SYMPOSIUM M
Thermal Barrier Coatings
November 28 – 30, 2000

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*Invited paper
SESSION M1: PLENARY I
Chair: Meera Aruna Anbel
Tuesday Morning, November 28, 2000
Room 209 (Hynes)

8:30 AM #M1.1
MECHANISMS CONTROLLING DURABILITY OF THERMAL BARRIER COATINGS
Anthony Evans, Princeton University, Princeton, NJ.

Thermal barrier materials are used in gas turbines to provide both thermal and oxidation protection. These materials consist of three basic layers. (i) An inner layer comprising a NiAl-based alloy is designed to resist viscous-flow while forming (ii) a thin thermally grown oxide (TGO, typically α-alumina), that restricts oxygen ingress and protects the substrate from oxidation. (iii) An outer layer comprises a low thermal conductivity oxide, generally stabilized zirconia. This layer is referred to as a thermal barrier coating (TBC). It is designed to provide a temperature drop of about 100°C on components subject to backside air cooling. It must also have the strain tolerance to withstand the thermal expansion mismatch with the substrate. The thermal barrier system is dynamic. The TGO thickness, the microstructure, and microstructure of the alloy layer changes as the Al is depleted, and, in some scenarios, the TBC microstructure changes. The durability of the system is linked to these changes. The major constituent governing performance is the TGO layer, which is highly stressed and which, while thin (in micrometers), is present in high energy density domains. The means whereby this energy density couples into the TBC to cause failure are described. Based on this understanding, approaches for addressing durability issues are discussed.

SESSION M2: FAILURE MECHANISMS AND LIFE PREDICTION
Chair: Meera Aruna Anbel
Tuesday Morning, November 28, 2000
Room 209 (Hynes)

9:15 AM #M2.1
THERMAL BARRIER COATING SYSTEM PERFORMANCE IN GE AIRCRAFT ENGINES
J. Lehey, GE Aircraft Engines, Evendale, OH.

Thermal barrier coatings (TBC) are used on a number of turbine components to increase engine performance through augmenting temperature capability and/or extending component service lives. For many high-pressure turbine airfoil applications, the TBC system is comprised of the base alloy, a Pd-based diffusion coating, and an electron-beam vapor-deposited (EB-PVD) yttria-stabilized zirconia ceramic layer. These coating systems have a high thermal mass and which, while thin (in micrometers), is present in high energy density domains. The means whereby this energy density couples into the TBC to cause failure are described. Based on this understanding, approaches for addressing durability issues are discussed.

9:45 AM #M2.2
CONTRIBUTION TO LIFE PREDICTION OF APS THERMAL BARRIER COATINGS

Thermal barrier coatings are exposed to complex thermo-mechanical loads during service leading to specific life limiting degradation and damage processes, in bond coat oxidation, sintering, phase transformation in bond coat and TBC, etc. In the case of a plasma-sprayed TBC under thermo-mechanical loading conditions, the cyclic deformation of the base material causes crack fields, consisting of segregation and delamination cracks. Further crack propagation results in a macroscopic delamination, i.e. failure of the TBC. The presented concept of critical strain enables to estimate the number of thermo-mechanical loading cycles to failure for a thermal barrier coated gas turbine component as a function of the base material strain range and time. Degradation processes as bond coat oxidation and sintering of the ceramic top coat are considered in that life prediction concept. TMF data was gained with IN 792 cc, a VPS NiCoCrAlY bond coat and an APS top coat of zirconia stabilized with 25% Y2O3. The applied thermal-cyclic mechanical cycle was defined by a temperature range between RT and 950°C and a varied total strain range between 0.2 and 0.8%. Calculations were applied to the experimental data using the concept of critical strain. The calculations reveal, that the strain range dependent number of cycles to failure is essentially decreased by sintering of the TBC and to a less extent by bond coat oxidation. Finally, a first approach of a critical energy density concept will be presented.

10:30 AM #M2.3
THE ROLE OF BOND COAT GEOMETRIC DEFECTS IN TBC FAILURE
Eric Jordan, Maurice Bell, Matt Backey, Joe Ambrico, Krishnakumar Vaidyanathan, Kathleen McCarron, Univ. of Connecticut, Mechanical Engineering Dept. and Dept. of Metallurgy and Materials Engineering, Storrs, CT.

Geometric irregularities can play an important role in TBC failure due to thermal cycling. Two contrasting examples will be described. In the first example a NiCoCrAlY bond coat with entrapped oxide defects is described in which the entrapped oxide results in the complete encapsulation of some bond coat sections. The fused bond coat defect is then observed to be a propagating crack and effectively the TBC failure site. In the second example a PdAl bond coat is described which has grain boundary ridge features that evolve into cavities. The selective damage at the ridges is explained using elastic plastic FEA. Growth of the cavities which involves cyclic plasticity is described in terms of an analytical model which utilizes about 20000 nodes. The model highlights the fact that maximum stress in the oxide occurs at a specific oxide thickness for any given loading. It is also shown that increased cavity growth occurs when the oxide is preferentially grown in the in-plane direction as would be expected in the case of oxide cracking, tensile creep or stress enhanced phase oxide growth. The oxide growth behavior needed to bring the model in agreement with the observed behavior of the PdAl bond coat will be presented.

11:00 AM #M2.4
FAILURE MECHANISMS IN PLASMA SPRAYED THERMAL BARRIER COATINGS.
Alphonse Ribiat, Harvard University, Division of Engineering and Applied Sciences, Cambridge, MA; Anthony G. Evans, Princeton University, Maxson Institute, Princeton, NJ.

The microstructure and durability of a thermal barrier coating (TBC) produced by the thermal spray method have been characterized. Upon exposure, the bond coat chemistry and microstructure change by interdiffusion with the substrate and upon thickening of the thermally grown oxide (TGO). A wedge impression test, in conjunction with SEM observations, has been used to probe the failure mechanisms. At short exposure times, when the TGO thickness is less than about 5μm, the growth of the TGO does not affect crack patterns in the TBC and delaminations induced by wedge impression propagate within the TBC about 3 μm from the interface. An aspheric phase at the split interfaces promotes this failure mode. As the thickness of TGO increases during exposure, cracks form in the TBC around imperfections at the interface. Moreover, induced delaminations develop a trajectory close to the interface, propagating not only through the TBC but also within the TGO and along the interfaces. A scaling rule based on the size of the local imperfections caused by TGO growth has been used to rationalize the critical TGO thickness when the TBC fails.

11:15 AM #M2.5
THE RELATIONSHIP BETWEEN BOND-COAT OXIDATION AND FAILURE OF THERMAL BARRIER COATINGS.
David R. Clarke, Vladimir K. Telinyan, Materials Department, University of California, Santa Barbara, CA.

Although zirconia thermal barrier coatings (TBC) are already widely and successfully used in aerospace and power generation gas turbine engines, there is a drive to use them at still higher temperatures. However, there are concerns about their usage under conditions at which failure cannot be tolerated. This has focused attention on trying to elucidate the underlying mechanisms that lead to TBC failure. In this presentation, a consistent model will be presented relating the factors that influence the formation and growth of the thermally grown oxide with the mechanisms that cause TBC failure. The model is based on a series of observations we have made of the oxidation of Ni-Co-Al bond coats demonstrating that surface preparation affects both the kinetic of the transformation of transient alumina to the final α-alumina phase and the parabolic rate constant during high temperature oxidation. Specifically, by combining photo stimulated luminescence spectroscopy, scanning electron microscopy and SIMS, we reach three major conclusions. Firstly, surface preparation affects the nucleation of α-alumina and hence the grain size of the thermally grown oxide. Secondly, ingenuity ions in the bond coat, as well as those introduced during surface preparation, are incorporated into the growing thermally grown oxide. The oxide growth rate is found to be correlated with the type of ingenuity, their concentration and the grain size of the oxide. Further observations indicate that the kinetic of the transformation to α-alumina depends on the bond coat and thermal barrier coating having local failure. As presently understood, this is produced by volumetric changes in the oxide.
bond-coat is associated with the beta NiAl to gamma-prime NiAl phase transformation and driven by aluminum depletion from the bond-coat during high-temperature oxidation.

11:45 AM M4.2 CYCLIC FAILURE OF A THERMAL BARRIER SYSTEM BY A DISPLACEMENT INSTABILITY IN THE THERMALLY GROWN OXIDE. Daniel R. Mann, and Anthony G. Evans, Princeton Materials Institute, Princeton University, Princeton, NJ.

Thermal protection systems based on ceramic thermal barrier coatings (TBCs) are widely used in turbine engines for propulsion and power generation, but are susceptible to delamination and spalling failure. These protection systems are complex materials comprising multiple layers having disparate thermo-elastic properties. Damage evolution is mediated by residual stresses that develop due to oxide layer growth and thermal expansion mismatch of the constituent layers, but is highly dependent upon the continuous chemical and microstructural evolution of the constituents during service. Particular attention is focussed on morphological evolution at the metal/oxide interface, and the role of the developing morphological features on the nucleation of interfaces and the propagation of cracks. The dependence of the microstructural oxidation studies, high-resolution imaging, chemical and microstructural analysis, and novel thermo-mechanical test methods are used in combination to elucidate failure mechanisms for EB-PVD TBCs. The propagation of Ni-PdAl bond coatings in such systems, damage evolution occurs during thermal cycling as the result of a displacement instability associated with the thermally grown oxide. Details of the mechanisms by which this displacement instability leads to nucleation and propagation of damage - and its implications for the design of TBC systems with improved durability - will be discussed.

SESSION M3: PLENARY II
Chair: Nitin P. Padture
Tuesday Afternoon, November 28, 2000
Room 209 (Hynes)

1:30 PM #M3.1 IMPROVING THE DURABILITY OF THERMAL BARRIER COATINGS. Maurice Gell, Eric Jordan, Krishnamoorthy Vudayaganapathy, Kathleen McCallon, Vaghoth Sohn, School of Engineering, University of Connecticut, Storrs, CT.

The durability and reliability of current thermal barrier coatings (TBCs) made of 6-8 weight percent yttria partially stabilized zirconia (YSZ) requires improvement to enable TBCs to become "prime reliable". Prime reliable TBCs would allow turbine airfoil designers to incorporate the TBCs in the basic design of the turbine blade, rather than add an overlay of partially stabilized zirconia. The design of the bond coat, the selection of the materials, and the fabrication process will allow the TBC to perform within the designed lifetime of the turbine blade. A significant improvement in the YSZ durability and reliability has taken place at the University of Connecticut through mechanized research and production TBCs. Five production TBCs, two manufactured by electron beam beamless vacuum deposition (EB-PVD) and 3 deposited by plasma spray have been thermally cycled to various life fractions at 1,121°C, and the mechanisms of spallation flow and fracture are being determined. For these TBCs, damage occurs at the spallation surface, was observed at low fraction life. For the EB-PVD TBCs, damage is initiated at microstructural features or defects on the bond coat surface. Removal of these defects prior to the deposition of the ceramic layer introduces a change in the spallation mode and as much as a 3X improvement in life. For the plasma sprayed TBCs, a variety of damage initiation and progression modes were observed. Based on these observations, recommendations will be made for improving the durability and reliability of these TBCs.

SESSION M4: MECHANICAL PROPERTIES
Chair: Nitin P. Padture
Tuesday Afternoon, November 28, 2000
Room 209 (Hynes)

2:15 PM #M4.1 DELAMINATION OF COMPRESSED COATINGS ON CURVED SUBSTRATES. John W. Hutchinson, Harvard University, Cambridge, MA.

Thermal barrier coatings are often applied to curved substrates, and oxidation barrier coatings form on wire bearing elements. When cooled, these coatings usually experience large compressive stresses which make them susceptible to interface delamination. The effect of substrate curvature on buckled-driven delamination is analyzed. Specifically, delamination propagation for coatings on cylindrical surfaces is considered. Propagation in both the axial direction and the circumferential direction is considered, for positive and negative curvatures. The sign of the curvature has a strong influence on the direction of propagation and on the energy release rate available to drive the interface crack.

2:45 PM #M4.2 MEASUREMENT OF INTERFACIAL TOUGHNESS LOSS IN THERMAL BARRIER COATING SYSTEMS SUBJECTED TO ISOTHERMAL EXPOSURES. Roy Harudoko, Jack Beal, Qin Ma, Carnegie Mellon University, Pittsburgh, PA; Matthew Skeggs, Frederick Pettit, Gerald Meier, University of Pittsburgh, Dept. of Materials Science and Engineering, Pittsburgh, PA.

A major concern with thermal barrier coatings (TBCs) is their loss of adhesion during service, leading to spallation. In this research, an indentation test is used to quantify decreases in interfacial toughness of TBC systems as a function of the duration of isothermal high-temperature exposures. A description is given of the indentation test, which involves penetration of the TBC and the oxide layer below it, inducing plastic deformation in the underlying metal bond coat and superalloy substrate. This plastic deformation induces a compressive radial stress away from the indent, which drives an asymmetric delamination of the TBC and oxide layers. Detailed elastic-plastic model results are presented which allow determination of the toughness of the oxide/bond coat interface from a measured radius of delamination. Test results are presented tracking the "apparent" loss of toughness (not accounting for changes in the TBC system) for EB-PVD TBC systems as a function of isothermal exposures from 1100°C to 1200°C. These results indicate a significant loss in apparent toughness occurs at a fraction of the total TBC system life. Apparent losses in toughness are correlated with observations of increasing oxide thickness and TBC spallation. These changes in the TBC system increase the energy driving delamination and could lead to apparent decreases in toughness even if the oxide/bond coat interface itself is not degraded. Further analyses and tests are presented which quantify the relative importance of oxide thickening, TBC spallation and interfacial damage in degrading apparent TBC system adhesion in these tests.

3:30 PM #M4.3 SIMULATING PHYSICAL PROPERTIES OF THERMAL BARRIER COATINGS VIA OOF. Edwin R. Fuller, Jr. and Stephen A. Langer, National Institute of Standards and Technology, Gaithersburg, MD.

Knowing basic physical properties of plasma-sprayed thermal barrier coating (TBCs) is essential to the design and reliability assessment of components using these coatings. In particular, mechanical properties, such as elastic behavior and residual stresses, have a strong influence on delamination behavior, and hence reliability. As mechanical properties are difficult to measure directly, an alternate strategy is to develop numerical schemes for determining these properties from the complex microstructure of these materials. One computational tool, called OOF, is being developed at NIST. OOF, which stands for Object Oriented Finite element analysis, is a computational tool that allows material scientists to simulate physical properties of complex microstructures from an image of that microstructure. Computer simulations using OOF have been conducted on TBCs to elucidate the influence of microstructural features, such as porosity, microcracks, interfacial surface roughness, and residual misfit strains, on mechanical behavior. Recent extension to incorporate fracture and damage accumulation and measurements of thermal conductivity will also be discussed.

4:00 PM #M4.4 MECHANICAL BEHAVIOR OF FREESTANDING TBC. Stefan Langer-Bergh, Dinoorah Steiner, Ulrich Bast, Siemens AG, Corporate Technology, Munich, GERMANY.

The mechanical behavior of plasma sprayed TBC-material was investigated under uniaxial compression. Freestanding TBC-rings were separated from the substrate using an etching technique and tested in a mechanical testing unit at RT and elevated temperature. The measured stress-strain curves of the coatings show a pronounced hysteresis and evidence of time-dependent (visco-elastic) material behavior. A simple model including microstructural information about the material is used to interpret the experimental results and to identify the relevant material parameters.

4:15 PM #M4.5 MICROSTRUCTURE-PROPERTY RELATIONSHIPS FOR PLASMA-SPRAYED COATINGS: ELASTICITY, THERMAL CONDUCTIVITY AND CROSS-PROPERTY CORRELATIONS. Mark Kirchmayer, Tufts University, Medford/Somerville, MA.

Effective thermal conductivities (strongly anisotropic) of sprayed and
PVD coatings are explicitly expressed in terms of the microstructure. The role of pore shapes and orientation in the distribution of solid coatings on the substrate are found to have an influence, but to some extent, the control and processing parameters - quantitatively established. Thermal conductivity of sprayed coatings in the direction normal to the substrate is substantially lower than that of PVD coatings. The orientational scatter of solid 'volumes' in PVD coatings is found to be responsible for reductions of thermal conductivity (as compared to the bulk material).

Effective elastic moduli (strongly anisotropic) are also expressed in terms of the microstructure. The results agree quite well with the available experimental data. They explain, in particular, the possibility of the "inverse anisotropy." Young's modulus in the direction normal to the substrate being higher than the one in the transverse direction that may occur in certain microstructures of plasma-sprayed coatings. It is shown that the orientational scatter of splats plays an important role. The phenomenon of inverse anisotropy is typical for PVD coatings.

Cross-property correlations between the elastic and the conductive properties are established in the explicit form. Possible applications:
A. Since the results apply to both thermal and electric conductivities, such correlations can be used to control the effective elastic moduli and electric conductivities are much easier to measure than the mechanical properties.
B. By measuring the elastic stiffness normal to the coating (say, from Hertz' contact problem) one may estimate the conductivity in this direction.
C. Understanding of such cross-property correlations is essential if one wishes to optimize the combined TBC/mechanical performance.

4:45 PM M4.6
MODELING EFFECTS OF MATERIAL PROPERTIES AND THREE-DIMENSIONAL SURFACE ROUGHNESS ON THERMAL BARRIERS
Chair: C. Michael Glyn, K.S. Ramaswamy, P.D. Wright and K. J. Hemberek Department of Mechanical Engineering, Johns Hopkins University, Baltimore, MD. GE Aircraft Engines, Materials and Process Engineering Department, Cincinnati, OH.

The effect of surface roughness on thermal barrier coatings (TBCs) leads to out-of-plane, tensile residual stresses that can eventually lead to spallation. Other factors, including modulus of elasticity, coefficient of thermal expansion, and stress relaxation of the bond coat, also play a significant role in the development of these residual stresses. TBC systems of Rene N5 test bars, coated with one of two different diffusion bonded bond coats and copped with a ceramic top coat using electron beam physical vapor deposition (EB-PVD), were supplied by GE Aircraft Engines and will be considered for this study. Materials properties of the different types of bond coats measured in an independent, Johns Hopkins study, along with surface roughness measured in this study, will be the critical input parameters in a finite element analysis (FEA) of the TBC systems. The modeled surface roughness will be based on scanning electron microscopy (SEM) images of the bond coat/top coat interface. The effect of an idealized three-dimensional surface roughness on residual stresses is also compared to residual stresses resulting from a grooved surface formed by revolving a sinusoidal wave about an axis of symmetry.

The resulting residual stresses calculated by the FEA are expected to be used as input parameters for future failure analysis studies.

SESSION M5: PLENARY III
Chair: Bruce A. Pint
Wednesday Morning, November 29, 2000
Room 209 (Hynes)

8:30 AM *M5.1
THERMAL BARRIER COATING LIFE PREDICTION FOR LAND-BASED GAS TURBINES
John G. Goedjen, Matthias Oechler, and Ramon Subramanian, Gas Turbine Materials Department, Siemens Westinghouse Power Corporation, Orlando, FL.

Industrial gas turbine Designers will continue to place greater reliance and emphasis on the use of Thermal Barrier Coating systems to improve engine efficiency. This increased reliance will depend, in part, on development and advancement of new coating material systems which can meet the increased performance objectives; to a great extent, it will come with ability to place greater confidence in the current materials systems through the use of life prediction methodologies. The time/temperature kinetics of bond coat degradation in service, such as oxidation and bond coat depletion, is well understood. The path to greater firing temperatures and reduced cooling flows has brought greater emphasis to degradation of the TBC, especially with regard to the effects of sintering. Efforts in understanding the kinetic processes and associated failure modes have begun to bring the bond coat and TBC time/temperature design limits for coating systems in industrial gas turbines. Extending these design limits will rely on a greater understanding of the systems; where the properties of both the bond coat and TBC contribute to the failure. Defining this region will come with an understanding of the fracture mechanism and strain energy of the bond coat TBC interface and the time/temperature properties of the materials in question. An analysis of the bond coat and TBC factors which bracket the operational regime will be reviewed; a discussion of the methods required to resolve the mixed mode failure regime will be presented.

SESSION M6: OXIDATION
Chair: Bruce A. Pint
Wednesday Morning, November 29, 2000
Room 209 (Hynes)

9:15 AM *M6.1
THE INFLUENCES OF SULFUR IMPURITIES AND PLATINUM ADDITIONS ON OXIDE SCALE ADHERENCE TO CVD ALUMINIDE BOND COATINGS. J. Allen Hynes, Karen L. More, Bruce A. Pint, Ian G. Wright, Oak Ridge National Laboratory, Oak Ridge, TN; Ying Zhang, University of TN, Knoxville, TN; Wei Y. Lee, Stevens Institute of Technology, Hoboken, NJ.

The adherence of the thermally-grown aluminia scale to a metallic bond coating is often the life-limiting factor for advanced thermal barrier coating systems. The objective of this work was to investigate the influence of Pt on the scale adherence and void growth behavior during oxidation of aluminide bond coats with concentrations of sulfur. Single-phase Nial and NiPtAl bond coats were fabricated on low-sulfur (LS) and high-sulfur (HS) single-crystal Rene N5 superalloys by chemical vapor deposition (CVD). Scale growth characteristics and adherence were investigated by isothermal and cyclic oxidation testing at 1150°C. Oxide and coring microstructures were evaluated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Scale adherence to CVD Nial on HS superalloys was very poor, whereas the scale adherence to NiPtAl on LS superalloys improved significantly. By comparison, the time to significant scale spallation on CVD NiPtAl was about 4X that of the best LS Nial coating. There was no observable influence of sulfur on the fretter corrosion content or scale adherence to Pt-containing coatings. Scales on NiPtAl typically failed due to formation of large voids at the oxide-metal interface, and void concentrations on isothermally-oxidized NiPtAl increased with increasing sulfur content. Interfacial voids were not observed on surfaces or cross-sections of oxidized CVD NiPtAl on LS or HS superalloys. The aluminia scales on both NiPtAl and NiPtAl contained numerous, very fine internal voids (by TEM), except when Hf from the substrate was present in the oxide, which resulted in a dense scale. It was concluded that the detrimental effects of sulfur are mitigated in Pt-containing coatings, primarily by elimination of void growth at the oxide-metal interface.

9:45 AM M6.2
INFLUENCE OF BOND COAT MICROSTRUCTURE ON OXIDATION BEHAVIOR AND STRESS EVOLUTION IN AN ELB-PVD TBC MODEL SYSTEM. Eric Chrapkowski, Carsten Menneker, Manfred Rehle, Max-Planck-Institut fur Metallforschung, Stuttgart, GERMANY; Scott G. Terry, Carlos G. Levi, University of California at Santa Barbara, Materials Department, Santa Barbara, CA; Jean Le Cozo, Ecole des Mines de Saint-Etienne, SM-C, Saint-Etienne, FRANCE.

Lifetime and adherence of Thermal Barrier Coating Systems (TBC systems) depend strongly on the formation of a thermally growing oxide (TGO) between Bond Coat (BC) and TBC. The influence of BC pre-treatment and morphology on the growth and the stress evolution in the TGO is not well understood. To address this question, TBC model systems were prepared consisting of NiCrAlY multiphase alloy substrates with different pre-treatments, GO and an ELB-PVD TBC top layer. The microstructural evolution of the TGO after isothermal and cyclic oxidation was studied by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Mechanical stresses in the TGO scale were measured non-destructively by optical piezospectroscopy. Stress state and microstructure of the TGO will be correlated with stress in the underlying BC, and will be discussed under the viewpoint of failure mechanisms.

10:30 AM *M6.3
COMPARATIVE STUDY OF THE OXIDATION OF SEVERAL BONDCOATS FOR TBC SYSTEMS. Daniel Mencane, Djur Ognib, Marie-Christine Lafont, Bernard Pieraggi, Centre Interuniversitaire d'ingénierie et de Recherche des Métaux, UMR CNRS-INPT-UPS 5085, ENSET, Toulouse Cedex, FRANCE.
The oxidation behavior of several bond coats was studied in a systematic manner. Most systems were tested with all combinations of the following parameters: 1/ alloy substrate: IN100 or AM3 (single crystal) Ni-based superalloys 2/ bond coats: VPS NiCoCrAlY or CoNiCrAlY, NiPtAl, NiPtAl 3/ bond coating: as-deposited, polished, grit-blasted, preoxidized 4/ test conditions: APS or EB-PVD ZrO2-Y2O3 ceramic coatings. The precipitate treatments of bond coats were determined from a careful study of (Ti,Al,Mg,Zr)-Ni-base superalloys. The preoxidation treatments of bond coats were determined from a careful study of (Ti,Al,Mg,Zr)-Ni-base superalloys. The preoxidation treatments of bond coats were determined from a careful study of (Ti,Al,Mg,Zr)-Ni-base superalloys. The preoxidation treatments of bond coats were determined from a careful study of (Ti,Al,Mg,Zr)-Ni-base superalloys.

11:00 AM M6.4 TEM INVESTIGATIONS OF OXIDIZED YTTRIA STABILIZED ZIRCONIA ON PLATINUM ALUMINIDE BOND COAT. Matthew D. Blanford, C. Yang, U. of Pittsburgh, Dept. of Materials Science & Eng., Pittsburgh, PA.

Determination of the microstructure and chemistry of the oxidized thermal barrier coatings (TBCs) is crucial to understanding their failure mechanisms. We are investigating oxidized TBCs by structural and analytical transmission electron microscopy (TEM) methods. The examined TBC material is yttria-stabilized zirconia on a platinum aluminate bond coat (BC) by electron physical vapor deposition. This melt-process was then oxidized at 1100°C in air to form polycrystalline alphas. It is well known that randomly oriented alphas on (thermally grown oxide TGO) forms due to high temperature oxidation of the BCs. Since spallation is observed at both the TBC/TGO and the BC/TGO interfaces, it is critical to determine the structure and chemistry at all interfaces. To obtain information about both interfaces, we are using advanced computer software to analyze the TEM chemical and diffraction data obtained from a Philips 200CM FEG microscope operated at 200kV. Preliminary energy dispersive X-ray spectroscopy data suggest that there is an interdiffusion between the TGO and BC, but the BC appears to be sharp. From this type of data, we will identify whether there is any texture of the alphas or sample in the TBC coating. We will also examine whether there exist metastable alphas, which are known to be detrimental to scale adhesion.

11:15 AM M6.5 COMPARISON OF THERMAL BARRIER COATINGS FAILURES ON NiCrAlY AND ON PLATINUM ALUMINIDE BOND COAT. Guy L. Meier, Materials Science and Engineering Department, University of Pittsburgh, Pittsburgh, PA.

Yttria stabilized zirconia (YSZ) thermal barrier coatings (TBCs) were prepared by electron beam physical vapor deposition (EB-PVD). These coatings were deposited upon NiCoCrAlY bond coats and platinum aluminate bond coats which in turn were on René N5 superalloy substrates. The NiCoCrAlY bond coats were prepared by two different powder types. These TBCs were characterized in as processed conditions as well as after cyclic oxidation exposures in air at 1100°C and 1200°C using optical metallography, x-ray diffraction and scanning electron microscopy. These bond coats on N5 substrates were also cyclically oxidized in air at 1100°C without TBCs in order to document and compare the oxide characteristics of the bond coats. After 3000 hours of cyclic oxidation without TBCs there was a substantial difference between some of the NiCoCrAlY bond coats and the platinum aluminate bond coats. Both of these coatings were depleted of aluminum, but a Al2O3 scale was still evident upon these bond coats. The surfaces of the platinum aluminate bond coats were more dense than the surfaces of the NiCoCrAlY bond coats and this difference was evident after 4000 hours of cyclic oxidation. It was also observed during the initial stages of oxidation of the NiCoCrAlY bond coats that transient oxides containing nickel were present at the interface. The bond coats failed after approximately 1000 to 2000 hours in air at 1100°C whereas the TBCs with platinum aluminate bond coats failed after 1000 to 1200 hours. The TBCs on both types of bond coats failed by fractures predominantly along the thermally grown oxide (TGO) and bond coat interfaces, but there were significant differences into the TGO. The failures of the TBCs on the two different types of bond coats will be compared and important factors that are believed to play significant roles in determining TBC lives will be presented and discussed.

11:45 AM M6.6 ON THE NATURE OF INTERFACIAL OXIDE AND TEMPERATURE OXIDATION STUDIES IN NI-10% Y / YTRIA-ZIRCONIA THERMAL BARRIER COATINGS. A.M. Varparasad, Defence Materials and Stores Research & Development Establishment, DMRDE (PO), Kanpur, INDIA.

Plasma sprayed Thermal Barrier Coatings that contain (i) NiCrAlY bond coat (50 microns) followed by (ii) 8% Yttria-Zirconia Ceramic top coat (250 microns) have been prepared on austenitic stainless steel substrates using powders of 8%. Yttria-Zirconia made by Polymer Matrix Method (Rej-I) and Yttria-Alumina made by Polymer Matrix Method (Rej-II). Furnace methods have been employed to conduct thermal cycle tests at 1000 degrees centigrade and the microstructure and compositional changes across the interface between bond coat and ceramic top coat have been examined on a Jeol Scanning Electron Microscope fitted with Energy Dispersive X-ray Analyzer (SEM-EDXRA), to study the nature of the interfacial oxide growing during thermal cycles. Initially, the region adjoining the ceramic top coat revealed the presence of Nickel, the major constituent of NiCrAlY bond coat and little of Aluminium and other elements. The results are in agreement with the existing data on the formation of Nickal rich phases grown from the melt during plasma spray process. Observations after 25, 50, 75 and 100 Thermal Cycles revealed that at the interface region, elements Aluminium and Silicon are negligible initially, but, the same grew steadily with increase in number of thermal cycles. The adhesion between bond coat and substrate is intact although the TBCs were subjected to 1000 thermal cycles and the Aluminia rich interface oxide is about 5 microns. The Coefficient of Thermal Expansion (CTE) of Aluminium Oxide (5 ppm) and Silicon Oxide (3 ppm) are low as compared to the substrate (16 ppm) and Yttria-Titanium top coat (11.6 ppm) and is adverse effect of the bonding between bond coat and ceramic top coat. The CTE of the substrate (16 ppm), the intermetallic phases of bond coat e.g. NiAl (13 ppm), ZrAl (15 ppm) and the substrate (11.6 ppm) form a gradient across the two Layer Thermal Barrier Coating. As thermal cycles proceed, there has been a gradual increase in the thickness of the interfacial oxide that is build-up of Alumina (CTE=6 ppm) and Silicon (CTE=5 ppm) and the CTE of the CTE gradient across the 5 microns wide interfacial oxide. At the end, delamination may be seen for the Zirconia Ceramic top coat leaving behind the bond coat adhering to the substrate. References: 1. P. Pramanik, Bull. Mat. Sci., Vol. 19, 1996 pp. 952-961. 2. A. M. Varparasad and P.T. Rajagopalan, Proc. Mat. Res. Soc. of India, AGM-7, Feb. 1996. 3. A. M. Varparasad, Amitab Chakraborty, Sanjay and P.T. Rajagopalan, Proc. Thermal Analysis Symposium, Dec. 1995, pp. 200-202. 4. A. M. Varparasad and P.S. Venkateswaran, Proc. Ninth National Congress on Corrosion Control, Sept. 1999, pp. 216-240.

SESSION M7: PLenary IV

Chair: Sanjay Symath

Wednesday, Afternoon, November 29, 2000
Room 209 (Hynes)

1:30 PM M7.1 FAILURE MECHANISMS OF THERMAL BARRIER COATINGS. L. Singha, R. Herwog, W.J. Quandt, R. Steinbrech, D. Clemens, T. Van Research Centre Julich, Institute for Materials in Energy Systems 2, Julich, GERMANY.

Using thermal barrier coatings (TBCs), gas inlet temperatures of aer engines as well as industrial gas turbines can be significantly increased, provided, TBCs can be used as integral part of blading design. In the past, the physical properties of TBCs will be described with special emphasis on the influence of the TBC microstructure on Young's modulus. Microindentation has been used to measure Young's moduli for different types of TBCs which have been produced by air plasma spraying. Young's moduli strongly depended on the porosity as well as on the microstructure of the TBC. At temperatures above 1000°C sintering of the TBC will result in increased Young's moduli. The sintering kinetics has been evaluated for selected TBCs. From these kinetic measurements it can be demonstrated that Young's moduli will increase up to a factor of 2 by changes in the TBC microstructure. These results are also supported by the TBC performance in the bond coat oxidation resistance. The chemical composition of the bond coating will influence the growth rate of aluminas scales between the ceramic TBC and the bond coat but also the microstructure and phase transformation of elevated...
TEMPERATURES. ESPECIALLY ABOVE 900°C DISSOLUTION OF GAMMA-PRIME PHASES WILL RESULT IN ABNORMAL HIGH THERMAL EXPANSION COEFFICIENTS, WHICH WILL RESULT IN MECHANICAL STRESSES IN THERMALLY GROWN OXIDE (TO). BY CONTROLLED ADDITIONS, THE GAMMA-PRIME SOLUTION TEMPERATURE CAN BE RAISED TO HIGHER TEMPERATURES. IT IS ALLOU TO REDUCE OR SUPPRESS GAMMA-PRIME PRECIPITATION BY FURTHER ADDITIONS. IN THESE CASES A SIGNIFICANT IMPROVEMENT OF SCALE STABILITY CAN BE OBTAINED.


SESSION MS8: CHARACTERIZATION AND NDE
Chair: Sunjay Sampath
Wednesday Afternoon, November 29, 2000
Room 209 (Hynes)

2:15 PM MS8.1

Thermal barrier coatings are increasingly used and their efficiency relies upon a high thermal conductivity ceramic layer, consisting, most generally, of a zirconia-based material deposited by plasma spraying or by EB-PVD for the most demanding applications. The thermal conductivity of the ceramic layer is a function of the thermal conductivity of the deposited material and the distribution of porosity within the deposited coating. In this paper, we propose a description of the thermal conductivity of bulk zirconia-based materials. Starting from the experimental data published by [1], we show that the thermal conductivity of pure zirconia as a function of temperature, which does not follow the conventional T^-1 law, can be interpreted by introducing a cut-off length for the phonon mean free path. Replacing tetragonal zirconium ions with tetragonal zirconium ions, for stabilizing the tetragonal or the cubic phase, is accompanied with the introduction of oxygen vacancies. As the point defect concentration increases, the thermal conductivity at room temperature first decreases and, above an oxygen vacancy content of about 5%, increases as shown by [2] on single crystals. The decreasing law can be described with a model invoking phonon-phonon and phonon-point defects scattering mechanisms. The results obtained are then used to calculate the variations of the thermal conductivity in the yttria-stabilized zirconia phase as a function of temperature, with a satisfactory agreement, in particular for the partially stabilized material. This approach is then extended to zirconia containing other stabilizers than yttrium to evaluate the effect of traces of tetragonal or the cubic phase, is accompanied.

4:25 PM MS8.2

The thermal conductivity of nanocrystalline yttria-stabilized zirconia (YSZ) coatings is of interest for metal-ceramic bond coatings (MOCVD) has been investigated for grain sizes of 10 to 100 µm at temperatures of 600-700°C. At room temperature, a grain-size-dependent reduction in thermal conductivity is observed for grain sizes smaller than approximately 30 nm, reaching a value of less than one-third the bulk value at the smallest grain size measured. As grown samples were found to exhibit about 90% of bulk density and the amount of porosity did not significantly vary with grain size. Hence, the observed changes in thermal conductivity is believed to be attributable to the effects of grain size rather than porosity. Measurements of the temperature dependence of the thermal conductivity from 80-700°C will also be described. The observed behavior is consistent with expectations based on a comparison of grain size with the phonon mean-free-path in single-crystal zirconia. Studies of YSZ grain growth during annealing found that rapid grain growth occurs above approximately 900°C. The potential benefits of grain refinement on the nanometer-scale in thermal barrier applications will be discussed. This work is supported by the U. S. Department of Energy, Office of Science, under Contract W-31-109-Eng-38.

3:30 PM MS8.3
PROCESSING EFFECTS ON POROSITY-PROPERTY CORRELATIONS IN PLASMA SPRAYED PARTIALLY-STABILIZED ZIRCONIA COATINGS. H. Herman, L. Kulkarni, A. Goland, and S. Sampath Center for Thermal Spray Research, SUNY Stony Brook, NY.

Thermal barrier coatings (TBCs) will impact protection to heat engine components against failure under excessive heat loads, to increase inlet temperatures with consequent improvements in efficiency, and to reduce the time to regen for cooled engines. Control of thermal conductivity is critical since low thermal conductivity depends not only on the nature of the yttria-stabilized zirconia (YSZ) TBC, but also on the morphology of pores and cracks, which are closely linked to process methodology and the form of the ceramic feed materials. A presentation will be given on the influence of feedstock characteristics (particle size distribution and powder morphology) and thermal cycling on porosity content and its resultant influence on thermal conduction and elastic modulus of plasma sprayed YSZ TBCs. Multiple- and Porod-small-angle neutron scattering (SANS) have been used to examine the three-void system (intergranular pores, cracks and globular pores). The void/crack system is quantitatively resolvable by SANS experiments demonstrating that intergranular pores are dominant in influencing the thermal conductivity and elastic modulus of the coatings. Variations in powder morphology significantly influence the results. Sintering during thermal cycling reduces porosity and increases thermal conductivity. On sintering, the microstructure was found to be more anisotropic, suggesting that the cracks sinter at a lower temperature than do intergranular pores. Work was supported by NSF through its Materials Research Program: DMR 9632570.

6:00 PM MS8.4
PHASE IDENTIFICATION IN HEATED THERMAL BARRIER COATINGS USING MICROBEAM X-RAY DIFFRACTION COMBINED WITH ELEMENTAL X-RAY MAPPING. Jennifer R. Verkouteren, Rynna B. Mariniello, David S. Bright, NIST, Chemical Science and Technology Laboratory, Gaithersburg, MD.

Compositional distinct micrometer-sized areas in plasma spray coatings were identified from elemental X-ray maps and characterized for phase content by using laboratory-based microbeam X-ray diffractometry. The elemental maps indicated that the phase containing very low concentrations of yttria (<0.8 mol fraction YO, <0.8 mol fraction YO) formed during heating of a homogeneous 0.82 mass fraction YO, 0.82 mol fraction YO) coating. This phase was found to be concentrated around cracks in the coating, and had maximum dimensions of approximately 10 µm x 30 µm. The microstructure was observed using a 10 µm X-ray beam and both a position-sensitive detector and a phosphor imaging plate. The phase was found to be cubic, rather than the monoclinic phase expected for such a low stabilizer content. The microdiffraction results were also used to resolve large inconsistencies between the bulk diffraction (neutron and X-ray) results and the elemental mapping results.

4:15 PM MS8.5
X-RAY MICROCOMPOSITION - ROUTINE TOOL FOR MICROSTRUCTURAL CHARACTERIZATION OF COMPLEX ANISOTROPIC STRUCTURES OF THERMALLY SPRAYED DEPOSITS. S. J. Bielew, University of Maryland, College Park, College Park, MD and National Institute of Standards and Technology, Gaithersburg, MD.

X-ray microtomography is a new technical tool that allows one to obtain a 3D visualization of a real object. The technique is based on the principle of tomography and it allows one to obtain the 3D reconstruction of the object from the 2D projections. In this way, it is possible to obtain a detailed picture of the internal structure of the object, which is not possible with other imaging techniques. The technique is currently used in various fields, such as materials science, biology, and medicine. In this talk, we will discuss the principles of X-ray microtomography and its applications in the field of thermal spraying.

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to address this issue and to allow high-throughput users to get prompt data analysis and 3D reconstruction. We present a review of microstructural methods obtained for a film as a function of by currently available techniques ranging from optical microscopy and intuition porosimetry to small angle scattering and x-ray tomography. The results are compared. The current status, future developments, and availability of tomography to a wide scientific community are discussed. Acknowledgement: ANL authors are supported by U.S. Department of Energy, BES, under Contract W-31-109-ENG-38 and CTSR authors are supported by NSF MSE/ award DMR-9621570.

4:30 PM M8.6
CHARGE TRANSPORT AND DEGRADATION EVALUATION OF THERMAL BARRIER COATINGS BY ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY. Jianqi Zhang, Danyash Tamboli, Vitali Desan, Univ of Central Florida, Advanced Materials Processing & Analysis Center, and Dept of Mechanical, Materials and Aerospace Engineering, Orlando, FL.

Advanced turbine engines are slated to operate at turbine inlet temperatures of nearly 2750°F so as to achieve 60% and higher overall efficiency. In the United States, the capability is often obtained for a film that will withstand such high temperatures. The use of thermal barrier coatings (TBCs) is essential to reduce the substrate skin temperatures to acceptable levels. The successful application of TBCs in land-based gas turbines is a greater technical challenge compared to zero-engine applications because there are significant differences ranging from the size/time/temperature/duty cycles between these two systems. Land-based gas turbines are exposed to long-term service while incurring harsh corrosive environment. Therefore, the long-term reliability of TBC is a far more critical concern in industrial gas turbines. The currently used monitoring, repair and maintenance techniques for time consuming labor intensive. Accordingly, development of non-destructive evaluation (NDE) techniques capable of determining the coating quality economically and easily becomes paramount importance. The impetus for this research was to develop electrochemical impedance spectroscopy (EIS) as a non-destructive technique for industrial turbines. In this study, EIS technique was used to examine the behavior of intact TBC at ambient temperature. Cross-sectional morphological evaluation of TBC was conducted by scanning electron microscopy (SEM). By correlating the SEM visual examination with EIS data, TBC was characterized non-destructively. A model of EIS alternative current equivalent circuit was proposed to establish the relationship between the EIS parameters in the circuit and the microstructural characteristics of TBC. A linear relationship was found to exist between the electrical impedence of TBC top coat and the thickness of the top coat. The porosity of TBC top coat showed a linear relationship with the capacitance of ceramic TBC, and the pore shape in the TBC top coat was represented by the value of the electrical impedence of the pore. The result in the study has demonstrated that EIS can be used as a NDE technique for quality assurance of TBC.

4:45 PM M8.7
NON-DESTRUCTIVE EVALUATION OF THERMAL BARRIER COATINGS USING IMPEDANCE SPECTROSCOPY. Xin Wang, Md. Shawkat Ali, Junxin Mei, Ping Xiao, Brunel University, Dept of Mechanical Engineering, Uxbridge, Middlesex, UNITED KINGDOM.

Determining the oxidation of thermal barrier coatings (TBCs) non-destructively is essential for monitoring the performance of TBCs and predicting the lifetime of TBCs in service. In this research, impedance spectroscopy was used, as a non-destructive tool, to examine the oxidation of thermal barrier coatings (TBCs). Impedance diagrams obtained from impedance measurements at 1350°C were analyzed according to the equivalent circuit model of the oxidized TBCs. TBCs after oxidation at 1350°C consist of yttria stabilized zirconia as a top coat layer, cubic oxides from the oxidation and a Ni-25Cr alloy as a bond coat. When the oxidation time is less than 200 hours, the impedance spectra of TBCs can be fitted by using an equivalent circuit model, which represents a discontinuous layer of alumina that is separated by an oxide layer and a bond coat. When the oxidation time is between 400 and 1500 hours, the impedance spectra of TBCs can be fitted by using a simple equivalent circuit model, which represents a three-layer structure consisting of a continuous alumina layer, a mixed oxide layer and a top coat layer. In this case, the thickness of the alumina layer can also be measured by simulating the electrical modulus spectra of TBCs. Therefore, impedance spectroscopy is a powerful tool for non-destructive evaluation of oxidation of TBCs.

SESSION M9: POSTER SESSION
Chair: Nik P. Padture
Wednesday Evening, November 29, 2000
8:00 PM
Exhibition Hall D (Hynes)

M9.1 SEPARATING INTERFACE FROM BULK EFFECTS USING ELECTRICAL TRANSPORT PROPERTIES OF THIN FILMS: AI/TI MULTILAYERS AND AI THIN FILMS. Daniel Joelle, J. Gonzalez, John E. Honeich and Grady S. White, National Institute of Standards and Technology, Gaithersburg, MD.

Multilayer materials are sometimes considered as thermal barrier coatings because they enable a thin film resistivity enhancement, the same as a close interface thermal resistance. The thermal resistivity associated with the interfacial layers becomes more significant as the layers become thinner, increasing the density of interfaces. The measurement of the properties of the material within the layers can also vary systematically with thermal conductivity divided by the specific heat per unit volume of a thin film that limits the thermal conductivity of the film. The thermal diffusivity was measured both perpendicular and parallel to the plane of the layers using the Mirage Spectroscopic Technique. Non-interfacial effects (e.g., systematic variation of microstructure with thickness) were determined from the in-plane thermal diffusivities. The interfacial thermal resistance was determined from the dependence of the perpendicular thermal thickness, which was corrected for the non-interfacial effects. Uncorrected for these effects lead to an over-large value of the interfacial resistance. The accuracy of the Mirage system was established by studying the thermal diffusivity of Cu films from 0.1 to 5 μm thick.

M9.2 POST-EXPOSURE EVALUATION OF THERMAL BARRIER COATINGS USING ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY. Jianqi Zhang, Vitali Desan, Univ of Central Florida, Advanced Materials Processing & Analysis Center, and Dept of Mech., Mat's and Aero, Engineering, Orlando, FL.

The application of thermal barrier coatings (TBCs) is one of the most critical approaches in the development of advanced turbine systems. It allows an increase in the turbine inlet temperature up to about 2750°F without an increase in the skin temperature of the substrate superalloys, thereby efficiently increasing the overall efficiency to 60% and higher. However, the application of the TBCs on the land based power generation systems is challenging because the land based gas turbine systems are expected to run several thousand hours while incurring severe hot corrosive environment without inspection. There is insufficient durability/reliability information to assure that the coating will remain protective during such continuous operation periods with far-in-between inspections. Thus, the evaluation of the TBCs becomes a paramount issue not only for quality assurance but for in-service performance monitoring and life time prediction. In this study, high temperature behavior (isothermal and cyclic oxidation and hot corrosion exposure) of TBCs was investigated by using electrochemical impedance spectroscopy (EIS) at ambient temperature. Scanning electron microscope (SEM) and optical microscope were used to examine cross-sectional and surface morphology of the exposed TBC. The correlation of SEM and optical microscope image on the exposed TBC with the EIS data, an NDE technique for TBC degradation was established. It was found that characteristic EIS spectra were obtained effectively to differentiate various post-exposed TBC such as isothermal oxidation, cyclic oxidation and hot corrosion. In addition, the type and length of high temperature exposure were qualitatively discernable from the EIS data. For a quantitative evaluation, a model of EIS equivalent circuit was proposed to relate the material parameters of the TBC with the EIS parameters. From the results, it was shown that EIS can be used to characterize and monitor the microstructure of post-exposed TBC and quantitatively evaluate EIS feasibility.

M9.3 HIGH TEMPERATURE MICROSAMPLE TENSILE TESTING OF DIFFUSION ALUMINIDE BOND COAT LAYERS. Deng Peng, The Johns Hopkins University, Dept of Mechanical Engineering, Baltimore, MD; David Wright, GE Aircraft Engines, Materials and Engineering Department, Cincinnati, OH; K.J. Henker, The Johns Hopkins University, Dept of Mechanical Engineering, Baltimore, MD.

One of the key components of a thermal barrier coating (TBC) is the bond coat layer, which provides oxidation resistance and a foundation
for the ceramic top coat. The physical and mechanical properties of the bond coat are believed to influence the development of stresses during thermal cycling. These stresses have been shown to play an important role in determining TBC life, but the use of standard tensile testing techniques for characterizing diffusion alumina bond coats has been greatly inhibited by their limited thickness (<100 µm). A high temperature, high strain rate, simple tensile testing technique has been developed and successfully employed to characterize PtAl/AlN bond coats in the temperature range from 650°C to 1100°C. The Young's modulus, coefficient of thermal expansion, yield strength and stress relaxation behavior of these two materials were measured as a function of temperature.

The results from this study are being used as material inputs for an independent finite element analysis (FEA) study of the development of stresses during thermal cycling. The results of both of these studies are expected to provide a foundation for understanding and modeling the role of bond coat properties in determining TBC reliability.

M9.4 A NUMERICAL SIMULATION OF RATCHETING IN THERMAL BARRIER SYSTEMS. Anette M. Karlsson, Anthony G. Evans, Princeton Materials Institute, Princeton University, NJ.

Ratcheting is a mechanical phenomenon that occurs when certain structures are subjected to cyclic thermo-mechanical loading where the structure yields during loading and again during unloading due to a redistribution of internal stresses. Ratcheting can cause the geometry of a structure to change significantly, which can sometimes lead to undesirable or catastrophic events. This paper discusses a numerical investigation of ratcheting as it occurs in a class of thermal barrier ceramic-alloy barrier systems. Ratcheting is associated with a process that eventually generates cracks between the thermally grown oxide (TGO) and the thermal barrier coating (TBC), ultimately causing spallation of the TBC. Ratcheting in these systems is caused by a combination of several factors: (1) cyclic thermal loading, (2) yielding and reverse yielding of the bond coat during each load cycle, (3) a bias and increasing in-plane stress in the TGO, and (4) existing morphological features. The bias stress is due to the in-plane oxidation of the TGO at elevated temperature since the TGO grows not only normal to the bond coat surface, but also in-plane, thus increasing in-plane “growth strain” during each thermal cycle. In this study, finite element analyses were conducted to simulate the development of the thermal barrier system as the oxide layer grows. The model consists of a three-layered structure: the bond coat (typically FeCrAlY), the growing oxide layer (alumina-aluminina), and the thermal barrier coating (partially-stabilized zirconia). The growth strain is simulated by adding a bias strain for each thermal cycle. The development of the structure is seen to be a function of pre-existing morphology, material properties, and the rate of oxidation. Results are presented that illustrate the development of internal stresses and the evolving deformations associated with the ratcheting process.

M9.5 MICRO-MECHANICS MODELS FOR FAILURE PREDICTION OF THERMAL BARRIER COATINGS. Ming Y. He, Materials Department, University of California, Santa Barbara, CA; John W. Hutchinson, Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA; and Anthony G. Evans, Princeton Materials Institute, Princeton University, Princeton, NJ.

The durability of thermal barrier coatings is governed by a sequence of crack nucleation, propagation and coalescence prior to final failure by large scale spallation of the ceramic top coat. The observation of undulations and imperfections on the nucleation and propagation stages of delamination of compressed thin films has been analyzed in several respects. 1) Calculations of the thermal fatigue have revealed that the interface undulations can result in cyclic straining of the substrate, near the interface, leading to crack initiation by fatigue. A thermal fatigue map, which characterizes the regions in which initial yielding, shakedown and cyclic plasticity occur, has been presented. 2) An analytical model for fatigue imperfections experienced upon thermal cycling has shown that, in some circumstances, ratcheting occurs. The undulation amplitude increases with each thermal cycle, which induces out-of-plane tensile strains in the TBC. These strains may cause cracks parallel to the interface. The analysis reveals that there is critical undulation amplitude, below which ratcheting does not occur. The critical amplitude is related to ratio of the thermal stress in the film to the substrate yield strength. 3) An analytical model for stress in the three-dimensional system of the TBC and substrate, taking into account the thermally grown oxide (TGO) growth strains in combination with thermal expansion mismatch. The results are used to identify a critical TGO thickness at failure and express it in terms of the governing materials variables.
ESTIMATION. Neil J. Goldfine, Yingke Sheiretov, Andrew Washabaugh, Darrell Schlicker, Vladimir Zilberstein, JENITEK Sensors, Inc., Watertown, MA.

New inspection methods use spatially periodic field eddy current sensors, called Measuring Windings MagnetoMeters (MWMs) and novel periodic eddy current field detectors, to measure coating thickness, electrical conductivity and permittivity. The coating porosity can be estimated from measurements of the conductivity for metallic coatings and permittivity for ceramic coatings. The sensors are conformable permitting characterization of both flat and curved parts in a contact mode. Non-contact mode characterization of metallic coatings is also possible with the MWM.

This paper describes a multiple frequency metallic coating characterization technique that uses three-dimensional data from pre-computed sensor responses to convert MWM impedance magnitude and phase into independent estimates of metallic coating thickness and porosity. Examples of results on curved turbine blade components are given. The technique developed in this technique can be visualized as measurement 'grid matrices' that permit estimation of three unknown properties (e.g., ceramic topcoat thickness, metallic bond coat thickness and metallic bond coat porosity). Ongoing work is focused on estimation of magnetic permeability as a fourth unknown to assess thermal aging of coatings and substrates. This work was supported in part by NASA and has continued under internal research and funding development at JENITEK Sensors, Inc.

M9.10 CHARACTERIZATION OF THERMALLY-SPRAYED DICALCIUM SILICATE BY ULTRASOUND-Angle X-RAY SCATTERING.
Jan Hlavsky, University of Maryland, College Park, MD and National Institute of Standards and Technology, Gaithersburg, MD; Andrew J. Allen, Gabrielle G. Long, National Institute of Standards and Technology, Gaithersburg, MD; Peter R. Janus University of Illinois, Argonne National Laboratory, Argonne, IL.

Dicalcium silicate feedstock has been atmospherically plasma-sprayed onto a steel substrate to a thickness of about 500 µm. Such deposits are currently being considered for the next generation of thermal barrier coatings. Currently, deposits thick cannot be characterized by the small angle neutron scattering methods that have proven so successful for thin films. Ultrasound ultrasonic angle X-ray scattering (USAXS) studies have enabled some of the microstructural void information to be obtained from these deposits. The high brightness and small beam size available at a third generation X-ray synchrotron source permit the study of deposits less than 500 µm thick in a plane perpendicular to the substrate. Our results show that we can obtain the complete microstructural Porod surface area distribution, and also the anisotropy in the multiple scattering that is associated with the orientation and size distributions of the intragranular cracks and interlamellar pores. USAXS imaging has been used to visualize the dominant microstructural features in the deposits. The microstructure was used for varying orientations of the Q vector with respect to the spray direction, highlighting the differently oriented features. We present this novel view of the microstructure and discuss it together with results from other techniques to show how such studies can enhance our understanding of the microstructural deposit properties.

M9.11 TRANSMISSION ELECTRON MICROSCOPY INVESTIGATION INTO THE OXIDATIVE FAILURE MODE OF 68 wt % Y₂O₃-STABILIZED ZrO₂/Na₂Cr₂O₇ THERMAL BARRIER COATINGS.

Field-emission transmission electron microscopy (TEM) was used to investigate the interfacial chemistry of thermally cycled air plasma sprayed Y₂O₃-STABILIZED ZrO₂ (YSZ)/Na₂Cr₂O₇ thermal barrier coatings (TBCs). Historically, TEM of failed TBC cross sections has been non-trivial due to specimen preparation difficulties. In the present study, TEM specimens of coatings on a low pressure plasma sprayed Ni-16 wt % Cr-7wt % Al-0.6 wt % Y alloy, cycled to failure, were prepared using the focused ion beam lift-out technique. Phase distributions within the oxide scale were determined by energy dispersive spectroscopy and electron diffraction. The results revealed the formation of single oxide phases as well as the相伴 presence of an additional aluminum scale, after prolonged thermal cycling. These discontinuous oxide phases were comprised primarily of Ni(Al)O₃ and Cr(Al)₂O₄ with minor amounts of yttrium containing oxides. Oxides other than those present at specific interfaces were formed following aluminum depletion in the vicinity of the oxidizing interface. Large particles (>1 μm) of unoxidized, pure nickel metal were also found within the discontinuous oxide phase. The elemental nickel may cause an increased coefficient of thermal expansion (CTE) mismatch between the discontinuous oxide phase and the YSZ topcoat. On the coating cycle, this CTE mismatch will lead to residual compressive stresses within the YSZ topcoat and cause the topcoat to buckle or delaminate.

M9.12 EVOLUTION OF THE METAL/OXIDE INTERFACE IN NIOCCIASYL-BASED THERMAL BARRIER SYSTEMS.
Daniel R. Munson, Caroline Liu, Anthony G. Evans and Nan Yao, Princeton Materials Institute, Princeton University, Princeton, NJ.

Thermal protection systems based upon thermal barrier coatings (TBCs) are widely used to protect metallic hot-section components in turbine engines. They comprise the thermal barrier coating (TBC) itself, a superalloy substrate, an aluminum-containing bond coat (BC) between the TBC and the metallic base material, and a thin thermal barrier oxide (TO) layer that forms between the TBC and BC. Each of the four constituents evolves in service, and all interact to control the performance and coating durability. Reactive element (RE) additions to the BC and substrate are known to significantly affect the durability of the TBC systems, the effect largely attributed to gettering of segregating species (such as sulfur) that degrade interface adhesion. There has also been recent realization that the morphology of the metal/oxide interface plays a key role in the spalling failure of the TBC systems. Recent investigations of NiCoCrAlY-based thermal barrier systems have shown that morphological features in the metal/oxide interface develop in relation to the distribution of reactive elements in the system, and are associated with RE-based precipitates in the developing TGO layer. High-resolution SEM and TEM-based imaging, chemical and microstructural analysis were used to characterize the microstructure of the spinel bond coat with an emphasis on the interfacial morphology. The mechanisms by which it develops, and its effects on thermal barrier coating durability.

M9.13 CHANGES IN LATTICE STRUCTURE AND MICROHARDNESS DURING THERMAL TREATMENT OF A NiCoCrAlY ALLOY.
Thomas Rehfeldt, Holm Meier-Institut Berlin, Berlin, GERMANY; Gerald Schmauscher and Helmut Klingsboeck, Bundesanstalt fuer Materialienforschung und -prufung, Berlin, GERMANY.

NiCoCrAlY alloys are being tested for application as bond coat material deposited between superalloys and ceramic thermal barrier coatings in turbine blades. The NiCoCrAlY alloy investigated in this work consists of an ordered phase with B2 lattice structure (beta phase), an ordered gamma prime phase with L1₂ lattice structure [Ni₃Al type structure] and a chromium rich phase [1]. The gamma prime phase was shown to transform into the disordering for gamma phase in the temperature range between 800°C and 1100°C [1]. In order to measure the microhardness of the gamma prime phase we prepared a single phase gamma prime alloy with approximately the same chemical composition as the gamma prime phase in the bond coat alloy. The chemical composition was measured locally by means of energy dispersive spectroscopy in TEM and in SEM. TEM investigation of the gamma prime phase alloy confirmed that the alloy has L1₂ lattice structure. The single phase alloy revealed an ordered-disorder transformation in the same temperature range as the gamma prime phase in the bond coat alloy. The critical temperature of the phase transformation is small compared to that of Ni₃Al due to the high contents of Cr and Co and the low content of Al. The microhardness of the single phase alloy was measured on specimens in the as produced state and after an appropriate heat treatment at high temperature and subsequent quenching into ice water in order to freeze in the high-temperature state. It was found that the microhardness decreases from Hv = 350 in specimens quenched from 800°C to Hv = 250 in specimens quenched from 1100°C. This decrease in microhardness is ascribed to changes in the atomic bondings during the order-disorder transformation.


M9.14 HARDNESS AND ELASTIC PROPERTIES OF ZIRCONIA-BASED ENHANCED THERMAL BARRIER COATINGS FROM ROOM TEMPERATURE TO 1472K. Brian D. Kernig, Anqi He, Arthur H. Heuer, Case Western Reserve University, Department of Materials Science and Engineering, Cleveland, OH.

A high temperature displacement-sensitive indenter was used to measure hardness and elastic properties from room temperature to 1472K of a Zirconia - 7 wt % Ytria thermal barrier coating made by ELOX. The samples were deformed in situ, and tested in temperature as subsequent to a 4 h anneal in air at 1472K. The hardness and effective stiffness decrease with increasing temperature. Hardness and
stiffness increase after the very modest aging process. The microstructure in the as-deposited and aged samples, and the damage zone around indentations were studied with TEM. The short aging treatment significantly concerned the intracrystalline pore structure.

M9 15
IN-PLANE CRACKING BEHAVIOR NEAR AND AWAY FROM INTERFACE OF THERMAL BARRIER COATINGS AND THERMALLY GROWN OXIDES. Z. Zhang, J. Kameda*, A.H. Swanson, Iowa State University, Ames Laboratory, Ames, IA; Office of Naval Research, Naval Research Laboratory, Washington, DC, Japan; S. Sakurai, Hitachi Ltd., Mechanical Engineering Research Laboratory, Hitachi, Japan.

The initiation characteristics of in-plane cracks near and away from the interface of thermal barrier coatings (TBC) and thermally grown oxides (TGO) have been studied using a protracted four-point bend testing technique together with a finite element analysis. In-plane TBC cracks initiated near or away from the TBC/TGO interface depending on the substrate thickness, and the root radius and position of a stress concentrator at the edge of protracted TBC. It has been shown that the onset of TBC cracks near or away from the interface has not to go beyond at least an in-plane TBC tensile stress component but not by a principal tensile stress acting upon an inclined plane to the interface. The critical local tensile stress (σ*, for the onset of TBC cracks near the interface was found to be much lower than that away from the interface. Thicker substrate specimen tests exhibited lower values of σ* for interface TBC cracking than thinner substrate specimens. Conversely, TBC cracking away from the TBC/TGO interface became much more difficult as the substrate thickness was increased. The inverse effects of the substrate thickness on the TBC cracking near and away from the TBC/TGO interface are rationalized by the tensile and compressive residual stress components distributed in the substrate and near TBC, respectively, which are affected by the thickness of the substrate. This work was carried out as part of a program approved by the US DOE, Office of Basic Energy Sciences, Division of Materials Science.

SESSION M10: PLANE V
Chair: David J. Wortman
Thursday, November 30, 2000
Room 209 (Hyatt)

8:30 AM *M10.1
R&D STATUS AND NEEDS FOR IMPROVED EB-PVD THERMAL BARRIER COATING PERFORMANCE. Christopher Legerski, Uwe Schulz, Klaus Fritscher, Manfred Peters, Wolfgang A. Kupper, Institute of Materials Research, DLR-German Aerospace Center, Cologne, GERMANY.

Thermal barrier coatings (TBCs) are currently used for lifetime improvement of highly loaded turbine blades and vanes in aeroengines and land-based gas turbines. Utilizing the insulating materials properties of ceramics in a ceramic top coating, TBCs predominantly reduce the beneficial effect by reducing the effective metal temperature and mitigating the effect of hot spots. However, the increasing demands placed on the high-temperature capabilities of future turbine components are beyond the requirements of TBC systems which are an integral part of the component and thus vital for its safe operation. Coating failure then essentially marks the end of component lifetime. Therefore, "prime-relent" coatings are necessary which performance has to be dependent on state-of-the-art TBC systems. The performance improvements needed undoubtedly require a systems approach, including consideration of environmental and mechanical properties of each part of the TBC system and their interplay and compatibility. Based on the extensive body of knowledge available from practical applications and laboratory tests, the paper highlights both research and development status and trends devoted to future generation electron beam physical vapor deposition (EB-PVD) TBC systems with significant performance improvements and reliability. The paper includes consideration of both the bond coat and the ceramic coating. Compatibility with the substrate and improved oxide scale spallation resistance at higher temperatures than currently employed are important issues for bond coat development. Growth of the oxide scale underneath the ceramic top layer is already affected during processing and is important in view of TBC durability. For the ceramic coating, improved water resistance, phase stability and lower thermal conductivity are much desired and will require advanced materials. In addition, material properties are closely linked to processing conditions, the paper addresses important relationships where appropriate. Examples are given of the significance of single layer property interactions with regard to overall coating system performance.

SESSION M11: PROCESSING
Chair: David J. Wortman
Thursday, November 30, 2000
Room 209 (Hyatt)

9:15 AM *M11.1
MICROSTRUCTURE EVOLUTION IN EB-PVD THERMAL BARRIER COATINGS. Scott G. Terry, Janghyun Cho, Charles G. Levi, Materials Dept., University of California, Santa Barbara, CA.

Current issues in understanding the microstructure evolution of vapor-deposited thermal barrier coatings (TBCs) and the development of the characteristic TBC columnar morphology will then be examined, with emphasis on the selection of in-plane and out-of-plane textures, and on the implications for the incorporation of porosity in different length scales. The relative role of crystallography, surface diffusion and local flux variations due to shadowing will be discussed in the context of experiments where temperature, vapor incidence pattern and substrate characteristics are varied in a controlled manner. Of particular interest is the effect of columnar growth on the evolution of morphology vis-a-vis deposition on stationary substrates. Additional insight on the interplay between the vapor flux and the surface morphology will be provided from continuum and ballistic deposition models. (Work supported by ONR under Grant N00014-94-1-0471.)

9:45 AM M11.2
NOVEL PROCESSES FOR SYNTHESIZING THERMAL BARRIER COATING SYSTEMS. J.F. Groves, D.D. Hess, H.N.G. Wadley, Univ of Virginia, Materials Science and Engineering Dept, Charlottesville, VA.

Directed Vapor Deposition (DVD) has been developed to facilitate rapid, efficient film coating with a range of compositions and microstructures. Conventional electron beam (e-beam) evaporation has a high vacuum at 10^-4 mbar or lower, vacuum e-beam technology (10^-4 - 1 mbar) and a flowing carrier gas to create and transport a focused evaporant stream from multiple crucibles. The mechanisms of gas and vapor transport in the DVD system have been examined experimentally and through use of vapor transport models. During operation, DVD generates luminescence from gas and vapor in the system, allowing visual control over the deposition process. Gas and vapor transport has also been studied using Direct Simulation Monte Carlo (DSMC) and bimolecular collision theory codes which follow atoms through the system. Additionally, these codes provide insight into vapor atom deposition location, angle, and energy, information critical to identifying appropriate coating applications. Early experiments and modeling suggested that DVD might be suitable for the creation of porous, columnar thermal barrier coatings (TBCs) for use in turbine power systems. Subsequent experimental work has demonstrated a TBC creation ability. Insight gained during early work also suggested that DVD microstructure control could be enhanced through plasma activation of the gas and vapor stream prior to deposition. Initial experimental work with a second generation DVD tool indicates that plasma activation does enhance DVD’s ability to deposit microstructure.Coupling plasma activation, a focused vapor stream, and low vacuum e-beam evaporation has generated a deposition technology of wide applicability. With this technology it appears possible to synthesize uniform columnar coatings over large areas. The use of useful microstructures and compositions using a single tool. Thus, novel materials systems can be developed to overcome current TBC system limitations, moving the field closer to discovery of a prime relevant coating system.

10:00 AM M11.3
MICROPHOTOGRAPHY OF YTTIRIA STABILIZED ZIRCONIA LAYERS DEPOSITED USING ELECTRON BEAM DIRECTED VAPOR DEPOSITION. D.D. Hess, J.F. Groves, H.N.G. Wadley, University of Virginia, Materials Science and Engineering Dept, Charlottesville, VA.

The thermal conductivity of porous yttria stabilized zirconia (YSZ) thermal barrier coatings are controlled by their pore morphology. YSZ coatings having porous, columnar morphologies have been grown using a low vacuum (0.1 to 1 Torr) electron beam directed vapor deposition process. This process approach employs a transonic helium carrier gas jet which transports an evaporated YSZ flux towards a substrate to create deposition conditions which vary greatly from conventional electron beam evaporation approaches. Using this technique, YSZ films were deposited on a range of deposition conditions. The resulting morphologies included highly porous (up to 50%) columnar grown structures with distinct intercolumnar porosity (up to 1.0 microns wide), denser coatings having textured columnar grains with limited intercolumnar pore width and granular coatings with columnar pores. The coating morphology was found to be affected by several parameters including the substrate temperature, evaporation/depotition rate, chamber pressure and the...
properties of the carrier gas jet (i.e. its speed, density, and interaction with the substrate). In order to link these parameters to more fundamental growth parameters (such as atom energy and random angle of incidence), the flow field of the helium gas jet and its interaction with a substrate was modeled using a direct simulation Monte Carlo (DSMC) approach and binary collision theory (BCT). The role of these deposition parameters plays in the development and coating morphologies desirable for use as thermal barrier coatings will be discussed.

10:45 AM M11.4
PROCESSING AND THERMAL CYCLING EFFECTS ON THE LIFE OF THERMAL BARRIER COATINGS FOR INDUSTRIAL GAS TURBINE APPLICATIONS. Zeher Motasem, PhD, Surface Engineering Solar Turbines Incorporated, San Diego, CA.

Industrial gas turbine combustion systems are currently designed with plasma sprayed thermal barrier coatings (TBCs) for combustor liner life extension. Lower combustor liner metal temperatures could be achieved when a prime-reliant TBC is applied onto a back-side cooled liner. TBC life is strongly dependent on many factors. These include bond coating chemistry, ceramic coating thickness, substrate material, test temperature and mode. Thermal cyclic testing was conducted on various TBC systems to study the effects of these factors on TBC life. This paper discusses these factors and their influence on TBC durability. Metallurgical evaluation of thermally-cycled TBCs was conducted to assess the failure mechanisms associated with plasma sprayed thermal barrier coatings.

11:15 AM M11.5
DEVELOPMENT OF PROCESS MAPS FOR PLASMA-SPRAYED PARTIALLY-STABILIZED ZIRCONIA. A. Vaidya, A. Kulkarni, H. Herman, S. Sampath, Center for Thermal Spray Research, SUNY, Stony Brook, NY.

The performance of Thermal Barrier Coatings (TBCs) is strongly dependent on porosity, thermal conductivity, phase composition and microstructure. A process map for atmospheric plasma spraying of 8% yttria-stabilized zirconia (YSZ) is under development. Process maps are an integrated set of relationships that link processing to performance, which provide a framework to achieve intelligent process control, optimize microstructure/properties and enhance reliability. The variation of microstructures and properties with key process parameters also provides insight into the mechanism of deposit formation. In this study a hollow sphere YSZ powder was processed using a commercial plasma spray torch. A variety of particle sizes were produced by changing the particle temperature and velocity during spraying. Diagnostic studies were carried out with different nozzle geometries to achieve a wide range of particle temperatures and velocities. Splat and coatings were then produced under these conditions. The effect of substrate temperature was also considered for each condition, since this has been shown to be significant in earlier studies. The morphology of splats formed under these conditions has been examined and correlated to the resulting coating microstructure. The coatings have been characterized for porosity, thermal conductivity, microstructure and mechanical properties. Such maps can be used as design tools to construct coatings with specified properties. The work was supported by NSF through its MARC program: DMR 96-32570.

11:30 AM M11.6
DURABLE THERMAL BARRIER COATINGS WITH NOVEL MICROSTRUCTURES DEPOSITED BY SOLUTION PRECURSOR PLASMA SPRAYING. T. Bhatin1, B. Cetegen1, M. Gell1, E.H. Jordan1, A. Ozurk2, N.P. Fauteux1, K.W. Schlichting1, P.R. Strutt2, and D. Xiao2, 1Inframat Corp., North Haven, CT, 2Inframat Corp., North Haven, CT.

Nano-crystalline, porous thermal barrier coatings (TBCs) of yttria-stabilized zirconia (YSZ) have been deposited by plasma spraying of inorganic liquid precursors (nitrates and acetates) onto bond-coated superalloy substrates. Under thermal cycling conditions, these new TBCs have a better spallation life than state-of-the-art conventional plasma-sprayed YSZ TBCs. These new TBCs display several unique microstructural features which are believed to contribute to the improved resistance to spallation under thermal cycling: (i) elimination of splat/splat boundaries and microcracking that are present in conventional TBCs made by powder feedstock plasma spraying, (ii) nano-crystalline grains which appear to be resistant to coarsening, (iii) higher and well-distributed porosity and (iv) presence of strain relieving cracks normal to the metal-ceramic interface. Experiments are being carried out to determine the complex interaction of liquid precursor droplets with the plasma and the metal substrate out using two different approaches. First, precursor droplets are being collected in the plasma by thermophoretic sampling at different locations in the flame, and are being characterized using scanning electron microscopy and transmission electron microscopy.