SYMPOSIUM M

Thermal Barrier Coatings

November 28 – 30, 2000

Chairs

Maria Arana Antelo
GTDBMS
ABB Alstom Power
Baden, CH-5401 SWITZERLAND
41-56-205-7733

Nitin Padture
Inst of Materials Science
Univ of Connecticut
97 North Eagleville Rd
Storrs, CT 06269-3136
860-486-4206

Bruce A. Pint
Oak Ridge National Laboratory
MS 6156
Oak Ridge, TN 37831-6156
865-576-2897

Sanjay Sampath
Dept of MS&E
SUNY-Stony Brook
Ctr for Thermal Spray Research
Stony Brook, NY 11794-2275
516-632-9512

David J. Wortman
Corporate R&D
General Electric Co
Bldg K1-Mb207
Schenectady, NY 12301
518-387-7725

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SESSION M1: PLENARY I
Chair: Maria Arana Antelo
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 visco-plastic flow while forming (ii) a thin thermally grown oxide (TGO, typically ∝-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 back-side air cooling. It must also have the strain tolerance to withstand the thermal expansion misfit with the substrate. The thermal barrier system is dynamic. The TGO thickens, the microchemistry 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 (a few microns), still represent a high energy density domain. The means whereby this energy density couples into the TBC to cause failure are described. Based on this understanding, approaches for addressing durability are discussed.

SESSION M2: FAILURE MECHANISMS AND LIFE PREDICTION
Chair: Maria Arana Antelo
Tuesday Morning, November 28, 2000
Room 209 (Hynes)

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

Thermal barrier coating systems (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 PtAl diffusion coating and an electron-beam physical vapor deposited (EB-PVD) yttria-stabilized zirconia ceramic layer. These coating systems have a practical service interval that is limited by several failure modes, including mechanical damage to the ceramic layer and thermal cycling degradation of the bond coat. This presentation will review the typical failure mechanisms observed on hardware, and where possible, compare the results to those obtained in laboratory engine-simulative testing of samples.

9:45 AM M2.2
CONTRIBUTION TO LIFE PREDICTION OF APS THERMAL BARRIER COATINGS. R. Herzog, F. Schubert, L. Singheiser, Research Centre Juelich, Institute for Materials and Processes in Energy Systems (IWV 2), Juelich, GERMANY.

Thermal barrier coatings are exposed to complex thermo-mechanical loads during service leading to specific life limiting degradation and damage processes, as 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 typical crack fields, consisting of segmentation and delamination cracks. Further crack propagation results in a macroscopical 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 7-8 wt% yttria. The applied thermo-mechanical cycle was defined by a temperature range between RT and 950 deg C and a varied total tensile 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 Gell, Matt Begley, 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 roll in TBC failure due to thermal cycling. Two contrasting examples will be described. In the first example a MCrAlY bond coat with entrapped oxide defects is described in which the entrapped oxide result in the complete encapsulation of some bond coat sections. The isolated bond coat depletes of aluminum prematurely and harmful non-alpha oxides form. In the second example a PtAl 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 an idealized cavity geometry. The model highlights the fact that maximum tensile stress in the oxide occurs at a specific optimal oxide thickness for any given loading. It is also shown that increased cavity growth occurs when the oxide preferentially grows in the in plane direction as would be expected in the case of oxide cracking, tensile creep or stress enhanced in plane oxide growth. The oxide growth behavior needed to bring the model in agreement with the observed behavior of the PtAl bond coat will be presented.

11:00 AM M2.4
FAILURE MECHANISMS IN PLASMA SPRAYED THERMAL BARRIER COATINGS. Afsaneh Rabiei, Harvard University, Division of Engineering and Applied Sciences, Cambridge, MA; Anthony G. Evans, Princeton University, Materials 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 inter-diffusion 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 5μ, the growth of the TGO does not affect the crack patterns in the TBC and delaminations induced by wedge impression propagate within the TBC about 30μ from the interface. An amorphous phase at the splat 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 result based on the misfit around 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. Tolpygo, Materials Department, University of California, Santa Barbara, CA.

Although zirconia thermal barrier coatings (TBC) are already widely and successfully used in both aerospace and power generation gas turbines, there is a drive to use them at still higher temperatures 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,Pt)Al bond-coats demonstrating that surface preparation affects both the kinetics of the transformation of transient aluminas to the final alpha-alumina phase and the parabolic rate constant during high temperature oxidation. Specifically, by combining photostimulated luminescence spectroscopy, scanning microscopy and SIMS, we reach three major conclusions. Firstly, surface preparation affects the nucleation of alpha-alumina and hence the grain size of the thermally grown oxide. Secondly, impurity 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 types of impurity, their concentration and the grain size of the oxide. Further observations indicate that the kinetics of the phase transformation to alpha-alumina in the thermally grown oxide as well as its subsequent growth rate cause depletion of aluminum from the underlying bond-coat. This, in turn, promotes "rumpling" of the bond-coat on cyclic oxidation and creates geometric incompatibilities between the bond-coat and thermal barrier coating leading to local failure. As presently understood, this is produced by volumetric changes in the bond-coat associated with the beta-NiAl to gamma-prime-Ni_3Al phase transformation and driven by aluminum depletion from the bond-coat during high-temperature oxidation.

11:45 AM M2.6
CYCLIC FAILURE OF A THERMAL BARRIER SYSTEM BY A DISPLACEMENT INSTABILITY IN THE THERMALLY GROWN OXIDE. Daniel R. Mumm 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 motivated 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 interfacial separations and the propagation of damage. Systematic oxidation studies, high-resolution imaging, chemical and micro-structural analysis, and novel thermo-mechanical test methods are used in combination to elucidate failure mechanisms for EB-PVD TBC systems comprising (Ni,Pt)Al 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, Krishnakumar Vaidyanathan, Kathleen McCarron, Yongho Sohn, School of Engineering, University of Connecticut, Storrs, CT.

The durability and reliability of current thermal barrier coatings (TBCs) made from 6-8 weight percent yttria partially stabilized zirconia (7YSZ) 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, reduce cooling air flow and thus improve engine fuel efficiency, and be assured that the TBC will not spall for the designed lifetime of the turbine blade. A significant approach to improving 7YSZ durability and reliability has been taken at the University of Connecticut using mechanisms-based research of production TBCs. Five production TBCs, two deposited by electron beam beam physical vapor deposition (EB-PVD)and 3 deposited by plasma spray have been thermally cycled to various life fractions at 1121°C, and the mechanisms of spallation were determined. For all TBCs, damage on the eventual spallation surface, was observed at low life fractions. For the EB-PVD TBCs, damage was initiated at microstructural features or defects on the bond coat surface. Removal of these defects prior to deposition of the ceramic produces 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 heating elements. When cooled, these coatings usually sustain very large compressive stresses which make them susceptible to interface delamination. The effect of substrate curvature on buckle-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 Handoko, Jack Beuth, Qin Ma, Carnegie Mellon University, Dept of Mechanical Engineering, Pittsburgh, PA; Matthew Stiger, 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 or cyclic 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 axisymmetric 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 EBPVD 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 sintering. 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 sintering and interfacial damage in decreasing 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 (TBC's) 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 stratagem is to develop numerical schemes for determining these properties from the complex microstructure of these materials. Such a 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 scientist to simulate physical properties of complex microstructures from an image of that microstructure. Computer simulations using OOF have been conducted on TBC's to elucidate the influence of microstructural features, such as, porosity, microcracks, interfacial surface roughness, and residual misfit strains, on mechanical behavior. Recent extension to incorporated fracture and damage accumulation and measurements of thermal conductivity will also be discussed.

4:00 PM M4.4
MECHANICAL BEHAVIOR OF FREESTANDING TBC. Stefan Lampenscherf, Dinorah Steiner, Ullrich 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 interprete 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 Kachanov, 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 orientational distribution of solid domains the factors that can, to some extent, be controlled by processing parameters - is 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 "columns" 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 utilized as a non-destructive quality control: the 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 BARRIER COATINGS. Michael Glynn, K.T. Ramesh, P.K. Wright[a] and K.J. Hemker Department of Mechanical Engineering, Johns Hopkins University, Baltimore, MD. [a]GE-Aircraft Engines, Materials and Process Engineering Department, Cincinnati, OH.

The effect of surface roughness on thermal barrier coatings (TBC's) 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 buttons, coated with one of two different diffusion annealed bond coats and capped 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. Material 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 microscope (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 Oechsner, and Ramesh 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 and predictable. The push 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 bracket 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 regime where the properties of both the bond coat and TBC contribute too the failure. Defining this region will come with an understanding of the fracture mechanics and strain energy of the bond coat TBC interface and the time /temperature properties of the materials. An analysis of those 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 Haynes, Karren L. More, Bruce A. Pint, Ian G. Wright, Oak Ridge National Laboratory, Oak Ridge, TN; Ying Zhang, University of TN, Knoxville, TN; Woo Y. Lee, Stevens Institute of Technology, Hoboken, NJ.

The adherence of the thermally-grown alumina 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 coatings with controlled sulfur contents. Single-phase NiAl and NiPtAl bond coats were fabricated on low-sulfur (LS) and higher-sulfur (HS) single-crystal Rene N5 superalloy by chemical vapor deposition (CVD). Scale growth characteristics and adherence were investigated by isothermal and cyclic oxidation testing at 1150°C. Oxide and coating 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 scale adherence to NiAl 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 superalloy sulfur content on scale adherence to Pt-containing coatings. Scales on NiAl typically failed due to formation of large voids at the oxide-metal interface, and void concentrations on isothermally-oxidized NiAl 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 alumina scales on both NiAl 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 EB-PVD TBC MODEL SYSTEM. Eric Sommer, Carsten Mennicke, Manfred Rühle, Max-Planck-Institut für Metallforschung, Stuttgart, GERMANY; Scott G. Terry, Carlos G. Levi, University of California at Santa Barbara, Materials Department, Santa Barbara, CA; Jean Le Coze, Ecole des Mines de Saint-Etienne, SMS-MHP, 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, TGO and an EB-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 nondestructively by optical piezospectroscopy. Stress state and microstructure of the TGO will be correlated with respect to the underlying BC morphology, 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 Monceau, Djar Oquab, Marie-Christine Lafont, Bernard Pieraggi, Centre Interuniversitaire d'ingénierie et de Recherche des Matériaux, UMR CNRS-INPT-UPS 5085, ENSCT, Toulouse Cedex, FRANCE.

The oxidation behavior of several bondcoats was studied through a systematic study. Many systems were elaborated and tested with almost all combinations of the following parameters: 1/alloy substrate: IN100 or AM3 (single crystal) Ni-based superalloys 2/ bond-coat: VPS NiCoCrAlYTa or CoNiCrAlY, (Ni,Pd)Al, (Ni,Pt)Al 3/ bondcoat surface finish: as deposited, polished, machine ground, grit-blasted, preoxidized 4/ topcoat: APS or EB-PVD ZrO2-Y2O3 ceramic coatings. The preoxidation treatments of bond-coats were defined from a careful study (TGA-GIXRD-SEM-SIMS) of their short-term (6 to 24 hours) isothermal oxidation behaviour as a function of test temperature (900 to 1100°C), oxygen partial pressure and also heating rate to test temperature. All bond-coats are alumina formers, but depending on the oxidation conditions, transient theta alumina or stable alpha alumina grow on nickel aluminides as well as on MCrAlY's. For all these systems, the conditions of exposure leading to the growth of a thin layer of alpha alumina was defined. The microstructure of these alumina thin layers and their underlying bondcoats was characterized through extensive SEM and TEM examinations. The characterisation of complete TBC systems was also performed to compare the studied systems and to determine the effect of the bond-coat preoxidation. TBC test specimens were subjected to different solicitations: isothermal oxidation, cyclic oxidation at 1100°C, cyclic corrosion at 900°C and thermal shocks (fast cooling from 1200°C). Among these numerous results, some points will be emphasized such as the effect of surface finish and oxygen partial pressure on the growth of transient alumina, and the differences in the oxidation behavior of palladium and platinum modified nickel aluminides.

11:00 AM M6.4
TEM INVESTIGATIONS OF OXIDIZED YTTRIA STABLILIZED ZIRCONIA ON PLATINUM ALUMINIDE BOND COAT. Mridula Dixit Bharadwaj, Judith C. Yang, Univ of Pittsburgh, Dept of Materials Science & Eng, Pittsburgh, PA.

Determination of the microstructure and chemistry of the oxidized thermal barrier coatings (TBC) are crucial to understanding their failure mechanisms. We are investigating oxidized TBC's by structural and analytical transmission electron microscopy (TEM) methods. The examined TBC material is yttria-stabilized zirconia grown on a platinum aluminide bond coat (BC) by e-beam physical vapor deposition. This multilayer was then oxidized at 1100°C to form polycrystalline alpha alumina. It is well known that randomly oriented alpha alumina (thermally grown oxide TGO) forms due to high temperature oxidation of the TBC's. 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 200KeV. Preliminary energy dispersive X-ray spectroscopy data suggest that there is intermixing between the TGO and TBC, but the TGO and BC interface is sharp. From this type of data, we will identify whether there is any texture of the alumina scale, or texture in the TBC coating. We will also examine whether there exists metastable aluminas, which are known to be detrimental to scale adhesion.

11:15 AM *M6.5
COMPARISON OF THERMAL BARRIER COATINGS FAILURES ON MCrAlY AND ON PLATINUM ALUMINIDE BOND COATS. N.M. Yanar, G.H. Meier and F.S. Pettit, 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 (EBPVD). These coatings were deposited upon NiCoCrAlY bond coats and platinum aluminide bond coats which in turn were on René N5 superalloy substrates. The NiCoCrAlY bond coats were prepared by two different powder spray processes. These TBC systems were characterized in the 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 oxidation characteristics of the bond coats. After 3000 hours of cyclic oxidation without TBCs there was not a substantial difference between some of the NiCoCrAlY bond coats and the platinum aluminide bond coat. Both of these coatings were depleted of aluminum, but α -Al_2 O_3 scales were still evident upon these bond coats. The surfaces of the platinum aluminide bond coats were more deformed than the surfaces of the NiCoCrAlY bond coats and this difference was evident after about 1000 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. The TBCs with NiCoCrAlY bond coats failed after approximately 100 to 200 hours at 1100°C whereas the TBCs with platinum aluminide 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 excursions into the TGO and the TBC. 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 HIGH TEMPERATURE OXIDATION STUDIES IN NiCrAlY: 8% YTTRIA-ZIRCONIA THERMAL BARRIER COATINGS. A.M. Varaprasad, Defence Materials and Stores Research & Development Establishment, DMSRDE(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 standard stainless steel substrates using powders of 8% Yttria-Zirconia made by Polymer Matrix Method (Ref:1-4) and commercial NiCrAlY (METCO make, contains 0.1% Silicon). 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-EDXA), 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 Nickel 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 were negligible initially, but, the same grew steadily with increase in number of thermal cycles. The adhesion between bond coat and substrate is intact althrough the thermal cycles and the width of the Aluminium rich interface oxide is about 5 microns. The Coefficient of Thermal Expansion (CTE) of Aluminium Oxide (6 ppm) and Silicon Oxide (5 ppm) are low as compared to the substrate (16 ppm) and Zirconia top coat (11.6 ppm) and it has adverse effect on 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), 3Ni:Al (15 ppm) and the Zirconia top coat (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 pp) and Silica (CTE=5 ppm) and the gradient of the CTE gets disrupted sharply across the 5 microns wide interfacial oxide. At the end, delamination if any, is limited to 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 957-961. 2. A.M. Varaprasad and P.T. Rajagopalan, Proc. Mat. Res. Soc. of India, AGM-7, Feb. 1996. 3. A.M. Varaprasad, Amitab Chakrabarty, Sanjay and P.T. Rajagopalan, Proc. Thermal Analysis Symposium, Dec. 1995, pp 200-202. 4. A.M. Varaprasad and P.S. Venkataramani, Proc. Ninth National Congress on Corrosion Control, Sept. 1999, pp 236-240.

SESSION M7: PLENARY IV
Chair: Sanjay Sampath
Wednesday Afternoon, November 29, 2000
Room 209 (Hynes)

1:30 PM *M7.1
FAILURE MECHANISMS OF THERMAL BARRIER COATINGS. L. Singheiser, R. Herzog, W.J. Quadakkers, R. Steinbrech, D. Clemens, R. Vaen Research Centre Julich, Institute for Materials in Energy Systems 2, Julich, GERMANY.

Using thermal barrier coatings (TBCs), gas inlet temperatures of aero engines as well as industrial gas turbines can be significantly increased, provided, TBCs can be used as integrated part of blading design. In the first part, 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 dependent on the porosity as well as on the resulting 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. A key issue for TBC performance is the bond coat oxidation resistance. The chemical composition of the bond coating will influence the growth rate of alumina scales between the ceramic TBC and the bond coat but also the microstructure and phase transformation at elevated temperatures. Especially above 900°C dissolution of gamma prime phases will result in abnormal high thermal expansion coefficients, which will introduce additional stresses in thermally grown oxide scales (TGO). By controlled alloying additions, the gamma prime solvus temperature can be shifted to higher temperatures. It is also possible to reduce or suppress gamma prime precipitation by further alloying additions. In both cases significant improvement of oxide scale adherence can be obtained. Low cyle fatique (LCF) and thermomechanical fatique (TMF) affect significantly TBC life. Examples will be presented to desribe the failure modes of TBCs under LCF- and TMF- conditions. The current state of the art of life prediction methodologies will be discussed in detail.

SESSION M8: CHARACTERIZATION AND NDE

Chair: Sanjay Sampath
Wednesday Afternoon, November 29, 2000
Room 209 (Hynes)

2:15 PM *M8.1

ON THE THERMAL CONDUCTIVITY OF ZIRCONIA-BASED MATERIALS. Berangere Leclercq, Remy Mevrel, Martine Poulain, Odile Lavigne, ONERA, Materials and Process Dept, Chatillon, FRANCE.

Thermal barrier coatings are increasingly used and their efficiency relies upon a low thermal conductivity ceramic layer, consisting, most generally, of a zirconia-based material deposited by plasma spraying or by EBPVD for the most demanding applications. The thermal conductivity of the ceramic layer is a function of the thermal conductivity of the bulk material and of the distribution of the 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 tetravalent zirconium ions with yttrium ions, for stabilising 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 involving 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-zirconia system as a function of temperature, with a satisfactory agreement, in particular for the partially stabilised material. This approach is then extended to zirconia materials containing other stabilisers than yttrium to evaluate the effect of trivalent, tetravalent and pentavalent ions on the thermal conductivity of bulk materials. 1. S. Raghavan, H. Wang, R.B. Dinwidie, W.D. Porter, M.J. Mayo, Scripta Mat. 39(8) 1119 (1998). 2. J.-F. Bisson, D. Fournier, M. Poulain, O. Lavigne, R. Mevrel, accepted for publication in Journal of the American Ceramic Society (2000)

2:45 PM M8.2

ON THE GRAIN-SIZE AND TEMPERATURE DEPENDENCE OF THE THERMAL CONDUCTIVITY OF NANOCRYSTALLINE YTTRIA-STABILIZED ZIRCONIA. H.-S. Yang, J.A. Eastman, G. Soyez[a], S.K. Streiffer, L.J. Thompson, G.-R. Bai, C.K. Henry, and C.W. Letourneau, Argonne National Laboratory, Materials Science Division, Argonne, IL; [a]Present affiliation: Carl Zeiss, Oberkochen, GERMANY.

The thermal conductivity of nanocrystalline yttria-stabilized zirconia (YSZ) coatings grown by metal-organic chemical vapor deposition (MOCVD) has been investigated for grain sizes of 10 to 100nm at temperatures of 80-700K. 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 sizes measured. As-grown samples were found to exhibit >90% of bulk density and the amount of porosity did not vary significantly with grain size. Hence, the observed changes in thermal conductivity are believed to be attributable to the effects of grain size rather than porosity. Measurements of the temperature dependence of the thermal conductivity from 80-700K 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 to 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 *M8.3

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

Thermal barrier coatings (TBCs) will impart protection to heat engine components against failure under excessive heat loads, to increase inlet temperatures with consequent improvements in efficiency, and to reduce requirements for cooling. 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 conductivity 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 (intersplat pores, cracks and globular pores). The void/crack system is quantitatively resolvable by SANS experiments demonstrating that interlamellar 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 interlamellar pores. Work was supported by NSF through its MRSEC program: DMR 9632570.

4:00 PM M8.4

PHASE IDENTIFICATION IN HEATED THERMAL BARRIER COATINGS USING MICROBEAM X-RAY DIFFRACTION COMBINED WITH ELEMENTAL X-RAY MAPPING.

Jennifer R. Verkouteren, Ryna B. Marinenko, David S. Bright, NIST, Chemical Science and Technology Laboratory, Gaithersburg, MD.

Compositionally distinct micrometer-sized areas in plasma-sprayed TBCs were identified from elemental X-ray maps and characterized for phase content by using laboratory-based microbeam X-ray diffraction. The elemental maps indicated that a phase containing very low concentrations of yttria (< 0.03 mol fraction $YO_{1.5}$) formed during heating of a homogeneous 0.08 mass faction Y_2O_3 (0.87 mol fraction $YO_{1.5}$) 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 phase content was determined by using a 10 μm X-ray beam and both a position-sensitive detector and a phosphor imaging plate. The phase was determined 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 M8.5

X-RAY MICROTOMOGRAPHY - ROUTINE TOOL FOR MICROSTRUCTURAL CHARACTERIZATION OF THE COMPLEX ANISOTROPIC STRUCTURES OF THERMALLY SPRAYED DEPOSITS. Jan Ilavsky, University of Maryland at College Park, College Park, MD and National Institute of Standards and Technology, Gaithersburg, MD; Francesco De Carlo, Derrick C. Mancini, Experimental Facilities Division, Advanced Photon Source, Argonne National Laboratory, Argonne, IL; Anand Kulkarni, Herbert Herman, Center for Thermal Spray Research, SUNY at Stony Brook, Stony Brook, NY.

Thermal spray deposits represent an example of complex microstructures which are challenging to characterize with high reliability. Their microstructure contains metastable phases and at least three anisotropic systems of voids of wide range of shapes and sizes. The deposits are often fragile (especially in case of ceramics) so that metallographic cross sections are neither representative nor reproducible. Therefore other characterization techniques, for example, small-angle scattering, which is independent of grinding/ polishing preparation, have been applied in recent years. However, direct visualization by microscopy techniques of the voids within cross sections is still a standard tool. Routine use of x-ray microtomography would bring to this field a microstructural characterization technique with a similar view of the microstructure, but independent of sample preparation. A characterization technique must be appropriate for the task and accessible to allow for its routine use. Recent developments in x-ray microtomography - namely reduction of resolution limit and an increase of throughput, now open this field to wide use. One of the major problems to be solved when dealing with high-throughput tomography is the complexity of the data analysis. This involves the data preprocessing, the sinogram generation and the 3D reconstruction. At the Advanced Photon Source, a system is under development to address this issue and to allow high-throughput users to get prompt data analysis and 3D reconstruction. We present a review of microstructure characteristics obtained for a plasma sprayed alumina by currently available techniques ranging from optical microscopy and intrusion porosimetry to small angle scattering and x-ray micro-tomography. The results are compared. The current status, future development and accessibility 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 MRSEC award DMR-9632570.

4:30 PM M8.6
QUALITY ASSURANCE EVALUATION OF THERMAL BARRIER COATINGS BY ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY. Jianqi Zhang, Danyash Tamboli, Vimal Desai, Univ of Central Florida, Advanced Materials Processing & Analysis Center, and Dept of Mechanical, Materials and Aerospace Engineering, Orlando, FL.

Advanced turbine system engines are slated to operate at turbine inlet temperatures of nearly 2750°F so as to achieve 60% and higher overall efficiency. No currently used superalloys can withstand such high temperatures so that 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 aero-engine applications because there are significant differences regarding the size/time/ environment/stress duty cycles between these two systems. Land based gas turbine systems are expected to give inspection free 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 are either time consuming or labor intensive. Accordingly, development of non-destructive evaluation (NDE) techniques capable of determining the coating quality economically and easily becomes paramountly important. The impetus of this research was to develop electrochemical impedance spectroscopy (EIS) as a NDE technique of TBC for industrial turbines. In this study, EIS technique was used to examine the behavior of intact TBC at ambient temperature. Cross-sectional morphological examination of TBC was conducted by scanning electron microscope (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 elemental parameters in the circuit and the microstructural characteristics of TBC. A linear relationship was found to exist between the electrical impedance 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 impedance 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, Junfa 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 350°C, were analysed according to the equivalent circuit model of the oxidised TBCs. TBCs after oxidation at 1100°C consist of yttria stablised zirconia as a top coat, oxide layers from the oxidation and a MCrAlY 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 between the top coat and 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 the top coat. 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: Nitin P. Padture
Wednesday Evening, November 29, 2000
8:00 PM
Exhibition Hall D (Hynes)

M9.1
SEPARATING INTERFACE FROM BULK EFFECTS IN THERMAL TRANSPORT PROPERTIES OF THIN FILMS: Al/Ti MULTILAYERS AND Cu THIN FILMS. Daniel Josell, Eduardo J. Gonzalez, John E. Bonevich and Grady S. White, National Institute of Standards and Technology, Gaithersburg, MD.

Multilayer materials are sometimes considered as thermal barrier coatings because such compositional variation enhances some apsect of oxidation resistance or mechanical strength. An additional motiviation is the possibility of reducing the thermal conductivity below the values of the bulk constituents through scattering of phonons at the interfaces (i.e., a nonzero interface themal resistance). The thermal resistance associated with interfaces between layers becomes more significant as the layers become thinner, increasing the density of interfaces. However, the properties of the material within the layers can also vary systematically with layer thickness. Accurate modeling of heat flow in multilayer or thin film thermal barrier coatings requires at least empirical understanding of these individual effects. We have, therefore, measured the thermal diffusivity (thermal conductivity divided by specific heat per unit volume) of Al/Ti multilayer thin films prepared by electron beam evaporation. All tested films were 3.1 μm thick with each specimen possessing a particular bilayer thickness (5nm or more). The themal diffusivity was measured both perpendicular and parallel to the plane of the layers using the Mirage (Photothermal Deflection) Technique. Noninterfacial effects (e.g., systematic variation of microstructure with layer thickness) were determined from the in-plane thermal diffusivities. The interfacial thermal resistance was determined from the dependence of the perpendicualr thermal diffusivity on bilayer thickness, suitably corrected for the noninterfacial effects. Uncorrected for, these nonintrerfacial effects lead to an overly large value of the interface 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 BY ELECTROCHEMCIAL IMPEDANCE SPECTROSCOPY. Jianqi Zhang, Vimal Desai, Univ of Central Florida, Advanced Materials Processing & Analysis Center, and Dept of Mech., Mat'ls 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 period 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 TBC was investigated by 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. Through the correlation of SEM and optical microscopic examination 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 variant post-exposed TBC such as isothermal oxidation, cyclic oxidation and hot corrosion. In addition, the type and length of high temperature exposure were qualitatively discernible from the EIS data. For a quantitative evaluation, a model of EIS ac equivalent circuit is proposed to relate the EIS elemental parameters to the physical morphology of the exposed TBC. Functional relationships have been established between the exposed TBC morphological properties (such as porosity and pore shape) and the EIS parameters. From the results, it will be shown that EIS can be used to characterize and monitor the microstructure of post-exposed TBC and qualitative and quantitative evaluation of TBC damage and lifetime prediction by EIS is feasible.

M9.3
HIGH TEMPERATURE MICROSAMPLE TENSILE TESTING OF DIFFUSION ALUMINIDE BOND COAT LAYERS. Deng Pan, The Johns Hopkins University, Dept of Mechanical Engineering, Baltimore, MD; P.K. Wright, GE-Aircraft Engines, Materials and Process Engineering Department, Cincinnati, OH; K.J. Hemker, 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 are known to play an important role in determining TBC life, but the use of standard tensile testing techniques for characterizing diffusion aluminide bond coats has been greatly inhibited by their limited thickness (<60 μm). A high temperature microsample tensile testing technique has been developed and successfully employed to characterize PtAl/NiAl bond coats in the temperature range from 650°C to 1150°C. The Young's modulus, coefficient of thermal expansion, yield strength and stress relaxation behavior have all been measured as a function of the 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 systems. In thermal 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 four principal 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 strain in the TGO, and (4) existing morphological features. The bias strain derives from 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 (alpha-alumina), 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
MICROMECHANICS 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 buckling and spalling. The influence of interface 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 analysis of displacements experienced by undulating thin films upon thermal cycling has shown that, in some circumstances, ratcheting occurs. The undulation amplitude increases with each thermal cycle, which induce 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 analysis on stresses near imperfections that develop because of the thermally grown oxide (TGO) growth strains in combination with thermal expansion misfit. The results are used to identify a critical TGO thickness at failure and express it in terms of the governing materials variables.

M9.6
MORPHOLOGY, MELTING AND SOLIDIFICATION OF PLASMA SPRAYED ALUMINA PARTICLES. Susumu Uematsu, Gang Li, Chiori Takahashi, Tetsuya Senda, Ship Research Inst, Materials and Processing Div, Tokyo, JAPAN.

This investigation describes the melting and solidification processes of injected particles during plasma spraying. The fused and crushed (FC) Al_2O_3 particles were sprayed in ambient condition after sieved as the range of -63 38, -38 20, -20 10 μm. The collection of free flying particles in plasma spraying has been performed to evaluate the degree of particle melting using particle collectors (adhesive paste and carbon adhesive tape), and subjected to scanning electron microscopy (SEM). The observation reveals that the fusion mechanism of large and thick ceramic particles is different from that of smaller ceramic or metal particles. Even in large size starting powders, most particles collected on the tape were spherical ones under 5 μm in size at short distance and around 10 μm at long distance. The particles collected on the adhesive paste observed the spherical as large as 40 μm in size. For the partially melted particles, the trace of liquid parts appeared on surface, especially at edge area. Furthermore, spherical particles of 1 E2 μm in size were observed in the shrink of melted parts, attached on the surface of the solid parts. These surfaces have been experienced with a various features of crystal growth according to pass through the different melting and solidification paths. The fact mentioned above, the progressive melting and solidification processes were discussed.

M9.7
MICROSTRUCTURAL CHARACTERIZATION OF YTTRIA-DOPED ZIRCONIA COATINGS WITH ELECTRON MICROPROBE WAVELENGTH DISPERSIVE COMPOSITIONAL MAPPING. Ryna B. Marinenko, Jennifer Verkouteren and David S. Bright, NIST, Surface and Microanalysis Science Division, Chemical Science and Technology Laboratory, Gaithersburg, MD.

Compositional mapping with the electron microprobe is an excellent analytical technique for studying the microstructure of cross sections of thermal barrier coatings. With a focused electron beam of about one micrometer, digital elemental x-ray maps of 50 μm by 50 μm regions of the coating can readily show whether multiple phases are present. In the work described here polished cross-sections of yttria-doped zirconia thermal-sprayed coatings prepared from different stock powder sources and prepared under different spray and annealing conditions were analyzed with the intention of identifying the phases present and possibly correlating results with other physical measurements such as x-ray diffraction. The presence of the cubic and tetragonal crystal phases of the yttria-doped zirconia (Y = 6-7% mass fraction) are preferred to the monoclinic phase (less than 3% mass fraction of Y) for a more protective coating due to the more favorable thermal expansion coefficient of the first two phases. Using four fixed wavelength spectrometers and digital beam control, 64 pixel x 64 pixel x-ray maps were recorded simultaneously for each of the elements Y, Zr, Hf (a trace element in the coating) and O. Data was acquired for 2s at each pixel. Quantitation of the element data at each pixel was done using pure element standards and a ZAF matrix correction procedure. Several maps were taken and quantified from specimens prepared from two different commercial feedstock materials. The distribution of the elements and the inferred percentage of each crystal phase in each specimen appears to be dependent on the feedstock and the annealing conditions. Details of the results observed in the x-ray maps will be discussed.

M9.8
GROWTH OF LOW THERMAL CONDUCTIVITY THERMAL BARRIER COATINGS VIA ELECTRON BEAM-DIRECTED VAPOR DEPOSITION. D.D. Hass, H.N.G. Wadley, Univ of Virginia, Materials Science and Engineering Dept, Charlottesville, VA.

Low thermal conductivity yttria stabilized zirconia (YSZ) coatings have been grown using a low vacuum (0.20 Torr) electron beam directed vapor deposition process. In this approach, a transsonic helium jet was used to entrain and transport an electron beam evaporated YSZ flux towards a substrate. This resulted in the growth of highly porous, columnar microstructures without substrate rotation because the interaction of the helium jet with the coating surface resulted in many of the evaporated species making oblique angles of contact with the substrate. By altering the properties of the gas jet and the evaporation rate the column width and intercolumnar spacing in these structures could be controlled. Coatings grown with the jet axis normal to the substrate had thermal conductivities comparable to YSZ layers applied using conventional electron beam evaporation processes (1.4 to 1.9 W/mK). By alternating the substrates inclination to the jet as growth progressed, coatings containing zig-zag shaped columns and pores were created. These YSZ coatings had thermal conductivities as low as 0.7 W/mK.

M9.9
THERMAL BARRIER COATING CHARACTERIZATION USING SPATIALLY PERIODIC MAGNETIC AND ELECTRIC FIELD SENSORS WITH PRE-COMPUTED DATABASES OF SENSOR RESPONSES FOR REAL-TIME THICKNESS AND POROSITY

ESTIMATION. Neil J. Goldfine, Yanko Sheiretov, Andrew Washabaugh, Darrell Schlicker, Vladimir Zilberstein, JENTEK Sensors, Inc., Watertown, MA.

New inspection methods use spatially periodic field eddy current sensors, called Meandering Winding Magnetometers (MWMs) and novel periodic and non-periodic field dielectrometers 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 databases of 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 and flat test specimens are presented. The databases used in this technique can be visualized as measurement “grid lattices” that permit estimation of three unknown properties (e.g., ceramic top-coat 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 JENTEK Sensors, Inc.

M9.10

CHARACTERIZATION OF THERMALLY-SPRAYED DICALCIUM SILICATE BY ULTRASMALL-ANGLE X-RAY SCATTERING. Jan Ilavsky, 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; Pete R. Jemian University of Illinois, Argonne National Laboratory, Argonne, IL.

Dicalcium silicate feedstock has been atmospheric-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 this thin cannot be characterized by the small angle neutron scattering methods that have proven so successful for thicker deposits. However, anisotropic ultrasmall-angle X-ray scattering (USAXS) studies have enabled some of the anisotropic 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 anisotropic Porod surface area distribution, and also the anisotropy in the multiple scattering that is associated with the orientation and size distributions of the intrasplat cracks and interlamellar pores. USAXS imaging has been used to visualize the dominant microstructural features in the deposits. The microstructure has been imaged for varying orientations of the Q vector with respect to the spray direction, thus 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 anisotropic deposit properties.

M9.11

TRANSMISSION ELECTRON MICROSCOPY INVESTIGATION INTO THE OXIDATIVE FAILURE MODE OF 6-8 WT.% Y_2O_3-STABILIZED ZrO_2/Ni-Cr-Al-Y THERMAL BARRIER COATINGS. Tabbetha A. Dobbins, Altaf H. Carim, The Pennsylvania State University, Dept. of Materials Science and Engineering, University Park, PA; Lucille A. Giannuzzi, The University of Central Florida, Dept. of Mechanical, Materials and Aerospace Engineering, Orlando, FL; Merrilea J. Mayo, The Pennsylvania State University, Dept. of Materials Science and Engineering, University Park, PA.

Field-emission transmission electron microscopy (TEM) was used to investigate the interfacial chemistry of thermally cycled air plasma sprayed Y_2O_3-stabilized ZrO_2 (YSZ)/Ni-Cr-Al-Y 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-7 wt.%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 additional oxide phases, beyond the protective alumina scale, after prolonged thermal cycling. These discontinuous oxide phases were comprised primarily of $Ni(Cr,Al)_2O_4$ and $(Cr,Al)_2O_3$ with minor amounts of yttrium containing oxides. Oxides other than protective alumina are believed to form upon aluminum depletion in the vicinity of the oxidizing interface. Large particles ($>1\mu$) 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 cooling 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 NICOCRALY-BASED THERMAL BARRIER SYSTEMS. Daniel R. Mumm, Caroline Lau, 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 substrate, and a thin thermally grown oxide (TGO) 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 effect the durability of the TBC coatings, the effect largely attributed to gettering of segregating species (such as sulfur) that degrade interface adhesion. There has also been a 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 present at 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 are used to characterize the evolution of interfacial morphology, elucidate the mechanisms by which it develops, and evaluate its effects on thermal barrier coating durability.

M9.13

CHANGES IN LATTICE STRUCTURE AND MICROHARDNESS DURING THERMAL TREATMENT OF A NiCoCrAlY ALLOY. Thomas Rehfeldt, Hahn-Meitner-Institut Berlin, Berlin, GERMANY; Gerhard Schumacher and Hellmuth Klingelhoeffer, Bundesanstalt fuer Materialforschung und - pruefung, 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 (Ni_3Al type structure) and a chromium rich phase [1]. The gamma prime phase was shown to transform into the disordered fcc 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 produced 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 alloy confirmed that the alloy has L12 lattice structure. The single phase alloy revealed an order-disorder transformation in the same temperature range as the gamma prime phase in the bond coat alloy. The crtitical temperature of the phase transformation is small compared to that of Ni_3Al 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.

1. T. Rehfeldt, G. Schumacher, R. Vaβen and R.P. Wahi, Scripta Mater., in press.

M9.14

HARDNESS AND ELASTIC PROPERTIES OF ZIRCONIA-BASED EBPVD THERMAL BARRIER COATINGS FROM ROOM TEMPERATURE TO 1473K. Brian D. Kernan, Anqiang 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 1473K of a Zirconia - 7wt % Ytrria thermal barrier coating made by EBPVD. Samples were studied in the as-deposited condition, as well as subsequent to a 4 hour anneal in air at 1477K. 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 coarsened the intracolumnar 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], A.H. Swanson, Iowa State University, Ames Laboratory, Ames, IA;. [a]Office of Naval Research International Field Office Asia, Tokyo, JAPAN; S. Sakurai, Hitachi Ltd., Mechanical Engineering Research Laboratoy, 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 protruded 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 protruded TBC. It has been shown that the onset of TBC cracks near or away from the interface in the protruded TBC tests is controlled by a transverse 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 near-interface TBC cracking than thinner substrate specimens. Conversely, TBC cracking away from the TBC/TGO interface became 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 stresses distributed in the near-interface and midst TBC, respectively, which are affected by the amount of machining the substrate side.
This work was carried out as Work for Other program approved by the USDOE, Office of Basic Energy Sciences, Division of Materials Sciences.

SESSION M10: PLENARY V
Chair: David J. Wortman
Thursday Morning, November 30, 2000
Room 209 (Hynes)

8:30 AM *M10.1
R&D STATUS AND NEEDS FOR IMPROVED EB-PVD THERMAL BARRIER COATING PERFORMANCE. Christoph Leyens, Uwe Schulz, Klaus Fritscher, Manfred Peters, Wolfgang A. Kaysser, 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 the ceramic top coating, TBCs predominantly exert their beneficial effect by reducing the average metal temperature and mitigating the effect of hot spots. However, the increasing demands placed on the high-temperature capabilities of future turbine components require 'designed-in' TBC solutions, i.e. the TBC system is 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-reliant' coatings are necessary which performance has to go beyond that of 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 changes during service. 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 depostion (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 sinter resistance, phase stability and lower thermal conductivity are major areas of interest. Since 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 Morning, November 30, 2000
Room 209 (Hynes)

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

Current issues in understanding the microstructure evolution of vapor-grown thermal barrier coatings will be reviewed. 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 roles 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 substrate rotation on the evolution of morphology vis--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 sponsored by ONR under Grant N00014-99-1-0471.)

9:45 AM M11.2
NOVEL PROCESSES FOR SYNTHESIZING THERMAL BARRIER COATING SYSTEMS. J.F. Groves, D.D. Hass, 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 occurs in high vacuum at 10^{-6} - 10^{-4} mbar. In contrast, DVD uses lower vacuum e-beam technology (10^{-4} - 10 mbar) and a flowing carrier gas to create and transport a focussed 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 atom transport to be observed visually. 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 suited to 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 vary deposit microstructure. Coupling plasma activation, a focussed vapor stream, and low vacuum e-beam evaporation has generated a deposition technology of wide applicability. With this technology it appears possible to synthesize bond coats, oxide layers, and top coats with useful microstructures and compositions using a single tool. Thus, novel material systems can be developed to overcome current TBC system limitations, moving the field closer to discovery of a prime reliant coating system.

10:00 AM M11.3
MORPHOLOGY OF YTTRIA STABILIZED ZIRCONIA LAYERS DEPOSITED USING ELECTRON BEAM-DIRECTED VAPOR DEPOSITION. D.D. Hass, J.F. Groves, H.N.G. Wadley, Univ 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 1.0 Torr) electron beam directed vapor deposition process. This processing approach employs a transsonic 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 over a range of deposition conditions. The resulting morphologies included highly porous (up to 50%) columnar grained 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 without columnar pores. The coating morphology was found to be effected by several parameters including the substrate temperature, evaporation/deposition 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 adatom energy and adatom 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 play in the development of coating morphologies desirable for use as thermal barrier coating 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. Zaher Mutasim, 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 processing 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 states 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. Splats 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 MRSEC program: DMR 96-32570.

11:30 AM M11.6
DURABLE THERMAL BARRIER COATINGS WITH NOVEL MICROSTRUCTURES DEPOSITED BY SOLUTION PRECURSOR PLASMA SPRAYING. T. Bhatia[1], B. Cetegen[1], M. Gell[1], E.H. Jordan[1], A. Ozturk[1], N.P Padture[1], K.W Schlichting[1], P.R. Strutt[2], and D. Xiao[2]. [1]Institute of Materials Science, University of Connecticut, Storrs, CT; [2]Inframat 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 splats/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 plasma and are being characterized using scanning electron microscopy and transmission electron microscopy. Second, the build-up of oxide coating on the metal substrate in the plasma is being studied as a function of time. These studies have contributed to our understanding of solution-precursor plasma-sprayed nano-crystalline YSZ TBCs. These studies also reveal the mechanism by which individual particles from precursor droplets form an adherent coating, and explain the phase and microstructural evolution in the coatings.

11:45 AM M11.7
Y_2O_3-STABILIZED ZrO_2 PARTICLE MELTING BEHAVIOR DURING HIGH VELOCITY OXY-FUEL THERMAL SPRAY DEPOSITION. Tabbetha A. Dobbins, Merrilea J. Mayo, The Pennsylvania State University, Dept. of Materials Science and Engineering, University Park, PA; Richard Knight, Drexel University, Dept. of Materials Engineering, Philadelphia, PA.

High velocity oxy-fuel (HVOF) thermal spray was used to deposit yttria-stabilized zirconia (YSZ) for thermal barrier coating applications. High velocity oxy-fuel (HVOF) deposited yttria -stabilized zirconia thermal barrier coatings were obtained, using hydrogen fuel gas, within a limited range of spray conditions. The affect of oxygen-to-fuel ratio, spray distance, and nozzle length on heat and momentum transfer were explored. These spray parameters were found to have a pronounced affect on particle melting behavior and hence, coating quality. The experimental results in the present work contradict many theoretical models, which predict that it should not be possible to manufacture viable YSZ coatings by HVOF.