspension allows nano-sized powders to be injected into the plasma flame, which has advantage of forming a variety of microstructures. However, there is a disadvantage of SPS that cannot be completely transmitted the enthalpy of plasma flame due to evaporation of solvent in the suspension, which causes decrement of coating formation rate.

In this study, disadvantages of the suspension atmospheric plasma spraying (SAPS) can be solved by forming YSZ coatings through suspension vacuum plasma spraying (SVPS). The length of plasma flame in vacuum condition becomes longer, powders can stay longer inside the plasma flame.

A variety of microstructured YSZ coatings were formed by SPVS at various spraying conditions. Microstructure of SVPS YSZ coatings were analyzed by SEM. Thermal conductivity of SVPS YSZ coatings were analyzed by laser flash method. Coating formation rate showed

## THERMAL BARRIER COATINGS ON POLYMER MATERIALS

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Key Words: Thermal barrier coatings; Polyimide matrix composite; Sol-Gel; Air plasma spraying.

Polyimide matrix composite (PIMC) has been widely used to replace metallic parts due to its low density and high strength. It is considered as an effective approach to improve thermal oxidation resistance, operation temperature and lifetime of PIMC by depositing a protection coating. The objective of the research was to fabricate a series of thermal barrier coatings (TBCs) on PIMC by a combined sol-gel/sealing treatment process and air plasma spraying (APS). By optimizing the experimental parameters, thermal shock resistance, thermal oxidation resistance and thermal ablation resistance of PIMC could be improved significantly. The ZrO<sub>2</sub> sol was prepared by sol-gel process and the effects of the different organic additions on phase structure, crystallite size and crystal growth behavior of the ZrO<sub>2</sub> nanocrystallite were investigated. The addition of HAc and DMF were beneficial to decrease the crystallite size and alter the activation energy for crystal growth, further inducing the crystallization of ZrO<sub>2</sub> nanocrystallite at low temperature (300°C) and the stability of tetragonal ZrO<sub>2</sub> at 600°C. Based on the optimized parameters of the sol preparation, the ZrO<sub>2</sub>/phosphates duplex coating was fabricated on PIMC via a combined sol-gel and sealing treatment process. The sealing mechanism of the phosphates in the duplex coating was primarily attributed to the adhesive binding of the phosphates and the chemical bonding between the sealant and the coating. It was demonstrated that the duplex coating exhibited excellent thermal shock resistance and no apparent delamination or spallation occurred. Relatively, the duplex coating with the thickness of 150 μm provided excellent thermal oxidation and thermal ablation resistance for the polymer substrate. However, the presence of cracks and delamination in the coatings provided the channels for oxygen diffusion, causing the final failure of the protection coating. The Zn/YSZ and Al/YSZ coating systems were successfully deposited on PIMC by APS. Metals with comparatively low melting point as the bond coats (Cu, Al, Zn) were beneficial to increase thermal shock resistance of the coating systems. In comparison with the Al/YSZ coating system, the Zn/YSZ coating exhibited the better thermal shock resistance, which was ascribable to the lower residual stress in the Zn layer after deposition and the lower thermal stress induced during thermal shock test. For these coatings, the increase in surface toughness of the substrate as well as the decrease in thickness of metal layer favored the improvement of thermal shock resistance of the coatings. With the temperature increases, thermal shock lifetime of the coatings decreased disastrously. However, the difference was that the slight increase of the thickness of YSZ layer favored the increase in thermal shock resistance of the Al/YSZ coatings, while for the Zn/YSZ coating systems the increase in the thickness of YSZ layer made thermal shock resistance weaken. Owing to the

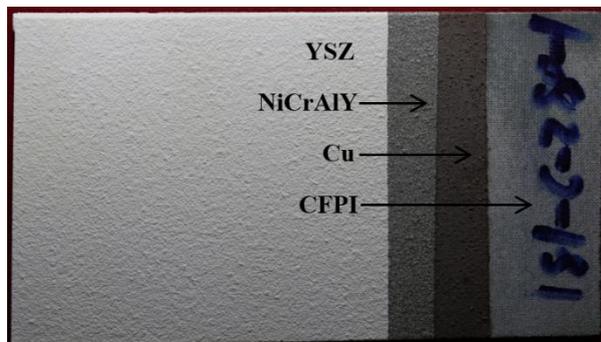


Figure 4– TBCs on CFPI

protection of Zn/YSZ and Al/YSZ coating systems, the time for 5 wt% weight loss of the sample was prolonged from 16 h to 50 h when oxidation at 400°C; as the oxidation temperature increased to 450°C, the time for 5wt% weight loss was extended from 5 h to 13 h. By depositing different coatings, the anti-ablation property of PIMC was significantly improved. During property testing, the formation of cracks and delamination in the coating and the occurrence of the spallation led to the failure of the coating systems, which was mainly due to the residual stress during the deposition process, thermal stress induced by the mismatch in thermal expansion coefficient and further oxidation of the substrate.

## PS-PVD THERMAL/ENVIRONMENTAL BARRIER COATINGS WITH NOVEL MICROSTRUCTURES

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**Keywords:** Plasma spray physical vapor deposition (PS-PVD); Electron beam physical vapor deposition (EB-PVD); Thermal barrier coatings (TBCs); Environmental barrier coatings (EBCs); Ceramic matrix composites (CMC).

Plasma spray physical vapor deposition (PS-PVD) technology has attracted increasing attention due to its promising potential in processing advanced functional coatings such as thermal/environmental barrier coatings (TBCs) by flexibly tailoring the coating microstructure architecture in a broad range. In this work, yttria stabilized zirconia (YSZ) TBCs with a novel quasi-columnar structure were prepared by co-deposition of vapor phase and nano-clusters using PS-PVD and the associated deposition mechanism was discussed. The thermo-physical and mechanical properties, sintering resistance and thermal shock life of the coating were investigated. The thermal conductivity is in a range of 0.7~1.0 W/mk between 200 °C and 1200 °C and the average life is ~4000 cycles during thermal shock testing in which the coating surface was heated to 1200 °C within 20 s and held at the temperature for 5 min by gas flame. Noted that the quasi-columnar TBC revealed much better resistance to glassy CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (CMAS) adsorption than those TBCs produced by air plasma spray (APS) and electron beam physical vapor deposition (EB-PVD) and some attempts were made to understand the related mechanisms.

Ytterbium silicate/mullite/Si environmental barrier coatings (EBCs) were sprayed onto SiC ceramic matrix composites (CMC) by PS-PVD. The dense ytterbium silicate coating deposited at 65 kw is mainly composed of ytterbium disilicate resulting from vapor-phase deposition, whereas the layered coating at 40 kw is mainly ytterbium monosilicate from liquid deposition.

## OPTICAL EMISSION SPECTROSCOPY FOR RATE AND COMPOSITION CONTROL OF PLASMA-ASSISTED EB-PVD PROCESSES

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Key Words: EB-PVD, plasma activation, TBC, EBC, composition control

Currently, EB-PVD of YSZ layers is the standard process for TBC on turbine components. Due to the similar vapor pressures of yttria and zirconia, processing is relatively uncomplicated, and the good performance of this material in various aspects is not easy to beat. However, the increasing need for enhanced turbine efficiency and reduced emissions requires new approaches and developments. This calls for improved TBC systems or ceramic-based turbine components coated with EBC systems, which go hand in hand with the use of new admixed materials and more complex coating compositions. Consequently, the corresponding PVD processes become more challenging as well and should be aided by enhanced monitoring and control means therefore.

Plasma activation of various PVD processes has been shown to be key to success in order to combine high-rate film growth with the requested film properties. The vapor and the reactive gas species are excited, ionized, and dissociated. The energy of charged particles impinging the substrate surface can be tuned resulting in layers with desired density, composition, hardness, or microstructure. The effect of plasma activation by using a hollow cathode arc discharge onto the morphology of YSZ layers [1,2] and its potential for coating of dense EBC's [3] have been discussed previously.

In this paper, another aspect of utilizing a plasma discharge in the vapor cloud will be discussed. Due to excitation of neutrals and ions, element-specific light emission occurs which can be analyzed by optical emission spectroscopy (OES). The spectrum can be used to monitor and control the PVD process. As an example, YSZ has been evaporated by EB-PVD, and an emission line of excited zirconium neutrals has been used to maintain a constant deposition rate. Moreover, metallic zirconium and yttrium have been co-evaporated in oxygen atmosphere by spotless arc-assisted EB-PVD [4], and the vapor species have been monitored by OES. In another project, co-evaporation of several metallic ingots has been performed by the jumping beam method, and an OES-based control loop is being developed to automatically control the EB power input and feeding speed of the individual ingots. This plasma-based OES control method has a considerable potential for the development of reliable, well-defined deposition processes. In addition, the co-evaporation approach may be of increased interest to deposit new complex TBC and EBC systems.

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[2] B. Zimmermann *et al.*: Poster presentation at ECI Thermal Barrier Coatings IV, Irsee, Germany (2014)

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## RELATIONSHIP BETWEEN MECHANICAL PROPERTIES AND MICROSTRUCTURE OF YTTRIA STABILIZED ZIRCONIA CERAMICS DENSIFIED BY SPARK PLASMA SINTERING

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Keywords: YSZ, Spark Plasma Sintering, Fracture surface, Mechanical properties

Yttria stabilized zirconia ceramics are well known in the field of thermal barrier coatings due to their high ability to thermally insulate hot metallic parts of turbo-engines. The present work is focused on the mechanical properties and the fracture behavior of such materials shaped by Spark Plasma Sintering.<sup>1</sup>

Two types of powders have been used: i) the first one is a commercial powder made of micrometric spheroidal agglomerates of nano-crystallites (Tosoh), and ii) the second one is a home-made Sol-Gel powder<sup>2</sup> consisting of dense agglomerates of micrometric non-spherical crystallites. Both powders were shaped by Spark Plasma Sintering. The microstructures and mechanical properties of the various samples were characterized for different porosity rates and composition. The adjustment of several SPS processing parameters such as the temperature and the applied pressure allowed to obtain ceramics with a porosity in the range from 0 to 50 % vol. with oriented microstructure.

It is shown that both powders exhibit a similar evolution of their mechanical behavior (Young modulus and hardness) versus the porosity even if the fractures surfaces are quite different (Figure 5). Indeed, while for the nanopowder the fracture surface is mainly intercrystallites, two fracture modes (intra and inter-agglomerate) are observed for the micrometer powder. Furthermore, we found from acoustic emission analyses that the nanometric powder induces higher Young modulus than those with micrometric powders.

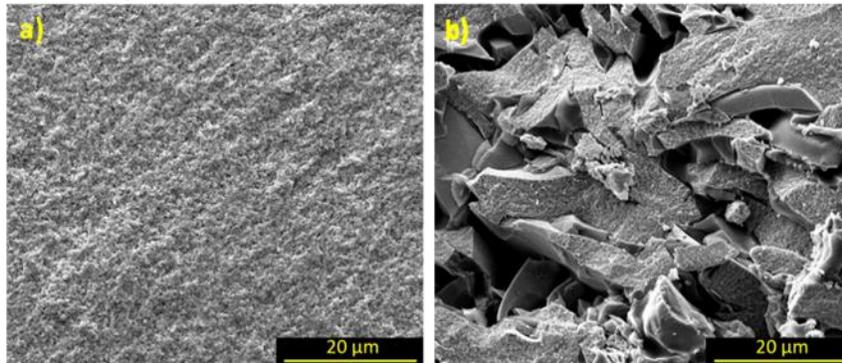


Figure 5 : Fractures SEM-FEG of pellets with an average porosity of 30%vol from powder a) Nano b) Micro powders

An hypothesis to explain the difference of fracture surface can be that the reactivity during sintering of the nanopowders is better than the micropowders one, due to higher exchange surfaces between the grains, leading to a more cohesive structure and better mechanical properties. Then the weak interface between the agglomerates of the micropowders leads to lower Young's modulus.

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# THERMOPHYSICAL, MICROSTRUCTURAL CHARACTERISATION AND NON-DESTRUCTIVE CONTROL OF TBCS BY PHOTOTHERMAL AND THERMOGRAPHIC TECHNIQUES: SOME LESSONS LEARNED

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Key Words: Photothermal techniques, NDE&T, thermography, thermal diffusivity, microstructure.

Since several years, photothermal and thermographic techniques have been used to perform the thermo-physical characterisation of TBCs and the non-destructive assessment of TBC integrity. Furthermore, in the last decade some attempts to use these techniques for carrying out a non-destructive microstructural characterization have been done, as well. In this talk the description of a thermographic technique able to simultaneously measure the through-the-thickness and the in-plane thermal diffusivity of free standing TBCs samples and thus giving evidence of the typical microstructural anisotropy of APS TBCs will be provided [1]. Furthermore, some effects of the laser radiation used in a laser flash experiment on the TBC thermal diffusivity and a new model for fitting the experimental data will be presented [2,3].

The main results of an activity focused to identify potentialities and limitations of using Laser flash experiments on multilayered samples for estimating thermal diffusivity of TBCs samples will be provided.

A theoretical and experimental analysis of the real capabilities of infrared techniques to estimate the porosity content and the microstructure of porous ceramic materials such as thermal barrier coatings (TBCs) by studying thermal diffusivity variations when pores are filled with air or vacuum will be provided [4,5].

The method [6] for the semi-quantitative estimation of the interface cracked fraction between the bondcoat and TBC, within coupons subjected to thermal cycling, will be proposed. It consists on the evaluation of the TBC thermal diffusivity evolution during ageing compared to the as sprayed value. A critical analysis, starting from the contradictory results obtained applying this method on several sets of APS TBC samples, complements the topic. A successful case of integrating the aforementioned approach with the apparent thermal effusivity method [7] to monitor damage progression of Bondcoat-TBC interface over thermal cyclic oxidation tests will be presented together with the comparison with computed tomography images of the same samples.

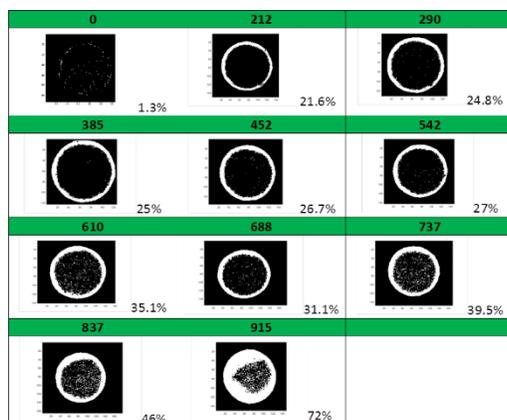


Figure 1 - Delamination evolution as a function of aging cycles (on top of each image) at high temperature estimated by the apparent effusivity method. Delaminations are represented as white pixels. The quantitative estimation of delaminated area is provided close to each image.

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## EFFECT OF COOLING RATE ON PHASE TRANSFORMATION IN 6-8 WT % YSZ APS TBCs

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In properly produced as-sprayed thermal barrier coatings of yttria partially stabilized zirconia (7YSZ) the only phase that can be found is the metastable tetragonal prime structure  $t'$ . Even though  $t'$  is sometimes called “not transformable”, because it behaves as practically stable up to rather high temperature, long term exposure much above 1200 °C produces its equilibrium transformation in tetragonal and cubic phases. During cooling down to room temperature the tetragonal phase will transform in monoclinic one. Although it is considered a martensitic transformation, fast cooling after prolonged high temperature exposure (over 1300°C) can avoid or limit the evolution from tetragonal to monoclinic structure. The effect of the cooling rate on this transformation has been investigated in free standing TBCs both with porous microstructure and dense vertically cracked one, exposed at 1400°C for 100 hours. The samples have been analysed by XRD and subsequent Rietveld refinement analysis to quantify the phase content: the results highlight that different cooling rates give different monoclinic contents, confirming the cooling rate effect on the transformation. If the phase equilibrium was not achieved due to fast cooling, it could be restored at low temperature for short duration independent of cooling rate. It was demonstrated that after exposure at 1400°C followed by fast cooling, the equilibrium phase composition could be achieved by a low temperature heat treatment of 12h at 200°C. For validation, the quantitative phase analysis has been performed before and after that low temperature heat treatment. Moreover the unit cell volume per each phase has been measured, for both samples at equilibrium and samples after fast cooling. Therefore the strain induced by the volume increase due to monoclinic phase formation has been calculated and compared with TBC maximum allowable strain.

## PHONON SCATTERING MECHANISMS CONTRIBUTING TO THE LOW THERMAL CONDUCTIVITIES OF ENTROPY STABILIZED OXIDES AND HIGH ENTROPY CARBIDES

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Key Words: thermal conductivity, entropy stabilized materials, phonon mass scattering, phonon strain scattering, high temperatures

The phonon thermal conductivity of solids is intimately related to any changes in atomic scale periodicity. As a classic example, the phonon thermal conductivity of alloys can be greatly reduced as compared to that of the corresponding non-alloy parent materials. However, the improved mechanical properties and environmental stability of alloyed materials makes these multi-atom solids ideal for a wide variety of applications. In this sense, entropy stabilized oxides and high entropy carbides are promising new materials that have potential to withstand extreme environments consisting of high temperatures and pressures. In these novel materials, thermal characterization is essential for understanding and predicting performance at elevated temperatures, as the presence of multi atomic species (5+ different atoms) in these solid solutions could lead to drastically modified phonon scattering rates and thermal conductivities. In this talk, we present recent measurements and molecular dynamics simulations on multiple atom alloys, including entropy stabilized oxides and high entropy diborides. We use time-domain thermoreflectance (TDTR), and optical pump-probe technique, to measure the thermal conductivity of these various systems. We also demonstrate the ability to extend TDTR measurements to temperatures above 1000 deg. C. The TDTR measurements show drastic reductions in the thermal conductivity of these crystalline solid solution materials, approaching values of the amorphous phases. These reductions in thermal conductivity can not be explained by phonon-mass scattering alone. Thus, to investigate the nature of the reduction in thermal conductivity of these multi-atom solid solutions, we turn to classical molecular dynamics simulations. In agreement with the Klemens' perturbation theory, the thermal conductivity reduction due to mass scattering alone is found to reach a critical point, whereby adding more impurity atoms in the solid solution does not reduce the thermal conductivity. A further decrease in thermal conductivity requires a change in local strain-field, which together with mass defect scattering can lead to ultralow thermal conductivities in solid solutions, which surpasses the theoretical minimum limit of the corresponding amorphous phases. These simulations qualitatively agree well with our experimental measurements, and add insight into the nature of phonon scattering in entropy stabilized materials.

## TEMPERATURE MAPPING ABOVE AND BELOW AIR FILM-COOLED THERMAL BARRIER COATINGS USING PHOSPHOR THERMOMETRY

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Key Words: thermal barrier coating, phosphor thermometry, air film cooling, cooling effectiveness.

Thermal barrier coatings (TBCs) are typically used in conjunction with air film cooling to maximize overall cooling effectiveness and reliability while minimizing sacrifices in engine performance. The effects of thermal barrier coating (TBC) thermal protection and air film cooling effectiveness have usually been studied separately; however, their contributions to combined cooling effectiveness are interdependent and are not simply additive. The combined cooling effectiveness is always less than the sum of the cooling effectiveness of stand-alone TBC protection and stand-alone air film cooling. These diminishing returns arise because adding the thermally insulating TBC between the cooling air and the surface to be cooled reduces the air film cooling effectiveness and because the air film cooling reduces the heat flux through the TBC and therefore reduces the temperature difference sustained across the TBC thickness. Due to these considerations, combined cooling effectiveness must be measured to achieve an optimum balance between TBC thermal protection and air film cooling. In this investigation, temperature mapping above and below air film-cooled TBCs was performed using luminescence lifetime imaging-based phosphor thermometry. Measurements were performed in the NASA GRC Mach 0.3 burner rig on a TBC-coated plate using a scaled-up cooling hole geometry where both the hot mainstream gas temperature and the blowing ratio were varied. Surface temperature maps were obtained from a Cr-doped  $\text{GdAlO}_3$  thermographic phosphor deposited on the surface of the electron-beam vapor-deposited yttria-stabilized zirconia (YSZ) TBC. From separate plates, temperature maps from the bottom of the TBC were obtained from a thin Er-doped YSZ layer integrated into the TBC below the overlying undoped YSZ. Procedures for temperature and cooling effectiveness mapping above and below the air film-cooled TBC surface are described. Most importantly, these measurements enable mapping the combined cooling effectiveness below the TBC, which is more important than surface cooling effectiveness when there is a barrier coating between the hot mainstream gas and the surface that needs thermal protection. Advantages of the luminescence lifetime imaging method over infrared thermography, as well as its limitations to steady-state conditions are discussed.

## PROGRESS ON LUMINESCENCE COATINGS FOR TEMPERATURE MAPPING ON TURBINE ENGINES

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As the operating temperature of thermal barrier coatings (TBCs) increase to accommodate the higher firing temperatures of new gas turbine developments, the need for accurate temperature measurements is becoming increasingly critical. Furthermore, the increasingly aggressive operating conditions also limit the number of suitable temperature measurement methods.

Thermocouples are practically very challenging to implement to measure TBC temperature, therefore, are not widely used. While infrared cameras enable the measurement of temperature profiles over the surface of components, the transparency of TBCs in the infrared range lead to significant errors. The technique is also susceptible to emissivity changes, which can occur during testing, and stray radiation from combustion can cause further errors. To overcome some of these limitations, there has been significant research and development interest in a relatively new technique called phosphor thermometry. In this technique a phosphor material is deposited on the surface of interest and the temperature dependent luminescence characteristics are used to measure the temperature during operation through interrogation by laser induced phosphorescence. This technique promises accurate temperature measurements in real-time and is under investigation by several research institutions.

The first implementation of this technique on an operating gas turbine demonstrated some of the capability of this method. The precision of the measurements was comparable to commercial thermocouples ( $\sim\pm 5K$ ) and transient temperatures were tracked at 8Hz, which is fast enough to follow a typical power generation gas turbine. More recent work has demonstrated the accuracy of the technique compared to commercial pyrometers and thermocouples on a burner rig. The effect of thermal gradients on the temperature measurements were also investigated through modelling and experimental testing. The research has indicated the possible capability of phosphor thermometry in gas turbine development.

While phosphor thermometry has great potential, the optical access required to make measurements during operation poses a significant practical challenge for implementation on commercial engines. The same restriction applies to infrared cameras.

To overcome this challenge, offline temperature measurement techniques are used to record peak temperature information. Thermochromic paint, the most widely used of these techniques, changes colour at predefined temperatures and is read-out afterwards by a trained expert. They are, however, not commonly used on TBCs because it can penetrate into the porous TBC material, causing ambiguous readings and potentially damaging the TBC system. In addition, the maximum temperature limit is restrictive for new engine developments. An alternative technique is thermal crystals, whereby silicon carbide crystals are embedded in the drilled holes in the surface. The crystals can be installed in TBCs but only give point measurements and have limited durability. A new technique is being developed at Sensor Coating Systems, which uses luminescence materials, similar to those used for phosphor thermometry but to record past peak temperatures. In this technique, the luminescence material is deposited as a paint or coating and on thermal exposure the microstructure permanently changes. The material can be deposited by atmospheric plasma spray making it very durable and compatible with TBC architectures. In one field test, the coatings survived 4,500 operating hours with less degradation than a standard TBC. Recent lab testing has demonstrated a measurement capability up to 1400°C and this presentation will discuss new development work taking the capability to higher temperatures. The research will provide a new and unique measurement capability at the upper temperature limit of current and future TBC systems, which will be critical for the development of new generation engines.

## FUNDAMENTAL CHALLENGES IN CMAS MITIGATION

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Key Words: Thermal/environmental barrier coatings, T/EBCs, silicate deposits, CMAS degradation

CMAS degradation of thermal and environmental barrier coatings (T/EBCs) is recognized as a fundamental barrier to progress in gas turbine technology; melting of the precursor silicate deposits, typically at  $\sim 1200^\circ\text{C}$ , limits the temperature capability of the coatings and by extension the achievable engine efficiency. Molten CMAS dissolves all coating materials of interest in the protection of superalloys and ceramic composites, sometimes with preferential grain boundary penetration, and often leads to the formation of new or modified crystalline phases. Notwithstanding the thermo-chemical attack, the more deleterious form of damage is arguably thermo-mechanical. In TBCs the CMAS melt flows into the network of pores and cracks/segmentations that enable strain tolerance during thermal cycling, stiffening the coating and elevating the strain energy available for delamination. The mitigation strategy is generally based on the reaction of CMAS with the coating material, consuming locally the melt and yielding the precipitation of crystalline phases in sufficient volume to fill in the flow channels and arrest penetration. The extent of stiffening scales with the penetration depth, which depends in turn on a complex interplay between the infiltration, dissolution and crystallization dynamics. Predictive models are hindered by uncertainty in the geometric features of the pore network as well as the paucity of information on the dissolution and crystallization rates, compounded with the evolving composition and viscosity of the melt under the thermal gradient within the coating. Ideally, the reaction should be sufficiently rapid to overwhelm the flow dynamics, so the stiffened layer thickness is minimized. However, most oxides that exhibit the desirable reactivity also lack significant toughening mechanisms, so the reduction in penetration and the increase in strain energy are counteracted by a lower toughness. In essence, a coating with no effective mitigation mechanism but reasonable toughness, like 7YSZ, could in some instances resist thermal cycling induced delamination better than an oxide more resistant to penetration but with a lower toughness. Balancing these attributes represents a grand challenge in TBC design.

Penetration is generally not the critical issue in environmental barrier coatings (EBCs), which must be dense to perform effectively as barriers to the permeation of water vapor and, ideally, of oxygen. Consequently, EBCs are selected to minimize thermal expansion mismatch with the CMC substrate. This constraint limits the choice of materials, with rare earth silicates being favored in current systems. These silicates, however, are rapidly attacked by CMAS, especially by melts with higher Ca:Si ratios. While the recession of the EBC material is problematic in itself, the reaction with CMAS results in a layer of reaction products that is poorly matched thermally with the substrate. A source of substantial strain energy arises from this reaction layer, leading to the evolution of cracks that may delaminate the modified layer and/or the underlying EBC, but also penetrate into the bond coat and the CMC. This may expose the latter to environmental degradation of the fibers and the fiber/matrix interfaces that enable damage tolerance. The robustness of the system thus depends not only on the chemical reactivity of the CMAS/coating system but also on the toughness of the different layers, which are generally low. The grand challenge in EBCs is to approach prime reliance because CMCs are arguably less environmentally robust than current superalloys. At a minimum, this demands low reactivity with a relevant spectrum of CMAS compositions, and sufficient toughness to mitigate impact and/or thermo-mechanical damage.

This presentation will discuss the state of understanding of these challenges and the tools available to assess the response of the system and effectiveness of the CMAS mitigation approach against a spectrum of melt compositions. The insight is complemented by the presentation of Prof. Poerschke at this conference.

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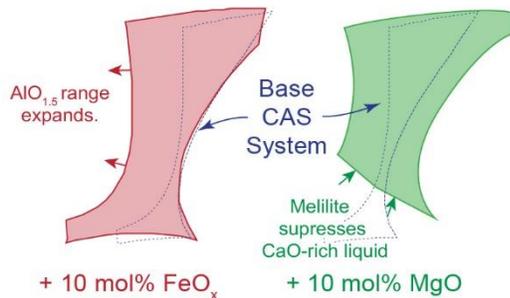
# APPLICATION OF PHASE EQUILIBRIUM MODELING TO UNDERSTAND AND MITIGATE THE CMAS THREAT IN THERMAL AND ENVIRONMENTAL BARRIER COATINGS

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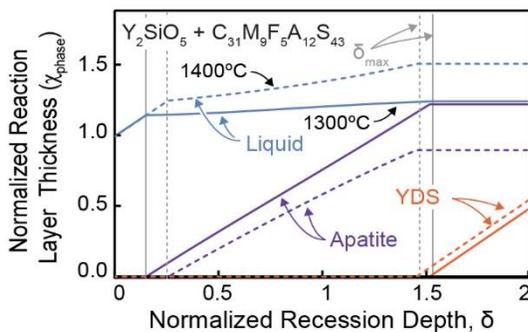
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Key Words: Thermal Barrier Coating (TBC), Environmental Barrier Coating (EBC), CMAS Degradation, Computational Thermodynamics Modeling

(a) Understanding Intrinsic Deposit Behavior



(b) Predicting EBC Recession Behavior



(c) Predicting TBC Crystallization Efficacy

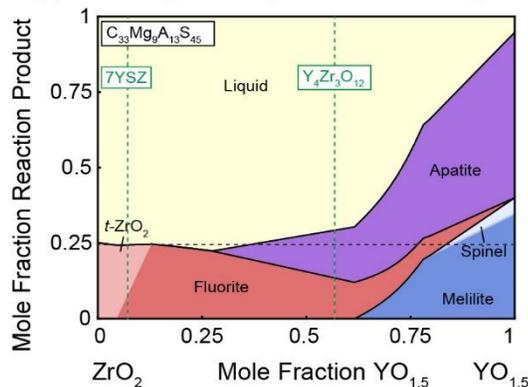


Figure 6 – The development of computational thermodynamics models seeks insight into (a) the intrinsic melting and crystallization behavior of the deposit itself, and the factors controlling (b) the recession of RE-silicate EBCs and (c) reactive crystallization in RE-zirconate TBCs.

The severity of thermal and environmental barrier coating (T/EBCs) degradation caused by molten silicate deposits (CMAS) is directly influenced by (i) the composition of the deposit, (ii) the component surface temperature and through-thickness gradient, and (iii) the composition of the coating material. Given the breadth of this parameter space, assessing the performance of even a single candidate coating material against all possible deposit compositions and thermal conditions is experimentally intractable. Instead, it is more efficient to develop computational thermodynamics models in order to select relevant conditions for testing and, ultimately, to guide the identification and selection of coating materials/architectures offering improved performance.

This presentation will describe efforts to develop robust thermodynamic models of the higher-order composition space (7+ components) relevant to the design of rare earth (RE)-containing T/EBCs. These efforts involve studying the detailed phase equilibria and crystal chemistry in key subsystems, validation of thermodynamic databases through targeted experiments in higher-order systems, and the development of modeling tools to predict compositional trends and reaction sequences.

The application of these tools will be demonstrated using case studies examining the reactions with RE-silicate EBC materials and RE-zirconate TBC materials in order to capture the variation in the compositional extent of melt-forming deposits due to the effects of temperature and composition variations on the extent of the molten region (Fig. 1 (a)). Because the recession of dense EBCs proceeds via progressive conversion of the coating into one or more reaction phases, it is useful to understand (and ultimately minimize) the thickness of the coating that will be consumed before the deposit is exhausted. In this context, parameterized models were developed to understand the evolution of stable reaction products as a function of EBC recession depth, and ultimately predict the maximum recession depth, e.g.,  $\delta_{max}$  in Fig. 1(b). Conversely, reactions with segmented TBCs ideally result in a rapid increase in the crystalline volume. Therefore, as illustrated in Fig. 1(c), the TBC modeling efforts aim to quantify the relative change in the crystalline volume and contributions from reprecipitation, extrinsic, and intrinsic crystallization pathways, on the due to variations in the deposit and coating composition. The results from these case studies offer insight into the factors controlling the crystallization reactions and provide guidance for the design of improved coating systems.

## CRITERION FOR DEVELOPMENT OF NOVEL CMAS/VA RESISTANT TBCS BASED ON MORPHOLOGY AND CHEMISTRY VARIATIONS

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**Key Words:** CMAS, EB-PVD 7YSZ, Microstructure modelling, Viscosity

The evolution of CMAS/VA resistant thermal barrier coatings (TBCs) has been the hot topic in the gas turbine industry and the inevitability is growing exponentially with the constantly increasing turbine inlet temperatures (TIT). Numerous research groups have acquired enormous amount of knowledge on the interactions of TBCs with CMAS, damage mechanisms and methods of analysing the CMAS attack. From all the current knowledge, most substantial parameters which define the CMAS/TBC interactions are shown schematically in Fig.1.

Chemical composition and microstructure are illustrated as highly influential parameters in case of CMAS/TBC interaction in Fig.1. Variation in the global CMAS/VA composition means difference in their melting points, viscosities, acidic/basic nature. Any developed novel TBC material will react differently to different CMAS/VA compositions and forms numerous reaction products which might bring a completely new effect in the end. In the presentation novel TBCs such as gadolinium zirconate, alumina and yttria rich zirconia coatings are introduced that were applied by means of EB-PVD method and their interactions with synthetic CMAS and natural volcanic ash was studied in detail. The reaction products heavily depend upon the CMAS chemistry and vary with respect to the crystallinity of the CMAS compound.

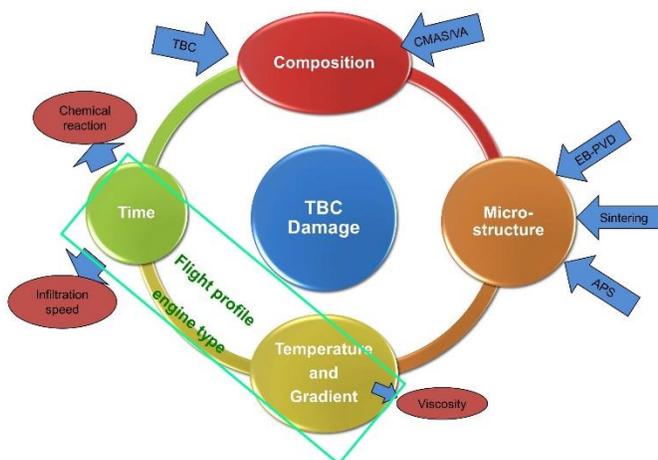
However, the TBC microstructure and the porosity define the kinetics of infiltration, reaction and hence play a vital role in hampering the CMAS infiltration. Two different coating methods electron beam physical vapour deposition (EB-PVD) and atmospheric plasma spray (APS) have entirely different microstructure and porosity network. Moreover, due to the contrastive porous geometries, the sintering of these ceramic coatings differs severely which would change the permeability of the coating. Temperature and time are other two important factors that define the melting process and reaction time for the CMAS and TBC to happen.

Two different EB-PVD microstructures were created and infiltration experiments were carried out at 1250°C and 1225°C for different time intervals. The 7YSZ coating with more 'feathery' features has resulted in higher CMAS resistance by at least by a factor of 2 than its less 'feathery' counterpart.

Moreover, these results are well supported by FEM simulations using ABAQUS and microstructural modifications where effects of feather arm lengths, inter-columnar gap width and feather inclinations on the infiltration kinetics are evaluated.

The experimental infiltration results were compared with theoretical infiltration estimations using a novel mathematical approach proposed in previous studies which assesses the permeability of the

coatings with two different methods called 'concentric pipe and open pipe models'. The infiltration depth was calculated using experimentally measured variables such as contact angle and viscosity. The theoretical and experimental results are in good agreement for CMAS infiltration confirming the validity of the physical model.



*Fig.7 – Schematic of influencing parameters on CMAS/TBC interaction*

## COMPUTATIONAL TOOL TO ACCELERATE CMAS-RESISTANT TBC DESIGN FOR AERO-TURBINE APPLICATIONS

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Key Words: CMAS, TBC design, CALPHAD, thermodynamics, ICME

Infiltration of molten Calcium-Magnesium Alumino-Silicate (CMAS) deposits is a primary cause of failure of thermal barrier coatings (TBCs) on aero-turbine engine blades. Cooling of infiltrated CMAS deposits leads to densification and subsequent cracking and delamination driven by internal strain energy due to the thermal mismatch between the solidified CMAS melt and the porous columnar TBC architecture. Infiltration kinetics, and thus onset of mechanical failure, are strongly affected by the thermodynamic properties of the CMAS melt (viscosity, melting point, etc.) and the crystalline reaction products formed due to the interaction between the CMAS melt and TBC material, which can block the channels in the TBC structure and inhibit further melt infiltration. Additional complexity is added due to the wide range of CMAS deposit compositions found in nature, which can lead to vastly disparate melt behavior and CMAS-TBC reactivity dependent on both deposit and coating composition.

A robust model to predict TBC failure and enable the design of novel CMAS-resistant TBC materials therefore relies on the ability to model CMAS melt properties and the reactivity between melt and coating. A computational design tool is currently under development to enable Integrated Computational Materials Engineering (ICME)-informed modeling of CMAS-TBC interaction and coating performance. This computational tool leverages Calculation of PHase Diagram (CALPHAD)-based thermodynamic databases which include the components of CMAS-Fe deposits as well as RE zirconate (RE=Y,Gd) TBC materials. A tool framework compatible with the Thermo-Calc software will allow for wide availability of the design tool across academic and industrial R&D communities. The tool enables TBC design by streamlining thermodynamic calculations related to CMAS melt properties and CMAS/TBC reactivity, feeding results into property and performance models. A CMAS selection module contains a compiled list of CMAS compositions while also allowing for user-defined compositions, allowing for quick assessment of CMAS melt properties across relevant deposit compositions and ranges. Efficient comparison of CMAS/TBC interactions can be performed across a large number of pre-defined or user-defined CMAS chemistries. CMAS reactivity may also be assessed across a range of RE/Zr ratios as well as compared between various RE systems. Examples of tool functionalities and relevant thermodynamic calculations will be presented. Future work includes integration with thermomechanical and kinetic infiltration models to predict TBC performance.

## MOLTEN VOLCANIC ASH DEPOSITION IN JET ENGINES

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Key Words: Volcanic ash, APS TBCs, EB-PVD TBCs, Deposition rate, Roughness

Safe air travel activity requires clean flight corridors. But in earth's atmosphere, volcanic ash is undoubtedly the major source to contaminate airspace by volcanic activity and thus present critical risks to aviation safety. A Jet engine is the central part to dominate the highest level of aviation safety but also the most vulnerable part by volcanic ash. The nature of volcanic ash damage to jet engines is the molten ash deposition on the hot-section airfoils in jet engines. These ash deposits can lead to the premature failure of the components in hot-section airfoils due to heat accumulation and, more importantly, can attack the protective ceramic thermal barrier coatings (TBCs). In a real jet engine, if few of the volcanic ash particles can adhere to the surface of hot-section airfoils and form an initial molten volcanic ash deposition layer, large ash deposition nodules (several cubic centimeters in volume) can quickly build up. Therefore, the formation of initial volcanic ash deposition layer plays a key role to mitigate the its detrimental effects on jet engines. However, constraining the initial formation process of volcanic ash deposition layer in jet engines is currently unknown due to harsh operation condition. Here, we present the formation process of initial volcanic ash deposition layer by applying the atmospheric plasma thermal spray technology to stimulate the 'in-flame generation' volcanic ash particles (from the 2010 eruption of Eyjafjallajökull volcano due to its potential hazard for current aircraft safety) with high-energy (e.g., temperature  $1833\text{ °C} \leq 2828\text{ °C}$ ; velocity  $146\text{ m s}^{-1} \leq 325\text{ m s}^{-1}$ ; and particles size  $\leq 62\text{ }\mu\text{m}$ ) to imping onto a solid substrate (Fig.1a). Subsequently, we quantitatively compared adhesive ability (i.e., deposition rate) of volcanic ash particles onto three categories of substrates (including traditional APS YSZ TBC, EB-PVD YSZ TBC and alumina substrate) under its increasing distance (50  $\leq$  125 mm) to nozzle. Finally, we analysed the formation mechanism of initial volcanic ash deposition layer. Our results demonstrate substrate characteristics (e.g., roughness,  $R_a$ ) and impact particle properties (represented by Reynold number) directly affect the adhesive ability of volcanic ash particle and subsequent layer formation. The deposition rate of volcanic ash particles decreased exponentially with increasing the distance with nozzle for all of substrates and also linearly decreasing with increasing the substrate surface roughness,  $R_a$  at each same distance to nozzle (Fig.1b). These observations indicate that volume density of particles and substrate surface roughness dramatically enhance the deposition rate of volcanic ash particles under plasma conditions. In addition, the final morphology of splats deposited by volcanic ash particles onto the different substrates were changed from disk-like to splash-like as decreased in roughness (Fig.1c). Overall, these observations and models offer important insights into the initial formation of molten volcanic ash layer for the tailoring of next-generation APS and EB-PVD TBCs that will be required to resist attack by volcanic ash in future higher-temperature jet engines.

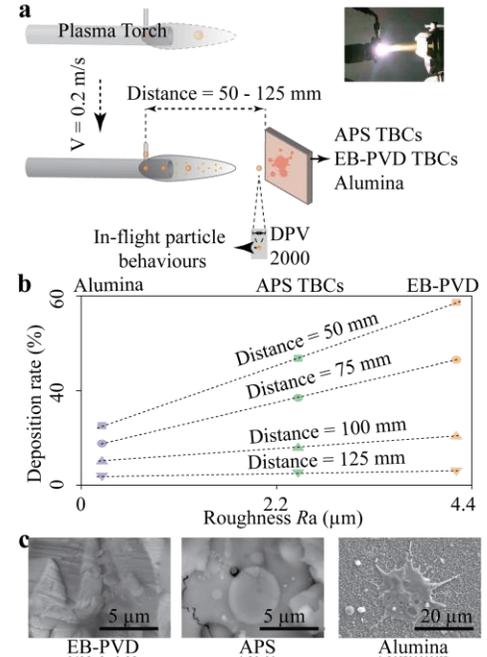


Figure 1. (a) A schematic of the experimental setup for capturing initial formation of molten volcanic ash layer under plasma spray conditions. (b) Roughness-deposition rate relationship for EB-PVD TBCs, APS TBCs and alumina substrate under different distance to nozzle, (c) The morphology of splats onto various substrates.

## ROLE OF MICROSTRUCTURE GEOMETRY AND CMAS VISCOSITY IN CMAS INFILTRATION

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Abstract-The most successful strategy to date to reduce the harmful effect of CMAS on TBC is by dissolution of elements from the TBC that form a blocking phase such as apatite in the case of gadolinium zirconate. Clearly there is a kinetic race of infiltration rate vs. rate of formation of the blocking phase. This race is influenced by CMAS viscosity, crack widths, availability lateral flow paths in addition to through thickness paths of and other factors influencing the dissolution rate of the TBC elements needed to produce the blocking phase. This behavior has been studied experimentally using interrupted tests and deliberate alterations of the microstructural geometry via both powder and solution precursor plasmas spray in two systems, gadolinium zirconate and yttrium aluminum garnet. In addition by changes in CMAS composition, viscosity was also strongly altered. Viscosity of several CMAS compositions was also measured in a high temperature viscometer. Results begin to provide a semi quantitative understanding of the factors involved. From a practical point of view it becomes clear that there is a critical size of through thickness crack that completely defeats this arrest mechanism and that this crack size is in the range of single digit microns or smaller. It is also clear that CMAS viscosity that is not an engineered quantity has important effects that will be difficult to predict in practice given the uncontrolled nature of CMAS composition.

## CMAS INTERACTION WITH YTTRIUM BASED SYSTEMS: TOWARDS A PROMISING SOLUTION?

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Key Words: CMAS, Ytria, Yttrium Zirconate, Gadolinium Zirconate, Reactivity

Anti-CMAS coatings are designed to protect thermal barrier coatings against degradations due to CMAS infiltration. They are dedicated to react as fast as possible with CMAS compounds in order to generate a new phase that will not let the CMAS infiltration going on. In addition to the fast kinetics, the preparation of large quantities of phases with as less as anti-CMAS material as possible is sought as well as the obtaining of a dense and impermeable phase. Reference anti-CMAS material is gadolinium zirconate, it has been demonstrated as efficient to block CMAS infiltration. The efficiency of yttria for the same application has been studied by previous works at the CIRIMAT laboratory [1]. The starting point of this work was first, to make a comparative study of the anti-CMAS properties of gadolinium zirconate and yttria based anti-CMAS compositions and secondly, to discuss on the behaviour of a mixed composition i.e. yttrium zirconate. This insight on the mechanism of interactions of CMAS with the yttrium based systems and gadolinium reference is obtained at the light of a large number of interactions experiments and characterizations. Interaction durations between 1h and 100h were investigated, with either 50/50 or 80/20 mass ratio of CMAS/anti-CMAS. Different temperatures of interaction between 1200°C to 1300°C were also scanned. The phases in presence were systematically characterized by XRD, SEM, EDX and Castaing microprobe local analyses and cartographies (Figure 1a)). In particular, the proportion and composition of phases are detailed as a function of the interaction time (Figure 1b) for each anti-CMAS-CMAS interaction system. From these experiments, the mechanisms of interaction between CMAS and  $Y_2O_3$ ,  $Y_2Zr_2O_7$  and  $Gd_2Zr_2O_7$  are evidenced. Whereas  $Y_2O_3$  interaction leads to the higher proportion of reaction products, the products impermeability is also superior for this composition. The depth of infiltration of CMAS into a dense pellet anti-CMAS material for a given time is longer for  $Y_2Zr_2O_7$  as compared to the two others. However  $Y_2Zr_2O_7$  benefit is due to a higher  $Ca^{2+}$  trapping capability with the formation of  $Ca_4Y_6$  like phase instead of  $Ca_2Y_8$  for  $Y_2O_3$  (Figure 1c)). In this respect, yttrium zirconate demonstrates a synergetic effect as compared to  $Y_2O_3$  and  $Gd_2Zr_2O_7$ . The origin of this synergy is interpreted as coming from the presence of both zirconium and yttrium. A large part of the discussion is based on the study of powders interactions, an insight into the interactions of CMAS with anti-CMAS pellets of the different compositions will also be presented and discussed. Fundamental and applicative aspects will be covered.

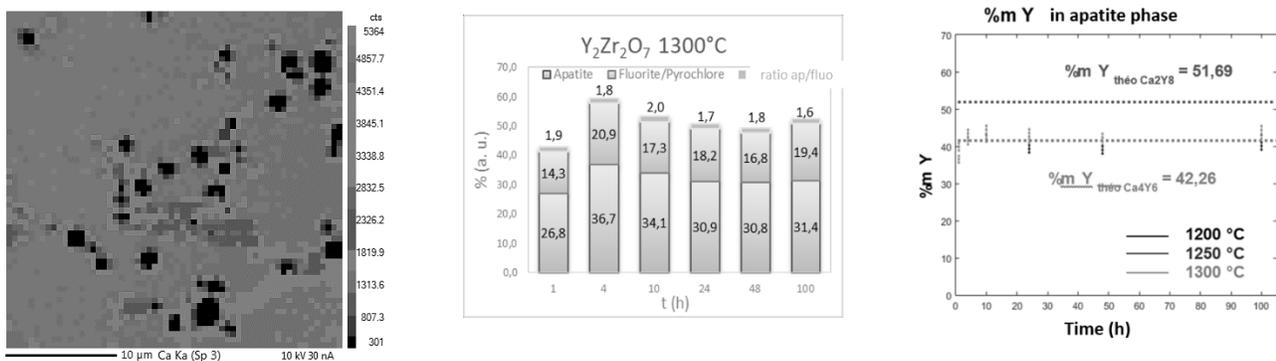


Figure 8 – a)  $Ca^{2+}$  element mapping by Castaing microprobe for  $Y_2Zr_2O_7$  powder after 1h interaction with model CMAS at 1300°C b) Surface repartition of apatite and fluorite phases for  $Y_2Zr_2O_7$  in interaction with the model CMAS for interaction times from 1h to 100h at 1300°C, c) Mass ratio of yttrium in the apatite phase as a function of the interaction time between  $Y_2Zr_2O_7$  and the model CMAS, the theoretical limits of mass ratio corresponding to  $Ca_2Y_8$  and  $Ca_4Y_6$  phases are given.

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# NOVEL THERMAL BARRIER COATINGS RESISTANT TO MOLTEN VOLCANIC ASH WETTING

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Molten environmental deposits primarily emanating from volcanic ash pose a serious threat to aviation safety. When ingested into a jet engine, the volcanic ash melts and adheres to the surface of hot regions (i.e., combustion chamber, turbine blade, and nozzle guide vanes) of jet engines. Virtually, these hot zones in jet engines comprise a two-layer thermal barrier coating (TBCs). These ceramic TBCs provide thermal insulation to the underlying nickel-based super alloy substrate, but these coatings are more vulnerable to the damage caused by molten volcanic ash deposits. Particularly, in the pursuit of high output efficiency, turbine operating temperatures increasingly exceed 1250°C, leading to detrimental effects on the TBCs. Introducing rare-earth oxides (eg. Gadolinium oxide) into TBCs is regarded as one of the main migratory approach to prevent the damage by ash, because the infiltration silica-rich molten volcanic ash deposit is slowed down by crystallising the melt, preventing deeper infiltration into the coating. However, the initial phase of the damage progression of volcanic ash into the porous texture of TBC has become unavoidable. Here, we utilised thermal spray technology to produce a novel thermal barrier coating consisting of the mixture of the hexagonal boron nitride (*h*-BN, 30 vol.%) and yttria stabilized zirconia (YSZ, 70 vol. %) (BN-YSZ coating).

Subsequently, we quantitatively analysed the wettability of three different types of volcanic ashes (Figure 1a) onto this new TBCs, compared with the traditional YSZ TBCs produced by atmospheric plasma spray (APS), using an optical dilatometer at 1250°C (Figure 1.b) in vacuum condition and dynamic spreading process in air condition. Our results indicate that the BN-YSZ coating (Figure 1.c) exhibits non-wetting ability with mean contact angles ranging from 92°-150° (figure 1.d), compared with the APS YSZ TBC coatings on which the ash was complete spread, for a period between 300-400 seconds in vacuum condition. Because *h*-BN are easily oxidised in atmosphere and are not stable, the contact angle of the BN-YSZ TBCs gradually decreased once the working environment in the dilatometer was brought to atmospheric condition. Therefore, the degradation of the TBCs are strongly dependent on the wetting nature of the molten volcanic ash. A solution to the mitigation of the molten environmental deposits without damaging the TBCs still remains elusive. This work not only elucidates the difference between BN-YSZ and YSZ coatings but also enables the development of novel materials for the next generation of TBCs.

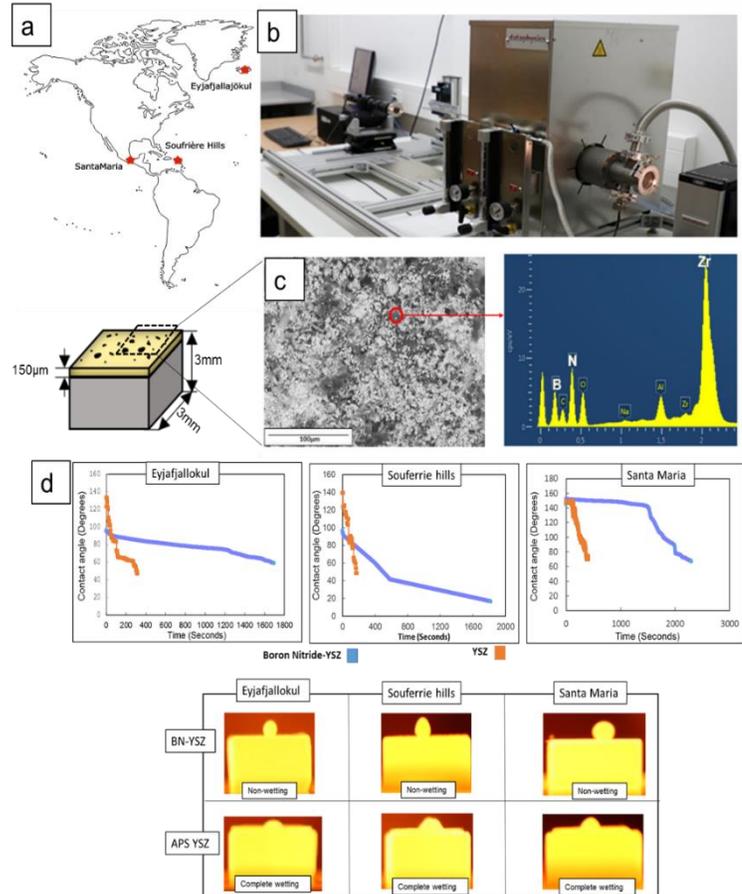


Figure 9. (a) Selection of volcanic ash for this research, (b) Optical dilatometer setup, (c) Surface morphology of BN-YSZ coatings, (d) Contact angle of the molten ash on BN-YSZ and YSZ coatings plotted against time.

## INVESTIGATION OF EROSION BEHAVIOR OF EB-PVD-TBCs AND SACRIFICIAL COATINGS AFTER CMAS INFILTRATION

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Key Words: Sacrificial coating, EB-PVD, Suspension thermal spraying, Erosion, CMAS

Aero-engines operating in sand laden environments often encounter severe problems with thermal barrier coatings (TBCs) due to erosion damage. Since the turbine entry temperatures are raising, the life-time of TBC coatings as well as its thermal conductivity are additionally influenced by molten sand (calcium-magnesium-alumino-silicate/ CMAS). Few attempts have been made in understanding the combined impact of both erosion and CMAS effects [1,2]. Wellman and Nicholls [1] have found that a fully CMAS infiltrated electron-beam physical vapor deposited (EB-PVD) TBC behaves like a continuum during erosion and slightly improves its erosion behavior under room temperature compared to pure TBC. Development of CMAS resistant coatings has been a hot topic for the last two decades and one of the proposed method is the application of sacrificial oxide layers such as  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{Sc}_2\text{O}_3$  et al. [3], on top of the TBCs. These sacrificial layers chemically react with the CMAS and modify the melting temperature or the viscosity of CMAS and thus the infiltration of CMAS into the TBC is inhibited.

Since both damage mechanisms (erosion and corrosion) occur parallel and competitively in a turbine, this study focuses on deeper understanding of the erosion behavior of CMAS-infiltrated 7wt.-% yttria stabilized zirconia (7YSZ) TBCs. 400  $\mu\text{m}$  thick 7YSZ coatings with two different microstructures were produced by EB-PVD. Additionally, sacrificial  $\text{Al}_2\text{O}_3$  coatings were also applied on the top of 7YSZ by means of suspension plasma spraying (SPS) and suspension high velocity oxy-fuel spraying (SHVOF) using water-based suspensions. CMAS infiltration experiments were carried out at 1250 °C using different CMAS compositions and different infiltration times. Erosion tests were realized at room temperature in an in-house erosion test rig and evaluated partly by confocal microscopy. Microstructural examinations as well as crack identification before and after testing were carried out using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX).

Infiltrated TBCs behaved as a continuum material during erosion exposure which lead mainly to surface spallation. Furthermore, the CMAS infiltration in the TBCs and partly the sintering effect at 1250 °C lead to a network of vertical cracks. These vertical cracks are weak areas where severe erosion occurs. The different TBC microstructures, infiltration times and CMAS compositions strongly influence the erosion behavior of the TBC. In case of alumina top coats the microstructure and especially the presence of porosity in the coating has strongly influenced the CMAS infiltration depth, the erosion behavior, and the stability of the entire coating system.

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# INTERFACIAL TOUGHNESS EVOLUTION UNDER THERMAL CYCLING BY LASER SHOCK AND MECHANICAL TESTING OF AN EB-PVD COATING SYSTEM

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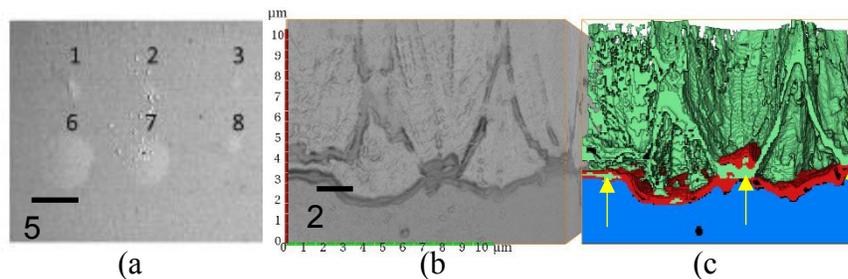
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Key Words: LASAT, FIB, EB-PVD, Fracture Mechanics

One of the major challenges for coatings on superalloys is to keep adherence during aging, where damage is mostly driven by thermal cycling. On the other hand, the methodology of the evaluation of the interfacial toughness should be consistent with in service loading. Recently, the use of LASer Shock Adhesion Test (LASAT) has shown its capability for both ranking different coating solutions and evaluating the evolution of a given coating as a function of aging [1-2]. The intent of this paper is to demonstrate the ability of LASAT to reproduce damage mechanisms observed under quasi-static in plane mechanical testing and to propose a general methodology to assess interfacial toughness evolution based on LASAT measurements. The material chosen in this study is a partially  $Y_2O_3$  stabilized EB-PVD zirconia layer coating deposited by Electron Beam – Physical Vapor Deposition (EB-PVD) onto a first generation Ni base superalloy. Aging has been performed using thermal cycling under laboratory air. Degradation of the coating system due to ageing is quantitatively assessed by LASAT and accompanied by different microstructural analysis methods. For LASAT, if laser flux is below a threshold, no delamination occurs. When increasing laser flux above this threshold, a systematic sequence is observed: i) delamination without buckling of the ceramic layer, ii) delamination and buckling, iii) partial cracking of the ceramic layer, and iv) spallation [1-2]. These different states are also achieved in compressive quasi-static testing and assessed by means of local strain measurement using digital image correlation technique [3]. Aging is evaluated through the evolution of both the delamination and the buckling behavior induced by the LASAT method or critical strain at ceramic spallation under compressive static load.



*Specimen after LASAT (a) top-view evidencing the contrast induced by debonding (b) FIB slice in BSE mode and (c) segmented image : bond-coat in blue, TGO in red, gaps between columns and crack in green and yellow arrows indicating micro-cracks within, below and above the oxide layer, TBC transparent*

The LASAT has shown to introduce very low scatter in delamination/buckling results when laser flux is low enough to avoid any cracking within the ceramic layer [2]. Thus, we choose to determine interfacial toughness from the specimen after LASAT leading to buckling without ceramic cracking. To determine the interfacial toughness between the ceramic layer and the substrate, a large variety of experimental techniques has been employed, including light profilometer, photoluminescence piezo-spectroscopy, infra-red imaging and image analysis. All these techniques enable to determine the precise 3D morphology of the ceramic blister obtained after LASAT and the size of interfacial crack. Further, mechanical elastic analysis of the blister shape is used to calculate the toughness of an interfacial crack at arrest as well as the residual stresses. At last but not least, 3D shape of the crack tip is measured by FIB and slice tomography to validate the size of the process zone and to determine the range of error including the global chain of measurements to the final evaluation of interfacial toughness.

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## THE INFLUENCE OF THERMAL TRANSIENT RATES ON TBC SPALLATION

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During rapid engine throttling operations, turbine airfoils can experience very rapid heating and cooling. These rapid transient events lead to the generation of very high thermal gradients, and consequently, larger non-uniform stress distribution through the thermal barrier coating (TBC) and substrate, which in turn leads to faster coating spallation. To study this phenomenon, a burner rig was designed and built to test coupons under these rapid transient thermal conditions. Coupons were tested to failure under different transient rates. The tests were also simulated using coupled aerothermal CFD and the thermal profiles were matched to the experiment. A fracture mechanics model was also developed to calculate energy release rates under these transient thermal loading. Rationalization of TBC spallation models reported in the literature and our own finite element model with experimental results was done. The details of the experimental set-up, coupon test results, and model correlation with test results will be presented.

## EXPERIMENTAL MEASUREMENTS OF THERMAL BARRIER COATING INTERFACIAL FRACTURE TOUGHNESS AS A FUNCTION OF MODE-MIX

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Key Words: TBC, delamination, interfacial toughness, mode-mix.

Mechanism-based lifetime assessment models of thermal barrier coating (TBC) systems rely on accurate knowledge of the experimentally measured interfacial fracture toughness over a range of mode mix and especially at mode II. Previously, no reliable test method had been employed to evaluate these properties under pure mode II conditions, which are most representative of critical TBC spall delamination upon turbine engine cool down. We have used conventional 4-point bend experiments and a newly developed compression edge-delamination (CED) methodology to make direct measurements of coating interfacial toughness as a function of mode mix. The material system examined was provided by collaborators at GE and consists of an Electron-Beam Physical Vapor Deposited (EBPVD) 7% Ytria-Stabilized Zirconia (YSZ) top coat, which is deposited on a Pt-modified diffusion aluminide  $\beta$ -(Ni,Pt)Al bond coat on a single crystal René N5 substrate. CED tests showed that thermal cycling caused a 50% reduction in mode II interfacial toughness. Results for as-deposited samples tested using a modified 4-point bend technique match previously reported data, and a toughness function for the as-deposited interfacial toughness vs. mode mix has been developed using results from this study and from previously reported values. Crack face friction has also shown to play a profound role in calculation of the interfacial toughness, and details regarding the characterization and implementation into the finite element model used to extract the interfacial toughness will be examined. Finally, microstructural observations, including morphological and chemical changes, linked to the degradation of the coating interfaces due to thermal cycling will be analyzed.

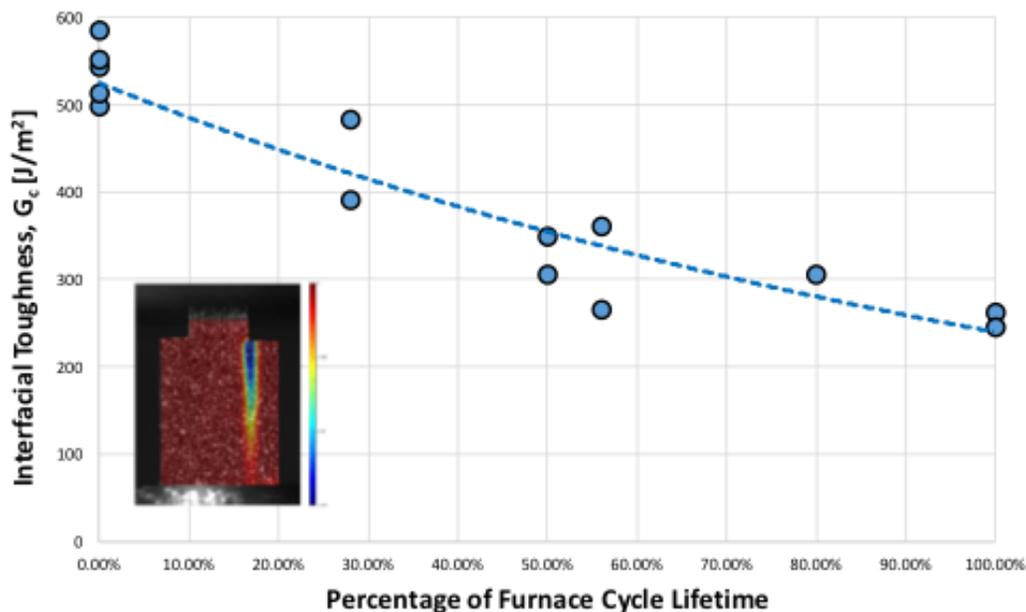


Figure 10 – Mode-II interfacial fracture toughness of an EBPVD 7%YSZ topcoat on a Pt-modified diffusion aluminide bond coat on a single crystalline René N5 substrate measured as function of furnace cycle lifetime.

## FAILURE BEHAVIOR OF MODERN DOUBLE-LAYER THERMAL BARRIER COATINGS SUBJECTED TO COMPRESSION TESTS

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Key Words: gadolinium zirconate, double-layer, thermal barrier coating, acoustic emission, digital image correlation

Demands for reduced emissions and higher efficiency of stationary gas turbines and jet engines lead to the necessity for increased operating temperatures. Therefore, thermal barrier coating (TBC) systems deposited to high-temperature impinged parts, e.g. turbine blades and vanes, as well as combustor liners, containing an yttria-stabilized zirconia (YSZ) top layer are well established. Currently, surface temperatures of YSZ coated turbine parts are limited to approximately 1250 °C in long-term operation, due to the rapid degradation of YSZ caused by sintering and phase instability. Double-layer TBC based on gadolinium zirconate (GZO) applied on top of a 7 to 8 wt. % YSZ layer seem to be proper candidates for advanced coating architectures to withstand temperatures up to 1550 °C. The present work investigates the failure behavior and fracture process of double-layer thermal barrier coatings under uniaxial compressive loading conditions. Coating systems of type GZO and YSZ with low and high GZO porosity (LP, HP) were fabricated, to examine the influence of microstructure and spray process parameter on failure behavior and compressive strain energy. A conventional YSZ-HP single-layer coating serves as a reference. All systems were deposited via atmospheric plasma spraying (APS) on cylindrical rods made from CoNiCrAlY (LCO-22) coated, nickel-based, single crystal superalloy (PWA 1483). The total thickness of ceramic layers was about 600 µm. Effects of thermal ageing were taken into account by isothermal pre-oxidation at 1050 °C and dwell-times of 100, 500 and 1.500 hours and compared to cyclic annealed TBC systems (50 to 1050 °C, up to 500 cycles). Failure and cracking processes during compression tests were monitored by an acoustic emission (AE) system and piezo-electric, wideband sensors. Furthermore, a stereo camera system provides information about three-dimensional displacements and TBC surface strain. In as-sprayed condition, the stored volume related strain energy to failure of double-layer coatings is comparable to the referenced single-layer system. AE analysis indicates coating failure at earlier stages after thermal ageing. Consequently, pre-oxidation leads to reduced strain energies with increasing dwell-time in all investigated coating systems. Based on digital image correlations (DIC), the failure behavior of as-sprayed GZO/YSZ coatings has been identified to be similar to the YSZ single-layer system. A different behavior was observed for pre-oxidized coatings, where cracking and spallation of GZO occurs predominantly.

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## THE INFLUENCE OF HEATING AND COOLING RATES ON TBC FAILURE IN HIGH HEAT FLUX TESTS

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Key Words: TBC failure, high heat flux testing, fracture mechanics

High heat flux testing is a commonly used procedure to investigate TBC failure modes. Samples of TBC on superalloy are thermally cycled, with the TBC being heated and the superalloy subjected to forced cooling in order to induce a temperature gradient. Typically conditions are deliberately chosen to be more aggressive than in the engine in order to induce TBC delamination or complete spallation within a few days. We have developed a test bench with a CO<sub>2</sub> laser as the heat source which, unlike the more commonly used burner rigs, allows exquisite control of the heating and cooling rates. An optical system detects the hot spots which are caused by TBC delamination. We experimentally validate a two-phase model for TBC failure. In Phase I a vertical crack is driven from the TBC surface down towards the bond coat, which requires a sufficiently high cooling rate. This acts as a starting defect for Phase II, in which a horizontal crack propagates and causes delamination / spallation, which requires a sufficiently high heating rate. In general, we find that heating and cooling rates are a more useful tool to probe TBC robustness than surface temperature or number of thermal cycles.

## THERMALLY SPRAYED PROTECTIVE COATINGS UNDER DEMANDING LOAD CONDITIONS

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Key Words: thermal barrier coatings, flexible operation, thermo-cyclic testing, lifetime

Materials in turbines are facing increasingly demanding conditions under operation. This is due to their diversifying field of application as e.g. in interplay with renewable energy sources. Each set of loading conditions, in terms of e.g. operation temperature, start/stop-frequency or contaminants present in the combustion atmosphere, shows a specific footprint of degradation pathways. Understanding and performance data are available for many individual degradation footprints as to date materials and coatings are developed in respect to each one of that kind of loading scenarios. Less often, materials are assessed at a wider range of conditions where changes and interplay of degradation modes can be observed.

Today's demand for design of material systems for flexible or volatile conditions of operation requires to consider the wider range of operation regimes including complex sequences of loading phases adding up to the overall degradation. Performance and degradation modes of APS TBC systems (both single layer YSZ as well as a double layer of YSZ plus  $Gd_2Zr_2O_7$ ) were studied under various conditions in cyclic testing. This includes scenarios with isothermal and gradient testing as well as sequential vs simultaneous loading with CMAS. Results are evaluated with respect to changes of (coexisting) degradation modes and spallation lifetime. Applicability of some modeling tools is discussed for lifetime prediction.

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## VIRTUAL TESTING AND DESIGN OF BARRIER COATING SYSTEMS

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Key Words: delamination, kinking, CMAS, failure maps.

The development of coating systems for high temperatures has two central challenges: (i) the selection of materials and layer architectures that are resistant to cracking and chemical attack, and (ii) the identification of active failure mechanisms and their dependency on the system's intrinsic properties. This talk will describe two modeling frameworks that are tailored to meet these challenges. In the first framework, an automated system for analyzing delamination and mud-cracking in complex multilayers; this enables system developers to consider a broad range of materials and architectures and in turn rapidly identify promising material systems. The impact of CMAS penetration on coating reliability will be briefly discussed to illustrate potential applications of the framework. In the second framework, distributed cohesive zone models are used to develop a virtual testing framework: the framework is capable of predicting a broad range of cracking modes without a priori assumptions regarding the evolution of damage. The simulation framework exploits highly parallel computing approaches that enable simulations covering a broad range of parameter space; this enables the construction of "durability regime maps", which indicate likely failure mechanisms as a function of material properties. Simulations will be presented illustrating the transition between crack penetration, kinking and delamination; the results demonstrate that crack kinking can occur even in the absence of a putative kink crack, and that in certain situations, cohesive strength plays a critical role in governing brittle failure modes (i.e. the relative toughness of the constituents alone is insufficient). The implications of these simulations for developing tough, CMAS resistant coatings will be discussed, with a particular focus on the role of microstructure in ceramic coatings.

## LIFETIME EVALUATION OF VARIOUS EB-PVD And APS TBCs IN THERMAL GRADIENT AND FCT UNDER THE ATTACK OF CMAS AND VOLCANIC ASH

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Key Words: CMAS, volcanic ash, lifetime, thermal gradient testing

Thermal barrier coatings (TBCs) are applied to increase lifetime and efficiency of highly loaded turbine components. Degradation of those coatings by volcanic ash (VA) and calcium-magnesium-alumino-silicate (CMAS) deposits is now recognized as an increasingly important fundamental degradation mechanism. The presentation attempts to quantify the damage and reduction in lifetime resulting from infiltration of TBCs by deposits. Comparing TBCs deposited by either electron-beam physical vapor deposition (EB-PVD) or air plasma spraying, the 7YSZ gets infiltrated in both versions at a comparable rate. Depending on the applied experimental condition such as CMAS composition, temperature, and time, the infiltration depth varies in different TBC morphologies.

Upon thermal cycling the infiltration causes severe mechanical stresses within the TBC, subsequently leading to crack formation and TBC spallation. Most of the life time assessment tests so far were conducted under isothermal conditions which generally does not represent real engine atmospheres. In this presentation a combined approach utilizing thermal gradient test rig and furnace cyclic testing has been used to study the TBC life time behavior under the influence of CMAS and volcanic ash. EB-PVD 7YSZ coatings on Ni-based superalloys protected by a NiCoCrAlY bond coat were infiltrated with CMAS and subsequently tested under isothermal and thermal gradient conditions. The CMAS infiltration depth has a direct impact on the life time of the coatings. Full infiltration leads to a life time reduction up to 90% compared to a non-infiltrated coating while the life time of a half infiltrated coating is reduced by approximately one third. Spallation occurs at the interface between infiltrated and un-infiltrated regions. This failure location is associated with local stress peaks arising from the infiltration.

New topcoat compositions such as Gadolinium zirconate (GZO) that mitigate damage by deposits were investigated as well. The presentation provides results on several new TBCs, especially on their behavior under the influence of deposits and under thermo-cyclic loading. The interaction of the coatings with volcanic ash and with CMAS was investigated at temperatures between 1200 °C and 1250 °C using several compositions of the deposits. The pyrochlore TBCs rapidly form crystalline phases which provides a potential for damage mitigation. The new topcoats were investigated as single and double layers in comparison to standard 7YSZ coatings. In the double-layered TBC systems, a thin layer (~25 to 30µm) of 7YSZ was used between the new topcoat material and the bond coat. All new coatings were deposited by EB-PVD. Special emphasis was put on the engineering of the interface between both layers that was systematically varied. Selected TBCs were tested in FCT at 1100°C. Both single and double-layered GZO have shown longer lifetimes than the standard YSZ samples. Changes in microstructure, growth of the TGO layer, and diffusion of elements are discussed. Finally, a more realistic test scenario is introduced by using a small-scale micro gas turbine that burns kerosene. A volcanic ash test stand has been built with a precise particle feeder, a concentration measuring unit and a full TBC system on the blisk of the turbine. This setup allows testing of melting, sticking, corrosion, and erosion behavior of volcanic ash in-situ at high temperature in a realistic manner in a gas turbine. Both 7YSZ and GZO TBC have been investigated showing distinct differences in erosion resistance.

**REAL WORLD DRIVERS TO THE DURABILITY OF COATING & MATERIAL SYSTEMS IN GAS TURBINES**

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## T-EBC COATING SYSTEM FAILURE MODES

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Key Words: Thermal barrier coatings, environmental barrier coatings, air plasma spray, electron beam deposition.

The failure modes during steam cycling between 110 ° and 1316°C of silicon-ytterbium silicate EBC systems applied to silicon carbide substrates have been investigated. Premature delamination failure at silicon-ytterbium monosilicate (YbMS) interfaces is shown to result from thermal expansion mismatch driven channel cracking of the YbMS layer. These coating penetrating cracks enabled water vapor and oxygen to reach the silicon bond coat layer outer surface from the start of the thermal cycling process, and resulted in the rapid growth of an upper (b-phase) cristobalite thermally grown oxide (TGO) layer on the silicon surface. This silica layer suffered rapid edge erosion followed by thermal contraction mismatch induced delamination crack extension from the edge of the samples during cooling. Replacement of the steam erosion resistant monosilicate by its disilicate counterpart eliminated the channel crack oxidizer pathways to the silicon surface and delayed the growth of the silica TGO. The eventual failure of this coating architecture was governed by the development of a significant delamination driving force at the silicon - ytterbium disilicate interface as the TGO thickness exceeded ~5 mm. Coating failure life was then governed by the rate of permeation of oxidants through the ytterbium disilicate and by the very large thermal stresses developed during the upper to lower cristobalite transformation. Interestingly, the oxidant permeation is likely to increase during prolonged cycling as the diffusion barrier disilicate layer thickness was decreased by steam erosion. Preliminary results from investigations of several concepts for extending the coating system life will be described. One sought to utilize a thermal barrier coating to reduce the EBC temperature and water vapor flow rate at the ytterbium disilicate outer surface. A second has investigated the use of thin hafnia layers applied to the silicon bond coat outer surface to induce the formation of a composite silica/hafnium silicate TGO to reduce the thermal strain energy for delamination.

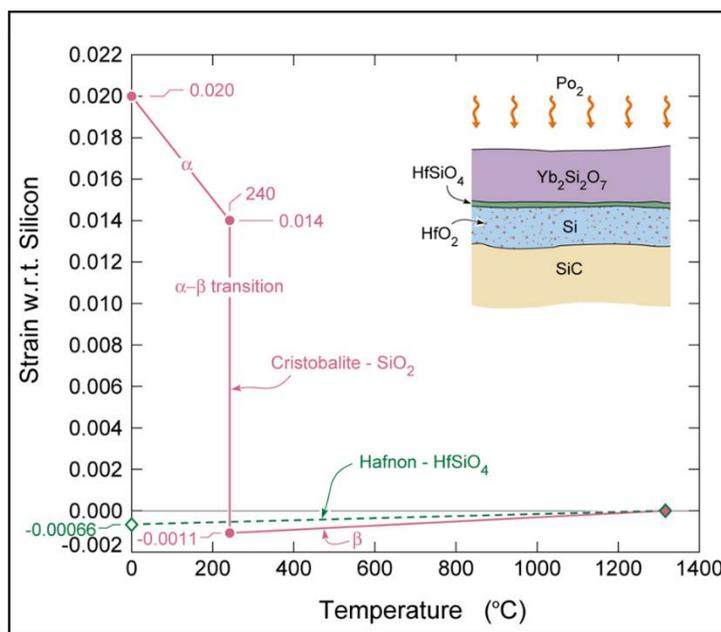


Figure 11 – Thermal expansion mismatch strain as a function of temperature during the cooling of a ytterbium disilicate – silicon EBC in which either a  $\beta$ -cristobalite or a hafnium silicate TGO had formed on the silicon bond coat.

## INTERFACE TOUGHNESS MEASUREMENT OF ENVIRONMENTAL BARRIER COATINGS FOR SiC/SiC COMPOSITES

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Key Words: Environmental barrier coating, Interface toughness, testing method

A simple interface fracture test for ceramics coatings on ceramics matrix composites was developed. A kind of asymmetric double cantilever beam (ADCB) test was proposed so that the interface fracture toughness could be measured by a small and simple-shape specimen without applying inter-laminar shear or tensile loading to CMC substrate. The proposed test was applied to a classic environmental barrier coating (EBC) consisting of mullite layer and Si bond coat on monolithic SiC substrate. A small block specimen of  $\sim 3 \times 4 \times 3$  mm was cut from the coated substrate, and a notch was machined along the interface. The notch was opened by inserting a wedge to the notch; the notch opening displacement at the notch root was measured. From the critical notch opening displacement and load where the crack starts to propagate, interface fracture toughness was calculated.

Several studies have reported that the reaction product is formed at the interface of various multilayer EBC systems with a Si bond coat, and the reaction product may cause the degradation of interface adhesion. To investigate the effect of such reaction products, the test was also applied to the heat-exposed EBC. The interface toughness after the heating was measured as a function of exposure time. The interface toughness varied with exposure time. Formation of a reaction products was observed at the interface during the heating; they grew with exposure time. The variation of the toughness was discussed based on the interface observation and was correlated to the interface reaction products.

# **THERMAL SPRAY PROCESSING ROUTES FOR ENVIRONMENTAL BARRIER COATINGS**

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## TOWARDS MULTIFUNCTIONAL THERMAL- AND ENVIRONMENTAL-BARRIER COATINGS

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Key Words: TBCs; EBCs; CMAS; mechanical properties; thermal properties

Gas-turbine engines are ubiquitous in aircraft propulsion, and land-based ones are used to generate ~20% of world's electricity. Ceramic thermal barrier coatings (TBCs) are used to insulate and protect hot-section metallic components in these gas-turbine engines. However, the higher temperatures and extreme conditions in high-efficiency engines are making TBCs prone to deposition of undesirable silicates ingested by the engines, engendering new materials issues that are becoming critical for the development of more efficient engines. The undesirable silicates (calcium-magnesium-alumino-silicate glass or CMAS) can be in the form of sand and volcanic ash in the case of aircraft engines, and coal fly ash in the case of syngas-fired engines used for electricity generation. The understanding of mechanisms by which molten CMAS deposits damage conventional yttria-stabilized zirconia TBCs is presented. Demonstration and understanding of approaches to mitigate this type of CMAS-induced damage in new TBCs are also presented, together with a discussion of guidelines for the development of new TBCs. However, state-of-the-art TBC-coated metallic components may not have the necessary high-temperature capabilities required for the next-generation engines with even higher operating temperatures and more demanding efficiency standards. In this context, ceramic-matrix composites (CMCs), combined with environmental barrier coatings (EBCs), are being implemented in gas-turbine engines. But the CMAS issue will need to be addressed in the context of EBCs-coated CMCs. Strategies for CMAS-attack mitigation of EBCs, which are different from those used in TBCs, are discussed and demonstrated. Finally, new concepts in CMAS-resistant T/EBCs that combine the thermal-barrier and environmental-barrier functions are discussed and demonstrated.

## ENVIRONMENTAL BARRIER COATINGS FOR SiC/SiC AND OX/OX CMCs

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Key Words: Environmental barrier coatings, ceramic matrix composite, thermal spray deposition, water vapor recession

Environmental barrier coatings (EBCs) are being developed for next-generation gas turbine engines to protect hot-section SiC/SiC or Ox/Ox (alumina-based) ceramic matrix composite (CMC) components in the harsh operating environments. In this paper, high-velocity water vapor recession ( $v=100\text{m/s}$ ,  $P_{\text{O}_2}=0.15\text{atm}$   $T=1200^\circ\text{C}$ ) and thermal gradient cycling behavior ( $T_{\text{surface}}=1250^\circ\text{C}$ ) of thermally sprayed  $\text{Yb}_2\text{Si}_2\text{O}_7/\text{Si}$  EBCs on SiC using different processing conditions will be presented. Phase composition and microstructural changes in the coatings prior and after the tests will be examined.

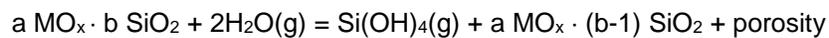
Furthermore, the potential of different (Yb, Sc)-zirconate and hafnate compositions with high melting points as EBC materials will be discussed based on their investigated bulk properties. Characteristics of the solid-state synthesized materials, which were high energy ball milled into submicron particle sizes and subsequently densified with field assisted sintering technology (FAST), such as phase stability (HT-XRD), thermophysical (dilatometry, thermal diffusivity) and mechanical properties (hardness, indentation fracture toughness) will be demonstrated.

# MICROSTRUCTURAL EVOLUTION OF ENVIRONMENTAL BARRIER COATINGS IN HIGH-TEMPERATURE STEAM

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Key Words: EBC, steam, porosity, faceting, sintering

Environmental Barrier Coatings (EBCs) are required for use of SiC-based composites in hot sections of gas turbine engines. The primary function of EBCs is to limit the interaction of SiC with steam in the combustion environment. Due to the additional constraints of thermal expansion match and chemical compatibility with the SiC substrate, state-of-the-art EBCs are typically fabricated from complex silicates. These silicates typically have sufficiently high silica activities that they also react with the steam by the following generic reaction.



This reaction has been extensively studied for the model EBC material  $\text{Y}_2\text{Si}_2\text{O}_7$  using  $1200^\circ\text{C}$  exposures in a steam-jet furnace [1]. Representative microstructures are shown in Figure 1. The amount of porosity formed at short times can be estimated from the volume change that accompanies the transformation from the high silicate to the low silicate, i.e., the transformation of  $\text{Y}_2\text{Si}_2\text{O}_7$  to  $\text{Y}_2\text{SiO}_5$  results in a volume reduction of  $\sim 30\%$ . Several features of note have been observed. First, the depth of silica depletion increases with time following parabolic kinetics in phase pure material. Second, the pore structure is faceted and columnar at short times. Finally, after longer term exposures the porous  $\text{Y}_2\text{SiO}_5$  surface layer sinters, the pores coarsen, the overall volume fraction of pores decreases, and the tortuosity of the porous structure increases. Given this observed microstructural evolution, we propose that an EBC silicate material can potentially be selected such that the silica-depleted surface layer sinters and self-heals, forming a more stable barrier layer that limits further reaction with high-temperature steam. Three silicates are investigated to explore *i*) the effects of volume change on silica depletion and *ii*) sinterability of the silica-depleted oxide. These silicates include  $\text{Ba}_{1-x}\text{Sr}_x\text{Al}_2\text{Si}_2\text{O}_8$ ,  $\text{Yb}_2\text{Si}_2\text{O}_7$ , and  $\text{HfSiO}_4$ . Preliminary results for the microstructural evolution of these silicates in high-temperature, high-velocity steam will be presented along with our more comprehensive study of  $\text{Y}_2\text{Si}_2\text{O}_7$  stability in steam.

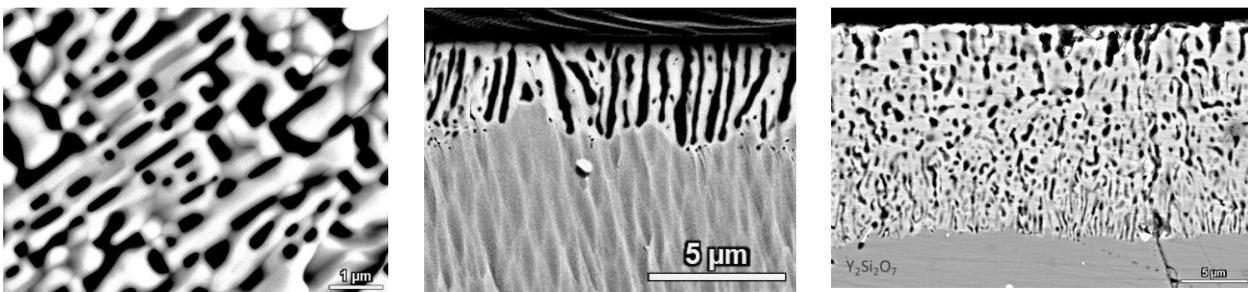


Figure 12 – Porous  $\text{Y}_2\text{SiO}_5$  surface layer formed on  $\text{Y}_2\text{Si}_2\text{O}_7$  after exposure at  $1200^\circ\text{C}$ , 1 atm steam flowing at  $\sim 160\text{m/s}$ . Left: surface view after 6h; Middle: cross-section after 12h; Right: cross-section after 250h.

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