RELIABLE THERMAL BARRIER COATINGS
FOR HIGH-LOADED TURBINE AND COMBUSTOR PARTS

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RESEARCH PROGRESS ON TBCS MATERIALS FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

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Recently, considerable efforts have been invested to explore new thermal barrier coating (TBC) materials with high temperature capability to meet the demand of advanced turbine engines. In this presentation, the research progress on TBC materials for ultra-high temperature applications in Beihang University is overviewed. The synthesis, coating processing, thermo-physical properties and thermal cycling performances of La-based oxides such as LaTi2Al9O19 (LTA) and modified La2Ce2O7 (LC) are investigated. Both the LTA and LC TBCs have exhibited very promising potential for applications at temperatures approaching 1573 K. Also, rare-earth oxides doped zirconia TBC with superior durability is reported here.
LIFING AND DEGRADATION OF EB-PVD THERMAL BARRIER COATINGS

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Electron-beam physical vapour deposition (EB-PVD) thermal barrier coating systems (TBC’s) have been used in gas turbine engines to successfully protect turbine aerofoils for several years. These coatings have been used to extend the life of components by lowering the operating temperature of the substrate alloy, reducing the amount of oxidation and thermal damage. However, to gain the greatest benefit from TBC systems, from the point of view of life and performance, the coating has to be considered early in the design process and the correct balance of life extension and aggressive cooling design chosen. To ensure that this process is robust, it is necessary for the surface engineer to understand the variation in spallation life of the ceramic and how this is related to temperature and the capability of the deposition process. This paper discusses failure mechanisms of EB-PVD TBC systems seen in service and laboratory validation testing, and the development of a probabilistic method to allow the development of a lifing method.
A combinatorial study of structure evolution and oxidation behavior of β-phase bond coats has been conducted. NiAl-based coatings with systematic variations in Pt, Pd, Cr and Hf have been fabricated by ion plasma deposition. Interdiffusion with the superalloy substrate, oxide spallation, and the rumpling behavior under thermal cycling conditions has been investigated, focusing on the relationship between these properties and the evolution of bond coat structure and composition. The durability of EB-PVD thermal barrier coatings deposited on the modified bond coats has been analyzed and the dependence of TBC failure on bond coat structure and properties will be discussed.
NEW BOND COAT MATERIALS IN TBC SYSTEM FOR ADVANCED SINGLE CRYSTAL SUPERALLOYS

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The bond coat in thermal barrier coating (TBC) system plays a very important role in determining thermal cycling durability of TBC. Interdiffusion between the bond coat and its underlying single crystal superalloy would cause degradation of oxidation resistance of the coating and significant reduction in mechanical properties of the superalloy. In this presentation, a NiAlX(X:Hf,Dy)/RuNiAl bond coat is proposed with the purpose of improving oxidation resistance and suppressing the precipitation of deleterious phases in superalloy such as secondary reaction zone (SRZ). The microstructure evolution, interdiffusion behaviors and the mechanism for suppress SRZ of the coating are investigated.
Advanced Ni-base single crystal superalloys have been developed to improve the thermal efficiency of aero jet engines. The coating compatibility is one of key issues to put them in practical use, because the Secondary Reaction Zone (SRZ) is easily formed in such new alloys once conventional bond coatings, e.g., Pt-modified aluminide and MCrAlY type coatings, are applied. Therefore, another bond coat system is required. In addition, the coating process temperature should be restricted to relatively low in the system, because the aging temperature of advanced alloys is required to be low. 1050 °C aging is the best for some advanced alloys, though the aging temperature of conventional CMSX-4 alloy is 1150 °C. In this study, Pt-γ+γ' type bond coatings were applied to advanced Ni-base single crystal superalloys, TMS-138 alloy and IHI-E5 alloy. As process parameters, the effects of Pt electro-deposition thickness, other element addition and diffusion temperatures on microstructures and creep rupture lives at 1100°C, 137MPa condition were studied. Other elements such as Ir, Al were added to coating by electro-deposition. And also, 7wt% yttria-stabilized zirconia (7YSZ) top coat was applied on samples by electron beam physical vapor deposition (EB-PVD) and the spallation lives at 1135 °C, 1h thermal cyclic condition were compared. The results show creep rupture life of the Pt-γ+γ' coated TMS-138 was longer than that of the Pt-Al coated TMS-138. No SRZ was observed in the Pt-γ+γ' coated TMS-138 after creep test, on the other hand, about 80 μm thick SRZ was observed in the Pt-Al coated TMS-138. The spallation life of TBCs on simple Pt-γ+γ' coating heat treated at 1050 °C did not show enough life time, but Ir addition Pt-γ+γ' coating show better spallation lives even though they were heat treated at 1050 °C.
COMPOSITIONAL FACTORS AFFECTING THE OXIDATION BEHAVIOR OF CURRENT AND DEVELOPMENTAL BOND COATING SYSTEMS

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Many high-temperature coatings rely on the formation of a continuous and adherent thermally grown oxide (TGO) scale of á-Al2O3 for extended resistance to degradation. For instance, the durability and reliability of thermal barrier coating (TBC) systems in gas turbines are critically linked to the oxidation behavior and stability of the alumina-forming bond coat, which may be based on á'-Ni3Al+á-Ni or á-NiAl (i.e., á, á+á or á+á'). This presentation will review research being conducted at the University of Pittsburgh to better understand the interplay between coating composition and oxidation behavior in order to guide both performance prediction and coatings development. Aspects to be discussed include the beneficial roles of Pt, Hf, Y, Si and Co, and efforts to develop Pt-free coating compositions that exhibit comparable or even improved performance compared to Pt-containing systems.
The formation of the thermally grown oxide (TGO) in thermal barrier coating (TBC) systems has been commonly considered as a factor, which has a significant impact on the system lifetime. In the present paper mechanisms of TGO formation in electron beam physical vapor deposited (EB-PVD) and air plasma sprayed (APS) TBC systems with MCrAlY (M = Ni,Co) type bondcoats are presented. The TGO-composition and growth kinetics are shown to be significantly affected by the chemical composition, microstructure and surface morphology of the bondcoat. The latter bondcoat properties are in turn determined by the bondcoat deposition and processing parameters prior to the application of the TBC coating. It is shown that for EB-PVD TBC systems with conventional MCrAlY-bondcoats the TBC lifetime can be related to a critical TGO thickness determined by the TGO growth rate and adherence and thus less sensitive to the temperature cycling parameters. In contrast for Zr and/or Hf containing MCrAlY-bondcoats forming faster growing, non-homogeneous TGO’s a stronger temperature cycling dependence is observed. For APS-TBC systems the time to macroscopic failure is much longer than the time for onset of TGO-delamination from the convex bondcoat surfaces. Consequently, for systems forming TGOs based on rather pure alumina the lifetime is mainly determined by the microstructural properties of the TBC and morphology of the TBC/bondcoat interface. The TBC lifetime can be shortened compared to alumina forming bondcoats if non-protective TGO’s based on Ni(Co)-rich spinels are formed. It is shown that such behavior can also be observed for MCrAlY-bondcoats with sufficiently high Cr (≥20% wt.) and Al (≥10% wt.) contents depending on the bondcoat Ni and Co contents as well as parameters of coating and processing treatments. The unintentional variation of the latter parameters can contribute to a large scatter in the thermal cyclic lifetimes observed for nominally the same TBC-systems.
Factors Controlling Adhesion of TBC Systems to Nickel-Based Superalloys

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Single crystal superalloys have traditionally been designed primarily with mechanical performance (i.e. creep and fatigue) in mind. With increasing operating temperatures (and hence efficiency) of gas turbine engines, the compatibility of these alloys with the thermal barrier coating systems placed upon them is also becoming an important design parameter. The current research involved a systematic study of the life-time of TBC systems on five different single crystal superalloys (SRR99, TMS-82+, PWA1484, CMSX-4 and TMS-138A) and three bond coat systems (Pt-diffusion, High Temperature Low Activity Pt-Al, and Low Temperature High Activity Pt-Al). An industry-standard yttria-stabilized zirconia (YSZ: \( \text{ZrO}_2/7\text{wt}\%\text{Y}_2\text{O}_3 \))-type ceramic top coat was used throughout this work, prepared using electron beam physical vapour deposition (EB-PVD) at a commercial facility.

Results of the study demonstrated that the compatibility of modern nickel-based single crystal superalloys with TBC systems is influenced strongly by the content of alloying element additions in the superalloy substrate. Electron microscopic characterization of the spallation interface showed that decohesion occurred at a position which depended on the substrate composition. It was observed that specimens with shorter TBC spallation life tended to fail at the TGO / bond coat interface; while more spallation-resistant coatings failed within the TGO or at the TGO / YSZ interface. No correlation was established between the oxide growth kinetics and the TBC spallation life. The results can be explained by postulating that the fracture toughness parameters controlling decohesion are influenced strongly by small changes in composition arising from interdiffusion with the bond coat, which itself inherits elemental changes from the substrate. This postulation, in fact, has been confirmed by preliminary results of a micro indentation-based assessment of the adhesion at the TGO / bond coat interface.
Industrial examples of platinum modified coating systems include the so-called platinum diffusion two phase \( f\alpha \) and \( f\alpha' \) bond coat, platinum aluminate bond coat of a single phase \( f\alpha'-(\text{Pt,Ni})\text{Al} \) and platinum modified EQ coatings based on a single phase \( f\alpha' \). Studies have indicated that the performance of thermal barrier coatings can be significantly improved by platinum modification of the bond coat. The reported benefits encompass improvement in oxidation resistance, suppression of interfacial rumpling, enrichment of aluminium population near the oxide-metal interface, enhancement of oxide adherence and most importantly, extension of the spallation life. Although the aforementioned beneficial effects have been extensively demonstrated, few studies have been conducted to elucidate the fundamental mechanisms underlying the apparent beneficial effects of platinum modification.

With this in mind, the current study was carried out to investigate both chemical and micromechanical influences of Pt in a systematic manner. Pt modified Ni-Al specimens were prepared with incremental addition of Pt (0, 5, 10 to 15 wt\%) while maintaining the aluminum content constant at 15 wt\%. Results of the study demonstrated that higher Pt content produced a thinner and more continuous oxide scale. The addition of Pt was also found to lower the coefficient of thermal expansion (CTE) of coatings at 1100 °C by approximately 5\%, and thereby, reduce the CTE mismatch between the \( \text{Al}_2\text{O}_3 \) scale and the intermetallic bond coat. This could partially explain the reason behind the suppression of interfacial rumpling with increasing platinum addition.

In order to rigorously manifest and explain some of the experimental observations and findings, a series of first-principles molecular-dynamics simulations comparing atomic bonding configurations through the analysis of the resulting electronic structure near the oxide-substrate interface with and without Pt-modification were also performed. By comparing the electron configuration of Pt-atoms with that of the substituted Ni-atoms, it was noticed that the delocalized 5d-orbitals of the Pt-atom participate more into the bonding hybridization with the 2p-orbitals of Al than the 3d-ones of the substituted Ni-atom do. Such a mechanism in the context of atomic bonding was also visualized as the Pt-atom near the top of the bond coat attracted the neighboring aluminum and oxygen atoms of the oxide scale and the topmost aluminum atoms of the bond coat to move more closely to itself. This resulted in a tendency for aluminum atoms to segregate in the interfacial zone that increased the number inter-atomic covalent bonds with oxygen atoms at the interface, therefore contributed to the formation of a dense and more protective oxide scale as well as the enhancement of the adhesion at the oxide-bond coat interface.
ON THE ORIGIN OF STRESSES IN ALUMINIDE BOND COATS DURING SERVICE AT HIGH TEMPERATURES

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The paper describes electron beam technology and equipment for single-stage deposition of graded thermal barrier coatings (TBC) by evaporation of composite ingots and their subsequent condensation in vacuum (EB-PVD). Design of a composite ceramic ingot is considered, as well as the available capabilities for controlling the composition, structure and properties of the deposited graded protective coatings and ensuring their high reproducibility. It is shown that use of a composite ingot allows deposition of a graded TBC on the surface of the items being protected in one technological cycle, including a metal bond coat, transition zones and outer ceramic layer. Use of the developed single-step electron beam technology of deposition of graded TBC allows an almost 2 times shortening of the duration and lowering of the cost of the technological cycle compared to the traditional multi-step technologies of deposition of multilayer TBC. Variants of graded TBC are given, containing a bond coat of NiAl (with Y and Hf additions) or MCrAlY+NiAl 25 – 125 microns thick and outer ceramic layer based on stabilized zirconium dioxide 125 – 250 microns thick, which were produced by the single-step cycle at composite ingot evaporation. Distribution of chemical elements in the substrate/coating system and microstructure after deposition and heat treatment were studied. The results of studying of stability of the graded outer ceramic layer based on ZrO2-Y2O3 with different additions against SMAS influence are demonstrated. Results of furnace thermal cycling tests of various types of graded TBC at 11500 C are given, demonstrating that the graded TBC 1.5 – 1.8 times exceed the traditional two-layer MCrAlY/ZrO2(Y2O3) as to thermal cyclic life-time. General views and main characteristics of industrial electron beam equipment designed for producing the above coatings, are demonstrated.
DEVELOPMENT OF A LOW PRESSURE PLASMA DEPOSITION TECHNIQUE TO IMPROVE THE PROPERTIES AND THE RESISTANCE OF THERMAL BARRIER COATINGS

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The Yttria partially Stabilised Zirconia (YpSZ) actually is the most employed thermal barrier coating (TBC) in aeronautics. Deposition techniques such as Electron Beam Physical Vapor Deposition (EBPVD) or (Air Plasma Spray) permit to obtain thick YpSZ layers with columns or vertical cracks and porosities (global porosity less than 25%). A new plasma process working under low pressure and power conditions (600 Pa, 200 W) was developed to deposit TBC exhibiting low thermal diffusivity and high resistance against the chemical attacks of the atmospheric dusts (CaO, MgO, Al2O3 and SiO2 – CMAS). In this way, the plasma reactor was used to deposit coatings such as YpSZ and YpSZ-Gd2Zr2O7 multi-stack. The Scanning Electron Microscopy analyses showed that the YpSZ layer was more than 80 µm thick (growth rate around 20 µm). The presence of micro, nano pores and vertical cracks was observed into the coating. The water porosimetry was used to estimate the porosity of YpSZ, which was determined to be around 50% (2 x higher as compared with atmospheric plasma spray). The morphology of the coatings synthesized in the low pressure plasma process was not observed in the literature. Several analyses such as Fourier Transformed Infrared Spectroscopy, X ray Diffraction and SEM confirmed that the chemistry and the low thermal conditions in the plasma discharge was responsible for the synthesis of YpSZ coating exhibiting this particular morphology. Contrary to YpSZ, Gd2Zr2O7 coatings were denser and did not contain vertical cracks. This property makes it possible this coating to resist against the penetration of the melted CMAS into the thermal barrier. Actually, an experimental set up equipped with an inductive 20 kW plasma torch is under development to inject and melt CMAS onto the thermal barrier coating. The aim is to validate the use of Gd2Zr2O7 as a protective layer for YpSZ against CMAS attack. The first results concerning the chemical attack of the zirconia by the CMAS performed in this plasma experimental se-up are reported.
Suspension or more general liquid precursor plasma spraying has received a lot of interest over the last decade due to the unique coating properties obtainable with this process. Especially in the area of thermal barrier coatings promising properties have been reported. The main advantage of the process for this application is the possibility to manufacture a high segmentation crack density in combination with a rather porous matrix. This specific microstructure leads to a rather low thermal conductivity in combination with a good thermal cyclic performance. Recent results related to these topics will be presented.

Additional issues which will be addressed in the paper are the requirements for an industrial application of the process. This will include a discussion of consequences of the typically applied very low stand-off distance and possible measures to overcome this limitation. In addition, characteristics of the process related to reproducibility and overspray will be highlighted.
Thermal barrier coating (TBC) systems are currently employed on gas turbine engine components to thermally and environmentally protect them from high gas inlet temperatures. These coating can result in the improved performance (fuel efficiency and thrust) of these engines and can also be used to increase component durability. The continual elevation of engine operation temperatures and the need to improve the reliability of these coatings has led to increased interest in TBC systems having enhanced thermo-mechanical durability, reduced top coat thermal conductivity and sintering rate and an increased resistance to high temperature erosive and corrosive environments. Alternative coatings and coating approaches are therefore of interest to potentially improve the performance of these multilayered coating systems. Directed Vapor Technologies International (DVTI), is currently investigating the use of an advanced electron beam vapor deposition approach, Directed Vapor Deposition (DVD), as a method for applying high quality thermal barrier coating systems at high rates onto engine components. The DVD process operates in a novel processing environment that employs a supersonic gas jet to “direct” vapor atoms onto components resulting in the highly efficient deposition of complex coating structures and compositions. Here, the use of this approach to deposit advanced TBC compositions, microstructures and architectures to achieve a comprehensive thermal barrier coating system that can provide improved performance and durability during elevated temperature exposures will be discussed.
MULTILAYER 3D PHOTONIC CRYSTALS FOR APPLICATION AS HIGHLY REFLECTIVE THERMAL BARRIER COATINGS (TBC)

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At temperatures in excess of 1200°C, the contribution of thermal radiation to the overall heat transfer inside of the gas turbines substantially increases. If the low thermal conductivity of conventional thermal barrier coatings (TBCs) would be combined with a high reflectivity in the infrared (IR) range, the thermal efficiency of the turbines could be improved and/or their lifetime could be substantially extended.

Three-dimensionally ordered macroporosity (3DOM) can provide TBCs with functionality of a photonic crystal (PhC). Radiation with wavelengths corresponding to the photonic bandgap (determined by the periodicity of the structure and the refractive index of the material) can be efficiently reflected. Coatings consisting of several PhC-layers with varying lattice constant can reflect light in a wide wavelength range and could potentially be used as IR-reflecting TBCs.

Test coatings with the inverse opal topology were obtained by self-assembly of monodisperse polystyrene (PS) particles of different diameters (400-1000 nm) followed by infiltration of the so-obtained templates with the ceramic phase by atomic layer deposition and subsequent removal of PS by calcination in air at 500°C. Titanium dioxide was used as ceramic phase due to its high refractive index. The samples demonstrated well-defined stopgaps in the IR-range. Multilayer inverse opals were produced by the repetitive self-assembly of PS particles of different sizes and ALD-infiltration steps.

The stability of the morphology and optical properties upon exposure to high temperatures was investigated. After the standard calcination procedure, the deposited titania was amorphous (there were no peaks in the XRD spectra). Amorphous TiO$_2$ turned into the anatase phase after annealing at 600°C. Only minor changes of the 3D-structure were found. The stopgap and thus the optical reflection properties in the IR did not change. After annealing at 900°C for 20 hours, considerable structural changes in the titania coating were observed although the pores were still highly periodical. It can be expected that PhC-coatings made of yttrium-stabilized zirconia would withstand much higher temperatures.
An intensive challenge for aircraft and industrial gas turbine engines in the recent decades is to increase operating temperature to a maximum without overheating the metallic parts during engine service. This demands the thermal barrier coating to have high thermal insulation capability with low thermal conductivity and high durability in the increased turbine inlet temperature and hostile environment filled with oxygen, erodents and various other contaminants. Chromalloy Gas Turbine LLC developed a new air plasma sprayed multilayer thermal barrier coating that shows a low thermal conductivity and an extended lifetime. The coating system has either a double layer structure of an alternative new chemistry Nd-Zr and typical 7YSZ or a triple layer structure of 7YSZ/Nd-Zr/7YSZ. The chemistry of the new Nd-Zr layer is NdₓZr₁₋ₓOᵧ with D dissolved in, where x is 0.1-0.5, y is 1.75-2.0 and D is an oxide of a metal selected from Y, Mg, Ca, Hf and mixtures thereof. The double and triple layer coating systems were sprayed onto Ni or Co based buttons, pins and engine components with MCrAlY bond coat under the typical and modified APS programs. The low thermal conductivity, extended cyclic oxidation lifetime, good phase stability, high sintering resistance, and enhanced erosion resistance in these coating systems are reported in this paper.
CONTROLLED INTRODUCTION ON ANELASTICITY IN PLASMA SPRAYED TBCS: IMPLICATIONS FOR PERFORMANCE AND RELIABILITY

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Mechanical compliance measurements of plasma sprayed ceramic coatings have revealed anelastic response i.e. the stress-strain relations are non-linear and hysteretic, collectively. Such anelasticity stems from the “brick” layered assemblage of spray deposited droplets along with the presence of porosity and other geometric discontinuities. This anelastic response is reproducible and can provide a quantitative description on the mechanical properties of the sprayed ceramic coating. It has further been observed that the anelasticity can be modified through plasma spray processing parameters and provides a framework for optimizing coating architecture design for enhanced performance. Furthermore, the anelastic parameters also provide a unique signature to describe the coating characteristics and as such provide a framework for monitoring process and coating reliability. This presentation will provide salient results in this integration of process-structure-property relations.
Plasma spray - physical vapor deposition (PS-PVD) is a low pressure plasma spray technology recently developed by Sulzer Metco AG (Switzerland) to deposit coatings out of the vapor phase. PS-PVD is developed on the basis of the well established low pressure plasma spraying (LPPS) technology. In comparison to conventional vacuum plasma spraying (VPS) and low pressure plasma spraying (LPPS), these new processes use a high energy plasma gun operated at a work pressure below 2 mbar. This leads to unconventional plasma jet characteristics which can be used to obtain specific and unique coatings. An important new feature of PS-PVD is the possibility to deposit a coating not only by melting the feed stock material which builds up a layer from liquid splats but also by vaporizing the injected material. Therefore, the PS-PVD process fills the gap between the conventional physical vapor deposition (PVD) technologies and standard thermal spray processes. The possibility to vaporize feedstock material and to produce layers out of the vapor phase results in new and unique coating microstructures. The properties of such coatings are superior to those of thermal spray and electron beam - physical vapor deposition (EB-PVD) coatings. In contrast to EB-PVD, PS-PVD incorporates the vaporized coating material into a supersonic plasma plume. Due to the forced gas stream of the plasma jet, complex shaped parts like multi-airfoil turbine vanes can be coated with columnar thermal barrier coatings using PS-PVD. Even shadowed areas and areas which are not in the line of sight to the coating source can be coated homogeneously. This presentation reports on the progress made by Sulzer Metco to develop a thermal spray process to produce coatings out of the vapor phase. Columnar thermal barrier coatings made of Yttria stabilized Zirconia (YSZ) are optimized to serve in a turbine engine. This includes coating properties like strain tolerance and erosion resistance but also the coverage of multiple airfoils.
To better understand the performance of thermal barrier coating systems a range of techniques have been developed which assess the interfacial adhesion, residual stress state and delamination behavior of EB-PVD and APS systems. In the case of a Pt- diffused gamma/gamma prime bond coat, both X-ray and wafer-curvature methods were employed to evaluate the residual stress in the bond coat. The residual stress measured by curvature method exhibits a decreasing trend from -147 MPa for as-processed bond coat to -10 MPa after 40 hours at 1150°C. Surprisingly, the residual stress measured by X-ray increases from -150 MPa for as-process bond coat to -460 MPa after 40 hours oxidation. All these phenomena can be related to the microstructure changes induced by Pt diffusion. Again for the Pt-diffused gamma/gamma prime EB-PVD system, using a previously established model for compression induced buckling, the estimated interface toughness was found to decrease with oxidation time. In this approach, although both nano-indentation and the small beam bending method have been used to determine the Young's modulus of TBCs, it is proposed that the Young's modulus derived from the beam bending method should give a Young's modulus related to the buckling phenomena. In this case, the mode I interfacial toughness was obtained as 10 J/m² for as-deposited TBCs to 0.79 J.m² for the 60 hour-oxidized TBCs. The decrease in the interface toughness due to oxidation can be attributed to changes in interfacial chemistry.

The delamination behavior of air plasma sprayed (APS) TBCs after annealing at 1050°C were investigated. A modified 4-point bending was employed to evaluate the interfacial fracture toughness. In all conditions, the delamination occurred primarily within the top coat, just several micrometers above the TGO layer. The energy release rate increases first to the maximum after 10h annealing, and then gradually decreases with further annealing. The reasons for this phenomenon could be related to the phase transformation and sintering occurring during annealing.

The electrical and mechanical properties of atmospheric plasma sprayed (APS) yttria stabilized zirconia (YSZ) thermal barrier coatings (TBCs) TBCs were determined using impedance spectroscopy and an indentation technique, respectively. Upon thermal exposure, sintering and phase transformation occurs in the YSZ TBCs, leading to changes in both the mechanical and electrical properties of the TBCs. After the thermal treatment, the formation of the monoclinic phase in the YSZ TBCs reduced the density of the TBCs and thus affected both the mechanical properties and conductivity of the TBCs.
THE EFFECT OF PROCESSING VARIABLES ON THE DURABILITY OF HIGH-PURITY YSZ-TBCS PREPARED BY APS

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The high-temperature behavior of high-purity, low-density (HP-LD) air plasma sprayed (APS) thermal barrier coatings (TBC) with NiCoCrAlY bond coats deposited by argon-shrouded plasma spraying will be described. The durability of thick HP-LD APS TBCs was found to be equivalent to or greater than that of thinner EBPVD TBCs. The high durability is postulated to result from several effects. The high purity resulted in very high resistance to sintering, which maintained a low value of the elastic modulus of the porous topcoat. Also, the phase transformation from the metastable tetragonal phase to the equilibrium mixture of monoclinic and cubic phases, which degrades fracture toughness, was suppressed. This presentation will focus on the effects of bond coat and topcoat architecture and the composition and CTE of the substrate on coating durability.
Ceramic environmental barrier coatings (EBC) and SiC/SiC ceramic matrix composites (CMCs) will play a crucial role in future aircraft propulsion systems because of their ability to significantly increase engine operating temperatures, reduce engine weight and cooling requirements. Advanced EBC systems for low emission CMC combustors and turbine airfoils are currently being developed under the NASA Fundamental Aeronautics and Intergraded System Research Programs to meet next generation turbine engine emission and performance goals. This paper will focus on NASA’s advanced EBC system approaches and technologies for SiC/SiC ceramic matrix composite combustors, turbine vanes and blades for next generation engines to significantly improve the engine component temperature capability and long-term durability. Degradation and failure modes of environmental barrier coating systems on SiC/SiC CMCs under various simulated engine testing environments, in particular in those with high pressure and high velocity, and with creep and fatigue loading conditions, will be addressed. The EBC improvements based on advanced testing in conjunction with modeling and design tools will be highlighted. Advanced EBC-CMC component testing and demonstrations under the current NASA programs will also be discussed.
WATER VAPOR RECESSION OF ENVIRONMENTAL BARRIER COATINGS FOR CERAMIC MATRIX COMPOSITES

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Si-based ceramics, such as silicon carbide (SiC) fiber-reinforced SiC ceramic matrix composites (SiC/SiC CMCs) and monolithic silicon nitride (Si3N4), are the leading candidate for next generation gas turbine hot section structural materials due to their high temperature strength and durability. Si-based ceramics, however, suffer from severe surface recession due to water vapor-induced volatilization of silica scale in high pressure, high velocity combustion environments, such as those in gas turbine hot section. Current solutions to preventing the recession include an external barrier coating, which is now known as environmental barrier coating (EBC), that shields Si-based ceramics from water vapor. Key components of current environmental barrier coatings include mullite, barium strontium aluminum silicate (BSAS), and rare earth silicates. EBC also recesses in the presence of water vapor and thus the accurate projection of EBC recession in service conditions is critical for EBC lifing. It is highly challenging to experimentally determine EBC recession because of the technical difficulty in simulating high temperature, high velocity and high pressure water vapor environments in a laboratory setup. This paper will discuss various experimental techniques for EBC recession measurement, EBC recession data in the literature, EBC recession measurement using water jet rig and computational modeling of EBC recession.
NEW THERMAL BARRIER COATINGS FROM COMPLEX PEROVSKITES

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The exceptional thermal properties and phase stability of ABO3 perovskite ceramics make them promising materials for high temperature insulation applications. In the case of thermal barrier coating (TBC) applied on gas turbine blades, several compositions from this class of materials have been considered. Most of them however fall short of the standard coating properties set by the state-of-the-art TBC composed of yttrium partially stabilized zirconia (YSZ). The major problem arises basically from coating deposition through plasma spraying whereby partial evaporation of feedstock components occurs. This leads to the deposition of non-stoichiometric phases which undergo catastrophic transformation on heating at high temperatures. Latest investigations involving complex forms of perovskites have shown that such partial evaporation can be minimized through systematic tailoring of spray parameters. Under burner rig cycling test at about 1400 °C surface temperature, the complex forms composed of Ba(Mg1/3Ta2/3)O3 and La(Al1/4Mg1/2Ta1/4)O3 show promising lifetimes especially when applied as an overlay coating to YSZ in a double-layer system. The bulk mechanical and thermal properties of these materials are comparable if not better than YSZ. Specifically, no catastrophic phase transformation occurs up to their melting point (~ 2800°C) hence they can be promising alternatives or supplemental coatings as the state-of-the-art YSZ TBC fails at long-term application temperatures higher than 1200°C.
IMPACT AND EROSION PERFORMANCE OF THERMAL BARRIER COATINGS

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Thermal barrier coatings (TBC) used on the hot section components of a gas turbine engine are susceptible to various life limiting issues that prevent current engine designs from taking more credit for the thermal gradients made possible by TBC. One of such life limiting issues is that particles ingested into and/or liberated in gas turbine engines collide with TBC coated parts at high speeds resulting in premature TBC failure. Lab test methods have been developed to investigate the impact and erosion performance of TBC and understand the mechanisms leading to TBC failure. The results from a number of lab tests are discussed and compared to the field experience of TBC coated parts in terms of impact and/or erosion damages. Improved impact and erosion resistance would enable a more durable TBC that could lead to significant efficiency improvements through savings in cooling air and higher operating temperatures.
For thin (less than 200 micron) air plasma spray (APS) and electron beam physical vapor deposition (EB-PVD) ceramic thermal barrier coatings (TBCs), some non-destructive techniques indicate damage at the bond coat-TBC interface during either ageing or cyclic oxidation tests. However, no technique is available for thick (more than 250 micron) APS TBCs. Several applications of transient thermography for detecting macroscopic coating detachments are reported in the literature. Most of these techniques work properly when a sound TBC area is available for being compared to the defected one. On the other hand, if diffused microscopic cracking of the interface all along the inspected area is expected, these techniques do not allow a clear integrity assessment of the interface. In fact, owing to the heat diffusion, each single crack is too small to produce a thermal indication on the TBC surface and for the same reason no sound reference area can be clearly identified. In this work, a semi-quantitative estimation of cracks at the interface of TBCs is obtained from thermal diffusivity values measured on coupons subjected to thermal cycling by using a single side thermographic technique. In fact, during thermal cycling, two phenomena occur: sintering that promotes a significant increase of thermal diffusivity, and cracking that, representing an additional thermal resistance, causes an apparent decrease of thermal diffusivity. The reported results refer to an experimental activity carried out on twenty-eight APS TBC samples cyclic aged at six different fractions of their lifetime. For each sample, the thermal diffusivity was measured at fixed lifetimes and the evolution of the cracked fraction of the interface was estimated by adopting a 2-D inversion model. Furthermore, at each of the six lifetime fractions some samples were destructively characterized by image analysis and the results were compared to the estimations given by the inversion model. A good agreement between the non-destructive estimations and image analysis results has been obtained. Moreover a figure of merit incorporating both the cracked fraction and the crack thickness is also proposed for ranking the damage.
CMAS: LESSONS LEARNED AND PERSPECTIVES

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Substantial progress has been made since the last Irsee conference on the understanding of the mechanisms of CMAS attack of thermal and environmental barrier coatings and the potential avenues for mitigation. Concurrently, awareness of the CMAS threat has broadened because of (i) increased evidence of CMAS damage in advanced commercial aero-engines, (ii) the recent disruption of air transport by volcanic ash plumes over Europe, and (iii) the growing interest in IGCC power generation plants where coal ash is a concern. The prospect of coating surface temperatures as high as 1500-1650°C in future gas turbines is severely undermined by CMAS melts, which can form at temperatures as low as ~1200°C and attack all oxide materials critical to the protection of metallic and/or ceramic components in the hot-gas path. Current mitigation approaches take advantage of the reaction to yield crystalline products that are more stable in contact with CMAS, but also consume a major fraction of the melt and reduce the volume available for further penetration or dissolution of the coating. Two critical issues in need of further understanding emerge. One relates to the effect of the chemical compositions of both the melt and the thermal or environmental barrier oxide(s) and another to the durability of the reacted layer under stresses produced by thermal gradients and cyclic thermal excursions, and/or chemical attack by combustion gases, notably water vapor. This presentation will review our current understanding of these issues based on recent studies of the melting and crystallization behavior of CMAS and CMAS+T/EBC combinations, as well as the response of the system to static and transient thermal gradients. The material challenges posed by the increasingly aggressive environments will also be discussed. (Presentation based on research performed by E.M. Zaleski, K.M. Grant, D.L. Poerschke, K.M. Wessels, C. Ensslen, R.W. Jackson, R.M. Leckie, J. Van Sluytman and S. Krämer. Work sponsored by the Office of Naval Research under grants N00014-08-1-0522 and N00014-06-1-0322, monitored by Dr. David Shifler.)
Y₂O₃ partially stabilized ZrO₂ (YSZ) is the state-of-the-art material for thermal barrier coatings (TBC) of turbine engine airfoils. YSZ TBCs for aircraft engines are usually fabricated by electron-beam physical vapor deposition (EB-PVD) which produces a characteristic columnar and highly porous microstructure showing beneficial strain-tolerance and low thermal conductivity. The most prominent and technologically most relevant degradation of TBCs is hot-corrosion induced by airborne inorganic particles ingested and subsequently deposited on hot turbine airfoils. This is referred to as CMAS-type hot-corrosion (calcia-magnesia-alumina-silica). In spring 2010, uncertainties on the performance and safety of aeroengines exposed to particles produced by the massive eruption of the Eyjafjallajökull volcano (Iceland) imposed serious limitations on European air traffic. Chemical analyses showed that the volcanic ashes have a much higher SiO₂ content and chemical complexity compared with the CMAS-type deposits commonly found on turbine airfoils. A key feature is also a much lower content of alkaline earth oxides (CaO, MgO) and, on the other hand, a significant content of alkaline oxides with Na₂O dominating K₂O. In the present work we report on the compatibility between standard 4 mol-% Y₂O₃ stabilized ZrO₂ EB-PVD thermal barrier coatings in the presence of artificial and genuine Eyjafjallajökull-type volcanic ashes. The microstructural features of the reactive interfaces and newly formed phases are monitored by electron microscopy. It turns out that a massive degradation of EB-PVD YSZ-TBCs is induced by volcanic ash deposits only after a few hours at 1200°C. The high silica activity of volcanic ashes triggers partial destabilization of tetragonal YSZ and subsequent formation of monoclinic ZrO₂ as well as significant crystallization of zircon (ZrSiO₄).
GARNET-TYPE REACTIVE INTERFACES FROM FE-TI-CMAS HOT CORROSION OF YSZ COATED ENGINE HARDWARE

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Crystalline CMAS-type surface deposits and CaSO₄ (anhydrite) pore fillings from an in-service EB-PVD 7YSZ coated 1st stage HPT airfoil are investigated in order to access the zirconia recession mechanism during thermal cycling. Small probe microanalysis reveals high lime-to-silica ratios and substantial amounts of Fe₂O₃ and TiO₂ indicating that an expanded Fe-Ti-CMAS system provides a more realistic hot corrosion scenario than amorphous model CMAS compositions. The Fe-Ti-CMAS composition proves to be an effective solvent for YSZ introducing solid-state reactions along the Fe-Ti-CMAS/YSZ interface which are investigated by scanning electron microscopy (SEM) and focused-ion-beam (FIB) assisted analytical transmission electron microscopy (TEM).

Upon partial dissolution of the YSZ column tips the reactive interfaces involve the garnet-type Ca₃(Zr, Mg, Ti)₂(Fe,Al,Si)₃O₁₂ phase, also known as the mineral kimzeyite, CaZrO₃ and Ca-doped FSZ particles. Phase compatibility at the interfaces confirms a two-stage hot corrosion process of the airfoil comprising (i) an early stage controlled by a Si-free Ca-source, most likely primary CaSO₄ producing a thin CaZrO₃ layer followed by (ii) a high Si-activity Fe-Ti-CMAS stage stabilizing kimzeyite instead. Due to its large homogeneity range the garnet phase provides an effective impurity sink at the Fe-Ti-CMAS/YSZ interface.
CMAS DEGRADATION OF EB-PVD THERMAL BARRIER COATINGS: FROM EX SERVICE EXAMINATIONS TO LABORATORY TESTS

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Thermal barrier coatings (TBC) have been used for more than fifteen years to protect turbines vanes and blades located in the hot sections of gas-turbine engines. The standard TBC system consists in an EB-PVD 8YPSZ layer (100-200µm thick) on top of a NiAl(Pt) or MCrALY bond coat. During fabrication and service, a thermally grown oxide (TGO) forms between the bond coat and the TBC. The component design optimization, the complex blade-cooling technology and the TBC use have allowed an increase in gas inlet temperature leading to temperatures on the order of 1200°C on the surface of the TBC. At such temperatures, under service conditions, TBC are susceptible to corrosion by molten calcium-magnesium-alumino silicates (CMAS) resulting from the ingestion of siliceous mineral debris (dust, sand, ash) contained in the hot gases arriving in the turbine.

In the literature, few studies can be found investigating the real interaction CMAS-TBC coating on ex-service blades or vanes, especially when the coating is elaborated by EB-PVD. The usual approach has mainly consisted in reproducing this corrosion in laboratory using a model synthetic CMAS and a thermal barrier directly coated on an alumina substrate.

This presentation aims to give new experimental data on the CMAS degradation of EB-PVD coatings in order to improve the understanding of the TBC-CMAS reaction. It firstly consists in a microstructural characterization of the interaction between CMAS and an EB-PVD TBC observed on a high pressure M88 turbine blade removed from service. In a second part, we compare these results with those obtained on a laboratory scale, under controlled conditions, using an original model CMAS composition (tridymite-pseudowollastonite-anorthite eutectic,1170°C).

In a last part, various CMAS resistant layers are tested, using dense materials or EB-PVD or PECVD coatings. All are zirconium based material doped with an effective amount of a lanthanum series based oxide, including pyrochlore. It is observed that the prevention of CMAS infiltration is obtained through the formation of a dense reaction layer under the main reaction zone between CMAS and doped zirconia.
The quest for higher efficiencies and performance demands higher operating temperatures in gas-turbine engines used in aircraft propulsion and electricity generation. Ceramic thermal barrier coatings (TBCs) used to protect and insulate hot-section metallic engine components are playing an important role in meeting those demands. However, the higher surface temperatures make TBCs more prone to deposition of undesirable silicates ingested by the engine, engendering new materials issues. The undesirable silicates can be in the form of sand (calcium-magnesium-alumino-silicate or CMAS) and volcanic ash in the case of aircraft engines, and coal fly ash in the case of synthetic-gas-fired engines used for electricity generation. The understanding of thermo-chemo-mechanical mechanisms by which these types of deposits damage conventional air plasma sprayed (APS) 7YSZ TBCs will be presented. Demonstration and understanding of approaches to mitigate this type of damage will also be presented, together with a discussion of guidelines for development of future TBCs.
Sintering- driven changes in the microstructure and properties of TBCs in gas turbines, due to prolonged exposure to high temperature in service, can impair their thermo-mechanical stability. In particular, sintering can cause substantial increases in stiffness and reductions in strain tolerance. These changes can be accelerated by the presence of impurities that segregate to the grain boundaries, where they enhance the solid state diffusivity [1] or, at sufficiently high concentrations, produce a vitreous phase that can dramatically accelerate sintering. The impurities that are most likely to have such effects are often termed CMAS (calcia-magnesia-alumina-silica), which are ingested into the engine in the form of particulates and may be deposited on the coating. Environmental deposits, such as volcanic ash, with particularly low melting points compared to typical gas turbine entry temperatures may pose a particular threat in this respect.

In this study, specimens have been subjected to extended periods at isothermal high temperature (up to 1500°C) and periodically quenched to room temperature using gas jets, with automatic monitoring of spallation events via a webcam. These specimens comprised partially stabilized zirconia (PSZ) coatings plasma- sprayed onto relatively thick (~5 mm) alumina substrates, with and without the subsequent surface addition of particulate designed to represent CMAS incorporation. Prior roughening of the alumina surface, via laser processing, was employed to ensure adequate interfacial toughness via mechanical keying. The thermal misfit strain induced during cooling of such specimens has a magnitude (~2 - 3 millistrain) similar to that for PSZ on a superalloy substrate, although it is of opposite sign. Since little or no chemical reaction is expected between substrate and coating at these temperatures, any observed spallation is likely to have been promoted by sintering- induced stiffness enhancement.

Experimental data will be presented concerning such observed spallation events. The penetration rate of the CMAS deposits into the TBC was determined via XRD measurements of the free surface, after serial mechanical polishing and by taking EDX profile of the transverse sections. The zirconia phase constitution, in particular the proportion of monoclinic phases and the mol.% of yttria present in the cubic/tetragonal phases, were monitored closely, in order to assess the thermomechanical stability of the PSZ, with and without CMAS. Thus conclusions will be drawn about the significance of (CMAS- assisted) sintering effects for TBC stability.

The utilization of fossil fuels for powering industrial gas turbines is expected to continue growing resulting in continued emphasis on increasing performance and reliability while simultaneously providing a cost effective, efficient, and environmentally sound power generation solution. The push to higher firing temperatures, increased efficiencies, reduced emissions and multiple fuel capability continues to demand more out of the gas turbine design and materials systems capabilities. Coatings are an integral part of many IGT materials systems, contributing several key functions such as thermal and oxidation protection, clearance control, wear resistance and sensing capabilities. Each of these coating functionalities presents unique challenges and requirements as they are super-imposed upon each other, especially with engine operating conditions becoming harsher and increasing service interval expectations. A full life cycle systematic approach in understanding the materials systems performance limits is essential for a successful engine implementation and enable robust materials system life prediction. As an example, thermal barrier coating (TBC) systems degradation mechanisms will be presented and examples of innovative systematic approaches towards engineering of production feasible, advanced high temperature capable coating systems will be provided.
During prolonged thermal cycling or isothermal exposure at high temperatures, both the physical properties of thermal barrier coatings (TBCs) evolve and damage accumulates at the interface with the underlying alloy so it is difficult to separate the individual contributions to the failure process and develop comprehensive failure models. To be able to do this, we have been exploiting a variety of methods for studying the crystallographic phase evolution, the evolution of thermal conductivity, the evolution of bond coat rumpling and the damage in the vicinity of the thermally grown oxide (TGO). The results of these studies on standard 8YSZ coatings will be summarized with particular emphasis on coatings deposited by electron-beam physical evaporation.

In addition to presenting some of the data we have obtained, we will also describe new insights obtained on the mechanisms of failure obtained using a piezospectroscopic luminescence imaging method. The piezospectroscopic imaging of the stresses in the thermally grown oxide formed by oxidation beneath thermal barrier coatings provides a form of in-situ “stress tomography” enabling the sub-critical separations between the TGO and TBC to be monitored and quantified. Analysis of the images reveals that small, isolated regions of damage initially form and then grow, linking up and coalescing to form percolating structures across the coating until the critical buckling condition is attained, the buckle extends and failure occurs by spallation. It remains to be established how these individual “damage” events are determined by the evolving physical properties of the coating and the TGO. This will form the basis for much of our future research.
Efficiency and reliability of modern jet engines strongly depend on the performance of thermal barrier coatings (TBCs) that prevent melting and oxidation of the turbine blades’ structural core. The system’s lifetime is limited by cracks appearing in and around an oxide layer that grows in the TBC under thermal cycling. High replacement costs have led to an increased demand to identify, quantify, and remedy damage in TBCs. An integrated experimental-numerical approach is presented for studying the main factors that contribute to damage, particularly interfacial irregularities. Damage at several stages of oxidation in TBCs is analyzed in samples with predefined interfacial irregularities. The model predicts the experimentally observed crack patterns, clearly quantifying the influence of imperfections and indicating that damage can be delayed by surface treatment.
EFFECT OF EXTRINSIC FACTORS FOR DEFORMATION OF EB-PVD THERMAL BARRIER COATINGS: SOME RESULTS OF THERMO-MECHANICAL FATIGUE TESTS

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Temperature and applied mechanical loading affect significant role on deformation behavior of EB-PVD TBCs. These behaviors usually influenced by temperature dependence of the deformability of substrate and TBCs under combined temperature and force relations. For example, out-of-phase TMF test shows complicated stress evolution under compressive strain controlled mode, i.e., tensile stress is born in the TBC system because of compressive creep deformation of a substrate superalloy. These behaviors, however, not explained quantitatively.

Attention of the present talk is focused on the unique deformation behaviors during in-phase and out-of-phase thermo-mechanical fatigue conditions with temperature gradient in through-thick direction. Some characteristic macroscopic behaviors have been analyzed using properties of constitutes. In addition, change of microstructure related behavior, e.g., TGO morphology and its stress, is also discussed in terms of the unique deformation behavior. Finally, degradation of TBC system caused by the unique deformation is discussed based on set of experimental and analytical results.
Modern thermal and environmental protection systems have multiple layers and functionalities. Important phenomena governing the life of these systems occur in each layer and especially at the interfaces between disparate layers. Mechanical characterization of these systems is complicated by their reduced dimensionality. Micro-scale tensile and bending experiments provide direct routes for characterizing the constitutive properties of individual layers and for quantifying delamination toughness. Experimental options for measuring delamination toughness with variants of the conventional four-point bend test will also be explored. Results involving both commercial thermal barrier coatings for turbine engines and developmental coatings for a solar probe satellite will be presented. The experimental insight gained in these experiments will be interpreted in context of the need for hierarchical models of layered protections systems.
INFLUENCE OF BONDCOAT CREEP AND ROUGHNESS ON TBC-DAMAGE

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To protect gas turbines components from overheating and corrosion, Y2O3 partially stabilized ZrO2 (PYSZ) thermal barrier coatings (TBC) are used with NiCoCrAlY bondcoats (BC) forming a thermally grown oxide (TGO) layer. Thermal stresses and TGO growth lead to TBC-cracking. BC- and TGO-creep and the roughness of the BC/TBC interface affect the stresses, damage evolution and lifetime. [1]

This was studied experimentally: Substrates made of FeCrAlY simulating the BC coated with a plasma sprayed PYSZ-TBC were thermally cycled. To vary BC creep, an oxide-dispersion-strengthened (ODS) and a non-ODS FeCrAlY-alloy with similar composition was used. Roughness was varied by sandblasting of the FeCrAlY with different parameters. Additionally, samples with periodic roughness were produced by turning. To vary TGO creep, the samples were coated with fine grained PVD-Al2O3 or with a coarser grained naturally grown TGO before applying the TBC. Thermal cycles were applied in air with Tmax=1050°C, Tmin=60°C and a dwell of 2 h at Tmax. Damage evolution was studied by infra-red-impulse-thermography.

It turns out, that the lifetime and damage evolution are significantly influenced by the BC- and TGO-creep, the BC/TBC interface roughness and the roughness profile type (sand blasted and turned). The results can be used to optimize the coating system and to enlarge the lifetime. By detailed analysis of the thermographies of sandblasted samples with creep weak BC and creep strong TGO a mathematical model was created which gives a good description of the increase of total delaminated area as a function of cycle number.

UNDERSTANDING APS TBC FAILURE BY SUFFICIENTLY REALISTIC MODELING AND SUPPORTING EXPERIMENTS

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It is typically observed that Air Plasma Sprayed TBCs fail in the Ceramic near the TGO (thermally grown oxide). Other failure modes do occur but this presentation only addresses this specific failure mode in a specific TBC system which we believe applies to many different versions of APS/bond coat systems. In the present work the goal is to show how a sufficiently realistic finite element modeling can shed light on the causes of this type of failure. Three sources of strain in the ceramic are recognized and are critical to understanding the causes of failure and these are: 1. The ceramic TBC layer experiences imposed strains due to the difference in coefficient of expansion of the TBC compared to the bond coat/TGO layer it is attached to. 2. The TGO thickness relentlessly increases in thickness causing geometry changes at the interface with the ceramic imposing a shape change. 3. The bond coat geometry changes dramatically due to rumpling. A finite element model is constructed and each of the three sources of strain is imposed individually to access their relative importance. The rate of TGO thickening and rumpling are determined from experimental observations and the thermal mismatch is based on published properties. The order of importance of these factors from highest to lowest turns out to be rumpling, oxide growth, and thermal mismatch. To determine the stress state induced by these strains it will be shown that a non-elastic constitutive model of the ceramic is a necessity and that this model must include: 1. much higher strength in compression than in tension. 2. rate dependence allowing relaxation. Elastic models yield stress that are many times (up to 100X) higher than the strengths measured in TBC experiments. Results using a very realistic viscoplastic model calibrated to NASA test data will be presented that show the necessity of bulk damage (non-fracture mechanics) approach. Predicted stresses at too low for successful prediction using fracture mechanics. Finally the challenge of predicting the observed fact that total hot time is shorter for short hold times will be discussed and the current model will be shown to represent that feature which is difficult to represent in most models.
ARE EB PVD TBCS MORE EROSION RESISTANT THAN PS TBCS?

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It is currently accepted that electron beam (EB) physical vapour deposited (PVD) thermal barrier coatings (TBCs) are more erosion resistant than their plasma sprayed (PS) counterparts. This paper looks at how various factors affect both the erosion mechanisms and rates of TBCs and how this affects the difference in performance between the two deposition processes.

Erosion mechanisms are not only affected by microstructure, temperature, particle velocity and size but also by the addition of dopents added to lower the thermal conductivity of the TBC. Furthermore, aging the TBC before erosion testing also has an effect on the erosion rate. In EB PVD TBCs aging promotes sintering of the columns which results in an increase in the material removed per impact resulting in an increase in the erosion rate. On the other hand for PS TBCs, which erode via a different mechanism than EB PVD TBCs, the erosion rate decreases with aging due to the sintering of splat boundaries. PS TBCs erode via intersplat cracking, thus any mechanisms which promotes the bonding between the splats, like sintering, will decrease the measured erosion rate. Thus the overall effect of aging is a convergence of erosion rates for the two different deposition processes.

Microstructural changes in EB PVD TBCs aimed at reducing the thermal conductivity of the system can also affect the erosion rates, normally increasing rates. Whereas microstructural changes in PS TBCs, for example vertical cracking which aims to increase the strain tolerance of PS TBCs, reduces the erosion rate. So bringing all these issues together raises the question as to whether EB PVD TBCs should still be considered to be more erosion resistant than plasma sprayed TBCs.

One final aspect that needs to be considered is how CMAS (or volcanic ash, VA) affects the erosion rate of TBCs. There is limited information on this, however, it has been shown that CMAS attack can increase the erosion rate of EB PVD TBCs.
Thermal barrier coating (TBC) systems are widely applied in modern gas turbine components to establish a thermal gradient between the hot operating gas and the air-cooled metallic base material. This allows an increase in operating temperatures and/or an extension in the service life of individual turbine components. Failure (i.e. spallation or cracking) of the ceramic top coating will result in loss of the thermal gradient and consequently increased corrosive attack of the spalled areas. Therefore, TBC lifetime prediction is not only of high interest for industry but also a challenge for academic research.

In most cases TBC failure occurs during the cooling-phase due to the mismatch in the coefficient of thermal expansion of the ceramic and the metal. In general however, not only thermal stresses, but also mechanically applied stresses can cause damage or spallation of the coating. The aim of this work is to use a fracture mechanics approach to model the tolerable strain limit at which cracking of the thermal barrier coating will initiate. Mechanical 4-point bending experiments with in-situ acoustic emission measurements were used to establish a data base for critical loading conditions as a function of thermal exposure, where use of the acoustic emission technique allowed one to distinguish the two failure modes “delamination” and “through cracking”. Specific results on atmospheric plasma sprayed TBCs are presented.
PROPERTY VARIATIONS IN TBC SYSTEMS
AND THEIR IMPACT ON TURBINE DESIGN

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For a further increase of gas turbine efficiency by increasing turbine inlet temperature, the combination of advanced cooling strategies and full consideration of ceramic TBCs in the thermal design of turbine blades and vanes is necessary. To avoid catastrophic failure of the engine due to TBC spallation followed by overheating of the substrate, in-depth knowledge of the damage behavior of TBCs under thermocyclic loadings as well as reliable life prediction methods are essential. In this context the present talk gives an overview about recent research of FZ Jüllich addressing the following topics: (i) Damage behavior of plasma sprayed TBC systems under thermocyclic and thermomechanical fatigue (TMF) loadings: The influence of high temperature dwell time, maximum and minimum temperature on crack growth kinetics in plasma sprayed TBCs is investigated using infrared pulse thermography, acoustic emission analysis and scanning electron microscopy. It is shown that delamination cracking starts with an incubation phase where crack length is correlated with the thickness of the thermally grown oxide (TGO) between bondcoat (BC) and TBC. As soon as a certain crack length which depends on the BC-TBC Interface roughness is reached, accelerated crack growth driven by TGO growth and thermal mismatch stresses is observed. Thermocyclic life in terms of accumulated time at maximum temperature decreases with increasing high temperature dwell time and increases with increasing minimum temperature. Acoustic emission analysis proves that crack growth mainly occurs during cooling at temperatures below the ductile-brittle transition of the BC. Superimposed mechanical load cycles accelerate delamination crack growth and, in case of sufficiently high mechanical loadings, result in premature fatigue failure of the substrate. (ii) Influence of bondcoat ductility on TMF life of TBC coated Ni-superalloys: Lifetime of a Ni-base superalloy coated with a ductile MCrAlY- and a brittle MCrAlY-NiAl bondcoat under out-of-phase TMF loading is analyzed. It is found that TMF life is nearly unaffected by the coating as long as its fracture strain at minimum temperature of the TMF cycle is larger than the strain range of the TMF cycle. In case of TMF strain ranges exceeding the fracture strain of the coating, a distinct decrease of TMF life is observed. (iii) Life prediction of plasma sprayed TBCs under thermocyclic loadings: Based on the results described in (i), a life prediction model based on TGO growth kinetics and a fracture mechanics approach has been developed which accounts for the influence of maximum and minimum temperature as well as of high temperature dwell time with good accuracy in a wide parameter range.
To prevent the formation of SRZ in the log-time high-temperature exposure of the turbine blades, thermodynamically equilibrium phase such as gamma-prime phase of the substrate is use as an oxidation-resistant bond coat. The previous study clarified that this "EQ coating" shows excellent interface stability and it does not degrade mechanical strength due to the SRZ formation.

In this study, TBC life test of EB-PVD ceramics coated EQ coating is investigated with other conventional MCrAlY coatings. 2nd generation superalloy CMSX-4 and 4th generation superalloy TMS-138A are used for substrates. About 150 μm thick of EQ coating, conventional NiCoCrAlY and CoNiCrAlY coating are deposited by LPPS and HVOF on the substrates. After polishing the surface of deposited bond coat, specimens are pre-oxidized in the EB-PVD chamber in 0.2 Pa of oxygen partial pressure. 150 μm thick of YSZ is deposited by EB-PVD on the pre-oxidized bond coat, following the pre-oxidation. Samples are heat treated cyclically in an electric furnace at 1135 °C with 1 h cycles. Fast cooling rate is obtained by air blow with each cooling cycle. As a result, it is found that TBC life of LPPS EQ-coated TMS-138A showed over twice of other conventional bond coats. Interrupted and failed samples are observed by SEM and EPMA. The differences of substrates, bond coats and its deposition processes in the microstructure, TGO growth and TBC life are discussed.
Understanding the mechanisms of thermal barrier coating (TBC) damage evolution is important for modeling, predicting, and improving TBC life and has been previously investigated primarily by inspection of TBC cross-sections at selected stages of TBC life. In contrast to the 1-D damage evolution revealed by destructive cross-section inspection, luminescence imaging techniques are shown to nondestructively monitor 2-D damage progression in TBCs. Taking advantage of the translucent nature of TBCs, luminescence excited from buried rare-earth-doped sublayers integrated into the TBC can be used to monitor TBC erosion, delamination progression, and temperature. In this presentation, delamination progression in TBCs composed of yttria-stabilized zirconia (YSZ) incorporating a thin base layer co-doped with erbium and ytterbium (YSZ:Er,Yb) is monitored by near-infrared and upconversion luminescence imaging. The co-doped base layer produces both near-infrared (NIR) luminescence emission at 1550 nm and upconversion luminescence emission at 562 nm using 980-nm laser excitation. It is demonstrated that integration of the co-doped YSZ:Er,Yb sublayer is achieved with no reduction in TBC life, whether the transition between co-doped and doped layers was by continuous or interrupted deposition. Delamination monitoring by NIR (1550 nm) and upconversion (562 nm) luminescence imaging is based on a reflectance-enhanced increase in luminescence produced in regions containing buried delamination cracks. Results are shown for both electron-beam physical-vapor-deposited (EB-PVD) and plasma-sprayed TBCs and it is observed that much finer grades of damage evolution can be observed for the EB-PVD TBCs. Delamination progression is monitored during interrupted thermal cycling of EB-PVD TBCs by both furnace and high-heat-flux laser heating. In both cases, delamination proceeds by generation, growth, and coalescence of microdelaminations, primarily at the TBC/thermally grown oxide (TGO) interface; however, it is shown that equivalent damage occurs much closer to the end of TBC life for high-heat-flux cycling than for furnace cycling.
LIFETIME ANALYSIS OF THERMAL BARRIER COATING SPALLATION

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The degradation of thermal barrier coatings (TBCs) namely used to protect aeronautical turbine blades from combustion gases involves complex mechanisms. Multiple failure modes leading to TBC spallation can effectively be observed on coatings that have experienced service conditions. Then, the lifetime assessment of TBC systems has been a challenge since their introduction in aircraft engines two decades ago. This paper proposed an energetic approach for the lifetime assessment of TBC systems. According to this approach, the TBC failure is induced by the accumulation of the strain energy density within the ceramic layer and resisted by the interfacial fracture toughness. The effect of thermal cycling on the delamination toughness of the TBC system is evaluated by means of two complementary experimental facilities, a modified four-point bending test and a specifically developed test for measuring the interface toughness under near-mode II conditions. The stored energy is then evaluated by the semi-analytical model of Balint and Hutchinson describing the behaviour of the TBC system under thermal cycling conditions. This model involves two length scales: a macroscopic one where each layer is represented by a beam. On the other hand, at the microscopic scale, by the use of nonlinear constitutive equations (to describe hardening, creep, oxidation, martensitic transformation) are derived the undulation growth, or rumpling, and the associated stresses in the bond coat, the ceramic outer layer and the thermally grown oxide. The evolution of the delamination toughness as a function of the thermomechanical history and the failure mode is then described by a damage model derived from this analytical model. The evolution of the microstructure and the composition of the bondcoat (Ni-Al based) during service conditions plays an essential role in the performance of the overall system. At high temperature, due to oxidation phenomena, the aluminium is progressively consumed by the growth of the interfacial alumina scale and interdiffusion phenomena occur between bondcoat and superalloy leading to a modification of the mechanical properties of this bondcoat. An original instrumented microindenter, developed at Onera, which allows characterising the mechanical properties of bondcoat materials up to 1000°C is then used. The available measurements go from the simple Vickers pyramid hardness to the force-penetration responses under complex loadings. This experimental technique combined with a modelling approach to solve the inverse problem, allows determining the evolution of the mechanical properties of the bond coat as a function of the thermal histories. Such evolution is finally introduced in the damage model describing the degradation of the adherence of the TBC system.
Optical diagnostics on thermal barrier coating structures maintain a critical role in gas turbine hot sections as performance demands continue to increase. In this presentation, we discuss the state of development of several optical methods for measurement of parameters relevant to TBC health monitoring, namely (1) hyperspectral luminescence imaging of bondcoat residual stress (via the piezospectroscopic effect); (2) phosphorescence-based temperature measurement within and on TBCs; and (3) low coherence interferometry as a depth sensitive probe of microstructure. The potential and limitations of each of these methods will be discussed in terms of their capability, sensitivity, and accuracy.
Morphological instability of the thermally grown oxide (TGO) is a fundamental source of failure in thermal barrier systems. The instabilities occur when initial non-planarity in the TGO grows in amplitude as the system experiences thermal cycling. By a numerical model, we explore how these instabilities are linked to constituent properties. The associated phenomena involve oxidation of the TGO, plastic flow of the bond coat, thermal expansion misfit between the TGO, bond coat and substrate, and stress relaxation in the TGO at high temperature. In this investigation, displacement instabilities in the thermally grown oxide originating from initial interface imperfections have been simulated by developing and using a numerical code. The simulation involves plasticity in the bond coat, growth strains in the TGO, thermal expansion misfit between the TGO, bond coat and substrate, as well as stress relaxation in the TGO at high temperature. In order to explore the fundamentals of the cyclic plasticity occurring in the bond coat, around the imperfections, plastic zone development upon temperature cycling has been simulated, as well as the associated plastic strains. Changes in the amplitude of the imperfections have been determined as the system cycles. The stresses in the TGO have also been monitored. One of the key implications is that the incidence of reverse yielding upon reheating differentiates between ratcheting and shakedown. That is, whenever the conditions for reverse yielding are satisfied during the initial cycle, the system ratchets. Otherwise, shakedown occurs. For a bond coat having temperature invariant yield strength, this transition occurs at a yield strength of about 300 MPa for the configuration analyzed. For the small overall thickening investigated, there is no significant change in transitional yield strength as the TGO grows.