Workshop Summary

Environmental Barrier Coatings for Microturbine and Industrial Gas Turbine Ceramics

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Introduction

Advanced structural ceramics are an enabling technology for significantly improving performance and reducing emissions of gas turbines for power and combined heat and power generation. However, achievement of the benefits of ceramics is hindered by in-service environmental degradation that results in recession of the ceramic material. In 2002, the DOE and Oak Ridge National Laboratory sponsored the first workshop addressing the need for environmental coatings (EBCs) for advanced silicon based ceramics for gas turbine applications. The workshop provided a forum for turbine and material developers and manufacturers to access the most recent innovations and test results on silicon nitride and environmental barrier coatings (EBC) development, mechanical reliability, and environmental stability. The nature of the problem, the requirements for protection, and a variety of approaches to providing the needed protection were presented. A detailed summary of the presentations of that workshop is available at https://www.ms.ornl.gov/DER/default.html

In 2003, DOE's Office of Distributed Energy and ORNL sponsored a second workshop to continue the information exchange regarding EBCs. This summary documents the 2003 workshop presentations.

Nature of the Problem:

Silicon nitride and silicon carbide ceramics rely on the formation of a self-replenishing surface layer of SiO_2 to resist oxidation at elevated temperatures. However, under the severe gas turbine conditions of pressure, temperature and velocity, water vapor reacts with the SiO_2 to form gaseous silicon hydroxide species that are swept away. The resulting and continuous loss of the SiO_2 layer allows oxidation of the substrate resulting in surface recession. The associated dimensional changes result in a loss of functional efficiency of the components. Significant recession was measured on silicon nitride turbine nozzles after only 1818 hours of engine testing. The predicted maximum recession on the leading edge of a vane after 25,000 hours is 3mm (0.127").

Requirements for Protection

Requirements for a protective EBC were defined in detail in last year's summary. However, several presentations this year provided updated or additional information regarding the needs previously identified.

John Holowczak, United Technologies Research Center, provided an overview of the benefits of ceramics for gas turbine engines for both power generation, aerospace, and military applications, indicating that the market for engine products incorporating ceramic turbine components is substantial. Even though the duty cycles for APUs, unmanned air vehicles, (UAVs) and microturbines, vary significantly, EBCs will be required for all static structures and some turbine rotor components. Blade tip and shroud regions present a unique requirement for EBCs due to the occurrence of rotor blade tip rubs. **Bjoern Schenk** of **Honeywell** added that during in-flight testing of ceramic nozzles in an APU application, the ceramic components experienced **hot corrosion**, apparently from corrosive constituents of ingested dust. The corrosive constituents could include CMAS or other elements not specifically determined. These field test results indicate that both hot corrosion and water vapor recession resistance are needed for hot gas path ceramic gas turbine components. One encouraging result is that dense zirconia coatings on metal components have shown resistance to the hot corrosion problem.

Irene Spitsberg, GE-AE, discussed the EBC needs for ceramic matrix composite (CMC) combustor, vane, and shroud components. The baseline Barium-Strontium-Aluminum-Silicate (BSAS) is limited to 300 hours at 2500°F and less than 50 hours at 2700°F. The 3-layer BSAS system plus a TBC is being considered. Considerations include the through-thickness delta T, CTE gradient, foreign object damage, and particle deposition and corrosion. Trade-offs are required because thicker coatings reduce the stresses in CMCs, but also increase the surface temperature of the coating. Sinter resistant TBC are needed for the higher temperatures.

Approaches and Results

In-situ or self generating approaches

Jim Smialek, NASA, explored the development of self healing scales in SiC by the incorporation of TiO_2 and/or Al_2O_3 formers. Self healing scales are preferred that grow faster than the SiO_2 under it. TiO_2 and Al_2O_3 grow at a rate 5 and 2 orders of magnitude faster than SiO_2, respectively. Thus, TiC, Ti_xSi_y, or TiAl particles in SiC should act as reservoirs for self healing scale formation. To evaluate this, TiC was incorporated in hot pressed SiC then furnace and burner rig exposed. Oxidized samples of 25 and 50% TiC-SiC composites formed regenerative TiO_2 scales, but oxidation rates were excessive due to porosity in the hot pressed material. Faceted continuous TiO_2 formed at the surface on a TiO_2+SiO_2 subscale with intact $SiC+TiO_2$ below that. Surface etch pitting found in the 2400°F burner rig test are consistent with volatility attack. Bulk $TiSi_2$ material was also furnace exposed. Initial furnace exposures from 1000 to 1300°C

showed oxidation weight gains well below the goal. Additional work is planned. **Bjoern Schenk** offered that Ti would form volatile hydroxides at the desired use temperatures.

[Reaction and Diffusion treatments](#)

Mike Brady, ORNL, is evaluating the feasibility of self-grading metallic precursor coatings as either EBCs or bond coatings on Si-based ceramics. Thin metal alumina forming alloy coatings are oxidized and reacted. The coating could act as an oxygen and H_2O barrier bond coating or just a water vapor barrier. To act as a bond coating, an Al-rich reservoir would remain to heal and maintain the anticipated alumina layer. To provide a water vapor barrier, all of the metal would be converted to an oxide.

Exploratory H_2O barrier precursors included sputter coated NiAl+Hf, NiCrAlY, $Cr_2Al(Y)$, FeCrAlY, and TiCrAl. Coated SN282 samples were oxidized at 1000-12000°C for 1 to 1000 hours. The typical oxidized and reacted coatings consisted of a duplex alumina outer layer and an Al-Me-Si-O layer on the Si_3N_4 or SiC. However, all but the NiAl and TiCrAl coatings spalled due to thermal expansion mismatch. The TiCrAl and NiAl coatings that adhered are not effective oxygen or water vapor barriers.

The alloy bond coating concept was evaluated using a sputtered TiCrAl layer followed by a low pressure plasma sprayed coating of the same composition on SN282. The sample was cyclically oxidized.

Challenges with alloy bond coatings include the potential formation of low melting silicides, Al may react with the substrate, CTE mismatch, and alumina growth rates are too fast at the temperatures of interest. TiCrAl family of bond coats may solve some compatibility issues:

- Ti-51Al-12Cr atomic % system develops gamma titanium aluminides
- Ti-Si eutectic melts above > ~1300°C
- The high affinity of Ti for N results in Ti migration toward the Si_3N_4 surface enriching the outer surface with Al. This self grading will provide Al_2O_3 at the surface and prevent Al loss/reaction to substrate
- Thin TiCrAl precursor coatings showed good compatibility and adherence to Si_3N_4 and SiC in exploratory experiments

However, Al_2O_3 growth, and phase transformation may limit the use temperature of the bond coating to 1100C, with the possibility of alloying to stabilize the phases. TBCs may be needed for higher temperature applications. Although crack blunting/healing may have occurred, further testing is needed to validate the proof of principle

Steve Nunn, ORNL continued discussion of a proposed a pack cementation/conversion approach to low cost tailored bond coatings or as stand-alone protective layers.   Pack cementation trials have been performed in an alumina powder bed with different substrate compositions (AS800, NT154, SN281), reactive powders ($AlCl_3$, $Sr(NO_3)_2$, $YrCl_4$, and $ZrCl_4$), and atmospheres (air, argon, nitrogen) at 1200°C and 1400°C.

Graded surface reactions have resulted in a large number of conversion chemistries. Composition and microstructural results vary with each processing variable. The results continue to show promise for this process for the formation of potential bond coatings or protective surfaces. Reactants migrated into the grain boundaries ~200 µm deep even though the "coating" may only be 20 microns thick. Some strength losses were demonstrated. Additional studies will focus on producing promising coating compounds such as $SrAl_2O_4$, $SrAl_2Si_2O_8$ and $Yb_2Si_2O_7$, and on exposure testing.

Paul Becher, **ORNL** summarized new approaches to tailoring the microstructure and mechanical properties of silicon nitride to achieve 1) a bimodal grain size with large acicular grains through -Si_3N_4 seeding, 2) a controlled size and aspect ratio of the acicular grains through selection of rare earth sintering additives, and 3) a reduced interface strength between the acicular grains and the intergranular film (IGF), also through selection of rare earth sintering additives. This tailoring can provide improved toughness. The differential binding energy – the measure of the preference of a RE for bonding with oxygen versus nitrogen relative to Si bonding with either oxygen or nitrogen - explains the diverse aspect ratios and IGF bond strengths obtained with different RE additions. When a RE-O bond is weaker than Si-O in glass, the RE concentrates at or near the Si_3N_4 surface. This impedes the attachment of Si and, thus slows the diametrical growth of the grain, which results in a higher aspect ratio. When a RE-O bond is stronger than Si-O in glass, the RE favors the SiO_2 rich triple point junctions, and, thus, RE migration to Si_3N_4 prism faces is weak. This allows faster diametrical growth of the grain, which results in a low aspect ratio. Even though the RE-bond strength for La and Lu are high, the La segregates more to the - Si_3N_4 prism planes, resulting in higher aspect ratio grains, a weaker IGF bond, and thus, increased toughness.

Further, **Becher** suggests that the surfaces of Si_3N_4 can be tailored for a higher thermal expansion to better match candidate EBC coatings. By incorporating RE silicates or SiREMe Oxynitrides, for example, which have a higher thermal expansion than Si_3N_4, the surface thermal expansion could be increased. As-sinter forged Si_3N_4 with 8 weight percent Lu_2O_3 and 2 weight percent SiO_2 produced a 200 µm surface layer rich in two lutetium silicate phases. A micro-FEA analysis of a reconstructed Si/Mullite/BSAS coating on Si_3N_4 with and without a 200 mm tailored layer at the Si_3N_4 interface resulted in a coating stress reduction from ~240 MPa to ~95 MPa

Ara Vartabedian of **St. Gobain** Ceramics and Plastics reported on an approach to incorporate protective surface layers on components by applying a coating prior to HIP processing. Preliminary results using an Y_2SiO_5 dip coating indicated that a 5 mil coating was too thick and that the coating no longer existed after the Hip process.

[Traditional ceramic powder based surface coating approaches](#)

Bjoern Schenk reported (printed copy not available) 2400 and 2700°F, 12 month and 36 month goals and approaches at **Honeywell**. A 2400°F isothermal system is expected to consist of an oxidation barrier coating (OBC)/environmental barrier coating

(EBC)/ corrosion shield. It is assumed that SiO_2 will always form at the Si_3N_4 surface. However, if the SiO_2 is kept below a critical 7-10 mm thickness, the damaging silica transformation will be prevented.   A 2700°F system will consist of a regenerating cation and oxygen diffusion barrier below the EBC to maintain the SiO_2 layer below the critical thickness and a TBC topcoating. Slurry coating approaches are preferred to avoid line of site limitations. A 12 month goal approach may consist of a slurry coated OBC/slurry coated EBC/plasma sprayed TBC-OBC/plasma sprayed TBC.

Honeywell and IKTS have performed 1450°C, 100 m/s, .27 bar p_{H2O} exposures for ~139 hours a variety of Si_3N_4 materials, alumina, mullite, YSZ, and RE silicates to rank recession performance. YAG appears stable; YSZ is inert, but most other materials recess. Disilicates and mullite form powder like surfaces that wipe off in the gas stream. All silicon nitrides recess at unacceptable rates.

Schenk also reported that **Honeywell** is developing a new gas pressure sintered high strength silicon nitride aimed at 1400°C capability with oxidation and creep properties similar to SN282, but with a Weibull modulus over 20 and a fracture toughness over 7 MPa⋅m$^{1/2}$.   The material is designed to be chemically compatible with Honeywell's developmental EBC (not disclosed).

Kang Lee, NASA, summarized enhanced durability and temperature approaches to the Si/Mullite or mullite+BSAS/BSAS EBC system. The NASA goal is a greater than 1000 hour life with a 1482°C surface temperature of the EBC and a 1316°C temperature at he EBC-CMC interface.   Recession of BSAS is a limiting factor in the current system. NASA is exploring topcoats with water vapor stability to 1482°C.   A water vapor TGA atmospheric pressure, high steam thermal cycling rig operating at p_{H2O} = 0.9 atm and a gas velocity of 2.2 cm/sec is being used to screen RE silicates. Weight change is monitored in real time. Initial results indicate that Y, Sc, Yb, and Er monosilicates have a lower weight loss than BSAS; however, testing must be re-performed because of the pick up of alumina in the rig. Previous researchers reported that monosilicates have better water vapor stability than disilicates, and the silicates have a low thermal conductivity that BSAS.   A mullite-Y_2SiO_5 couple exposure to 1400°C resulted in a reaction forming Y-Al-Silicate bubbles. Sc silicate on mullite performed better.

Si/Mullite+SAS/Sc-silicate and Si/mullite/Sc-silicate coatings were applied to SiC-SiC and AS800 substrates and exposed to 1380°C for 200 to 300 one hour cycles in NASA's High Steam Thermal Cycling rig. Through thickness cracking was a consistent problem. Cracks into the Si bond coat can allow for rapid oxidation of Si.

Tania Bhatia, UTRC, addressed the needs for EBC systems for Si_3N_4. Efforts have grown from experience with EBCs for SiC. The baseline EBC for SiC has been the Si/BSAS or BSAS + mullite/BSAS system. This EBC system has been successfully engine tested on SiC seal coated SiC CMCs for 15,144 hours max time exposures up to 2200°F. Where the EBC was intact, good protection was provided. A mullite coated BSAS Hexaloy SA coupon survived 100 atmospheric burner rig cycles to a 2700°F surface temperature and a 300°F EBC thermal gradient. SAS is being evaluated as an

improvement for the BSAS layer. The SAS based EBC has been engine tested for 8368 hours.

Application of the baseline EBC to Si_3N_4 was tested on AS800 in an FT8 vane rig exposure to 1260°C and in the ORNL Keiser rig to 1200°C for 2000 hours. Effective protection was provided where the coating remained in-tact, but through-thickness cracks occurred due to the CTE mismatch.

Strength measurements of Si alone and the 3-layer baseline coated substrates resulted in a ~50% strength loss compared to non-coated material. Additionally, a transient thermal stress analysis indicated that the stresses in EBC coated Solar ceramic stationary gas turbine nozzles are increased by from 6 to 48% over non-coated nozzles. The level of stress is strongly dependent on the CTE mismatch and on the extent of residual stress relaxation. Cracks in the coating, which act as strength controlling flaws, were determined to be the cause of the strength loss. Future work is focusing on EBC systems with a better CTE match. Plasma sprayed Y-silicate is being evaluated. Additional work is needed to understand and predict recession mechanisms in complex silicates in the gas turbine environment.

HT Lin, ORNL also reported that AS800, SN282 and SN88 exhibited significant strength loss when coated with the baseline, 3-layer BSAS EBC system. Contributing factors considered included the grit blasting conditions, Si bond coating thickness, Si bond coating surface roughness, and CTE mismatch induced residual stresses. The grit blasting conditions can result in strength loss if it is too aggressive, especially for low fracture toughness materials, but is not the primary cause of the strength losses in the coated material. Similarly, Si bond coating thickness and Si bond coating surface roughness were not found to be primary contributors. The formation of "zipper" cracks at the origin of failures suggested that CTE mismatch is a significant contributor. This suggestion was supported by mirco-FEA analysis of the coated Si_3N_4 that predicts high residual stresses in the Si bond coat and Si/ Si_3N_4 interface.

Jim Guiheen, Honeywell, provided an update on the application and control of Ta_2O_5 and Ta_2O_5-based alloys on AS800. Ta_2O_5 is of interest even though it does not prevent oxygen or water vapor transport, but because of its thermal match with AS800, its corrosion resistance, and microstructural stability. It may be beneficial as a bond coating. Small Particle Plasma Spraying (SPPS) has been optimized to provide dense, adherent coatings 2 to 4 mils thick. Additions of 1.5 to 3% Al_2O_3 or 1.5 to 5% La_2O_3 suppress the catastrophic to transformation at 1400°C. The La_2O_3 also results in an acicular microstructure. Nb_2O_5 additions are also of interest to provide CTE matching. Combinations of these additives can provide CTE and microstructure control as well as phase stabilization. Cyclic testing to 1200 and 1315°C resulted in spalling of pure Ta_2O_5 and Ta_2O_5 + 2, 3, and 5 weight % Al_2O_3, but no spallation of Ta_2O_5 +1.5% Al_2O_3 or Ta_2O_5 + 1.5 or 3 % additions of Al_2O_3 and La_2O_3. Residual stress changes occur as a function of exposure time.

Rishi Raj, Univ of Colo updated his work on the use of polymer-derived ceramic (PDC) Si-C-N based EBC system. The benefits of the PDC route are that it is apparently compatible with oxides, apparently has an ultra low slow diffusion at ultra high temperatures. The proposed EBC will use an oxide topcoat with a graded SiCN/SiCN+oxide nanocomposite interlayer. The oxide topcoat will provide stability with water vapor and have impermeable grain boundaries. Topcoat candidates include transition metal oxides (ZrO_2, HfO_2, Ta_2O_5, TiO_2), base metal oxides (Al_2O_3, MgO, etc), complex oxides (YAG, Perovskites, etc) or silicates (mullite, etc). The graded SiCN-nanoscale oxide dispersion interlayer will provide a CTE gradient for low energy interfaces, and a diffusion and silica formation barrier. The incorporation of SiCN in Al_2O_3 produced nanocomposites with retarded creep and grain growth, and low energy interfaces. The reduced creep is due to the extremely low diffusion of the large mobile molecules (1-2 nm). Further, ZrO_2 nanocomposites exhibit extremely small grains, high strength (2-3 GPa), and are thermally stable.

The SiCN bond coat on Si_3N_4 would provide a low energy covalently bonded interface, and may inhibit the nucleation of silica. A 0.1-0.2 µm thick CVD SiCN film on Si_3N_4 demonstrated low oxygen diffusion and a good bond, preventing the nucleation of SiO_2 at the interface. Basic research is needed to confirm that these aspects can be achieved together in an effective EBC. An "ABC" (SiCN-Oxide-Si_3N_4") system will be used to evaluate thermal shock and interfaces after exposure in the Keiser rig.

Excess carbon is apparently critical to high temperature properties for SiCN. Also, a small amount of boron can improve the weight loss and increases the resistance to crystallization. The properties are explained by the nanodomain microstructure that remains intact to ultrahigh temperatures. The emerging picture of the unit SiCN is a carbon gage structured with sequestered nanodomains of silica or Si_3N_4 which are unable to coarsen by diffusion, are too small to nucleate crystals. The structure can tolerate a high oxygen content without degradation of the high temperature properties.

The ABC composite study will identify the progression of oxidation overgrowth, thermal stress damage as a function of particle size and three interfaces, and the nucleation of oxide/SiCN and SiCN/ Si_3N_4 interfaces.

Evaluation methods

Beth Opila, NASA, exposed dense sapphire coupons in a TGA apparatus to confirm that alumina volatility will limit the lifetime of components and coatings for long term applications in combustion environments. Samples were exposed to 1250 to 1500°C at p_{H2O} of 0.15 to 0.68 atm at p_{total} of 1 atm. Recession of 250 µm in 10,000 hours is predicted at 1300°C in a 10 atm total pressure at 50 m/sec velocity in a combustion

environment. Porous alumina coatings in a turbulent environment are expected to volatilize more rapidly.

Peter Tortorelli, ORNL discussed the possibility of extending the usefulness of the Keiser rig used to expose candidate materials to high pressure and humidity conditions. Currently, the Keiser rig provides good evaluations of thermal stability, substrate-coating interactions, and the effectiveness of the coating to provide an oxygen barrier. Lacking is the evaluation of the volatility due to high velocity gas streams. Studies are currently being performed to determine whether the volatility issue also can be assessed by significantly increasing the p_{H2O} in the rig. The results of the study are expected to be reported next summer.

Bill Ellingson, **ANL**, illustrated the ability of elastic optical laser scattering to detect debonds in TBC coated superalloys and also the ability of this method to detect EBC coating thickness variations that developed on AS800 turbine vanes exposed for 1621 hours in the Rolls Royce/Allison 501K engine.

Bill illustrated the ability of Argonne's optical coherence tomography (OCT) system to characterize defects in both cross sectional and in-plane directions. The OCT system was used to detect an EBC coating spallation and characterize a crack the below the surface on a Si_3N_4 bearing ball.

J.P. Singh, Argonne National Labs, used indentation methods to measure the fracture toughness at and away from the EBC-substrate interface, and the elastic modulus and hardness in each layer of a 3-layer Si/BSAS coated SN282. Fracture toughness anisotropy was observed, with values of 3 and 6.5 MPa·m– in the directions parallel and perpendicular to the interface, respectively. The anisotropy was thought to be a result of residual stresses at the interface. Residual stresses were estimated based on the interface and away-from-interface K_{IC} values. The results were also supported by the results of an FEA model of the coating. The FEA model also illustrated the influence of the elastic modulus of the Si bond coating on the residual stress and the location of failure. These results support the reduced strengths measured for coated ceramics. Fractography showed interfacial cracking and voids/pores as sources of failure in BSAS-based and Ta_2O_3 EBCs.

Observations & Recommendations

Several issues are noteworthy from last year's workshop:

- The challenge of corrosion has been added to the list of concerns and requirements for EBC (Schenk)

- The list of materials that are not resistant to water vapor volatility is growing. For example data is being developed for volatility kinetics for alumina (Opila), and other materials experiences are sited (Schenk), but the data for many of the other compositions is still lacking to be able to rank them.

- It continues to be evident that an EBC systems performance in Si_3N_4 (microstructure, reactivity, adherence, etc) will be strongly influenced by the composition of the substrate. The CTE mismatches, albeit small can also be a crucial issue for success. Tailoring the substrate and coating system together may be required.

- The use of a TBC on top of the EBC is becoming of greater interest to extend temperature capability and durability. This interest is also supported by the need to also provide hot corrosion resistance, since TBCs developed for metals have shown some resistance to hot corrosion.

- Studies continue to improve the understanding of the problem, have identified many of the critical issues and options, but have not provided conclusive insight into a significant down selection of materials and processes.

Continued studies are needed to accelerate the protection development. The recommendations from last year's workshop continue to be applicable:

- Continuing the broad approach including further maturation of the current most promising approaches, as well as the exploration of new ideas.
- Establishing a material property database resource of critical properties, identify data that is needed, summarize results of prior evaluations, and provide references.
- Identifying low cost test methods for experimentally screening material candidates for water vapor resistance.
- Continue studies to identify materials and application methods with chemical and phase stability, bond strength, and retain or improve the substrate properties, and possibly provide impact resistance.
- Identify the bond strength requirements, and continue methods development for assessing the coating adherence.
- Continuing modeling and testing methodology development to bonding integrity.
- Emphasize low cost application processes suitable for complex gas turbine components.
- Continue conducting long term and cyclic exposure stability in combustion atmospheres.
- Continue the development of NDE methods for EBC coatings