Coatings for Si3N4 and SiC Ceramics: an Historical Perspective

Presented at the ORNL EBC Workshop

Nashville, TN, Nov 6-7, 2002

By

Dave Carruthers

Dave Carruthers & Associates

davecarruthers@prodigy.net

Presentation Outline

- Background
- Approaches to Environmental Corrosion
- Recommendations

Advanced Gas Turbines Provide a Material Challenges

- High Temperatures: 1900 to 2500F
- High and Cyclical Stresses: thermal and mechanical
- High Velocity Gases: approaching (exceeding) Mach 1
- High Pressures: ~ 4 to 10 atmospheres (for small turbines)
- Exposure to combustion products
- Combined Temperature, Pressure, Velocity, & Atmosphere which accelerate the detrimental effect, i.e., slow crack growth, corrosion

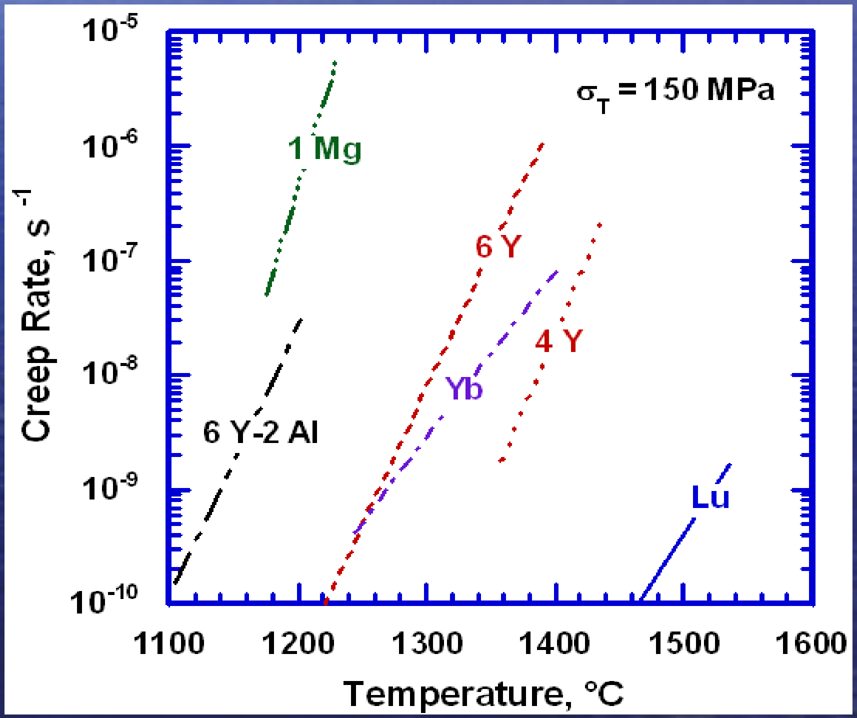
Microturbine Requirements Identified

[Ref DOE Microturbine Peer review, 2002]

OEM	Max Temp, F	Pressure, Atm	Life Goal, hrs Overhaul/ Service
GE	2130	4.2	8000 – 11,000/ 45,000 - 80,000
Capstone	2100	4.1	
UTRC [Shi, 2002]	2200	8	
IR	1902	4.8	

Advanced Si_3N_4 Show Significant Capabilities

- Creep and oxidation resistance have improved with improved compositions
- Available in gas pressure sintered complex shapes
- Decreasing ionic radius of RE increases oxidation resistance [Cinibulk, 1992]
- Single additive system: reduced oxidation, e.g.., SN282, Lu_2O_3, low Lu ion content glass, oxide growth : 0.004 μm^2/hr @ 1400C [Klemm, 2001a]
- Multiple additives system: increased oxygen diffusion , e.g.., AS800, Y_2O_3 + La_2O_3 +SrO , high ion content glass, growth rate 0.4 μm^2/hr @ 1400C [Klemm, 2001a]



from S. M. Wiederhorn and M. K. Ferber

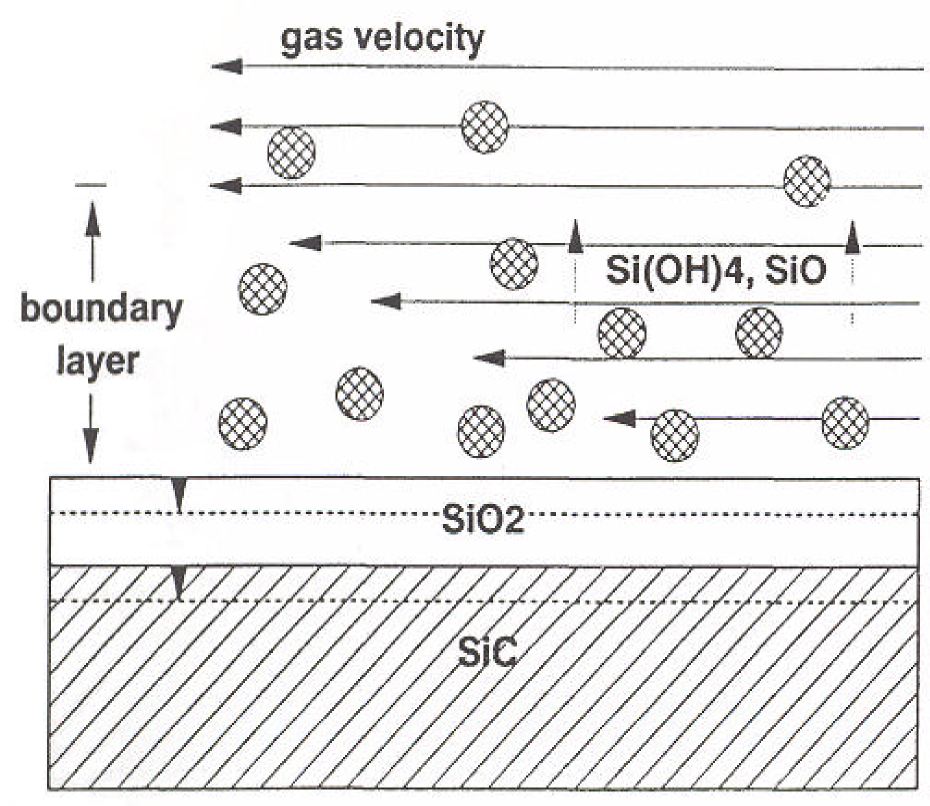
Today's Ceramics Are Not Adequate

- Vulnerability to Impact Damage
  - Air Research DARPA program [Richerson et al, 1982b]
  - Allied Signal AGT101 program [Boyd & Kreiner, 1987]
  - Solar Centaur 50S [van Roode et al, 1997]
- Poor resistance to water vapor and oxidation under advanced gas turbine conditions
  - Simulated Engine conditions [Smialek et al,1999, & Schenk et al, 2001]
  - Allison 501K Engine conditions [Lin et al, 2001]

Environmental Resistance is Major Challenge

- Water vapor degrades silicon based ceramics
  - H_2O enhances transport of impurities from the atmosphere to the surface
  - Increases oxidation rate of silica-formers: Relative to O_2, H_2O diffusion is ~1/10th, but solubility is ~1000x. Results in bubble formation
  - SiO_2 layer volatized by water vapor: $SiO_2 + H_2O$ --> Si(OH)x + SiO

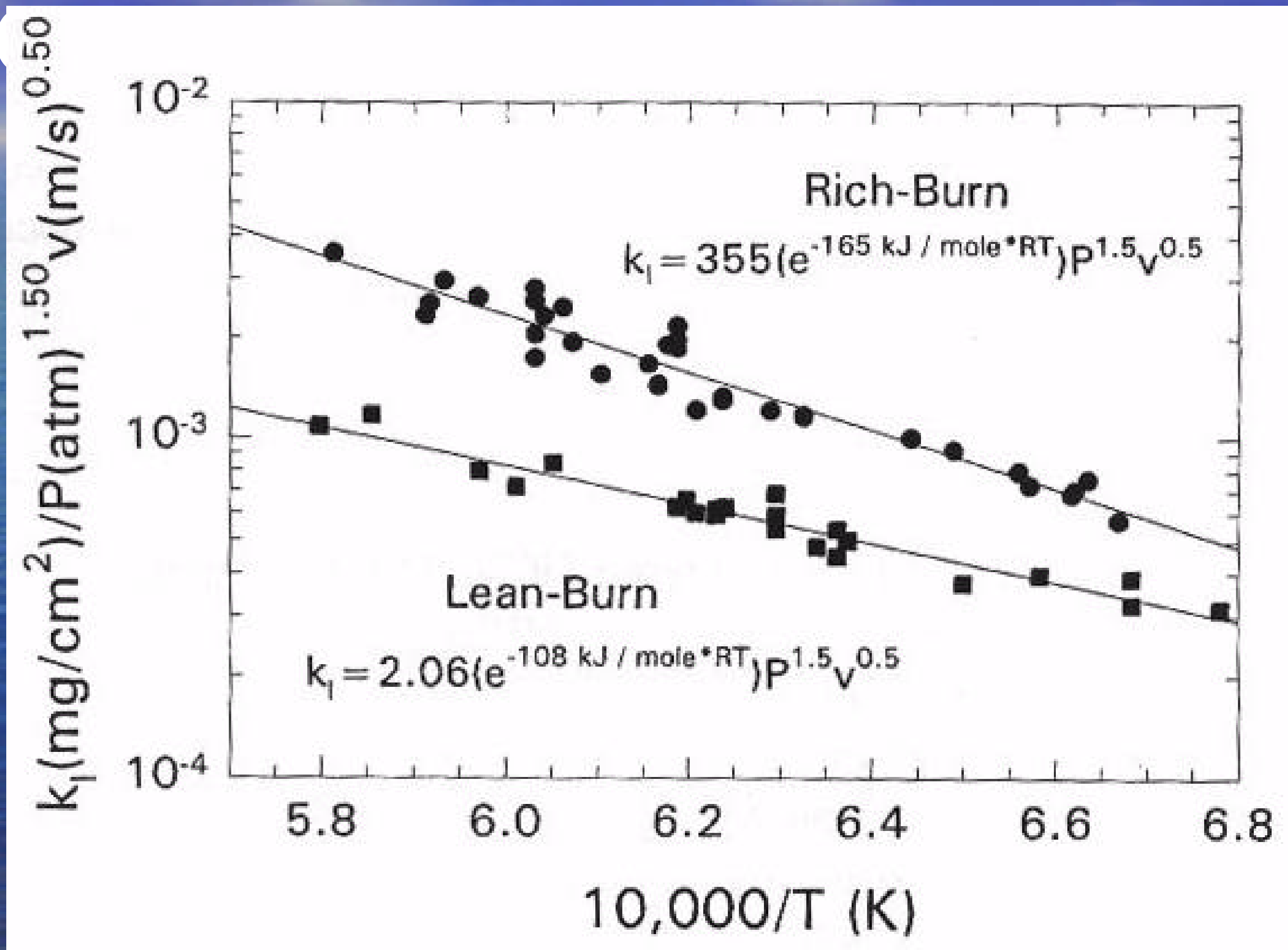
SiC and Si_3N_4 recession under combustor conditions



Smialek, et al, Adv Comp Mater, 1999

Unprotected Oxidation Leads to Recessi

Loss of SiO_2 layer allows substrate oxidation & recession



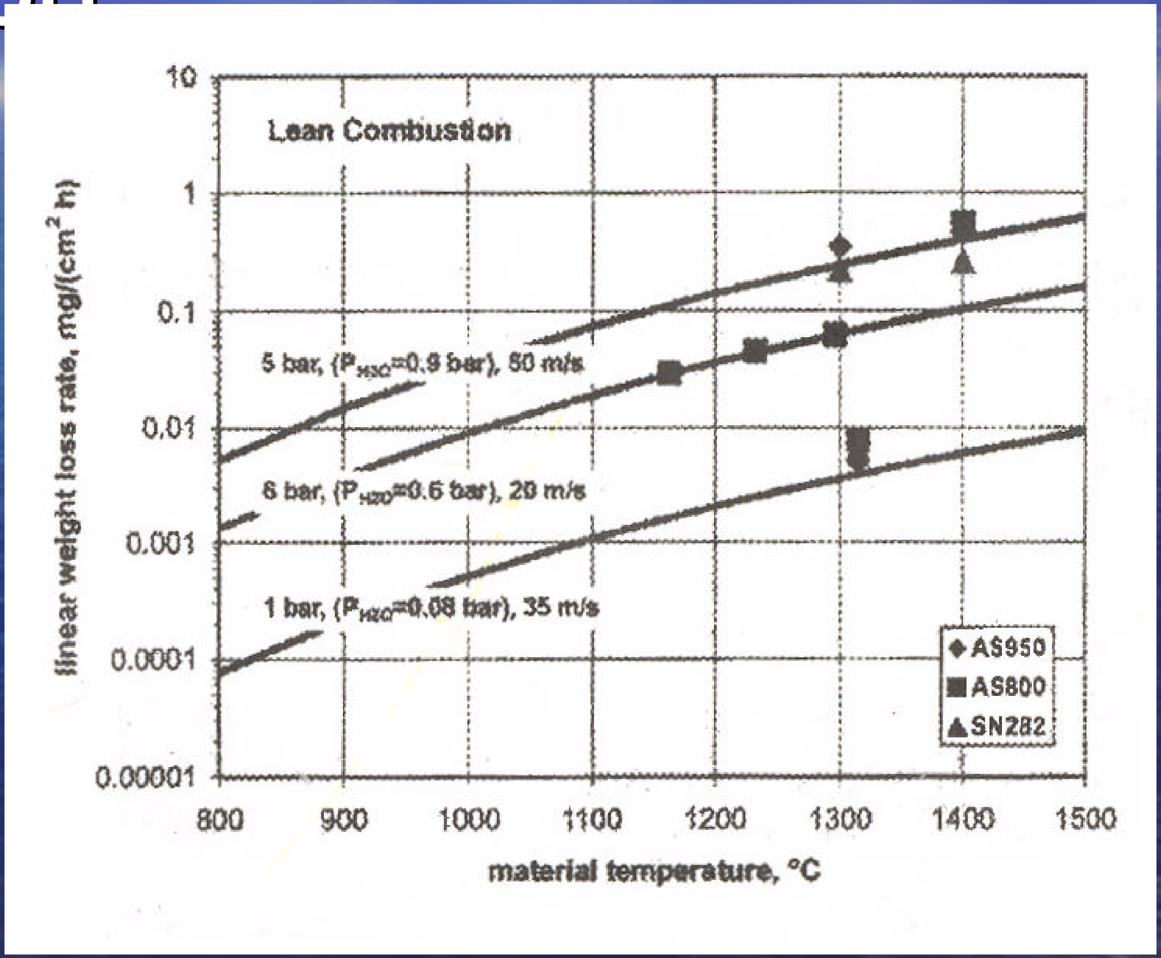
Smialek, et al, Adv Comp Mater, 1999

Advanced Si_3N_4s are Vulnerable to Recession

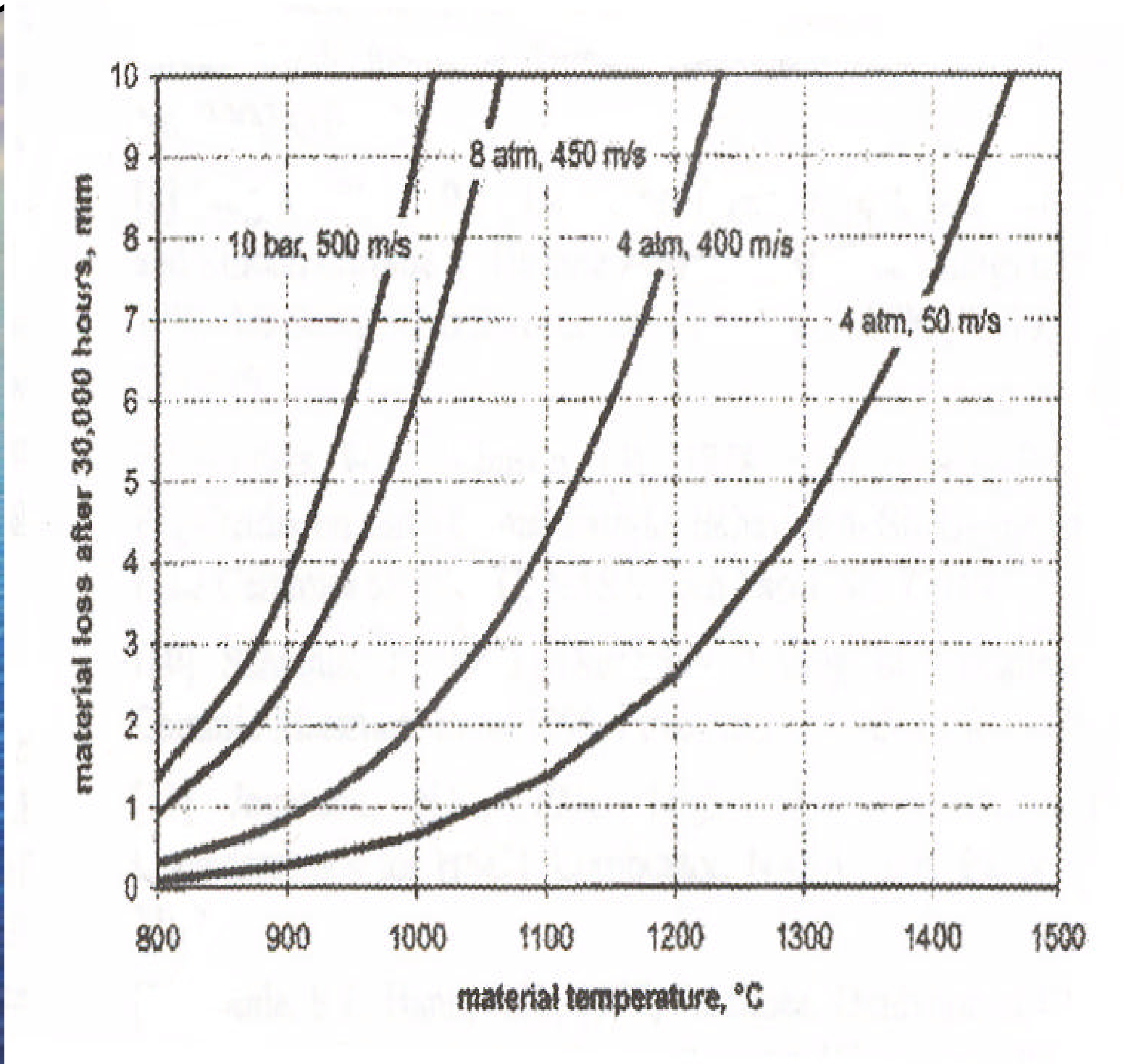
- •SN282
- •AS800
- •AS950
- •Si_3N4/MoSi2 +Y or Yb

• All recessed at .24 to .6 mg/cm2/hr in a combustion environment, 1400C, 5 bar

[Klemm, 2001a; Schenk et al, ASME 2001-GT-459]



Microturbine Conditions Require EBC Protection



Schenk, et al, 2001

Providing Environmental Resistance is Challenging

- Self healing SiO_2 not effective against water vapor
- Transport in SiO_2 is affected more by low level impurities than Al_2O_3 and Cr_2O_3 [Pareek et al, 1991, Zheng et al, 1992]
- Additives or impurities in surface layers increase oxidation rates, oxygen diffusion rate, change the rate controlling mechanism, and alter the oxide scale structure [Opila et al, 2000]
- Even with low oxygen diffusion coatings, silica will form under coatings
- Si_3N_4 & SiO_2 have low CTE: CTE mismatch leads to interface cracks & debonding
- Surface treatments to enhance adherence may

Requirements for Environmental Protection

- Environmental Durability in a hot gas environment
  - Oxidation resistance, low oxygen permeability
  - Resistance to Water vapor
  - Stability against hot gas constituents
  - Low volatility
  - > 10,000 hour life
  - Resistant to erosion, impact
- Chemical compatibility with SiO_2 that will form on substrate
- Stable microstructure & phases – grain size, porosity, non sintering or cracking
- Thermal expansion compatibility
- Must survive cyclic exposure
- Prefer a low elastic modulus

Solutions to Corrosion Must Not Conflict with Other Needs for Ceramics

- Reliability
  - High Fracture toughness w/ low scatter
  - Resistance to slow crack growth and creep
  - Oxidation, corrosion resistance
  - Impact resistance
- Formability
  - Complex, thick and thin shapes
  - Stringent dimensional control
  - Smooth aerodynamic surfaces
- Sinterability w/o expensive HIP processing
- Inspectability
- Affordability

- All needs must be achieve for success

Approaches to Protection

- Atmosphere control: minimize formation of corrosive species
- Alloy improvements
  - In situ or Self Generating protective surface layer
- Protective Coatings

Corrosion (Oxidation) Challenge of C-C, C-SiC, SiC-SiC

- Vulnerability to attack of fibers, interfaces or matrices via cracks from CTE mismatch and strain cracks.
- Approaches:
- Surface coatings: Si_3N_4 and SiC identified as good candidates [Strife et al, 1988]
- Glass forming compounds containing Si, B, Hf, Cr, Ti [Boullion, et al, 2002, Joshi et al, 1996]
- Y_2SiO_5 low CTE, plasma sprayed with YSi_X intermediate layer survived 1 hr at 1800C on C/C [Ogura, et al,1995] Spalled in 7 cycles to 1700C [Ogura, et al, 2001]

Self Generating Protection is Attractive

- Use additives that produce or self repair oxide coating with H_2O resistance.
- May not add expensive steps to processing

- Combustion results with Yb_2O_3 sintering additive [Klemm, 2001a]
  - Exposure removed SiO_2, but left a $Yb_2Si_2O_7$ layer
  - Disilicates has a higher chemical stability, but spalled (CTE ~ 5 x 10^{-6}/C,

- Combustion results, Yb_2O_3 as sintering additive and disilicate EBC [Klemm, 2001a]
  - Homogenious, crack free E- beam coating obtained
  - Exposure resulted in cracks from SiO_2 crystallization
  - SiO_2 below the EBC was protected, recession prevented

$MoSi_2$, SiC_p in Si_3N_4 Influence the Oxidation Process

- Both composites form Si_2N_2O interlayer below SiO_2 surface [Klemm, 1997]
  - Si_2N_2O beneath SiO_2 in pure Si_3N_4 is responsible for lower oxidation rate for Si_3N_4 than SiC [Du et al, 1989a, Ogbuji & Opila, 1995]
  - Si_2N_2O has a low oxygen diffusion [Du et al 1989b, Tressler, 1990]
  - Si_2N_2O has good oxidation resistance and high temperature strength (~600 800 MPa) [Park, D. S. et al, 2002; Ohashi et al]
  - Si_2N_2O reduces cation driving force to the surface
- $MoSi_2$ phase may provide high temperature ductile-phase toughening [Petrovic, 1997]

Early Environmental Coatings Addressed Corrosion

- Solar study for RB SiC & SiC. [Price et al, 1994]
- Plasma sprayed mullite, graded mullite, cordierite, zircon, alumina, yttria, chromia, hafnia, and YSZ
- Plasma spraying, 5-15% porosity typical
- Best corrosion resistance/adherence to 1204C:

  Single layer mullite

  Graded mullite to Al_2O_3

  Graded mullite to Y
- Best results for mullite adherence with surface prep: 1) SiC particles brazed to surface, or 2) proprietary etching: implies mechanical bond
- Surface treatment degraded the strength, but coating restored it

Alternate Approaches Evaluated

- Slurry coatings containing mullites: cracked in thermal exposure [Federer, ’98, ’90]
- CVD Ta_2O_5 stable to 1000C, but reactive with Na_2SO_4 [Lee, W.Y. et al, 1995]
- Fully crystallized PS mullite adhered to 1200 hr up to 1300C, still cracks [Lee, K.N. et al, 1995]
- CVD Mullite developed [Mulpuri, R.P et al, 1996]
- CVD crystalline mullite on SiC provided

Coating Development Continued

[Lee, K.N. 2000a, 2002b, 2000c]

- In the 90's, focus shifted to silicon volatility in water vapor:
  - SiC surface roughened by Na_2CO_3 etching for adherence
  - PS mullite lost silica during exposure, high silicon activity(0.3-.04)
  - Mullite w/YSZ top coat suppressed SiO_2 volatization, but H_2O penetrated cracks
- Lessons learned:
  - PS Mullite bond primarily mechanical, weak,
  - Residual amorphous mullite and alumina, impurities resulted in phase instability/shrinkage/cracks
  - CTE mismatch (5.6 vs 4.7 ppm/C for mullite and SiC) stresses resulted in cracking

Modified Mullite System Improves EBC on SiC

[Lee, K.N., 2000a; Sun, 2002b]

- BSAS attractive: low CTE and low silica activity (<0.1), crack sealing capability. [Lee,2002a] ,but reacts with silica
- $MoSi_2$ /Mullite + BSAS / BSAS delayed onset of accelerated oxidation in water vapor [Lee et al, 2000c; Lee, et al, in press]
- Si found to be excellent bond coat for mullite on SiC
- Si reacts with BSAS, so mullite or mullite + BSAS used as intermediate layer
- Initially mullite+BSAS intermediate layer preferred due to difficulty in achieving crack free mullite
- Both mullite and mullite +BSAS intermediate systems provided ~14,000 hours on SiC/SiC in engine; some EBC volatility & spalling observed [Eaton et al, 2001]
- Long term temperature limit ~1200C, adherence

UTRC Showing EBC Progress on Si_3N_4

[Sun et al., 2002b]

- Si_3N_4: CTE mismatch increase of 1.5 ppm/C from SiC
- EBC on Si_3N_4 FT8 vane: 31 hours/ 15 atm/ 1200 to 1230C/ max velocity ~.7 M: No spalling, strong bond, protected substrate
- 1204C / 2000 hr Keiser rig exposure shows protection on SN, but CTE cracks will reduce long term effectiveness
- At 1350C, Si bond coat oxidizes, Eutectic in BSAS/SiO_2 system estimated at 1350C. Could last few 1000 hours
- BSAS/mullite--B SAS interface stable for 500 hours in 1450C steam
- System temp capability can be increased by

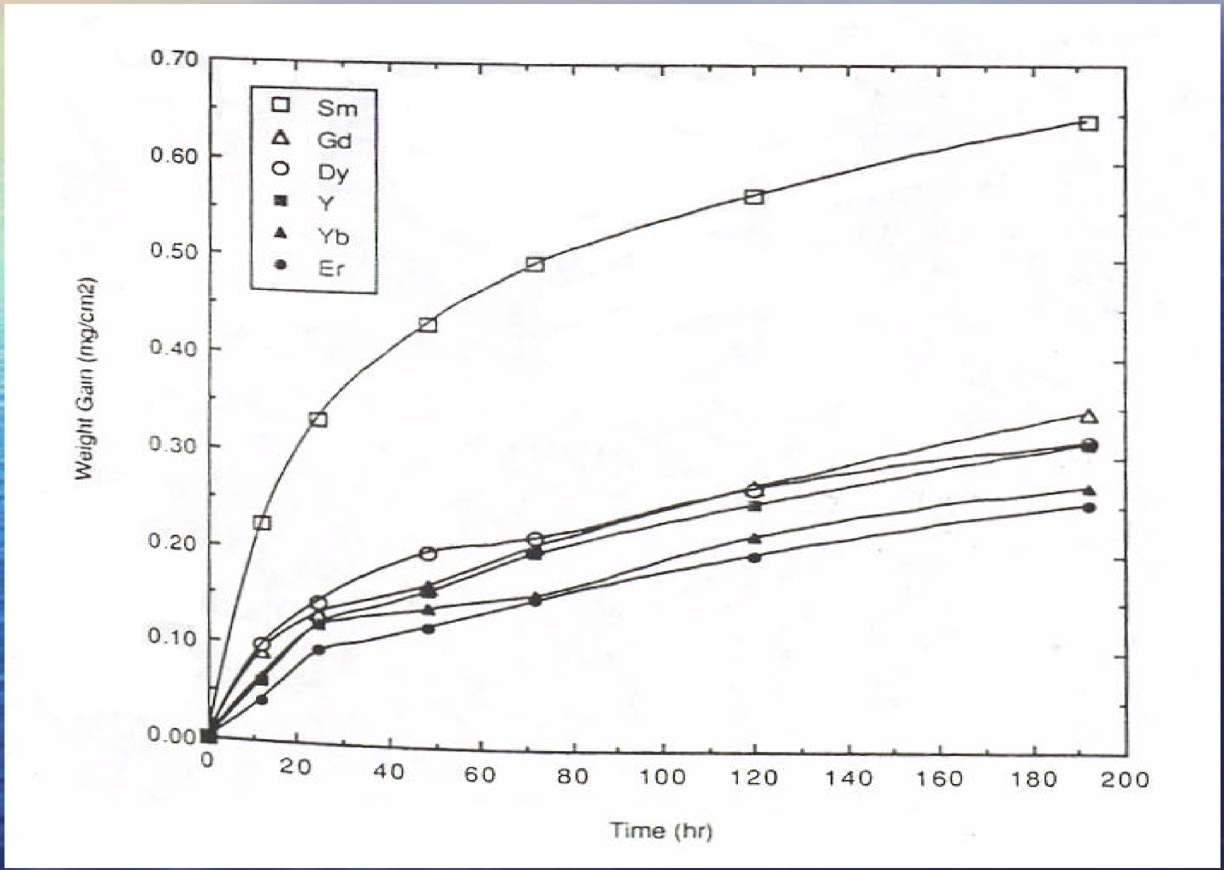
NASA Focusing on EBC's for SiC/SiC

- Focusing on 1482C (2700F) use temperature, 166C (300F) temperature drop through coating
- Currently identifying temperature limit for Si/mullite/BSAS + YSZ systems
- Si/Mullite EBC crack, provide water vapor path
- BSAS recession significant above 1400C [Lee et al, in press]
- Mullite an effective chemical barrier between mullite + BSAS and YSZ to 1500C
- Si/Mullite + BSAS/graded mullite+YSZ/YSZ partially spalled after 370 hours at 1400C

Challenges Remain for Si-Mullite-BSAS EBC [Lee, 2002b; Sun et al, 2002b]

- Non uniform coating thickness, Si porosity on non line-of-sight areas "Smoothing" observed on BSAS topcoat after engine exposure: erosion possible
- Long term stability of multi-component system on multi-constituent Si_3N_4 unknown
- Sintering aids may influence stability of Si bond coat
- Surface treatments to enhance adherence of bond coat often degrade substrate or strength
- 500-750 um thickness
- Implications of slow hexagonal to monoclinic celsian conversion are unknown, particularly for high temperature applications
- Potentially vulnerable to erosion in high velocity areas
- Durability demonstration of BSAS EBC on SN for long term is needed
- Critical to optimize the coating for CTE match and

Disilicates Offer Low Oxidation Rates



RE Disilicates show parabolic weight loss in oxidation

Er, Yb show lowest oxidation rate

[Cinibulk, et al, 1992]

Disilicate CTE related to Ionic Radius

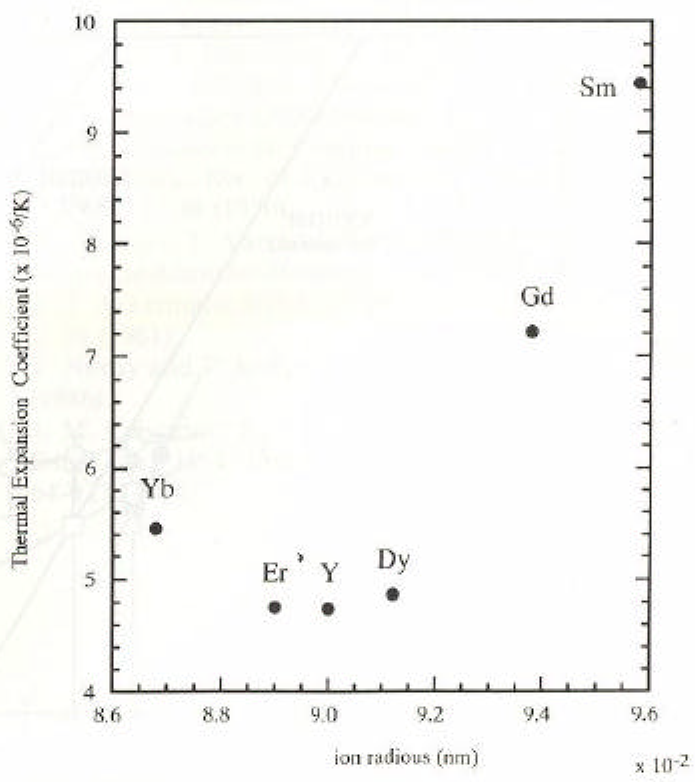
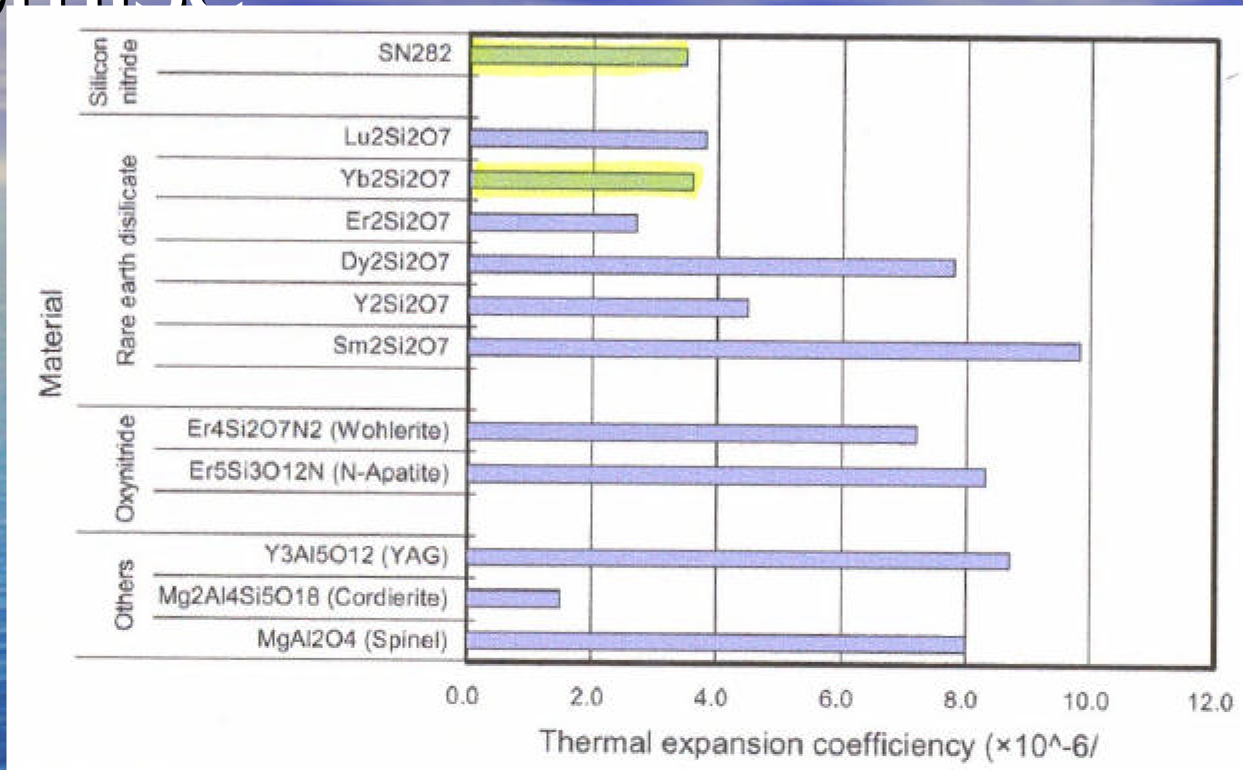


Fig. 11. The relationship between CTE and ion radius of lanthanide.

CTE tailoring may be possible with blended RE disilicates

Morimoto, et al, 1995

Disilicate Coating Shows Promise



- Candidates experimentally screened for water vapor resistance & CTE
- $Yb_2Si_2O_7$ and $Lu_2Si_2O_7$ did not lose weight after 15 atm saturated water vapor pressure @ 200C
- $Yb_2Si_2O_7$ has best CTE match with Si_3N_4 **[Fukudome et al]**

$Yb_2Si_2O_7$ Continues to Show Promise

- $Yb_2Si_2O_7$ Coated SN282 did not cracking or show crystal structure change in cyclic exposure + 20 hr burner rig exposure
- Engine components coated by slurry, ~30μm thick
- Turbine nozzles and combustor liner coated, to be tested in 2002

Y_xSiO_y offers Tailorable CTEs

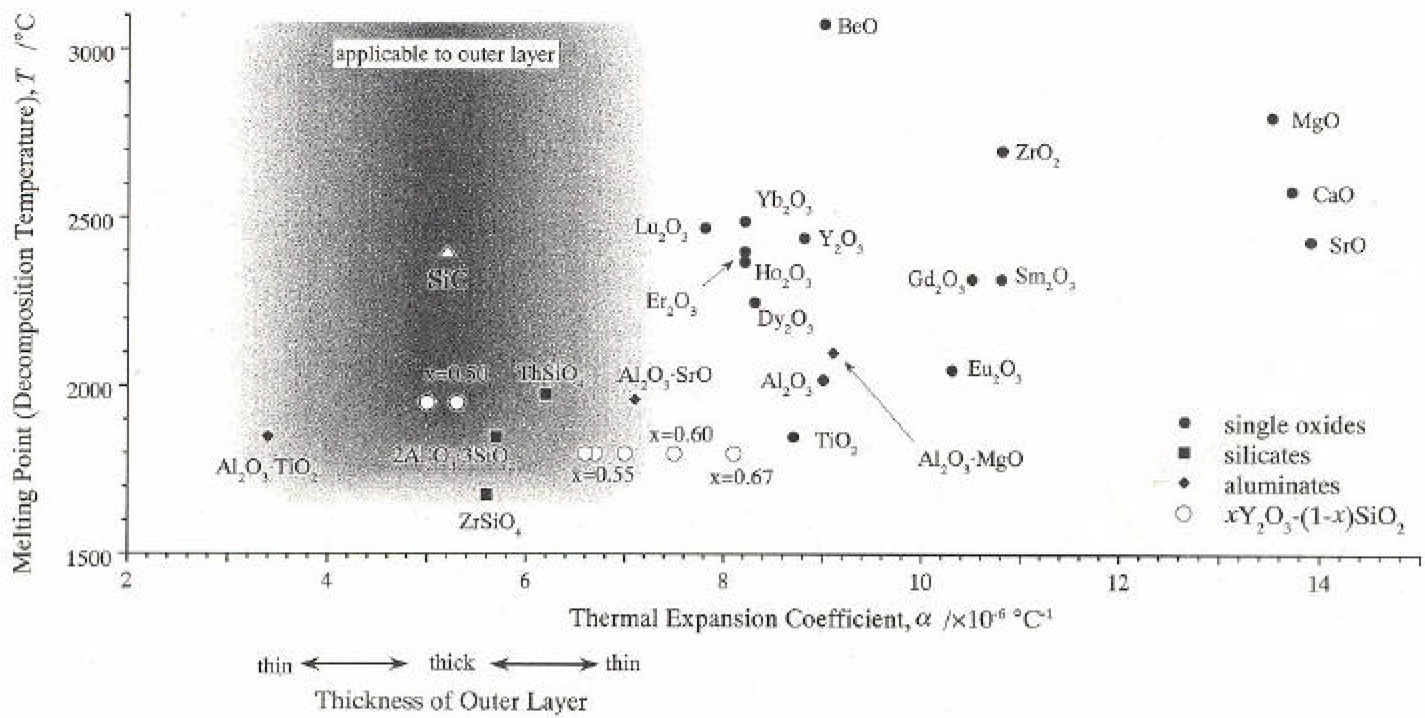


Fig. 11 Thermal expansion coefficients[24] and melting points of refractory oxides. The area shown by shadowing indicates applicability to the outer layer of our oxidation resistant coating.

Ogura, et al, 1999

Lessons Learned for Coatings on Si_3N_4

[Lee et al. in press]

- Application methods
  - Plasma spray: layered, porous microstructure, strain tolerant, cost effective, scale-up capability, wide use, non uniform thickness, line of sight application.

    Key Issues must be economical, and applicable to small, complex shapes
- CTE mismatch is a significant concern.
- Mechanical bonds are typically weak, especially when CTE mismatch is large. Mechanical bonding to rougher surfaces improves adherence but may reduce strength of

Lessons cont'd

- Low modulus systems help, e.g.. BSAS, mullite + BSAS
- Si, and possibly $MoSi_2$, are beneficial bond coatings
- During combustion atmosphere exposures, sintering additives can remain and concentrate on the surface, providing a possible means o developing a protective surface oxide
- Phase changes, such as amorphous to crystalline, can be problematic.
- Systematic, continuous improvement approach such as NASA & UTRC appears to be fruitful
- Disilicates, which are compatible with substrates, have water vapor resistant, and CTE match may

Lessons cont'd

- A successful coating will require:
  - A chemical bond to provide good adherence to SiO_2
  - A CTE match or low modulus for strain tolerance
  - A top coating for water vapor resistance
  - A TBC for higher temperature applications
- These requirements may be met in a single or multiple layer coating.

Cyclic Testing has not been adequately Addressed [He et al]

- Thermally grown oxides often develop at substrate-coating interface during high temperature exposure
- Growth strains may relax at high temperatures.
- Upon cool down, other components of the coating may yield with temperature dependent yield strength
- Tensile stresses increase with cyclic exposures
- This effect is not evaluated in static durability testing

Alternate Systems Worth Assessing

- Coatings
  - RE disilicates
  - YAG, YBAG, $ZrSiO_2$ ($ZrSiO_2$ incompatible with SiC, harmful to mullite [Price et al])
  - YAlSi – Amorphous YAS showed no degradation in 250C /15 atmosphere steam for 8700 hrs [Armstrong]
  - CaMgAlSi system
  - Others
- Bond Coat: Si_2N_2O, $MoSi_2$, disilicates, others

Alternate Application Methods Worth Assessing

- Focus on application methods suitable for complex shapes:
  - Displacement Reactions [Tiegs, Lowden]
    - Liquid metal
    - Pack cementation
    - Gas phase
  - Slurry, [Armstrong] sol gel, or polymer precursors applications
    - Dip coating
    - Spray coating
    - Spin coating
    - Vacuum infiltration
    - Reaction sintering of multilayer dipped coatings [Asayama et al, 2002]

Analytical Screening Approaches Should be Included

- Examples
  - Coatings for fiber coating candidates analytically screened for Thermodynamic, Physical, Mechanical, Stability [Gonczy et al, 2002]
  - Ceramic Materials analyzed for Chemical Stability in H_2 and $H_2 + H_2O$ [Misra, 1990]

Recommendations for Improved Environmental Resistance

Roadmap for Improved Materials Data Base for Environmental Resistance

- Establish a database resource for thermodynamic, physical, and chemical properties important to coating analysis and evaluation
- Data base:
  - For candidate bond coats: assess chemical bond to SiO_2
  - CTE
  - Silica activity
  - Water vapor resistance
  - Chemical & phase stability couples
  - Bond strength
- Perform testing to characterize the effect of the protection system on fast fracture and time dependent properties for use in life analysis codes
- Continue the development of test techniques to measure

Roadmap of Material Development for Environmental Resistance

- Screen and analyze candidates and candidate couples based on database knowledge
- Identify thermo-chemical data base needs
- Perform experimental evaluations of couples for bonding, chemical and phase stability, cyclic durability
- Perform experimental multilayer compatibility & stability evaluations
- Consider a porous surface layer between the substrate and EBC to provide strain tolerance and potential impact energy absorption?

Roadmap for Design and Life Prediction for Environmental Resistance

- Determine coating bonding strength requirements for static and rotating parts
- Effect of protection system on fast fracture and time dependent properties
- Incorporate the effect of coatings into the life analysis codes

Roadmap for <u>Non Destructive Evaluation</u> for Environmental Resistance

- Continue the development of NDE methods to assess coating adherence and integrity
- Continue to correlate coating bonding and integrity in service with NDE results
- Develop effective methods to detect coating deterioration before it becomes critical.
- Develop a low cost method to assess coating thickness/uniformity on complex

Roadmap for Fabrication and Process Development for Environmental Resistance

- Develop Low cost, robust application methods suitable for complex shapes
- Surface treatments to improve adherence without inducing strength loss
- System must be cost competitive

Acknowledgements

- DOE and ORNL for funding support
- Jerry Brockmeyer, Ultramet
- Munjal Chheda and Rajendra K. Bordia, Univ. of Washington
- Hagen Klemm, Fraunhofer Institute
- NASA Staff: Doug Kiser, Kang Lee, Jim Smialek, Michael Virrelli
- ORNL Staff: Beth Armstrong, Paul Becher, Craig Blue, Mike Brady, Matt Ferber, Allen Haynes, Edgar Lara-Curzio, HT Lin, Rick Lowden, Karren More, Steve Nunn, Dave Stinton, Terry Tiegs, Peter Tortorelli
- Dave Richerson, Dave Richerson & Associates
- Mark van Roode, Solar Turbines
- Bjoern Schenk, Honeywell
- Ellen Sun, UTRC

References, alphabetical order

- Armstrong, Beth, personal communications, also this meeting
- Asayama, M., Ando, M., Ohji, T., “Reaction bonding of oxide coatings on silicon nitride,’ Ceramic Engineering and Science Proceedings, Vol 23, No 4, 2002, Presented at the 26th Annual Conference on Composites, Advanced Ceramics, Materials, and Structures, Cocoa Beach, Jan 13-18, 2002
- Bouillon, E., Lamouroux, F., Baroumes, L., Cavalier, J. C., Spriet, P., Habarou, G., “An Improved Long Life Duration CMC for Jet Aircraft Engine Applications,” ASME GT-2002-30625, presented at the ASME Turbo Expo, land sea & Air, 2002, June 3-6, 2002, Amsterdam, The Netherlands
- Boyd, G. L, and D. M. Kreiner. "AGT101/ATTAP Ceramic Technology Development. " Proceeding of the Twenty-Fifth Automotive Technology Development Contractors Coordination Meeting, pg. 1011987
- Cinibulk, M. K., G. Thomas, S. M. Johnson, “Oxidation Behavior of Rare Earth Disilicate-Silicon Nitride Ceramics”, J. American Ceramic Society, **75,** [8] 2044-49 (1992).
- DOE Microturbine and Industrial Gas Turbine Peer Review meeting, March 12-14, 2002, Fairfax, Va., http://www.eren.doe.gov/der/micro_indgas_conf_02.html
- Du, H., Tressler, R. E., Spear, K. E., Pantano, C. G. ”Oxidation Studies of Crystalline CVD Silicon Nitride,” J. Electrochem. Soc. 136, 1527-1536, (1989a)
- Du, H., Tressler, R.E., Spaer, K.E., “Thermodynamics of the Si-N-O System and Kinetic Modeling of Oxidation of Si3N4,” J. Electrochem. Soc., 136 [11] 3210-15 (1989b)
- Eaton, H.D., Linsey, G.D., Sun, E.Y., More, K.L., Kimmel, L.B, Price, J.R., Miriyala, N., ”EBC Protection of SiC/SiC Composites in a Gas Turbine Combustion Environment – Continuing Evaluation and Refurbishment Considerations,” ASME GT 0513 2001, Presented at the ASME 2001 Turbo Expo, New Orleans
- Federer, J.I., “An investigation of the Ceramic Coatings for Protection of sic from High-Temperature Corrosion,” ORNL/TM-10606, 1988
- Federer, J.I., “Alumina Base Coatings for Protection of SiC Ceramics,” J. Mater, Eng vol. 12, 141-149,1990
- Fukudome, T., Tsuruzono, S., Karasawa, W., Ichikawa, Y., “Development and Evaluation of Ceramic Components for Gas turbine,” ASME paper GT-2002-30627, from presented at the ASME Turbo Expo, Land, Sea & Air 2002, June 3-6, 2002, Amsterdam, The Netherlands
- Gazza, G., Robinson, B., “Sintering of Si3N4 –Y2O3 – SiO2 Compositions wit5h Mo2C,” Third International Symposium on Ceramic Material and Components for Engines, Las Vegas NV, November 27-30, 1988, edited by V.J. Tennery, p 390-398, American Ceramic Society, 1989
- Gonczy, S., Brockmeyer, J., Easler, T. “Oxide Compositions for Fiber Interface Coatings in Ceramic Composites, Cocoa Beach Restricted Session, 2002
- Haynes, J. A., Cooly, K. M., Stinton, D.P., Lowden, R. A., Lee, W.Y., “Corrosion-Resistance CVC Mullite Coatings for Si3N4,” Ceramic Engineering & Science Proceedings, 20 [4] 355-362, 1999
- Haynes, J.A., Lance, M.J., Cooley, K.M., Ferber, M.K., Lowden, R.A., Stinton, D.P., “CVD Mullite Coatings in High Temperature, High-Pressure Air-H_2O”, J. Am. Ceram. Soc., 83 [3] 657-59 (2000)

References, cont’

- Joshi, A., Lee, J.S., “Coatings with particulate dispersion for high temperature oxidation protection of carbon and C/C composites,” Composites, Part A, 1997, pp 181-89, Published by Elsevier Science Limited
- Klemm, H., Hermann, M., Schubert, C., “Silicon Nitride Composites Materials with an Improved High temperature Oxidation Resistance”, Ceram eng Sci Proceedings, 18, No3, 1997, pp.615-623 Klemm, H., “Corrosion of Silicon Nitride Materials in Gas Turbine Environment,” Presented at the Structural Ceramics and Ceramic composites for High Temperature Applications, Seville, Spain, Oct 7-12, 2001a, submitted to J. Europ Ceram Soc.
- Lee, W. Y., Bae, Y. W., Stinton, D. P., “Na_2SO_4-Induced Corrosion of Si_3N_4 Coated with Chemically Vapor Deposited Ta_2O_5,” J. Am. Ceram. Soc., 78[7]1927-30, 1995
- Lee, K. N., Miller, R.A.,, Jacobson, N.S., “New Generation of Plasma-Sprayed Mullite Coatings on Silicon-Carbide, J. am. Ceram. Soc., 78 [3], 705-710 (1995) and US Patent No. 5,391,404
- Lee, K. N., “Current status of environmental barrier coatings for Si-based ceramics”, Surface and Coatings Technology, 133-134 (2000a) 1-7
- Lee, K. N., Fox, D., Eldridge, J., Zhu, d., Robinson, R., Bansal, N., Miller, R., “Upper Temperature Limit of Environmental Barrier Coatings Based on Mullite and BSAS”, NASA/TM 2002-211372, March 2002a
- Lee, K.N., “Environmental Barrier Coatings Having a YSZ Top Coat”, GT-2002-30626, Presented at the ASME Turbo Expo 2002, June 2002b, Amsterdam, The Netherlands
- Lee, K. N., “Key Durability Issues with Mullite-Based Environmental Barrier Coatings for Si-based Ceramics,” Transactions of the ASME, 122 pp 632-636, 2000c
- Lee, K. N., Fritze, H., and Ogura, Y., “Coatings for Engineering Ceramics,” in Progress in Ceramic Gas Turbine Development, Vol. 2., M. van Roode, M. Ferber, and D.W. Richerson, (eds) ASME (in press)
- Lin, H. T., Ferber M. K., van Roode, M., “Evaluation of Mechanical Reliability of Si3N4 Nozzles after Exposure in an Industrial Gas Turbine, Design and Testing of Ceramic Components for Industrial Gas Turbines,” in Ceramic Materials and Components for Engines. Edited by Heinrich JG, Aldinger A, Wiley-VCH, Weinheim-New York-Chicester-Brisbane-Singapore-Toronto, 2001, in press.
- McCluskey, P.H., Eaton, H.E., Godin, D. R., Foster, G.E., Harter, H.D., Chin, S., Cotnoir, G., Ellis, C.A., “Plasma Sprayed Mullite coatings on Silicon based Ceramic Materials,” US Patent 5,869,146
- Morimoto, T., Ogura, Y., Kondo, M., Ueda, t., “Multilayer Coatings for Carbon-Carbon Composites,” Carbon, Vol 33, No. 4, pp. 351-357,1995
- Misra, A.K., “Thermodynamic Analysis of Chemical Stability of Ceramic Materials in Hydrogen-Containing Atmospheres at High Temperatures,” NASA Contract Report 42721, 1990
- Mulpuri, R.P., Sarin, v. K., “Synthesis of mullite coatings by chemical vapor deposition,” J. Mater Res., Vol. 11, No 6, Jun, 1996]
- Ogbuji, L.U., Opila, E. J., “A comparison of the Oxidation Kinetics of SiC and Si3N4,” J. Electrochem. Soc. 142 [3] 925-30

References, cont'

- Ogura, Y., Kondo, M., Morimoto, T., Sekigawa, T., Notomi, A., "Oxidation Behavior of T2SiO5/SiC Coating for C/C Composites," High Temperature Materials Chemistry Proceedings, Part II, Eds, Hilpert, Froben & Singheiser, p. 561-64, Forschungzentrum Julich, (2001).
- Ohashi, M. et al, J. Am. Ceram Soc.,1991
- Opila, E.J., Jacobson, N.S., "Corrosion of Ceramic Materials", in <u>Corrosion and Environmental Degradation of Materials</u>, Wiley-VCH, Jan 2000
- Pareek, V,. Shores, D.A., "Oxidation of Silicon Carbide in Environments Containing Potassium Salt Vapor," J. Am. Ceram. Soc., Vol 74, pp. 556-63, 1991
- Petrovic, J.J., Pena, M.I., Kung, H.H., "Fabrication and microstructures of $MoSi_2$ Reinforced-Si_3N_4 Matrix Composites," J. Am Ceram. Soc., 80 [5] 1111-16 (1997)
- Price, J. R., van Roode, M., "Corrosion Resistant Coatings For Ceramic Heat Exchanger Tubes Operating in Highly corrosive Environments," Final Report GRI-94/0353 for the Gas Research Institute, Contract number 5086-232-1233, July, 1994.
- Richerson, D. W., and K. M. Johansen. Ceramic Gas Turbine Engine Demonstration Program, Final Report Contract N00024-76-C-5352. 1982b
- Schenk, B., Strangman, T., Opila, E., Robinson, R., Fox, D., Klemm, H., Taut, C., More, K., Tortorelli, P., "Oxidation Behavior of Prospective Silicon Nitride Materials for Advanced Microturbine Applications," ASME 2001-GT-459, Presented at the International Gas Turbine & Aeroengine Congress & Exhibition, New Orleans, LA, June, 2001
- Shi, J., Vedula, V. R., Holowczak, J., Bird, C. E., Ochs S. S., Bertuccioli ,L., Bombara, D. J.,, "Preliminary Design of Ceramic Components for the ST5+ Advanced Microturbine Engine,' GT-2002-30547 Presented at the ASME 2002 Turbo Expo, Amsterdam, The Netherlands, June 3-6, 2002
- Smialek, J.L., Robinson, R.C., Opila, E.J., fox, D.S., and Jacobson, N.S., "SiC and Si3N4 Scale Volatility under Combustion conditions," Adv. Composite Mater., 8 [1] 33-45 (1999)
- Strife, J.R., Sheehan, J.E., "Ceramic coatings for Carbon-Carbon Composites," Bulletin of the Am Ceram Soc., Vol 67, No. 2, 1988
- Sun, E., Eaton, H. E., Holowczak, J.E., Linsey, G.D., "Development and Evaluation of Environmental Barrier Coatings for Silicon Nitride,' ASTM 2002-GT-30628, presented at the IGTI Conference, Amsterdam, The Netherlands, June, 2002b
- Tiegs, T., Crow, J.B., Bawazer, L., Barker, D.L., "Oxide Coatings on Silicon Nitride by Displacement Reactions", Engineering Sci Proc. Vol. 22 [4] 2001, American Ceramic Society
- Lowden, R, Nunn, S., this conference
- Tressler, R. E., Spear, K. E., Zheng, Z., Di, H., "Fundamental Studies of the Oxidation of Silicon Carbide Crystals and CVD Silicon Nitride" in <u>High Temperature Corrosion of Technical Ceramics</u>, R. J. Fordham, ed., Elsevier applied Science (1990) , pp 69-89