

SEMICONDUCTOR PROCESS CHAMBER COATINGS: IMPROVING PERFORMANCE AND UPTIME

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Key Words: Semiconductor, Yttrium Oxide, Hafnium Oxide, Aluminum Oxide, Silicon Carbide, Thermal Spray, Physical Vapor Deposition, Chemical Vapor Deposition

Corrosion resistance is a critical property for semiconductor processing chamber components. Corrosive plasmas are omnipresent in semiconductor deposition processes, including plasma enhanced chemical vapor deposition (PECVD), physical vapor deposition (PVD), and etching. Process chamber cleanliness during plasma processing is becoming increasingly important as device feature sizes shrink. Particles that originate from erosion of the chamber components can lead to device yield losses, and eventually will result in the process chamber requiring the replacement of chamber components that are exposed to such plasmas. Thus the chamber components coatings are critical for tool performance and uptime.

I will review how the semiconductor process industry approaches ceramic coatings on complex metallic parts. Aluminum oxide and yttrium oxide based coatings that have shown significant benefit in application versus alternatives (Figure 1). These coatings can be deposited using anodization, CVD, PVD, and thermal spray. Material choices and deposition techniques are chosen based on coating performance, compatibility with substrates, and cost. In some instances, ceramic components are used where metallic components are not suitable, such as high temperature susceptors. I will compare how coatings used in the semiconductor industry are similar and different to those in the aerospace industry.

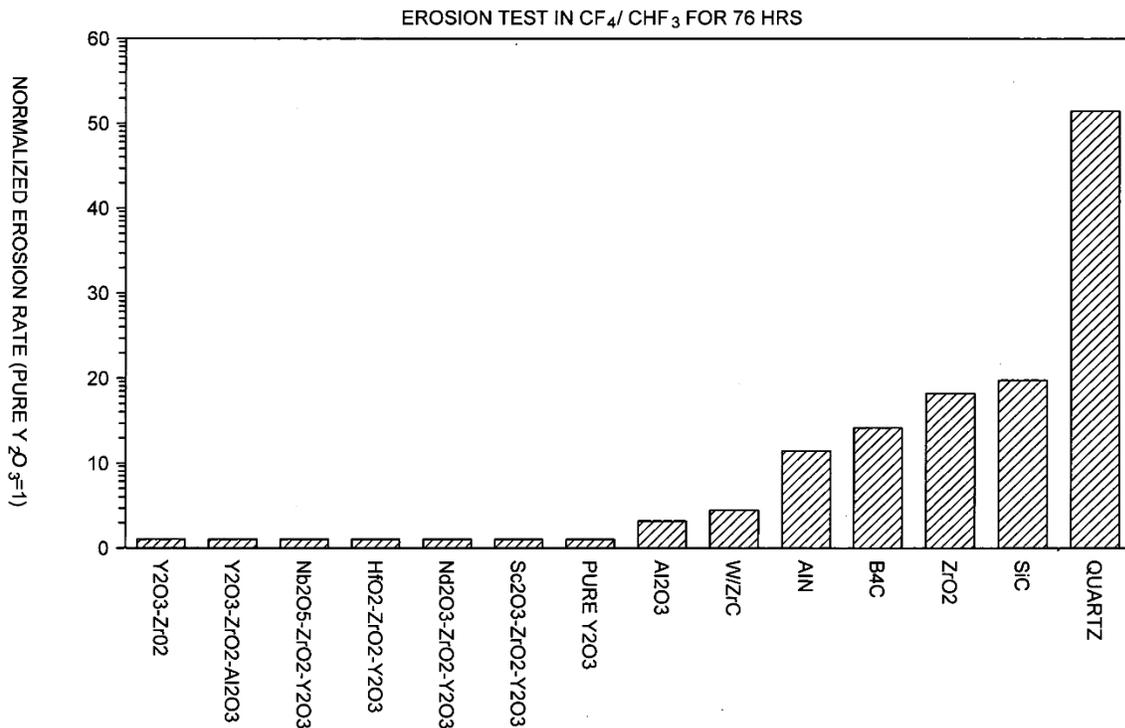


Figure 1 – Erosion of various materials in fluorine plasma

OXIDATION BEHAVIOR OF TWO-PHASE ($\gamma'+\beta$) Ni-Al COATINGS DOPED WITH Dy AND Hf

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Key Words: reactive elements, coating, oxidation, segregation, interface.

Dy/Hf co-doped two-phase ($\gamma'+\beta$) Ni-Al coatings were prepared by electron beam physical vapour deposition (EB-PVD). Cyclic oxidation behaviour of the coatings were investigated at 1100°C. The addition of 0.1at% Dy or 0.05at% Dy +0.3at% Hf to two-phase ($\gamma'+\beta$) Ni-Al coating significantly improved cyclic oxidation resistance, while addition of 0.5at% Hf to ($\gamma'+\beta$) Ni-Al coating no obvious effect on scale adhesion. The 0.1at% Dy doped and 0.05at% Dy +0.3at% Hf co-doped two-phase ($\gamma'+\beta$) Ni-Al coatings yielded mass gain of 1.24 mg/cm² and 1.04 mg/cm² after 100h cyclic oxidation. The Dy/Hf co-doped coating showed even further lower oxidation rate as compared to the corresponding Dy doped. In order to sufficiently exert reactive element effect (REE), extremely low solubility of the reactive element in each phase of the coatings should be guaranteed.

MULTIPLE-SCALE MODELING of PT EFFECT ON DURABILITY OF ALUMINIDE COATINGS

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Key Words: multiple-scale modeling, Pt effect, aluminide coating, durability, diffusivity.

The beneficial effect of Pt on the durability of aluminide coatings subjected to thermal cycling was studied by first-principles density functional theory (DFT) calculations, thermal physical analysis, atom diffusion simulation and mechanics-based modeling. This presentation will highlight these analytical approaches and research findings in three subject areas. First, the effect of doping elements (S, Pt, Cr, Y, Zr, Hf) on work adhesion, W_{ad} , of the β -NiAl coating/ Al_2O_3 scale interface was investigated. S was found to significantly reduce, while Y, Zr and Hf to largely increase W_{ad} of the interface, with Pt having a minimal effect. The bonding characteristics of the interface associated with the elemental doping were used to explain the trend of W_{ad} . Furthermore the X-S (X=Pt, Y, Zr, Hf) co-doping effects were also examined to elucidate the potential of these dopants in suppressing the detrimental effects of S. Second, the beneficial effect of Pt on reducing the β -NiAl/ Al_2O_3 interfacial tensile stress was assessed. The coefficients of thermal expansion (CTE) of Pt, β -NiAl and β -NiAl+Pt were obtained using DFT calculations and thermal physical formulas. The calculated CTE of the coatings, along with the experimentally measured CTE of Al_2O_3 , were then incorporated to evaluate thermal cyclic tensile stress at the undulated β -NiAl/ Al_2O_3 interface. The results showed that the addition of Pt to β -NiAl coating reduced the interfacial tensile stress, thus contributing to the improvement of thermal cyclic durability of the coating. This beneficial effect of Pt was more pronounced with a thicker oxide scale and a larger ratio of interfacial wave amplitude over wavelength. Third, the beneficial effect of Pt on lowering the diffusivity of S in β -NiAl coating was evaluated. The apparent activation energy and the pre-exponential factor of diffusivity via the next nearest neighbour (NNN) atom transportation as well as via interstitial jumps were analyzed, and the bonding characteristics of S with its surrounding atoms were calculated and compared with experimental results in the literature to elucidate the diffusion process of S. The addition of Pt in β -NiAl was found to significantly reduce the diffusivity of S, thus suppressing the detrimental segregation of S to the β -NiAl coating/ Al_2O_3 scale interface.

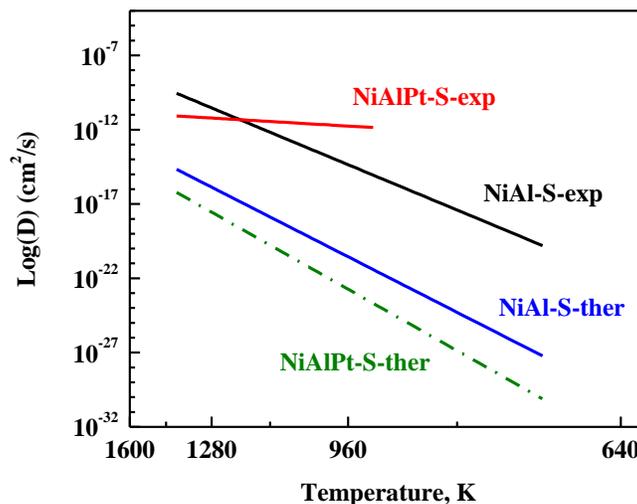


Fig.1 Diffusion coefficient of S in β -NiAl. The black solid curve (NiAl-S-exp) represents experimental measurement without Pt addition; the red solid curve (NiAlPt-S-exp) stands for the experiment value with Pt addition. The blue solid line (NiAl-S-ther) is referred to the calculated S diffusivity without Pt addition, while the dash green line (NiAlPt-S-ther) plots the calculated S diffusivity considering Pt effect. mechanism

DESIGN OF NOVEL γ' BONDCOATS AND INTERDIFFUSION WITH Re-RICH SUPERALLOYS

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Key Words: Thermal Barrier Coating; Bondcoat; Ni-based Superalloy; Durability; Interdiffusion.

Increasing the life of thermal barrier coating (TBC) systems critically relies on maintaining good adhesion between the bondcoat, the thermally grown oxide (TGO) and the topcoat. A common cause of failure, rumpling occurs as stress generated by oxide growth and thermal cycling results in creep of the mechanically weak bondcoat – this currently limits the life of EB-PVD TBCs with β coatings used in aircraft turbine blades and vanes. γ' coatings are known to present a better creep strength than β coatings and thereby markedly reduce rumpling, while still offering adequate oxidation resistance. The higher solubility of reactive elements (RE) in γ' also provides more flexibility in optimizing RE additions, as it limits the risk of overdoping; this can be used to further improve TGO adhesion. Furthermore, γ' compositions can, by essence, be adjusted to reduce the chemical potential mismatch with the substrate; this in turn will help curb the development of secondary reaction zones, which have become an issue when β coatings are used on Re-containing superalloys.

The poster will present recent efforts made at ONERA in the development of new γ' compositions for Re-rich substrates. Our current design strategy focuses on limiting substrate-coating interdiffusion and the associated loss of load-bearing section in the alloy. As mechanical properties improve and the bondcoat Al content is reduced, however, the bondcoat ability to maintain exclusive Al_2O_3 formation throughout extended cycling becomes critical to the system durability. Coating compositions are thus adjusted to a given alloy following the “equilibrium coating” concept, and then slightly modified to help maintain an appropriate composition relative to oxidation resistance. Compositions are assessed through the study of interdiffusion profiles obtained from both experiments and numerical simulations via a finite-difference method.

SUSTAINED PEAK LOW-CYCLE FATIGUE: THE ROLE OF OXIDATION RESISTANT BOND COATINGS

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Key Words: Bond coat, low-cycle fatigue, creep, TGO

Important developments in turbine blade technology, including cast thin-walled airfoils with complex internal cooling passes, place significant thermal gradients and stresses on the multilayered coating systems used to thermally insulate the blade from the hot combustion gases. As gas turbine engine operating temperatures increase, the intermetallic bond coatings traditionally used in thermal barrier coating systems undergo increased



Figure 2 – Structure of a (Pt,Ni)Al coating after SPLCF cycling. Cracks are outlined in white.

creep deformation. Bond coats for single crystal turbine blades have been designed primarily for oxidation protection with minimal consideration of mechanical and microstructural optimization. At higher temperatures, intrinsic failure mechanisms of coatings such as rumpling and cracking due to sustained peak low-cycle fatigue (SPLCF), limit the lifetimes of engine blades [1]. Bond coatings have been shown to extend or reduce the SPLCF lifetime of a specimen as compared to uncoated single crystals. The mechanical and microstructural properties bond coatings and their oxides that impact fatigue crack propagation rates have been investigated.

Cylindrical fatigue bars of single-crystal René N5 were machined for loading along the nominal [001] direction. The gage length of the fatigue bars was coated with various bond coatings for investigation. Two traditional β -phase coatings were examined: a Pt-free vapor phase aluminide coating (VPA) and a (Pt,Ni)Al coating. Additionally, a γ' coating developed at UCSB and a $\gamma-\gamma'$ coating developed at NIMS were considered [2,3]. Isothermal strain-controlled fatigue tests were completed at 982 °C and 1093 °C with a strain ranges of 0.60% and 0.35%, respectively. Specimens were loaded compressively to the maximum strain, held for two minutes, then unloaded to zero strain.

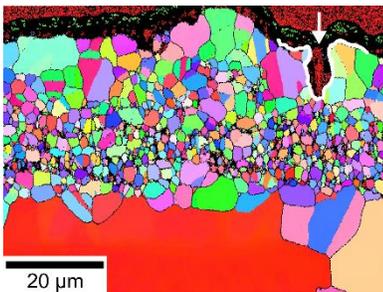


Figure 2 – Microstructure of a γ' bond coat produced via Ion Plasma Deposition (cathodic arc method)

During compressive dwell low-cycle fatigue, oxide filled cracks initiate at and subsequently propagate through the bond coating before entering the substrate. EBSD characterization shows cracks tend to propagate along grain boundaries in the bond coat, Figs 1 and 2. The microstructure of the bond coating depends heavily on the composition/phases present as well as the processing. Diffusion coatings produce large grains with a single grain frequently spanning the entire thickness of the coating, Fig 1. Overlay, or spray coatings, result in finer grain sizes and provide many boundaries for cracks to propagate along, Fig 2.

Finite element modeling suggests resistance to SPLCF cracking can be achieved via improvements in both the oxidation behavior and creep resistance. Changes to the oxidation behavior that either reduce the scale thickness or lower the oxide growth strains will decrease the TGO penetration

rate in the bond coat. However, designing a bond coat with such properties remains a challenge. γ' coatings have the potential for higher strength, but with lower Al content, these coatings would require Pt-modification to prevent less desirable spinels and mixed oxides. β -NiAl coatings have excellent oxidation resistance but poor high-temperature strength. The influence of these competing bond coating properties on crack propagation will be discussed as well as important considerations for future coating design.

References

- [1] C.G. Levi, J.W. Hutchinson, M.H. Vidal-Sétif, C.A. Johnson, MRS Bulletin 37 (2012)
- [2] D. J. Jorgensen, A. Suzuki, D. M. Lipkin, and T. M. Pollock, Surf. Coatings Technol. (2016).
- [3] K. Kawagishi, H. Harada, A. Sato, Superalloys 2008.

SUPERIOR PERFORMANCE OF PLASMA SPRAYED YSZ THERMAL BARRIER COATINGS WITH OXIDE DISPERSION STRENGTHENED BOND COATS

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Key Words: Oxide dispersion strengthened, thermal spray, advanced bond coats

Advanced thermal barrier coatings are essential to increase the efficiency of next-generation gas turbine engines. Different materials and process technologies give the possibility to extend the lifetime of TBCs. One limiting factor of the TBC lifetime is the growth of the TGO during thermal exposure resulting in an accelerated crack growth at the top coat- bond coat interface. The oxidation resistance and the temperature of the bond coat are key factors influencing the TGO growth rate. Oxide dispersion strengthened (ODS) bond coats have a slower oxygen scale growth during thermal exposure in comparison to standard bond coats.

In previous studies TBC systems with an additional thin ODS bond coat on top of a standard bond coat showed a higher thermal cycling performance. These studies used Inconel 738 and Amdry 386 as substrate and bond coat material, respectively.

This study investigates the thermal cycling performance of the ODS bond coat TBC systems combined with a different substrate ERBO 1 and bond coat material Amdry 995. TBC systems with the new material combination show high cycling lifetimes and superior performance in comparison to previous samples.

Samples were tested by a cyclic burner rig facility. Surface was heated by a gas burner to 1400°C while the backside is cooled by pressurized air to 1050°C. One cycle consists of 5 min heating followed by 2 min cooling. Cross sections of the samples were analyzed by SEM and laser microscope. The lifetime of the samples was evaluated especially with respect to diffusion processes, material properties, and bond coat temperature.

ODS powders with higher aluminum oxide additions were produced by high energy milling to fit the CTE of the ODS bond coat to the one of the top coat. This will reduce the initial crack formation on the top a wavy top coat - bond coat interface and increase lifetime. The advanced bond coats were applied by low pressure plasma spraying, the standard YSZ top coat by atmospheric plasma spraying. The performance was evaluated by a gas burner rig test.

MICROSTRUCTURAL EVALUATION WITH TYPE I HOT CORROSION DEGRADATION OF GAS TURBINE ALLOYS DURING BURNER-RIG TESTING

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Key Words: Characterization, TEM, Type I, hot corrosion, Gas Turbine Alloy

The hot corrosion resistance of selected gas turbine alloys was evaluated, as a baseline for assessing candidate new hot-section materials. The alloys were tested under burner rig exposures, using ASTM standard seawater for the salt contaminant and combustion conditions that provide representative materials evolution and degradation behavior relative to what is observed with marine gas turbines under service environments. Modern characterization techniques were utilized to evaluate the hot corrosion behavior and resistance of the evaluated material systems, to observe the degradation of the alloys and to study the underlying degradation mechanisms active during hot corrosion attack.

The burner rig test protocols were used to accurately simulate exposure conditions and materials evolution under extended service conditions in marine turbines. The burner rig test protocols achieve the following desired properties:

- Combustion by-products of shipboard and aero-turbine fuels
- Constant flow of contaminants, such as salt water
- Thermal cycling aimed to duplicate engine cycles.
- Accurate sample characterization.

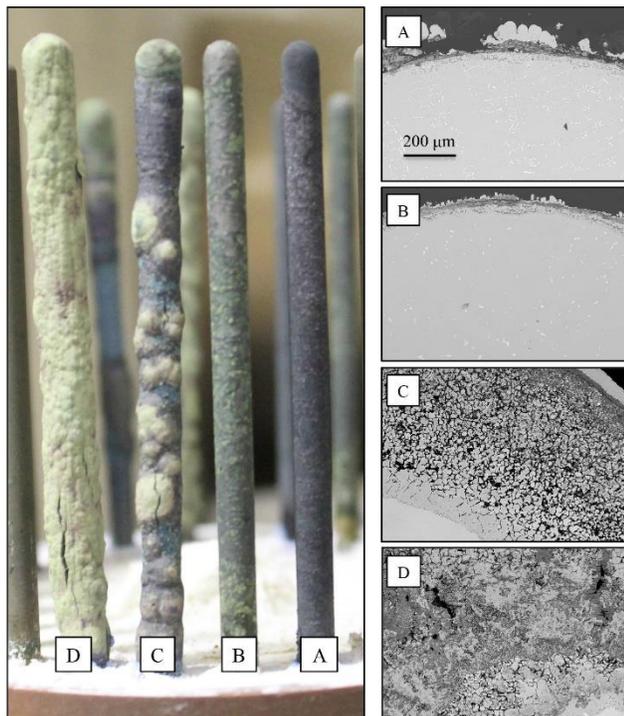


Figure 3 – The pins after 500 hrs at 900°C in burner rig test and the cross section view of the pins.

The extent of attack was distinctly different in the alloys. Figure 1 shows 4 different marine alloys after 500 hours of burner rig testing at 900°C. Presence or formation of carbides and second phases close to the surface, affect the corrosion mechanism in different ways.

After the test, Cr₂S₃ was observed at the reaction front in all alloys. The sulfide reacts with oxygen when the partial pressure of oxygen increases. The sulfur that is released from the sulfides by the oxidation reaction penetrates the material in front of the oxide, even if no additional sulfur is supplied. Subsequently, healing of the oxide scale is no longer possible.

Alloys A and B have higher Cr content (>15W%) compared to alloys C and D (~6W%). Overall the alloys with higher Cr content underwent milder hot corrosion attack. In these alloys, the high Cr phases, especially chromium carbides, seem to be the first region to face S attack.

Alloy C is a single crystal alloy with regular γ/γ' arrangement within the whole volume of the crystal, while in alloy D the shapes and sizes of the γ' precipitates are highly irregular, and distinct carbides are formed in different regions. The excessive different extent of attack in alloys C and D, despite the similar composition, illustrates the microstructural dependence of hot corrosion resistance of the alloys.

THE MODIFICATION OF RARE EARTH YB DOPED YTTRIUM ALUMINUM GARNET CERAMIC THERMAL PROTECTIVE COATING MATERIAL

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Key Words: yttrium aluminum garnet ceramics, thermal protection coating (TPC), rare earth Yb dope, thermal conductivity

The development of a new generation of ultra-high temperature thermal protection coatings will be an urgent requirement for the rapid development of aerospace. The yttrium aluminum garnet ceramics with high melting point, high strength and excellent high temperature stability will be a potential high temperature coating candidate material. However, its high conductivity will limit its use as a coating material. For the issue of heat insulation poor in yttrium aluminum garnet ceramic, the design and modification on ceramic materials were researched. The results have shown that it is doesn't change the YAG crystal structure and keep the original garnet crystal structure that the rare earth Yb doped YAG ceramic, yttrium aluminum garnet. The grain microstructure in YAG was significantly refined and the porosity was increased. The porosity increases with the increase of doping rare earth Yb in YAG. Obviously the specific heat capacity was reduced with the doping of the rare earth Yb in YAG, as so to reduce thermal conductivity of YAG. When the doping amount was up to 0.9, the grain size was small at 1.2-1.5um and the thermal diffusion and thermal conductivity were the lowest in YAG. Meanwhile, the thermal expansion coefficient of YAG ceramics was little variation and the phase change has not taken place with rare earth Yb doping in YAG. So there were excellent thermal expansion matching properties and good structure stability in the rare earth Yb doped yttrium aluminum garnet ceramic.

MECHANICAL AND THERMAL PROPERTIES OF NANOSTRUCTURED Gd₂O₃ DOPED YSZ COATINGS PREPARED BY ATMOSPHERIC PLASMA SPRAYING

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Keywords: atmospheric plasma spraying, nano-YSZ coatings, nano-GdYSZ coatings, properties

Four nanostructured Y₂O₃-ZrO₂(YSZ), 4mol%Gd₂O₃-YSZ(4Gd-YSZ), 6mol%Gd₂O₃-YSZ(6Gd-YSZ), 8mol%Gd₂O₃-Y₂O₃-ZrO₂(8Gd-YSZ) coatings were prepared by atmospheric plasma spraying (APS) technology under the same spraying parameters. The phase composition, microstructure, hardness, adhesion strength, thermal shock behavior and failure mechanism of nano-YSZ and GdYSZ were investigated systemically. The results showed that the as-sprayed GdYSZ coatings were consist of tetragonal ZrO₂ (t-ZrO₂) and Gd element was in solid solution with t-ZrO₂. The value of hardness, adhesion strength and thermal shock life for the as-sprayed nano-YSZ, 4Gd-YSZ, 6Gd-YSZ, 8Gd-YSZ coating were: YSZ > 4Gd-YSZ > 6Gd-YSZ > 8Gd-YSZ. Our investigations proved that the dopants Gd₂O₃ had the obvious effect on YSZ, that is Gd₂O₃ decreased the hardness, deteriorate the adhesion strength, and reduced thermal shock life. The more of Gd₂O₃ and the effect is obvious. Reasons of different properties for them were also analyzed in detail.

SYNTHESIS AND PHASE STABILITY OF THE $ZrO_2-Ln_2O_3-Ta_2O_5$ COMPOSITIONS FOR HIGH TETRAGONALITY ZIRCONIA-BASED THERMAL BARRIER COATINGS

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Key Words: Zirconia, Rare earth tantalate, High tetragonality, Phase stability

State-of-the-art TBC topcoat material is zirconia partially stabilized by 6-8% of yttria (ZY). The temperature limit for ZY coatings was determined to be 1200°C on the basis of phase transitions and sintering properties. Rare-earth zirconates ($Ln_2Zr_2O_7$) with pyrochlore structure were found to be very promising for thermal barrier coating materials. They possess high thermal stability up to the melting point (around 2300°C), low thermal conductivity (1.5 W/m·K at 1000°C for bulk material) and low sintering rate, but their fracture toughness is very low.

On the other hand, a lot of experimental work was carried out on the search of alternative tetragonal zirconia stabilizers. Rare-earth oxides (neodymia, samaria, gadolinia, dysprosia, ytterbia, scandia and others) stabilized zirconia coatings were proved to have excellent mechanical properties combined with low thermal conductivity. It was found, that co-doped stabilized compositions offer better properties than ones with single stabilizer. Usually in the co-doped compositions the primary component is yttria and the secondary is rare-earth oxide, both components are stabilizers for zirconia. These compositions were shown to be effective in decreasing thermal conductivity, but their fracture toughness was decreased too. On that reason there is a trend on zirconia doping with destabilizing oxides to increase the tetragonality index and have low thermal conductivity at the same time.

The present paper focuses on the co-precipitation synthesis and properties of the yttrium ($YTaO_4$), neodymium ($NdTaO_4$), gadolinium ($GdTaO_4$) and dysprosium ($DyTaO_4$) tantalate powder and tantalate-stabilized zirconia powders ZrO_2-YTaO_4 , $ZrO_2-NdTaO_4$, $ZrO_2-GdTaO_4$ or $ZrO_2-DyTaO_4$. Their phase composition was investigated at different calcination temperatures. Both yttrium and rare earth tantalates were shown to have two types of monoclinic structures (M and M'). As to zirconia-based compositions, both single and multi-phase samples were obtained depending on the tantalate amount and calcination temperature. Tetragonality indexes up to 1,027 were obtained.

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.

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FIBERS AND SOL-GEL MATRIX BASED THERMAL BARRIER COATING SYSTEMS FOR OUTSTANDING DURABILITY

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Key Words: Ceramic fibers, Sol-gel, Thermal barrier coatings, Cyclic oxidation, Durability

Thermal barrier coatings (TBC) are critical elements of the turbomachines. On turbine blades for aircraft engines, their preparation is based on EB-PVD industrial process. Such TBCs on first generation AM1 superalloy with a beta-NiPtAl bond coating exhibit 20% of surface spallation after about 600 1h oxidation cycles at 1100°C. In this work, a new method of TBC preparation was proposed and high durability of such structures was obtained with more than 1000 1h cycles at 1100°C before 20% of spallation. More than 1400 1h cycles was even obtained with the most performing formulations. A key point was that the surface spallation was lower than 10 % after 1000 cycles for TBCs made with the 70% and 80% fiber mix (*Figure 1a*). In the same conditions, EB-PVD TBCs exhibit 50-80% of spallation. The preparation process relied on the addition of a high temperature binder, namely a zirconia sol, to a mix of zirconia powder and fibers. TBCs with equiaxed porosity were obtained (*Figure 1b*). After thermal treatments, ceramic sintering bridges between the powder, the fibers and the ceramic derived from the sol transformation formed (*Figure 1c*). Another benefit was obtained from the anchoring of the fibers in the thermally grown oxide (TGO), inducing a tougher TGO layer. The outstanding durability of these fibers and sol-gel matrix based thermal barrier coatings is believed to be the consequence of higher toughness of both the TBC coating and modified TGO. Indeed, crack deviations were observed in these two elements. Moreover, contrary to EB-PVD TBCs, the porosity is isotropically distributed, limiting heat diffusion towards the superalloys.

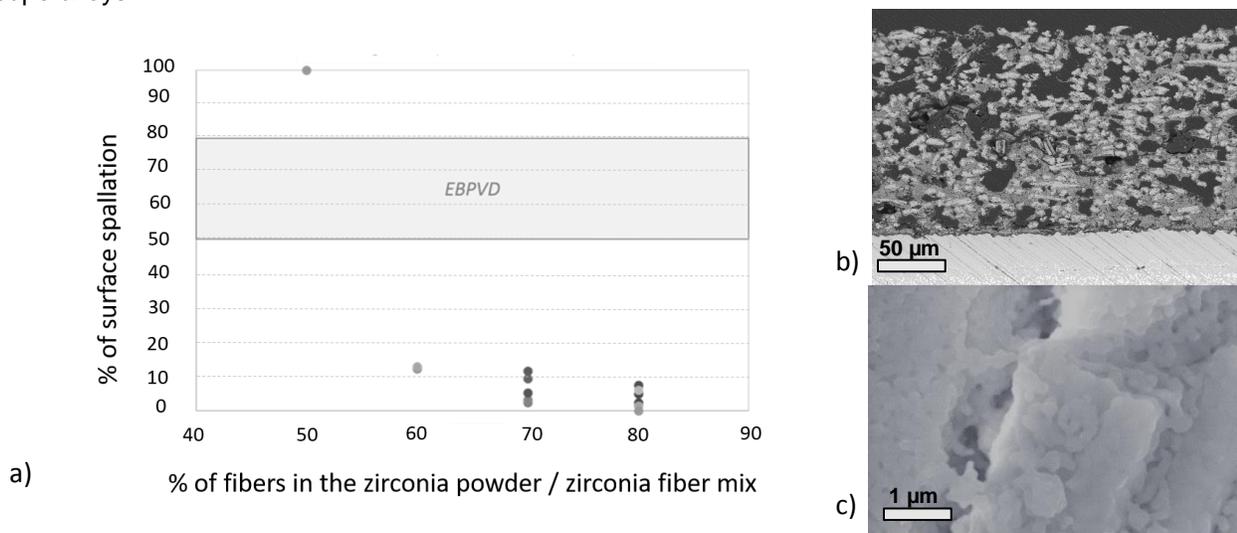


Figure 4– a) Percentage of surface spallation after 1000 1h cycles at 1100°C (with a 15 min cooling down to room temperature) versus the percentage of fiber in the zirconia powder/ fiber mix. The average values for industrial EB-PVD are given as a reference (specimen provided by Safran group). b) SEM micrograph of the cross-section of a 70% fibers sol-gel TBC c) SEM micrograph of ceramic sintering bridges in the fiber based TBCs after heat treatment at 1250°C.

STRUCTURE AND PROPERTIES OF CONDENSED GRADIENT COATINGS WITH NiAl-BOND COAT DOPED WITH Y OR Dy

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Key Words: EB-PVD, thermal barrier coatings, Ni-base super alloy, NiAl bond coat, active elements.

Doping of reactive elements (RE) as Y or Dy into the composition of NiAl bond coat in EB-PVD thermal barrier coatings (TBC) leads to an increase of performance characteristics of the latter. The report contains results of structure and property investigation of NiAl / ZrO₂-8% Y₂O₃ condensed TBC. Thickness of the condensed TBC is 40 ... 50/140 ... 160 μm done on Ni-based super alloy samples-buttons. The effect of Y or Dy dopants into NiAl bond coat, including their gradient distribution through-the-thickness of NiAl layer was considered as well. It was found that the additions of REs reduce the average grain size of the condensed NiAl layer by 4-5 times. It was shown that REs precipitate both inside the NiAl grains and along boundaries in the form of particles ranging in size from 5 nm to 20 μm, depending on the level of their concentration. REs optimal content was estimated to ensure the highest thermal cyclic durability. It is noted that positive effect of Dy doping into NiAl (in comparison with Y) occurs due to improvement of adhesion of the scale layer because of the growth of spindle-shaped precipitates of dysprosium oxides in it, slowdown of the growth rate of Al₂O₃ scale at the metal-ceramic interface and inhibition of interdiffusion of Al (about 1,2 times) in TBC-super alloy system.

TAILORED THERMAL BARRIER COATINGS DEPOSITED BY HYBRID WATER-STABILIZED PLASMA TORCH

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Key Words: hybrid plasma torch, water-stabilized plasma, suspension/solution plasma spraying, tailored microstructure

High enthalpy plasma generated by hybrid water-stabilized plasma (WSP-H) torch enables spraying of dry powders, suspensions as well as solutions with superior feed rates, which makes this technology ideal for cost-effective spraying of thick and/or large-area coatings. Moreover, the versatility of the deposition process enables individual tailoring of the coatings compositions, microstructures and properties for various novel applications. In this study, feasibility of high throughput deposition of TBCs with WSP-H technology will be illustrated for selected model materials (e.g., YSZ, $Gd_2Zr_2O_7$, YAG) deposited from conventional powders as well as from liquid feedstocks. Application-relevant properties of these coatings (thermal conductivity, wear resistance, mechanical properties, high-temperature behavior, etc.) will be discussed and related to the wide range of achievable microstructures (see figures below for illustration). Examples of perspective multiphase coatings having layered, intermixed or functionally graded microstructures will be also provided.

Comparison of the TBC deposition carried out with WSP-H and conventional gas-stabilized plasma torches (i.e. torches providing plasma with vastly different properties) will provide a new perspective on the processes governing plasma-matter interactions and coating build-up phenomena.

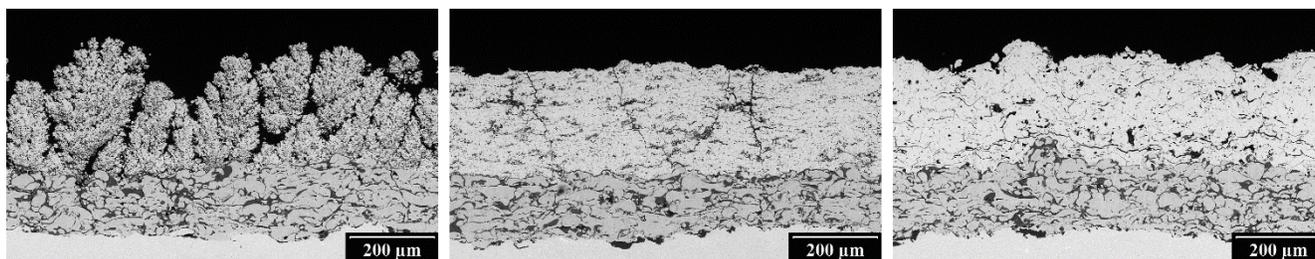


Figure 1 – Examples of TBCs deposited by WSP-H technology. NiCrAlY bond coat (deposited from coarse powder) covered by YSZ top coats (deposited from suspension – left, solution – center, powder – right).

MUSALEK, R.; MEDRICKY, J.; TESAR, T.; KOTLAN, J.; PALA, Z.; LUKAC, F.; ILLKOVA, K.; HLINA, M.; CHRASKA, T.; SOKOLOWSKI, P.; CURRY, N. Controlling Microstructure of Ytria-Stabilized Zirconia Prepared from Suspensions and Solutions by Plasma Spraying with High Feed Rates. *Journal of Thermal Spray Technology*, 2017, Vol. 26, Issue 8, p. 1787-1803

MUSALEK, R.; MEDRICKY, J.; TESAR, T.; KOTLAN, J.; PALA, Z.; LUKAC, F.; CHRASKA, T.; CURRY, N. Suspensions Plasma Spraying of Ceramics with Hybrid Water-Stabilized Plasma Technology. *Journal of Thermal Spray Technology*, 2017, Vol. 26, Issue 1-2, p. 37-46

DENSE CERAMIC COATINGS DEPOSITED BY AEROSOL DEPOSITION FOR MULTILAYERED ARCHITECTURE TOWARDS THERMAL/ENVIRONMENTAL BARRIER COATINGS

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Key Words: aerosol deposition (AD), mesoplasma, yttria-stabilized zirconia, alumina, dense ceramic coatings

The demands for thermal/environmental barrier coatings (T/EBCs) have been increased as the operating temperature of gas turbines increased in harsh environment [1]. Multilayered and multifunctional coatings are required for advanced T/EBCs [2], varied from porous insulative layer to dense environmental barrier layer. Aerosol deposition (AD) method is a unique deposition method that enables the deposition of dense ceramic coatings with high adhesion strength without melting of injected powder based on room temperature impact consolidation (RTIC) phenomena [3-5]. Thus, it will be interesting to apply this process for T/EBC applications. However, in order to apply the AD method to these applications, the deposition rate and the ability of three-dimensional coverage should be improved. Mori et al. preliminary reported that the introduction of plasma assistance drastically improved the deposition rate for lead zirconate titanate [6]. Thus, it would be worth to try to enhance aerosol deposition by introduction of plasma assistance [7]. The use of mesoplasma flow, which is transitional state from thermal plasma to low-pressure plasma, is the key to the deposition [8]. Fine powder of 8-wt% yttria-stabilized zirconia was sprayed by an rf-inductively coupled plasma at a reduced pressure. The effect of plasma assistance was confirmed at the power input of several kilowatts, which was much smaller compared to conventional plasma spray. Coatings with uniform thickness of 5-20 μm was obtained. The Vickers hardness of the coating reached to 1200 HV. This coating will be useful for the architecture of multilayered advanced T/EBCs.

References

- [1] J. M. Drexler et al., *Adv. Mater.*, 23 (2011) 2419-2424.
- [2] V. Viswanathan et al., *J. Am. Ceram. Soc.*, 97 (2014) 2770-2778.
- [3] J. Akedo and M. Levedev, *Jpn. J. Appl. Phys. Part 1*, 38 (1999) 5397-5401.
- [4] J. Akedo, *J. Am. Ceram. Soc.* 89 (2006) 1834-1839.
- [5] J. Akedo, *J. Therm. Spray Technol.* 17 (2008) 181-198.
- [6] M. Mori et al., *Proc. IEEE Int. Symp. Appl. Ferroelectric.* 1-2 (2007) 454-456.
- [7] A. Vardelle et al., *J. Therm. Spray Technol.* 25 (2016) 1376-1440 (J. Akedo and K. Shinoda, Section 2.2, 1379-1383).
- [8] T. Yoshida, *Pure Appl. Chem.* 78 (2006) 1093-1107.

2-LAYERS TBC BY EBPVD

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Key Words: EB PVD, bond coat, high-rate evaporation, leader-free, TBC

Although EB PVD metal coatings have been widely used for many years, one of their drawbacks is the presence of growth defects, so-called leaders. Leaders are the linear structural defects that allow for such reactive elements as oxygen to infiltrate (penetrate) to the substrate surface along the inner surfaces of the leaders, and oxidation or corrosion of the substrate surface (airfoil surface) takes place. This problem was solved by application of EB PVD high-rate metal ingot evaporation method for deposition of metal coating having general composition of $M\text{CrAlY}(X)$ where M is Fe, Ni, Co, or Ni/Co and X – Si, Ti, Zr, Ce etc, it allows us to solve the problems with adhesion, make this method less expensive with good performance rate and form the leader-free structure. Selection of parameters provides full reproduction of evaporated material composition in deposited coating and obtaining leader-free structure. A deposited material has some growth defects that can be easily eliminated by thermal treatment at moderate temperature. The structure of the as-deposited coating is characterized by the non-equilibrium fine grain microstructure that features abnormal physical properties, including accelerated internal boundary diffusion. In this case, the phase composition has been identified as supersaturated M-based solid solution with extremely large area of interfaces. During exposure at the temperatures below the transition temperature, the as-deposited structure evolves towards the more equilibrium configuration. Diffusion activated transformations of γ -supersaturated phase into γ/β equilibrium state is the cause of volume change, effective «healing» of the existing defects and reducing possibility of new 'leaders' appearance. Over the last years, the EB PVD process has been widely used for metal coating deposition on the 1st and 2nd stages blades and vanes of gas turbine Aero and Industrial engines, having $M\text{CrAlY}(X)$ general composition. Metal chemical composition depends on the superalloy type and operation conditions. Metal coating has been used either by itself as a protective (barrier) coating (overlay) or as a bond coat for multi-layer coating system (TBC). 2-layers TBC deposited by EBPVD onto the airfoils where the ceramic top coat layer of yttria stabilized zirconia (YSZ) has the strain columnar structure that prevents the failure due to thermocycling stresses and shows the perfect adhesion, smooth airfoil surface and no cooling holes blockage.

THERMAL SHOCK PERFORMANCE OF PS-PVD YSZ COATING THROUGH WATER QUENCHING CYCLE TEST

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Key Words: PS-PVD, YSZ coating, Thermal shock, Microstructure.

PS-PVD technology has been considered as one of the competitors for conventional APS and EB-PVD thermal barrier coatings due to its flexibility in coating microstructure regulation, good coating thickness distribution for twin-vane and high coating deposition efficiency. However compared with typical columnar microstructure of EB-PVD YSZ, the PS-PVD YSZ coating has cauliflower-like microstructure which will result in distinct difference in coating performance. Thermal shock is one of the most significant factors for the durability of TBCs. Water quenching cycle test is an efficient and fast method to discriminate the thermal shock performance of TBCs. In this paper, 2 TBCs samples with a dimension of 25.4mm in diameter and 5mm in thickness were obtained with 100 μ m LPPS CoNiCrAlYTa as bond coat and PS-PVD YSZ coating (120 and 250 μ m) as top coat. The water quenching cycle test is as follows: coated sample was put into furnace at a temperature of 1100 $^{\circ}$ C, holding for 5min; then the sample was poured into deionized water at ambient temperature directly; photographing and recording the surface appearance; after drying the sample, then the test is cycled again.

The SEM image shows that PS-PVD YSZ coating has a typical columnar structure, but at the bottom of YSZ coating a relatively dense and laminar layer is observed. The typical surface photos of samples are presented in Figure 1 after water quenching cycles test. Different from spallation in the form of blocks for conventional APS YSZ coating, PS-PVD YSZ coated sample demonstrate a distinct point peeling, but the YSZ column is not completely delaminated. With the increase of water quenching cycle test, the amount of point peeling rise. However the coating thickness has significant effect on the thermal shock performance. The thermal shock performance for YSZ coating with a thickness of 120 μ m and 250 μ m are presented in Figure 2. The result reveals that the thicker the YSZ coating is, the better Thermal shock performance is. The partial peeling off of PS-PVD YSZ coating is the reason for the different thermal shock performance.

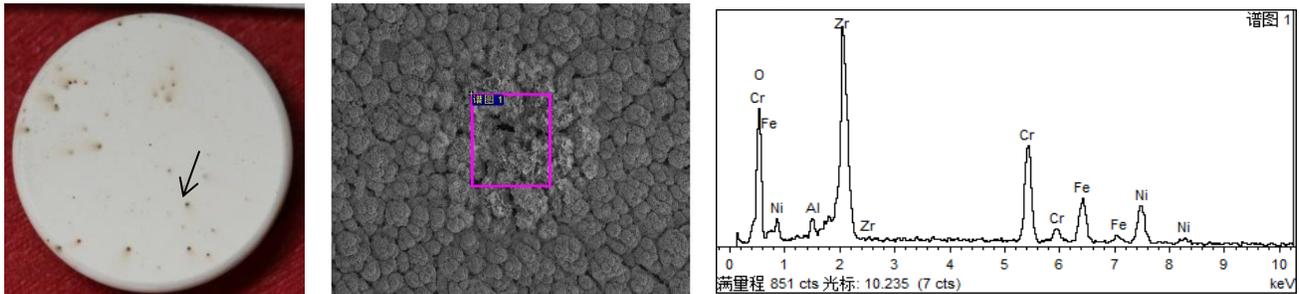


Figure 1 – Typical spallation behavior of PS-PVD YSZ coating after thermal shock test

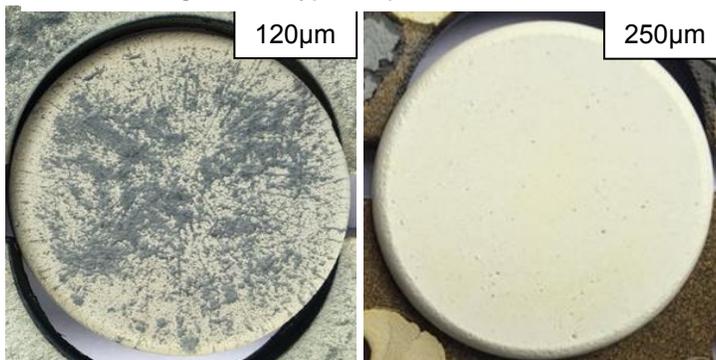


Figure 2 – Pictures of PS-PVD YSZ coating after water quenching for 20cycles

LASER FLASH TECHNIQUE: A CRITICAL ANALYSIS OF TESTING PARAMETERS AND MODELS FOR FITTING EXPERIMENTAL DATA

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

Laser Flash is considered the standard technique for measuring the thermal diffusivity of solids. To avoid any permanent damage of the sample when a LF measurement is carried out on brittle materials, characterized by very low values of thermal diffusivity, thermal effusivity, and toughness, as the case of freestanding APS TBC samples, the energy density deposited onto the sample surface should be minimized. The damaging effect of the energy deposited on the surface of free standing TBC samples during LF measurements has been experimentally investigated. The damage has been evaluated experimentally and analyzed by suitable heat conduction modeling and some suggestions are provided [1]. ZrO₂ is semitransparent to near IR radiation. This is the typical wavelength range of the laser heating source of the laser flash equipment. Moreover, the characterization of TBCs at high temperatures is particularly interesting as the typical working temperature of gas-turbine is >1000 °C [2]. At these temperatures the radiative heat transfer through the TBC becomes more and more relevant. The effect of blackening surfaces by a thin layer of graphite is considered [3]. Experiments are carried out at ambient temperature by means of a thermographic camera, at higher temperature in vacuum until 1200 °C and in argon atmosphere until 1000 °C. Data are analysed taking into account the heat exchange with the environment [4]. Successively, the possibility of radiative exchange between the two blackened sides of the sample [5] is taken into account. Finally, the possibility of simultaneous heating of the two sides of the sample, due to the semitransparency of the material is considered. This last model explains the anomalous immediate heating of the side facing the detector as shown in Fig. 1 Laser Flash is a very reliable technique for measuring thermal diffusivity of single layer samples but, especially for coatings, measuring their thermal diffusivity directly on a component they are deposited onto is a need. To satisfy this request in-reflection configuration photothermal techniques have been developed and successfully applied [6]. Furthermore, when the thickness of the substrate is not too thick, also the LF technique can be used on two-layer samples as some algorithms for estimating thermal diffusivity of a single material in a two layer sample have been developed since many years [7,8]. In particular all these models require to know the density, the specific heat and the thermal conductivity of the second layer. The effects of the uncertainty in the evaluation/estimation of the thermophysical parameters of the second layer will be discussed theoretically and compared with some experiments designed to highlight the most critical issues in this type of measurement.

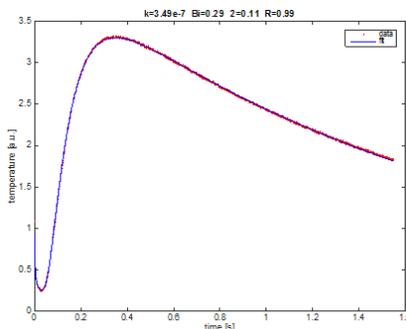


Figure 1 – laser flash experimental data with radiation heating also the rear face.

1. P. Bison, F. Cernuschi, S. Capelli, Surf. Coat Technol. Vol. 205, Issue 10, 2011, Pag.3128-3133.
 2. J. Manara, M. A. Schuster, H. Ratzler-Scheibe, and U. Schulze. Surf. Coat. Technol., (203):1059 – 1068, 2009.
 3. F. Cernuschi, L. Lorenzoni, P. Bianchi, and A. Figari. Infrared Physics & Technology, 43:133 – 138, 2002.
 4. J. A. Cape and G. W. Lehman. J. Appl. Phys., 34(7):1909–1913, July 1963.
 5. H. Mehling, G. Hautzinger, O. Nilsson, J. Fricke, R. Hofmann, and O. Hahn, International Journal of Thermophysics, 19(3), 1998.
 6. F. Cernuschi, P.G. Bison, S. Marinetti and P. Scardi, Acta Mater.56 (2008) 4477 – 4488.
 7. K. B. Larson and Karl Koyama, J. Appl. Phys. 38, 465 (1967)
- D. Maillet, S. André, J.C. Batsale, A. Degiovanni, C. Moyne. Thermal quadrupoles : Solving the heat equation through integral transforms. Wiley, London, 2000

THE POSSIBILITIES OF USING OPTICAL PROPERTIES MEASUREMENT METHODS FOR TBC RESEARCH

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Key Words: emissivity, reflectivity, transmissivity, spectral dependence, room and high temperature.

The main task of the thermal barrier coatings (TBC) is to protect the base material from the effects of high temperatures and thermal shocks. Heat transfer through the multilayered structure of TBC is performed by conduction and radiation. It is important to know not only the thermal conductivity and specific heat capacity of individual materials, but also the reflectivity, transmissivity and emissivity of the individual layers and the entire structure of TBC.

Several measurement methods of material optical properties have been developed at the New Technologies Research Centre. The methods are suitable for measuring reflectivity, transmissivity and emissivity of coatings and bulk materials at room temperature (SNHRRT, SNHTRT) and high temperature (SNEHT, EDEHT). The results are usually in the form of spectral dependent quantities, the total or band values can be further evaluated. The measurement method of emissivity of semitransparent coatings itself, although it is deposited on a substrate, is available for the room temperature measurements. The poster introduces a specification of measurement methods including example results for high emissivity layers.

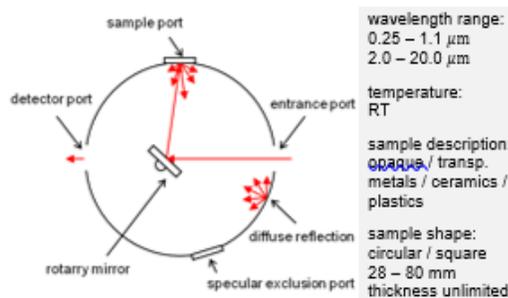


Figure 1 – spectral normal hemispherical reflectivity at room temperature (SNHRRT)

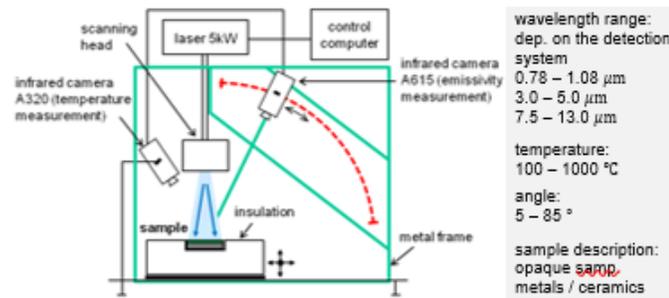


Figure 2 – effective directional emissivity at high temperature (EDEHT)

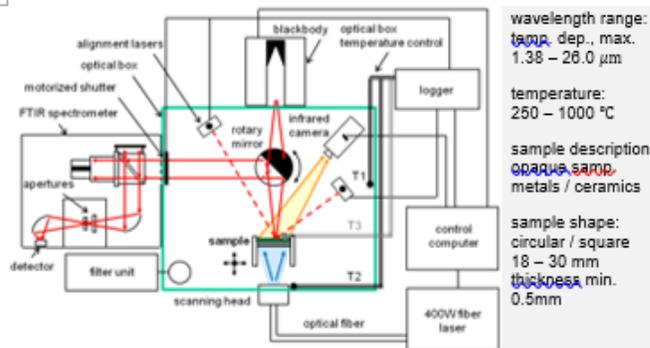


Figure 3 – spectral normal emissivity at high temperature (SNEHT)

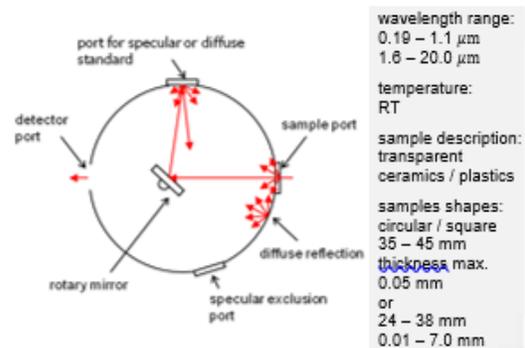


Figure 4 – spectral normal hemispherical transmissivity at room temperature (SNHTRT)

Using these measurement methods, it is possible to characterize the TBC properties important for the radiative heat transfer from the surrounding environment to the protected part.

More info about coating and bulk material measurements at <https://ntp.zcu.cz/en/laboratories/optical-properties>

FACTORS AFFECTING CERAMIC ABRADABLE COATING DAMAGE ACCOMMODATION

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Key Words: zirconia, air plasma spray (APS), abrasible coating, damage.

High temperature abrasible coatings are based on thermal barrier coating compositions and play an integral role in not only providing thermal protection for turbine shrouds, but also in maintaining blade tip clearances for increased turbine efficiencies. As turbine material technologies advance, there is a push for the development of abrasible coatings that can withstand more severe operating conditions and retain the optimum balance of abrasibility and durability. However, as abrasible coating technologies are pushed to higher temperatures and greater capabilities, such as compatibility with ceramic matrix composites, there are significant challenges in understanding the underlying mechanisms that aid the design of these inherently brittle materials enabling them to accommodate damage in a controlled manner. This study will first discuss the theories for fracture mechanics and wear mechanisms in ceramics and how they can be related to abrasible coatings. The influence of microstructural defects present in current technology ceramic abrasible coatings on the preferred wear behavior of these systems will then be investigated. The coatings to be compared are air plasma sprayed dysprosia- or yttria- stabilized zirconia with varying fractions of pore former and secondary phases. The wear of both as-received and aged coatings will be tested, and deformation mechanisms will be reported. Links between different defects, their evolution with aging, and observed wear behavior will be compared with two competing definitions of desired abrasible damage accommodation mechanisms, with one being energy dissipation through plastic deformation and the other depending on crack propagation and frictional sliding of the removed material to dissipate energy.

SEGMENTATION CRACKS IN PLASMA SPRAY COATINGS: FORMATION DYNAMICS AND CHARACTERIZATION

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Key Words: Segmentation Cracks, Evolving Stress, Curvature measurements.

Segmentation cracks in Air Plasma Sprayed (APS) Thermal Barrier Coatings (TBCs) have been recognized as crucial micro-structural asset for increasing the in-plane strain tolerance of the coatings and thus enhancing the TBC durability. These vertically cracked coatings also show excellent in-plane fracture toughness. This combination has allowed wide spread use of these coatings in gas turbine engines. Although industrially successful, there is limited scientific studies on the formation dynamics of such cracks, and their relationship to process conditions and performance. This is especially of importance as efforts are underway to find alternative to Ytria Stabilized Zirconias for higher temperature thermal barrier applications.

This study seeks to characterize the formation dynamics of such cracks through monitoring of real time curvature evolution of a beam during plasma spraying. The concept here is to understand stress evolution from the curvature measurements which then will allow identification of conditions at which cracks initiate and progress through successive coating build up. Examples are presented for Ytria Stabilized Zirconia as well as Gadolinium Zirconate and Titanium Oxide.

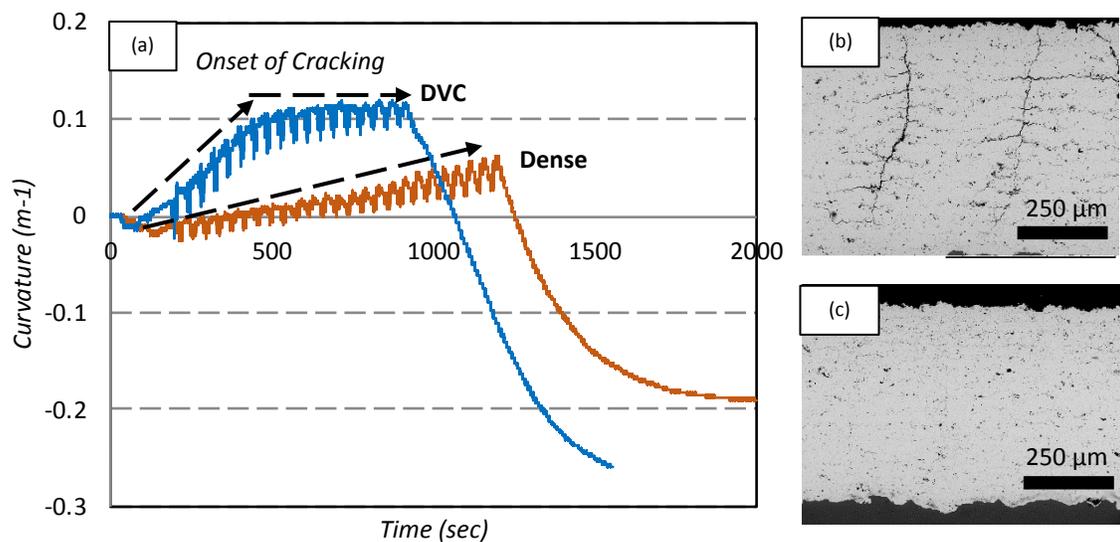


Figure 5: The change in evolving stress on onset of cracking as monitored by an ICP sensor for the as-sprayed YSZ coatings (a) Curvature -Time data and the corresponding microstructure of (b) Segmented (Vertically Cracked) coating (c) Dense coating.

CMAS-RESISTANCE OF A YITTRIA GRADED THERMAL BARRIER COATING FABRICATED BY PLASMA ACTIVATED EB-PVD

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Key Words: CMAS; Thermal Barrier Coating; EB-PVD; Plasma activation

EB-PVD yttria stabilized zirconia (YSZ) thermal barrier coatings (TBCs) are susceptible to calcia-magnesia-aluminum-silicate (CMAS) corrosion. The service lifetime of typical 8YSZ TBCs can be significantly reduced by CMAS attack. Currently, composition and microstructure modifications are the most commonly used methods for CMAS infiltration resistance. It has been reported by previous researchers that reactive elements, including Y, Gd, La, and etc., doped in TBCs can promote the formation of a dense protective layer by a sacrificing reaction with CMAS. It is therefore that the CMAS infiltration can be retarded. Besides, tailored columnar grains of TBCs are also proved to be effective for CMAS mitigation.

In this work, TBCs specimens with graded microstructure were fabricated by EB-PVD. The upper region of the TBC was doped with a higher Y_2O_3 content up to 25 wt.%, compared with the conventional 8YSZ composition. Besides, plasma activation was also introduced in the EB-PVD process to yield a tailored coating morphology and prosity. The coating specimens were tested at 1250 °C for evaluating CMAS resistance. Conventional YSZ coatings and graded coatings without plasma activation were also investigated for comparison.

GRADIENT DAMAGE SPREADING OF MOLTEN VOLCANIC ASH ON THERMAL BARRIER COATINGS

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Key Words: TBCs, volcanic ash, spreading ring

Aviation safety and aero engine life are always threatened by dust or ash suspending in the air route which derive from inevitable natural phenomena (volcanic eruption and sand storm) and human productive activity (run way debris, industrial fumes, and coal ash emission). Those floating silicate ash with the low melt temperature (lower than 1100 °C) will be easily ingested into jet engine and quickly melted due to the fact that the turbine inlet temperature of the current advanced jet engine at cruising altitude (1200-1450 °C) far exceed the melting point of those silicate ash. Subsequently, these molten ash are deposited on the surface of thermal barrier coatings (TBCs). TBCs is a refractory ceramic layer deposited on the surface of super alloy and can protect these metal at the hot parts (such as combustion chamber, blade and nozzle) from high temperature. However, these silicate deposits will lead to serious spallation and even failure of TBCs. Once the TBCs exfoliate under stress or chemical corrosion because of ash deposition, the engine may stop running during the flight and cause air disaster. Therefore, silicate ash deposition undoubtedly pose a huge obstacle in the development of jet engine. Here, to comprehensively understand the effect of silicate deposits on TBCs, we investigated the subsurface-transverse spreading ring of re-melted volcanic ash (obtained from Tungurahua Volcano, Ecuador, 2014) with various droplet size on the APS TBCs and EB-PVD TBCs respectively at the temperature from 1200 °C to 1600 °C over a wide range of duration (Figs. 1a and b). Our results demonstrate that the gradient change of concentration of volcanic ash melt onto TBCs directly leads to the formation of spreading ring in the subsurface-transverse of molten volcanic ash located in the edge of main spreading area (Fig. 1c). These observations imply that the interaction process of molten silicate ash with TBCs is driven not only by vertical infiltration due to gravitation but also by horizontal spreading owing to capillary force. Notably, the infiltration depth of the ring area was deeper than that of the main liquid area, which closely resembles previously observed in ceramic plate (Figs. 1d and e). Overall, we summaries the influence of temperature, holding time and size of droplet on spreading radius and conclude the mechanism of vertical infiltration. Those work is the first step to improving the TBCs and serve as the basic of developing the new generation of aeroengines.

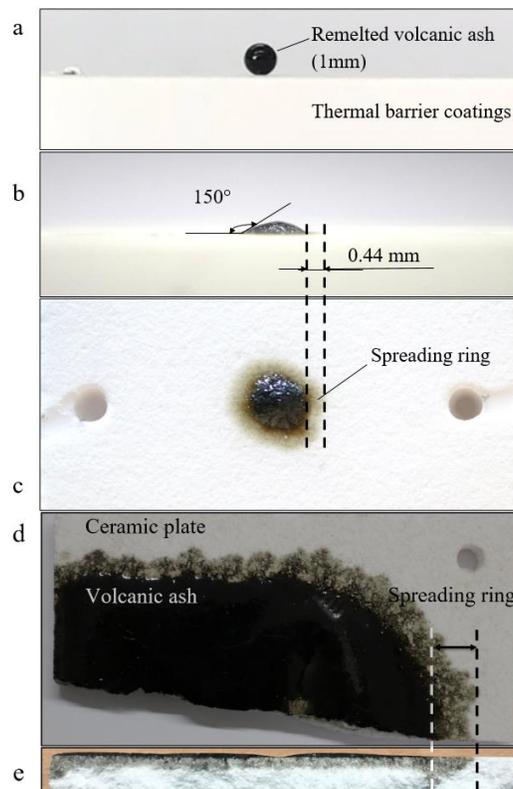


Figure 6. (a) A re-melted volcanic ash with the size of 1mm on TBCs before spreading. (b) The side view of spreading ring after spreading under 1200°C for 10⁴ h. (c) The top view of (b). (d) Spreading ring of volcanic ash on a ceramic plate. (e) Cross section of the ceramic plate.

HIGH TEMPERATURE INTERACTIONS BETWEEN ENVIRONMENTAL BARRIER COATING (EBC) CERAMICS AND CALCIA-MAGNESIA-ALUMINA-SILICATE (CMAS) GLASS

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Key Words: environmental barrier coating; CMAS glass; yttrium disilicate; yttrium disilicate; ytterbium disilicate; scandium disilicate

Ceramic-matrix-composites (CMCs) are being researched to replace current metallic hot-section components, which would allow for higher operating temperatures. Due to the oxidation of CMCs (usually SiC-based) in the presence of water vapor, dense environmental barrier coatings (EBCs) are needed. At temperatures above 1200 °C, silicate particles (sand, volcanic ash, fly ash, etc.) enter the engine, melt on the hot surfaces and form calcia-magnesia-alumina-silicate (CMAS) glass deposits. The molten CMAS glass can penetrate grain boundaries and cause dissolution, which leads to premature failure. New coatings are needed to protect CMCs from CMAS attack.

A new model, based on optical basicities, has been used to predict the reactivity between CMAS and potential EBC ceramics. Based on this analysis, several potential EBC ceramics have been identified: yttrium aluminate (YAIO₃), yttrium disilicate (γ -Y₂Si₂O₇), ytterbium disilicate (β -Yb₂Si₂O₇), and scandium disilicate (β -Sc₂Si₂O₇).

High-temperature (1500 °C) interactions of these four promising dense, polycrystalline EBC ceramics with a CMAS glass have been studied systematically. Although the optical basicities of all the EBC ceramics and the CMAS are similar, Y-bearing EBC ceramics react more with the CMAS. In Si-free YAIO₃, the reaction zone is small and it contains three regions of reaction-crystallization products: (i) needle-like Y-Ca-Si apatite(ss) grains, (ii) blocky grains of YAG(ss) or Y₃Al₅O₁₂(ss), and (iii) a mixture of Y-Ca-Si apatite(ss) and YAG(ss) blocky grains. In contrast, only Y-Ca-Si apatite(ss) forms in the case of Si-containing γ -Y₂Si₂O₇, and the reaction zone is an order-of-magnitude thicker. These CMAS interactions are analyzed in detail, and are found to be strikingly different than those observed in Y-free EBC ceramics (β -Yb₂Si₂O₇ and β -Sc₂Si₂O₇). This is attributed to the presence of the Y in the YAIO₃ and γ -Y₂Si₂O₇ EBC ceramics. There is little or no reaction found between the Y-free EBC ceramics and the CMAS. In the case of β -Yb₂Si₂O₇, a small amount of reaction-crystallization product Yb-Ca-Si apatite(ss) forms, whereas none is detected in the case of β -Sc₂Si₂O₇. Instead, the CMAS glass

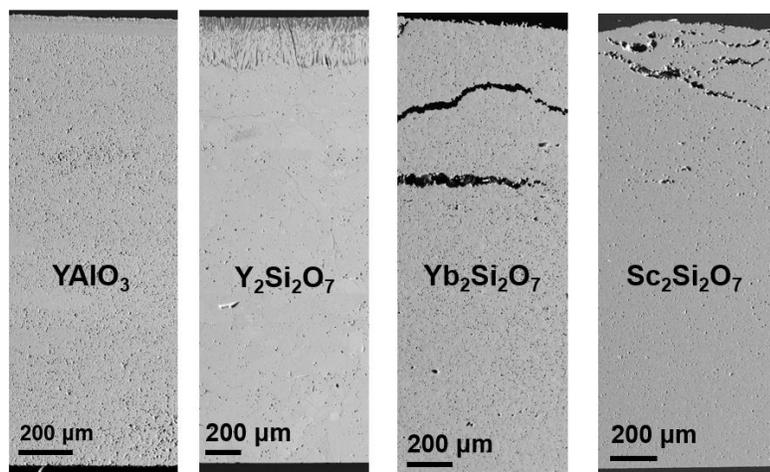


Figure 7 – Cross-sectional SEM images of CMAS-interacted (A) YAIO₃, (B) Y₂Si₂O₇, (C) Yb₂Si₂O₇ and (D) Sc₂Si₂O₇ after 24 hours at 1500 °C. Y-bearing EBC ceramics (A,B) show a reaction zone on the surface of the pellet (top), whereas Y-free EBC ceramics show 'buckling' cracks and a very limited or no reaction zone.

penetrates the grain boundaries and triple junctions of both Y-free EBC ceramics, and they suffer from a new type of 'blistering' damage comprising of large and wide cracks (Figure 1, C and D). This is attributed to the through-thickness dilatation-gradient caused by the slow grain boundary penetration of the CMAS glass. Based on this understanding, a 'blistering' damage-mitigation approach is devised and successfully demonstrated, where 1 vol% CMAS glass is mixed into the β -Yb₂Si₂O₇ powder prior to sintering. The resulting EBC ceramic does not show the 'blistering' damage, as the presence of the CMAS-glassy phase at the grain boundaries promotes rapid CMAS-glass penetration, thereby eliminating the dilatation-gradient.

HIGH TEMPERATURE INFILTRATION BEHAVIOR OF THREE VOLCANIC ASHES OF YSZ APS-DEPOSITED THERMAL BARRIER COATINGS

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Key Words: Volcanic ash, Thermal Barrier Coatings, Atmospheric Plasma Spray

Thermal Barrier Coatings (TBC) have enabled the increase of the operational temperature of aero engines. Raise in the turbine inlet temperatures (TIT) poses a threat to phase stability and safety for the state of the art material 7-8 wt% yttria stabilized zirconia (7YSZ). In addition to the inherent physicochemical restrictions of this material at high temperatures, the interaction of 7YSZ with siliceous airborne particles at temperatures above 1200 °C has been a major concern since the last decades. Sediments of Calcium-Magnesium-Aluminum-Silicates (CMAS) have been found in failed engines and have been correlated to the failure mechanisms of high temperature components. In 2010 the eruption of the Eyjafjallajökull volcano in Iceland heavily disrupted air traffic in Europe. This volcanic event led to regulations regarding volcanic ash (VA) concentrations in the atmosphere at which aircrafts are allowed to safely fly. Also, it brought to light the risks associated to VA in the safety of aircrafts with routes close to active volcanos. Nevertheless, reports of the assessment of the high temperature risk using real volcanic ashes is still limited in comparison to analyses carried out with CMAS.

Additionally, most reported studies have been focused on the study of electron beam physical vapor deposition (EB-PVD) rather than atmospheric plasma spray (APS) produced TBCs. This contribution addresses the study of the infiltration mechanisms of VA from three sources: Colima and Popocatepetl Mexican volcanoes as well as Eyjafjallajökull Icelandic volcano.

Infiltration experiments were carried out using two microstructures with different porosities (8.5 and 11.6%) produced by APS. 7YSZ was deposited over a ~68 μm NiCoCrAlYTa bond coat, using a M247-graded superalloy as substrate. Characterization of the volcanic ashes include DSC and DRX analyses as well as ICP chemical composition measurements. Infiltration experiments were conducted with a concentration of 20 mg/cm² of volcanic ashes in a form of an overlay over 7YSZ TBCs. Infiltration temperature was chosen as 1250 °C for isothermal

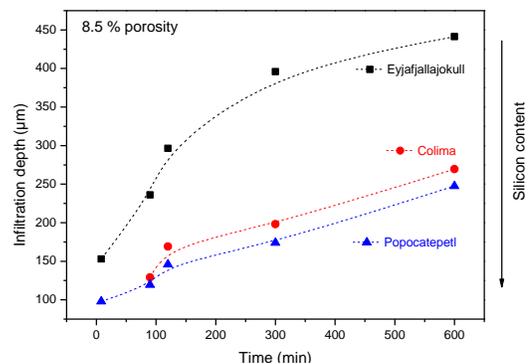


Figure 8 – Infiltration depth of the VA as a function of time on 8.5 % porosity coatings

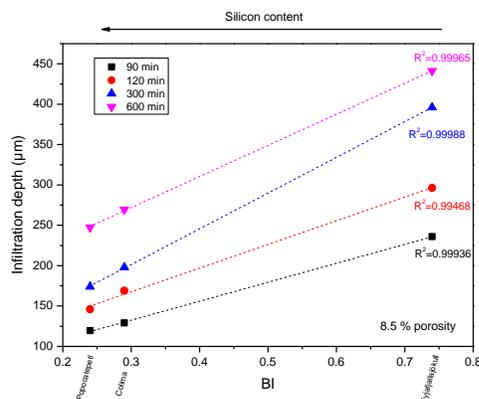


Figure 2 – Infiltration depth as a function of Basicity Index (BI) showing near-to linear correlation

heat treatments with heating rate of 10 K/min. Such temperature corresponds to the melting range VAs. Infiltration depth was determined as a function of time from 0 to 600 min. From this work, it was found that the chemical composition of the VA is a determinant factor in the infiltration depth of the coatings. For higher values of SiO₂, lower infiltration depths are seen. It was also observed that the greatest infiltration rate took place in the first 120 min of heat treatment (fig. 1). An attempt has been made in co-relating basicity index (B.I) of the VA melt and their infiltration kinetics. It was found out that the infiltration depth vs basicity index curves suggest an almost linear behavior irrespective of infiltration time (fig. 2). Further studies are now in progress in an attempt to set the basis for an infiltration model which may help to predict infiltration behavior for a wider number of VA based in chemical composition and basicity index.

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 impinging 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 ($50 \leq 125\text{ mm}$) 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.

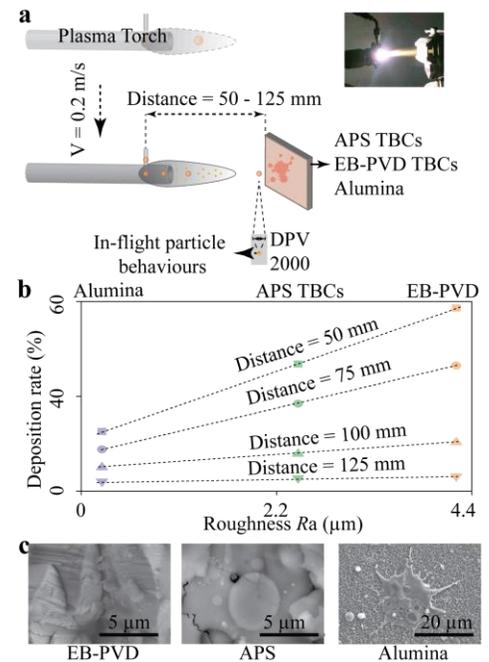


Figure 1. (a) A schematic of the experimental setup for capturing initial formation of molten volcanic ash layer under plasma spray conditions. (b) Roughness-deposition rate relationship for EB-PVD TBCs, APS TBCs and alumina substrate under different distance to nozzle, (c) The morphology of splats onto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

VOLCANIC ASH VERSUS THERMAL BARRIER COATINGS OF JET ENGINES – A HOLISTIC EXPERIMENTAL APPROACH

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Key Words: TBC, yttria-stabilized zirconia, YSZ, gadolinia zirconate, GZO

Since the heavy interruption of North Atlantic air traffic by volcanic ash in 2010 many experimental investigations have been done in order to better understand the influence of volcanic ash on the functionality of jet engines and in particular thermal barrier coatings (TBCs) on turbine blades within them. Some of these studies used natural volcanic ash while others used a synthetic mixture from the Calcium-Magnesium-Aluminum-Silicon system (CMAS). To this day, a holistic experimental investigation on TBCs, using various natural volcanic ashes, is missing. In the framework of the CORNET research project VAsCo (“Volcanic Ash resistant thermal barrier Coatings for jet engines” – www.vasco-cornet.eu), we are going to close this gap. We use four different volcanic ashes, which represent the chemical range of possibly produced ash by explosive volcanic eruptions. As TBCs, atmospheric plasma sprayed (APS) and electron-beam physical vapor deposited (EBPVD) coatings of yttria-stabilized zirconia (YSZ) and gadolinium zirconate (GZO) were chosen as state-of-the-art materials for first experiments. While YSZ EB-PVD coatings are prone to be fully infiltrated by molten silicates, GZO exhibits a higher resistivity against the infiltration through a rapid re-crystallization of the dissolved coating, thus closing the pathways of infiltration. This contrasting behavior of both materials makes them good candidates to study the influence of different chemical and mineralogical compositions of various volcanic ashes. The experiments are based on static and dynamic experiments: Static experiments include measurements with the heating microscope, to study the wetting and spreading of the molten ash sample on the TBC surface, and muffle furnace experiments with ash covered TBCs to study their chemical interactions. For dynamic experiments we thermally spray the ash on the TBC surfaces in order to simulate real conditions within the combustor/turbine section of a jet engine. Findings are used to modify TBCs and to improve their resistivity against molten volcanic ash. In addition to that, a feasibility study will be conducted in order to create a model synthetic volcanic ash for standard tests in the aviation industry.

**MATERIAL DAMAGE IN TBCS BY A SYNTHETIC CMAS AND THE NON-DESTRUCTIVE DETECTION:
-AN EXPOIRATION VIA A SINGLE CRYSTAL YSZ-**

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Key Words: Calcium-magnesium-alumino-silicates, Thermal barrier coatings, Single crystal yttria-stabilized zirconia, Crystallographic plane, Non-destructive detection List up to five key words.

More recently a new type of damage has been pronounced in thermal barrier coatings (TBCs) by calcium-magnesium-alumino-silicates (CMAS) from ingestion of siliceous minerals under certain operating conditions, based on synthetic material in Table 1. In order to understand material aspect of CMAS damage, a study on material interaction between a synthetic CMAS and a single crystal yttria-stabilized zirconia (YSZ) was studied in this work. Here, the effect of crystallographic orientation on the interaction was also investigated. The experimental works clearly showed that the material interaction between the CMAS and YSZ was significant, resulting in the change in microstructural morphology(Fig. 1(a)). The extent of interaction depended on the crystallographic factor of the YSZ (Fig. 1(b)). The CMAS damage developed depending on the crystallographic plane of YSZ; it was the lowest onthe {111} plane.This is a noteworthy finding tomitigate the CMAS damagein EB-PVD top coat. The change in physical properties was also found to be pronounced at the CMAS damaged area. Based on these findings the non-destructive detection was also tried for engineering applications.

Acknowledgement

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Table 1 Chemical composition of model CMAS.

	SiO ₂	CaO	Al ₂ O ₃	MgO
Mol.%	51.5	39.2	4.1	5.2

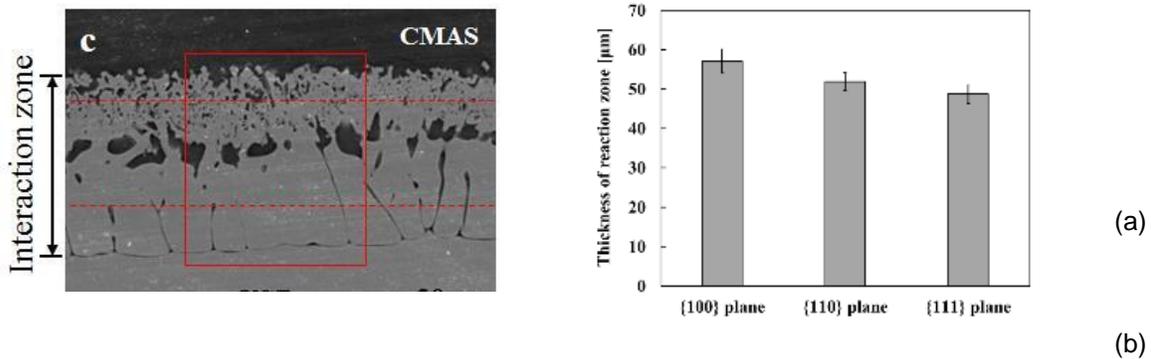


Fig. 1 CMAS attack on a single crystal YSZ.

RE₂O₃ DISSOLUTION KINETICS AND MECHANISMS IN CAS SILICATE MELTS: INFLUENCE OF THE RARE-EARTH

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Key Words: CMAS, Thermal Barrier Coating, Rare-earth silicates, Reaction kinetics, Basicity

Fine particles of sand, dust or volcanic ashes ingested by aircraft engines are well-known to damage 8YPSZ Thermal Barrier Coating (TBC). In service, these particles deposit on hot TBC surface ($\geq 1200^\circ\text{C}$) as molten silicate and infiltrate coating porous microstructure. They are mainly constituted of CaO-MgO-Al₂O₃-SiO₂ (CMAS) in variable proportions and also contain metallic oxides. Gd₂Zr₂O₇ TBC has shown efficiency to mitigate synthetic CMAS infiltration due to its reactivity with CMAS [1]. Indeed, the dissolution reaction leads to rapid formation of a sealing-layer in the topcoat mainly constituted of crystalline Ca₂Gd₈(SiO₄)₆O₂ apatite. However, this phase is not always stable in contact with CMAS and many rare-earth silicates may compete with apatite crystallization [2]. Several rare-earth oxides RE₂O₃ can be considered to replace yttria in ZrO₂-based TBC but little is known on reaction kinetics and thermodynamics involving RE₂O₃ and multi-component CMAS system.

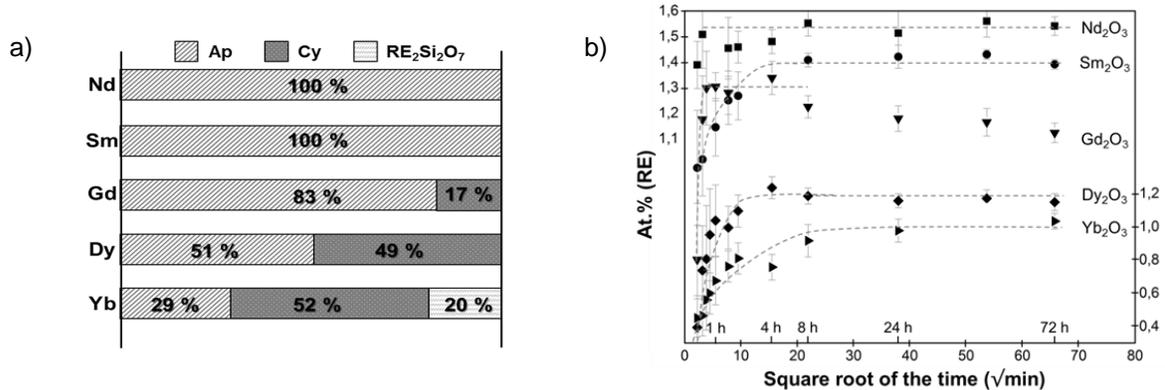


Figure 9 – a) RE-silicates proportion in RE₂O₃/CAS-bead mixtures after 1h at 1200°C and b) RE₂O₃ dissolution kinetics measured by EPMA (1200°C)

In this study, a simplified CMAS was selected with eutectic (1170°C) 65SiO₂-26CaO-9Al₂O₃ (mol. %) composition. Investigation on RE₂O₃ (RE = Nd, Sm, Gd, Dy and Yb) dissolution mechanism in CAS-melt was then performed at 1200°C. For this, CAS-glass beads containing dispersed RE₂O₃ solid powder in adequate amount to reach oversaturation were elaborated. Beads were then annealed in air for several durations and quenched. SEM observations coupled with XRD analysis gave information about dissolution/precipitation sequences and phase equilibria. The evolution of RE content dissolved in CAS over time and chemical evolution of CAS-melt was measured by EPMA. Reaction mechanism in CAS of RE₂O₃ was identified to be incongruent dissolution leading to precipitation of different RE-rich silicates. Dissolution of Nd₂O₃, Sm₂O₃, Gd₂O₃ and Dy₂O₃ in CAS results in formation of metastable apatite, and then stabilization of cyclosilicate. Disilicate Yb₂Si₂O₇ was also obtained in Yb₂O₃ bead-sample. The silicate precipitations induced significant variations of local CAS composition resulting in CaAl₂Si₂O₈ anorthite formation. The RE₂O₃ basicity has a direct influence on silicates solubility limits in CAS and on reaction kinetics (Fig.1).

[1] S. Krämer et al., Journal of the American Ceramic Society, 91 (2008) 576-583

[2] D.L. Poerschke et al., Journal of the European Ceramic Society, 36 (2016) 1743–1754

[3] F. Perrudin et al., Journal of the European Ceramic Society, 37 (2017) 2657–2665

CALCIUM–MAGNESIUM–ALUMINA–SILICATE (CMAS) RESISTANCE OF LAPO₄ THERMAL BARRIER COATINGS

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Key Words: Thermal barrier coatings (TBCs); Air plasma spraying (APS); Calcium–magnesium–alumina–silicate (CMAS); Corrosion resistance; Apatite

Nanostructured LaPO₄ thermal barrier coatings (TBCs) were prepared by air plasma spraying, and their resistance to calcium–magnesium–alumina–silicate (CMAS) attack at 1250 °C, 1300 °C and 1350 °C was investigated. The reaction products were characterized by X-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy and transmission electron microscopy. Exposed to CMAS attack for 0.5 h, a continuous dense reaction layer formed, which was mainly composed of P–Si apatite based on Ca_{2+x}La_{8-x}(PO₄)_x(SiO₄)_{6-x}O₂, anorthite and spinel phases. Beneath the reaction layer, little evidence of CMAS trace could be found. With the increase in temperature and heat treatment duration, the reaction layer became thick, while penetration depth of the molten CMAS changed slightly. Due to the formation of a reaction layer suppressing CMAS further infiltration, LaPO₄ TBCs are highly resistant to CMAS attack.

AN EXPERIMENTALLY-VALIDATED COMPUTATIONAL FRAMEWORK FOR CMAS DEGRADATION OF ENVIRONMENTAL BARRIER COATINGS

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Key Words: Environmental Barrier Coatings, CMAS, Silicate Deposit, SiC/SiC Composite.

The work addresses reactions between silicate deposits, generically known as CMAS, and yttrium disilicate (YDS), a candidate environmental barrier coating (EBC) for SiC/SiC composites. The primary goal is to elucidate effects of deposit composition, exposure temperature and time on the extent of YDS recession as well as the associated compositional and morphological evolution of reacting phases. Phase equilibrium calculations are used to assess deposits of twelve different compositions at 1300°C and 1400°C; experimental observations of YDS recession are reported for three of these compositions at both temperatures. The results show that recession depths reach terminal values for exposure times ≥ 100 h. Terminal recession depths are sensitive to deposit composition but only weakly affected by temperature. Deposits with high initial Ca:Si ratio react most severely with YDS, forming a thick layer containing an apatite reaction product interpenetrated by residual melt. The severity of the reaction decreases with decreasing Ca:Si ratio, and is least severe for deposits with insufficient Ca:Si ratio to produce apatite.

The accuracy with which the phase equilibrium calculations predict terminal recession enable an integrated modeling framework for simulation of consumption and failure of rare-earth silicate EBCs. In addition to the phase equilibrium calculations, the framework consists of two further components: (i) models for thermoelastic and physical properties of reacting phases and products; and (ii) high-throughput finite-element analyses to compute the energy release rates for steady-state channel cracking and steady-state delamination cracking after cooling. This capability is used to explore the effects of amount and composition of deposits on the propensity for fracture of YDS EBCs. The results reveal that the factors which affect coating recession, namely the deposit Ca:Si, correspondingly influence the energy release rates for fracture, due to the increased volume of thermally-mismatched reaction products.

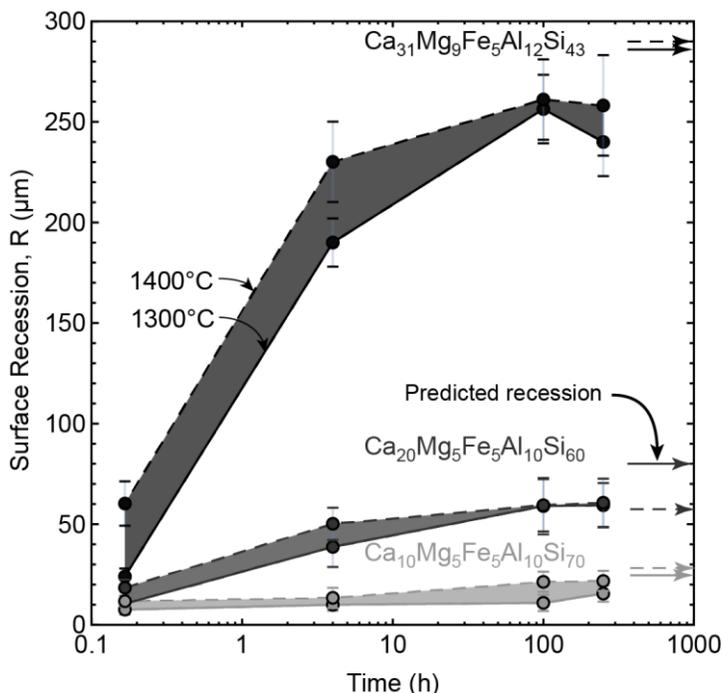


Figure 1: Measured recession and predicted terminal recession for three deposit compositions show remarkable agreement.

KINETICS OF THERMAL BARRIER OXIDE INTERACTIONS WITH MOLTEN SILICATES

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Key Words: Thermal Barrier Coating (TBC), Calcium-Magnesium-Aluminosilicates (CMAS), Dissolution, Diffusion, Kinetics

The degradation of thermal barrier coatings (TBCs) by molten silicates (CMAS) represents a significant barrier to increased operation temperatures of gas turbine engines and thus fuel efficiency. A promising mechanism for CMAS mitigation has been found in certain TBC chemistries (e.g. $\text{Gd}_2\text{Zr}_2\text{O}_7$) that undergo reactive crystallization – the crystallization of new, thermodynamically favored phases, which contain both melt and TBC constituents (e.g. apatite). Significant work has been undertaken to understand the thermodynamics of TBC-CMAS systems and the possible reaction phases, but little quantitative data on the kinetics of these interactions exists today; this includes: the (i) rate of TBC dissolution into the melt, (ii) diffusion of TBC constituents within the melt, and (iii) reaction product crystallization rates.

To better understand what limits kinetically the rate of thermal barrier oxide (TBO) saturation in the melt (a prerequisite of reactive crystallization), the effect of temperature, melt composition, and TBO composition on the dissolution and diffusion rates were quantitatively studied. TBOs in the $\text{REO}_{1.5} - \text{MO}_2$ systems ($\text{RE}=\text{Y} \ \& \ \text{Gd}$, $\text{M}=\text{Zr} \ \& \ \text{Hf}$) were placed in a semi-infinite, 1-D diffusive contact with one of two model silicate melts at either 1300 or 1400°C, an example of which can be seen in Figure 1. The reaction products and morphology were analyzed (Figure 1 (a) inset), and composition profiles of TBC constituents in the melt were measured using an electron microprobe equipped with wavelength dispersive spectroscopy. The resulting compositional data, e.g. Figure 1 (b), was fit to crystal dissolution and diffusion models, which enabled the quantification of TBO dissolution rates and TBO diffusivities in the model silicate melts.

Preliminary work has elucidated that the diffusivities of TBOs are strongly effected by the melt composition (i.e. the melt viscosity), but only weakly effected by the chemistry of the dissolving TBO. However, the TBO composition is seen to be an important parameter for controlling the dissolution rate. Modeling the dissolution and diffusion process on length scales relevant to TBCs (e.g. an EB-PVD intercolumnar gap) reveals that the time to reach melt saturation is only weakly dependent on the diffusivity but is strongly dependent on the dissolution rates. Thus, these results imply that the TBC dissolution rate should be a key optimization parameter for the design of novel TBC chemistries and coating architectures. With further investigation and determination of kinetic data, this work can be coupled with existing thermodynamic, thermomechanical, and infiltration models to enable the development of a fully-integrated, ICME based modeling approach to predict TBC-CMAS interactions and accelerate novel TBC development.

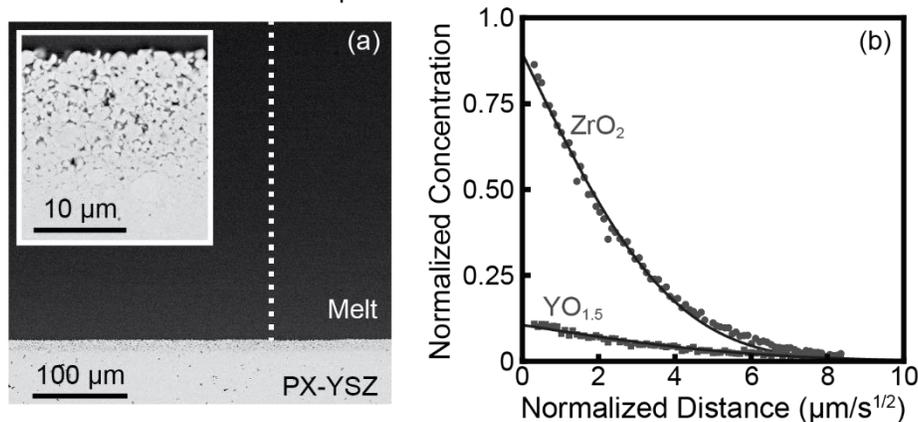


Figure 10 – 1-D TBC-CMAS diffusion couples enables the (a) analysis of the reaction zone (inset) and (b) collection of TBO (e.g. ZrO_2 and $\text{YO}_{1.5}$) concentration in the melt.

RAMAN STUDIES ON EB-PVD 7%YTTRIA- STABILIZED ZIRCONIA COATINGS WITH CMAS DEPOSITS

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Key Words: Thermal barrier coatings (TBCs); Calcium–magnesium–alumina–silicate (CMAS); Microstructure; Raman Spectroscopy

Thermal barrier coatings (TBCs) benefit the performance of turbine blades under operational conditions by successfully maintaining their integrity. However, reduced effectiveness of TBCs is experienced when foreign materials deposit on their surface, specifically those leading to infiltration of siliceous debris and calcium-magnesium-alumina silicate (CMAS) deposits. In this paper, the microstructural properties of Electron Beam Physical Vapor Deposition (EB-PVD) 7%YSZ coatings exposed to CMAS deposits were investigated. Raman spectroscopy was used to track the phase transformation of Zirconia from its tetragonal (*t*) to its monoclinic phase (*m*). Our results show that the behavior of the TBCs is location and temperature-dependent. For coatings heated at 1250° C for 10 hours, the YSZ top coat was partially dissolved in the CMAS, resulting in a decreasing monoclinic phase volume fraction further into the coating and away from the CMAS infiltrated region. These results suggest that the band corresponding to the monoclinic phase of the material can be used to detect the CMAS within the TBC.

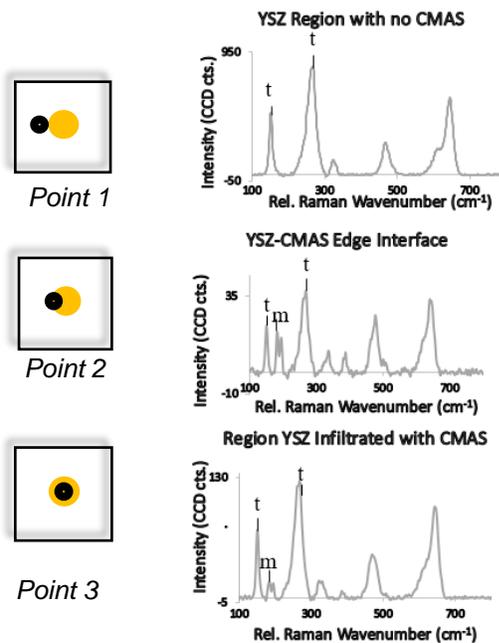


Figure 1 – Raman spectra (right) representative of the variation in phase composition from tetragonal (*t*) to monoclinic (*m*) at three different points (left) from in the sample heated at 1250°C for 10 hours: points 1 (CMAS free region), 2 (edge of infiltration), and 3 (infiltrated region).

Reference:

Bohorquez E., Sarley B., Hernandez J., Hoover R., Tetard L., Naraparaju R., Schulz U., Raghavan S., *Investigation of the Effects of CMAS-infiltration in EB-PVD 7% Ytria-Stabilized Zirconia via Raman Spectroscopy*. Extended abstract accepted for the 59th AIAA/ASCE/AHS/ASC Structural Dynamics, and Materials Conference, AIAA SciTech Forum, 8-12 January 2018, Orlando, FL.

Y₂O₃-ZrO₂ RATIO STUDIES FOR CMAS RESISTANT THERMAL BARRIER COATINGS PREPARED BY EB-PVD

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Key Words: CMAS/VA, reaction products, infiltration resistance, threshold point.

Thermal barrier coatings based on the yttria-zirconia system with compositions over 50 mol. % YO_{1.5} rest ZrO₂ have shown potential as CMAS/Volcanic ash (VA) resistant coatings¹⁻⁴. However, it is still not clear what Y-Zr ratio is the optimal to promote effective CMAS/VA arrest. A previous study has shown that pure Y₂O₃ coatings are not as effective as their yttria-zirconia counterpart⁴ making this topic of high relevance for the development of CMAS/VA resistant coatings. Therefore, this study is based on the determination of the optimal Y-Zr ratio for EB-PVD TBCs produced with compositions ranging from 40-70 mol. % YO_{1.5}. Preliminary results for short term infiltration (up to 7 min.) at 1250°C with natural VA from the Eyjafjallajökull volcano show a tendency of increased infiltration resistance with coatings having a higher yttria composition (70 mol. %) seen from Figure 1⁵. The experiments indicate formation of reaction products when a 50 mol. % YO_{1.5} coating composition is used and no significant reaction with lower yttria compositions. Thus, it appears that the threshold point to saturate the glass promoting formation of reaction products (apatite and garnet) is for compositions with at least 50 mol. % YO_{1.5}. A systematic study will be presented to determine the optimum yttria content in EB-PVD coatings for effective glass crystallization.

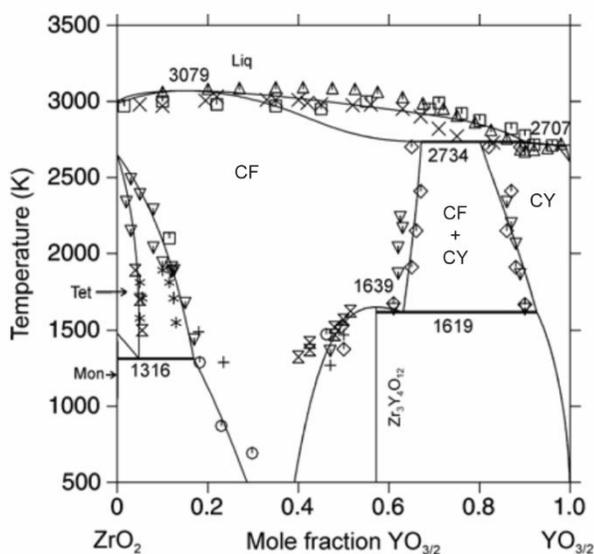


Figure 11 – Yttria-zirconia phase diagram where CF refers to the cubic fluorite YSZ phase and CY to the cubic yttria phase.

References:

1. Naraparaju R, Gomez Chavez JJ, Schulz U, Ramana CV. *Acta Mater.* 2017;136:164-180.
2. Krause AR, Li X, Padture NP. *Scr Mater.* 2016;112:118-122.
3. Krause AR, Garces HF, Senturk BS, Padture NP. *J Am Ceram Soc.* 2014;97(12):3950-3957.
4. Eils NK, Mechnich P, Braue W. *J Am Ceram Soc.* 2013;96(10):3333-3340.
5. Fabrichnaya O, Aldinger F. *J Mater Reserach Adv Tech.* 2004;95(1):27-39.

CALCIUM-MAGNESIUM-ALUMINO-SILICATE INDUCED DEGRADATION OF $\text{La}_2(\text{Zr}_{0.7}\text{Ce}_{0.3})_2\text{O}_7/\text{YSZ}$ DOUBLE-CERAMIC-LAYER THERMAL BARRIER COATINGS PREPARED BY ELECTRON BEAM-PHYSICAL VAPOR DEPOSITION

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Key Words: Thermal barrier coatings; CMAS; $\text{La}_2(\text{Zr}_{0.7}\text{Ce}_{0.3})_2\text{O}_7$; double-ceramic-layer; EB-PVD.

During last decades, much effort has been made to develop new alternative thermal barrier coating (TBC) to traditional YSZ for applications above 1250°C. $\text{La}_2(\text{Zr}_{0.7}\text{Ce}_{0.3})_2\text{O}_7$ (LZ7C3) is deemed as a very promising TBC candidate for advanced gas turbine because of its extremely low thermal conductivity, high sintering resistance and phase stability from room temperature to 1600°C. Thermal cycling with a gas burner showed that the LZ7C3/YSZ double-ceramic-layer (DCL) coatings prepared by electron beam-physical vapor deposition (EB-PVD) or atmospheric plasma spraying had a much longer lifetime than that of YSZ coating at 1250± 50°C. The use of the new TBC can allow higher gas temperatures, resulting in further improved thermal efficiency and engine performance. However, at these high operating temperatures, TBCs become susceptible to attack by calcium-magnesium-alumino-silicate (CMAS, relative to the main chemical components Ca, Mg, Al and Si) deposits resulting from the ingestion of siliceous minerals (dust, sand, volcanic ash, runway debris) with the intake air. CMAS becomes molten at temperatures above 1200°C and then rapidly penetrates the TBCs by capillary force, resulting in the loss of strain tolerance and premature failure of the coatings. In this paper, CMAS induced degradation of LZ7C3/YSZ DCL coatings prepared by EB-PVD method were investigated. Hot corrosion tests were performed at 1250°C at durations varying from 0.5 h to 24 h. It is observed that the infiltration of CMAS in the intercolumnar gaps was largely suppressed in the case of EB-PVD LZ7C3 coating. The penetration depth rarely exceeded 40 μm below the original surface even after 24 h exposure at 1250°C. This was ascribed to rapid dissolution of the LZ7C3 and essentially concurrent formation of a sealing layer made of crystalline apatite and fluorite phases, which is consistent with the observation on $\text{Gd}_2\text{Zr}_2\text{O}_7$. However, large vertical cracks would form in the EB-PVD LZ7C3 coating during thermal cycling as a result of re-crystallization, sintering and thermal expansion mismatch between ceramic coating and substrate. These vertical cracks can also act as channels to CMAS melt infiltration. Since the kinetics of the "dissolve-precipitation" reaction was slower than the infiltration rate of CMAS in the vertical crack, the majority of vertical cracks were not sealed. As a result, CMAS flowed down to the LZ7C3/YSZ interface along the vertical cracks, and then easily penetrated the YSZ buffer layer by capillary force. Chemical interaction also occurred in the YSZ buffer layer. What's more, the YSZ layer in the DCL coating even underwent a severer CMAS attack than the single YSZ coating. After 4 h CMAS exposure, the YSZ layer of the LZ7C3/YSZ bilayer coating was totally dissolved by molten CMAS followed by precipitation of a large number of globular ZrO_2 particles, while the single YSZ coating just suffered a slight degradation in the same experimental conditions and still kept its columnar structure. The probable reason was that the CMAS melt in the YSZ layer of the DCL coating had a higher CaO/SiO₂ ratio than the original CMAS composition due to the formation of apatite phase when CMAS reacted with the upper LZ7C3 layer. The initial Si: Ca ratio (Si: Ca≈1.4) in CMAS melt is less than the corresponding apatite (Si: Ca≈3), leading to progressive CaO enrichment during apatite crystallization. For this reason, it is suggested that the effectiveness of the CMAS mitigation strategy for YSZ TBCs by adopting a so-called CMAS-resistant top layer needs to be assessed in the context of more realistic conditions. If the formation of large vertical cracks in TBCs was not avoided, this CMAS mitigation approach may not as effective as expected.

CORRELATION BETWEEN POROSITY, AMORPHOUS PHASE AND CMAS CORROSION BEHAVIOUR OF LaMgAl₁₁O₁₉ THERMAL BARRIER COATINGS

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Key Words: LaMgAl₁₁O₁₉ coating; heat treatment; porosity; amorphous phase; CMAS corrosion

Calcium-magnesium-alumino-silicate (CMAS) attack is one of the significant failure mechanisms of thermal barrier coatings (TBCs), which can facilitate TBC's degradation at elevated temperatures. To clarify the correlation between the porosity, CMAS corrosion behaviour, lanthanum magnesium hexaluminate (LaMgAl₁₁O₁₉, LMA) TBCs were prepared by atmospheric plasma spraying (APS) and then heat-treated at 1173K and 1523K, respectively. For comparison, LMA tablets were prepared by mechanical and cold isostatic pressing. CMAS attack at 1523K was carried out both for LMA tablets and LMA coatings. Their microstructure, phase composition, and crystallization behavior after CMAS attack were investigated using scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS), X-ray diffraction as well as differential scanning calorimetry (DSC). The results indicated that CMAS attack was arrested for LMA tablets due to the formation of a dense crystalline layer induced by the chemical interactions between LMA and CMAS glass, while the as-sprayed LMA coatings were completely penetrated by molten CMAS due to the presence of amorphous phase and connected pores. Although the isothermal heat-treatment promoted a crystallization of LMA coatings, much vertical cracks formed during heat-treatment. The heat-treated LMA coatings suffered a severer CMAS attack than the as-sprayed one, since the vertical cracks inevitably provided efficient infiltration paths for molten CMAS.

Moved to Wednesday, June 27, 09:30 – 10:00

INVESTIGATION OF CMAS RESISTANCE OF SPS- AND SHVOF-ALUMINA TOPCOATS ON EB-PVD 7YSZ LAYERS

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Key Words: CMAS/VA, SPS, SHVOF, alumina sacrificial layer, EB-PVD 7YSZ layer

Thermal barrier coatings (TBCs) undergo severe degradation by interaction with molten calcium-magnesium-aluminum-silicate (CMAS) minerals that are found mainly in volcanic ashes (VA) or desert sands. After the infiltration of the CMAS, chemical reactions, diffusion and phase transformation can lead to residual stress, cracks and spallation and thus significantly shorten the life-time of the components. As the state-of-the-art material 7 wt.-% Y_2O_3 stabilized ZrO_2 (7YSZ) offers limited resistance to the CMAS attack, development of CMAS-resistant TBCs has undergone intense research during the last decades. One of the proposed approaches is the application of a sacrificial layer on top of the TBC which reacts with the molten CMAS/VA to crystalline phases and in this way inhibits further infiltration by sealing the gaps and pores. Al_2O_3 is one candidate for such a sacrificial layer which exhibits good CMAS resistance by formation of arresting phases. However, EB-PVD Al_2O_3 -topcoats suffer locally from cracks that arise from crystallization and sintering shrinkage, thereby providing only a discontinuous protection against CMAS infiltration due to their characteristic morphology. Even though the alumina is a candidate material, the coating density and the arrangement of porosity has been found to be a critical factor for restricting CMAS infiltration.

In this work alumina coatings were sprayed on top of EB-PVD 7YSZ TBCs using suspension plasma spraying (SPS) and suspension high velocity oxygen fuel spraying (SHVOF) starting from an aqueous suspension containing fine dispersed Al_2O_3 (d_{50} about 2.3 μm). The spray parameters were optimized in order to produce Al_2O_3 topcoats with homogeneous distributed porosity from very porous (porosity about 30 %) to denser (porosity about 10-15 %). These coatings were tested under CMAS attack by performing infiltration experiments at 1250 °C for different time intervals from 5 min to 10 hours. One Island volcanic ash from the Eyjafjallajökull volcano (IVA) and two types of synthetic CMAS compositions were tested in this study. The infiltration kinetics and reaction products were studied by SEM, energy-dispersive spectroscopy (EDS) and x-ray diffraction (XRD).

It was observed that the microstructure and especially the presence of the porosity in the Al_2O_3 coatings strongly influenced the CMAS infiltration kinetics. Due to its high and non-uniform porosity, CMAS/VA melt infiltrated the 100 μm thick, very porous alumina SPS-coating inhomogeneously and reached the subjacent 7YSZ layer already after one hour of annealing at 1250°C. Additionally, it was found that the infiltration kinetics varies also with the chemical composition of the CMAS/VA. Different crystalline phases such as anorthite, spinel or others were formed as reaction products of the SPS-Alumina-TBC with the CMAS/VA-melt. The exact phases and its location depend on the used CMAS/VA composition. Furthermore, the annealing time has a major influence on the presence of the various phases. The infiltration kinetics of the SHVOF-coatings was different due to a change in morphology. The current experiments clearly demonstrate that CMAS/VA mitigation depends on the interplay between morphology of the coating which dictates the driving force for infiltration, the reaction speed between alumina and the deposit, and the deposit chemistry.

ON COATINGS DELAMINATION; SOME ANALYTICAL SOLUTIONS

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Key Words: Delamination, mode mixity, equivalent boundary conditions, elastic compliance, buckling

A set of analytical solutions has been obtained related to crack growth along the boundary of a layer adjusting to another layer or half-plane. In particular, for the second Dundur's parameter vanishing the exact analytical solutions have been obtained for the two particular cases:

- semi-infinite crack separating two layers of equal thickness;
- semi-infinite crack separating a layers from a half-plane.

Two modes of stress intensity factors (SIFs) were obtained in terms of three force parameters: the total moment and two components (normal and shear) of the total force of stresses acting on the continuation of the crack line. The elastic clamping conditions [1-3] for a plate modelling the delaminated part of coating have also been obtained. According to these conditions the rotation angle and two components of displacement vector at the clamping point are related to the acting moment and two components of the total force by means of 3x3 matrix of compliance [4].

All functions involved are expressed in terms of single integrals of algebraic functions. For very small and very large ratios of Young's moduli simple asymptotics are derived.

The obtained solutions has been applied for the problems of buckling driven delaminations. It has been shown that for a wide range of parameters the ratio of the buckling stress and the critical stress of a rigidly clamped plate is determined by a single non-dimensional parameter, composed by the ratio of the elastic constants of the coating and substrate, and the ratio of the delamination length and the coating thickness. The solution has ben generalized for anisotropic and multilayered structures.

The problem of coating delamination from the cylindrical compliant substrate has also been addressed. Two types of prolonged blisters have been considered – along axial and circumferential directions: for each type of blisters the energy release rates have been calculated for their propagation in both axial and circumferential direction. For both cases tendencies for blister elongation has been observed.

From the practical point of view the obtained results is appeared to be useful for calculation parameters of coatings including TBC and for verifying precision of the program codes designed and to be designed for solving the wider range of problems of the kind. The results may also be useful for other applications such as interpretations of the results of blister tests.

1. Cotterell B., Chen Z. Int J Fract. V.104 (2000) 169-179.
2. Yu H.-H., Hutchinson J. W. Int. J. Fract. V.113. (2002) 39–55.
3. Begley, M.R, Hutchinson, J.W." The Mechanics and Reliability of Films, Multilayers and Coatings" Cambridge University Press, (2017).
4. Ustinov K.B. Eng. Fail. Analysis V.48B (2015) 338-344.

CRACK MORPHOLOGY IN A COLUMNAR THERMAL BARRIER COATING SYSTEM

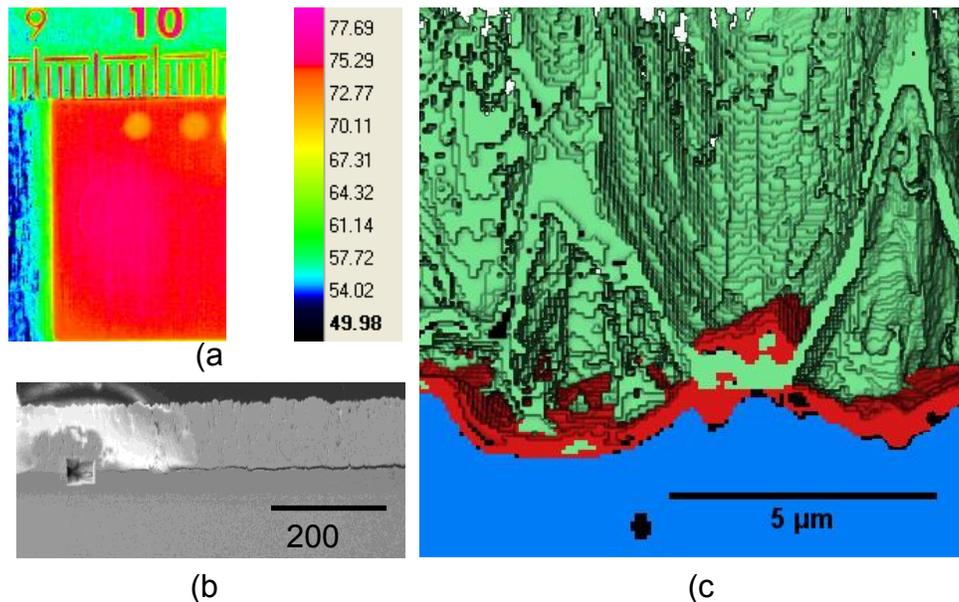
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Key Words: LASAT, FIB, EB-PVD, 3D morphology, crack tip

For high temperature application, EB-PVD ceramic layers are commonly used as thermal barrier coating. During thermal transients, the thermal expansion mismatch between coating and substrate drives failure of the TBC mainly by interfacial cracking. Laser Shock Adhesion Test (LASAT) provides stresses at the ceramic/metal interface enabling controlled interfacial cracking [1-2]. For achieving a clear understanding of the influence of local morphology on interfacial toughness, this study aims at characterizing the 3D morphology of a crack at the interface between metal and an EB-PVD TBC having a columnar structure.

Cracks were produced by LASAT. Surface infra red measurement yields to the localisation of the crack, that is detailed using cross-section, Fig (a) and (b) respectively. The crack tip was documented further in SE and BSE image stacks collected simultaneously during subsequent slice and view operations using a focus ion beam (FIB) and a scanning electron microscope (FIB slice & view). The segmented 3D data gives clear understanding of the columnar structure of the ceramic and of the interaction between the crack and the TBC microstructure, Fig (c).



- (a) IR analysis: yellow spots evidence interfacial crack
- (b) SEM cross-section: square on left side corresponds to the FIB location at the crack tip
- (c) Segmented images obtained from FIB: bond-coat (blue), oxide layer (red) both voids and cracks (green). ceramic (transparent)

References

- [1] Guipont, et al (2010). Journal of Biomedical Materials Research Part A, 95(4), 1096-1104.
- [2] Sapardanis, et al (2016). Surface and Coatings Technology, 291, 430-443.

EXPERIMENTAL CHARACTERIZATION OF ELASTIC STIFFNESS AND DELAMINATION TOUGHNESS IN COMMERCIAL THERMAL BARRIER COATING SYSTEMS

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Key Words: Compression Edge-Delamination, Elastic Stiffness, Delamination Toughness, 4-point bend

Layered thermal barrier coating (TBC) systems used in jet engines consist of a nickel-based superalloy substrate, intermetallic bond coat, thermally grown oxide (TGO) and a electron beam physical vapor deposition (EBPVD) 7% yttria-stabilized zirconia (7YSZ) top coat. Thermal protection is only provided when the TBC remains attached to the substrate, and mechanism-based lifetime assessment models rely on accurate knowledge of the experimentally measured interfacial fracture toughness and the topcoat modulus. We are employing 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. Of special interest are the CED specimens, which provide a direct measure of mode-II delamination toughness of the coating. In a parallel study, novel micro-bend techniques are being employed to measure the elastic modulus of both attached and freestanding EBPVD 7YSZ topcoats. Results for commercial TBC systems provided by industrial collaborators will be presented and used to characterize the effect of mode mix and various manifestations of thermal cycling on these material properties.

THERMAL STRESS ANALYSIS OF DOUBLE-CERAMIC-LAYERED THERMAL BARRIER COATINGS BASED ON RARE EARTH ELEMENT

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Key Words: Thermal Barrier Coatings, Rare Earth Element Oxide, Thermal Stress, Double Ceramic Layer.

So far, many studies have been conducted to increase the operating temperature of gas turbine engine because it enables to achieve the high efficiency with lower emission. As a part of continuous studies, various thermal barrier coatings (TBCs) have been applied onto hot-components as an efficient thermal insulating system. A typical TBC system consists of four layers: a metallic substrate, bond-coats, top-coats and thermally grown oxide between bond-coats and top-coats. Conventionally, top-coats are made of ceramic material such as 8% mol yttria stabilized zirconia (8YSZ) because of its low conductivity. However, 8YSZ based TBC suffers from considerable damage during the operating above 1200° due to the phase transformation and sintering, resulting in volume change and a decrease of strain tolerance.¹ Therefore, several oxide groups having the pyrochlore or fluorite structure are recommended to replace 8YSZ. To date, La₂Zr₂O₇ (LZ), La₂Ce₂O₇ (LC), LaTi₂Al₉O₁₉ (LTA) and Sr(Zr_{0.9}Yb_{0.1})O_{2.95}(SZYb) are of high interest.¹⁻³ Besides, double ceramic layer (DCL) is also applied on the bond-coats to improve the durability of TBC. Generally, the first top-coat (TC1) is made of the conventional 8YSZ as stress buffer on the bond-coats. Then, an alternative material is deposited as the second top-coat (TC2). In this study, using finite element (FE) analysis, we investigate thermal stress of the DCL typed TBC based on candidate materials when they have the same thermal insulating capacity above 1200°. As shown in fig. 1, a periodic FE model is constructed by taking both thermo-mechanical behavior and topological characteristics into account. Assuming that the turbine inlet temperature is 1500°, the surface of TC2 is heated by impinging gas of 1300° and the substrate is cooled by the internal cooling air equivalent to 700° for 3 cycles. As a result, the system having the lowest thermal stress is LC, followed by LTA, SZYb, and LZ. For all materials, the maximum stress always occurs during the heating period. Remarkably, the position and the moment where the maximum stress occurs are all different. The maximum stress is observed at the vicinity of the wavy oxide layer or TC2. But its moment is irregular such that it may occur at either the highest temperature or the room temperature. Consequently, it can be assumed that the service life is affected by not only the highest temperature but also the temperature difference during the operating cycle. Although LC is determined as the most suitable system to the given specific operation condition, there would exist the other optimal systems for different operation conditions, which can be further investigated by the proposed FE analysis in this study.

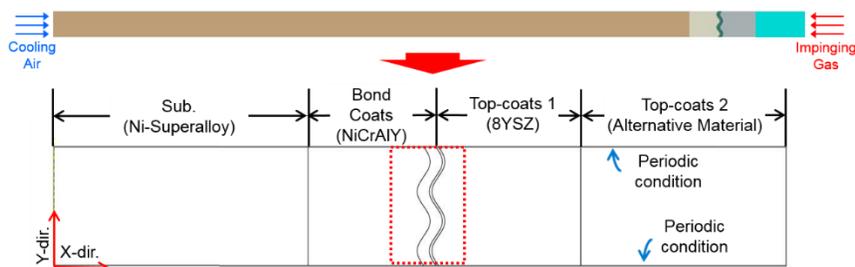


Figure 12 - An FEM model and its boundary conditions

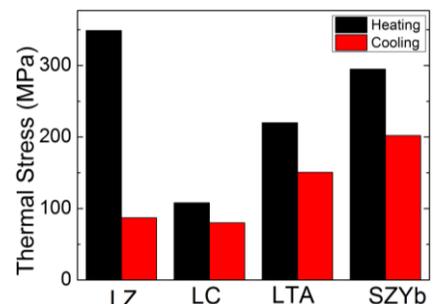


Figure 13 - Thermal Stress of DCL typed TBC based on alternative materials

1. Sadowski, T. and Golewski, P., 2016. *Loadings in thermal barrier coatings of jet engine turbine blades: An experimental research and numerical modeling*. Springer.
2. Darolia, R., 2013. Thermal barrier coatings technology: critical review, progress update, remaining challenges and prospects. *International materials reviews*, 58(6), pp.315-348.
3. Kumar, V. and Balasubramanian, K., 2016. Progress update on failure mechanisms of advanced thermal barrier coatings: A review. *Progress in Organic Coatings*, 90, pp.54-82.

DEVELOPMENT OF ENVIRONMENTAL BARRIER COATINGS FOR Al_2O_3/Al_2O_3 CMCS WITH IMPROVED ADHESION BY TEXTURING WITH LASER ABLATION

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Key Words: Environmental Barrier Coatings, Ox/Ox CMCs, surface structuring, thermal spray

Al_2O_3/Al_2O_3 ceramic matrix composites (CMC) are candidate materials for high-temperature applications such as gas turbines. As water vapor corrosion of oxide/oxide CMC is a major issue, the application of suitable environmental barrier coatings (EBC) is inevitable. Besides the gas tightness a good adhesion of the EBC is a crucial aspect for providing an effective barrier against the combustion atmosphere. Due to the brittleness of the ceramic matrix conventional surface treatments like grinding and sandblasting fail to increase roughness without causing damage to the substrate. Therefore there is a need for new methods of surface preparation of CMCs. This work examines the suitability of surface preparation with laser ablation for use prior to air plasma spraying (APS) on an oxide/oxide-CMC. Laser ablation allows controlling of the surface's structure and roughness. The effects of different laser parameters on the alumina surface were examined and a variety of different structures, for example a honeycomb or a cauliflower like structure, were prepared.

The laser treated surfaces were coated with potential EBC-candidates, such as Y_2O_3 and $Gd_2Zr_2O_7$ and the impact of laser textures on the coating adhesion was examined. Evaluation of the coated samples was done by pull-off adhesion testing and thermal cycling. Results indicate that laser pretreatment helps to increase the adhesion strength of the EBC-system.

ADVANCES IN THE DEPOSITION OF CERAMICS BY SOFT CHEMISTRY PROCESS: EXAMPLE OF RARE-EARTH SILICATE COATINGS

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Key Words: Dip-coating, rare-earth silicates coatings, suspension stability, microstructure

The dip-coating process consists in immersing a sample to be coated in the liquid medium and then removing it at a controlled speed in order to obtain a film of regular thickness, as shown in Figure 1a). Dip-coating technique is now used in many industrial fields (biomedical, transportation, optics...). It is a very simple, and easy process to implement for the deposition and shaping of different natures of coatings (ceramic, metallic and polymer). In the case of ceramic coatings, after the dip-coating operation, the layers undergo a sintering post-treatment leading to the consolidation and/or the densification of the deposit. The corresponding mechanisms need a rigorous control of many parameters. The parameters involved in the dip-coating process are related to the medium and to the process. Concerning the medium, the dispersion medium nature, the particles concentration, viscosity, and stability are the main ones. The stability of the suspension is a first-order parameter and a preliminary formulation work has been carried out to cope with it. Moreover, parameters relative to the fabrication process such as the number of layers and the thermal profile (intermediary and final temperatures), will also be key factors to be taken into account in the formation of homogeneous and reproducible coatings by dip-coating. This work highlights the influence of these various parameters in the case of rare earth silicates based coatings. The various experiments were carried out in correlation to the coatings quality and microstructure. Homogeneous and conformal ceramic coatings of few tens of micrometers thick, as shown in Figure 1b), were obtained. A multi-layers deposit in a sol loaded at 40% mass generally allows to reach the desired thickness. With these experiments relationship between dip-coating parameters and coatings microstructure and morphology can be established.

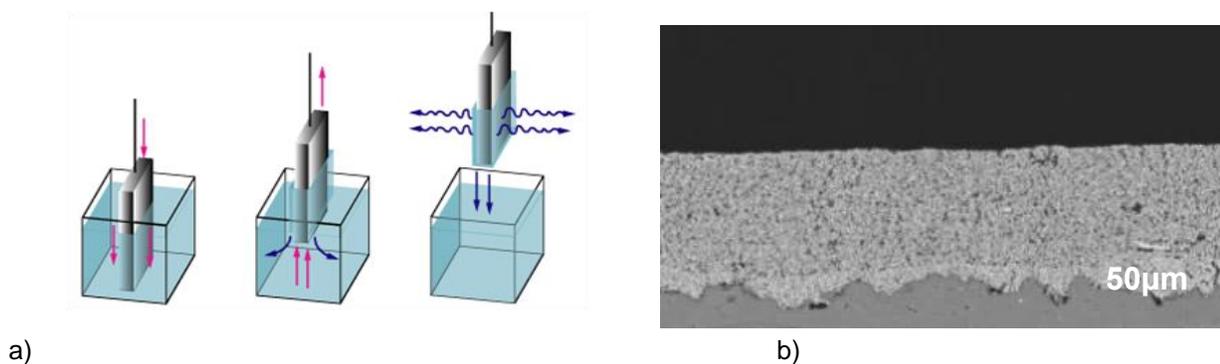


Figure 1: a) Schematic illustration of dip-coating process, b) SEM image of the cross-section of silicate based ceramic coating obtained by dip-coating"

DEVELOPMENT OF YTTRIUM AND YTTERBIUM SILICATES FROM THEIR OXIDES AND AN OLIGOSILAZANE PRECURSOR FOR COATING APPLICATIONS TO PROTECT Si_3N_4 CERAMICS IN HOT GAS ENVIRONMENTS

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Key Words: silazane, rare-earth silicates, polymer-derived ceramic, environmental barrier coating, hot gas corrosion

Environmental barrier coatings are required to protect Si_3N_4 against hot gas corrosion and enable its application in gas turbines. In comparison to other environmental barrier coatings, rare-earth silicate-based coatings stand out due to the very low corrosion rates in moist environments at high temperatures and the compatibility of thermal expansion coefficient to Si_3N_4 ceramics. Thus, the polymer-derived ceramic route was used to synthesize yttrium and ytterbium silicates in the temperature range of 1000-1500 °C for basic investigations regarding their intrinsic properties from a mixture of Y_2O_3 or Yb_2O_3 powders and the oligosilazane Durazane 1800. After pyrolysis above 1200 °C in air, the corresponding silicates are already the predominant phases. The corrosion behaviour of the resulting composites was assessed after exposure to flowing moist air at 1400 °C for 80 h. The material containing Yb_2SiO_5 and $\text{Yb}_2\text{Si}_2\text{O}_7$ as main crystalline phases undergoes the lowest corrosion rate ($-1.8 \mu\text{g cm}^{-2} \text{h}^{-1}$). In contrast, the corrosion rate of yttrium-based composites remained at least ten times higher. Lastly, the processing of Y_2O_3 /Durazane 1800 as well-adherent, crack-free and thick (40 μm) coatings on Si_3N_4 was achieved after pyrolysis at 1400 °C in air. The resulting coating consisted of an $\text{Y}_2\text{O}_3/\text{Y}_2\text{SiO}_5$ top-layer and an $\text{Y}_2\text{Si}_2\text{O}_7$ interlayer due to diffusion of silicon from the substrate and its interaction with the coating system.

FROM the LAB to the INDUSTRIAL SCALE: EBC THERMAL SPRAY POWDERS

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Key Words: EBC Powders, F&C, A&S, Flowability

The quality and performance of the feedstock material plays a key role in achieving a robust Environmental Barrier Coating (EBC) for Ceramic Matrix Composites (CMCs). As CMCs become commercialized there is a great need to implement the industrial-scale manufacture of EBC thermal spray powders from its current position as a laboratory-scale process. The challenges and the necessary development required to design a manufacturing process route from the raw materials to the RE-silicates thermal spray powder will be discussed. The fused and crushed (F&C) manufacturing process, including the new morphology of the agglomerated and sintered (A&S) RE-silicate powders, will be presented. The results of the influences of the process parameters on the evolved phases, particle size distribution, homogeneity, chemistry, purity and morphology will be discussed in detail. We will show that the selection of the best-performing material can be made based on the results from the correlations between flowability, apparent density, mechanical strength and morphology.

MEASUREMENTS OF MECHANICAL PROPERTIES OF AN AIR PLASMA SPRAYED THERMAL BARRIER COATING USING MICRO-CANTILEVER BENDING

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The elastic modulus and fracture toughness of an air plasma sprayed thermal barrier coating (APS TBC) were measured using the micro-cantilever bending technique. The micro-cantilevers were machined by a focus ion beam with their central arms either parallel or normal to the bond coat/topcoat interface. Such orientations allowed direct measurements of both the in-plane and out-of-plane elastic moduli as well as mode I fracture toughness by bending. The micro-cantilevers showed linear behaviour during bending. The calculated elastic modulus along the in-plane and out-of-plane direction is ~ 144 GPa and ~ 110 GPa, respectively, suggesting that the APS TBC is elastically anisotropic at microscale. The derived mode I fracture toughness along the plane parallel to the interface is ~ 0.40 MPa m. This relatively low toughness reflects the weak fracture resistance of the highly-flawed APS for short cracks at microscale. The measurements in this study can be incorporated into micromechanical life time prediction models of the APS TBCs.