Two concepts for EBC coatings with low silica activity: geomimetic compositions and coatings derived from polymer precursors

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Outline

- **Objectives**
- **Company background and capabilities**
- **Coating Requirements**
- **Material choices**
- **Coating concepts**
  - **Polymer derived coatings**
  - **Geomimetic coatings**
  - **Composite Coatings**
  - **Graded Coatings**
- **Development tasks**
- **Summary**

Technical Contributors

- **Ceramatec:**

  Charles Lewinsohn

  Preceramic precursor processing, materials testing and analysis.

  Balakrishnan Nair

  Geomimetic materials processing, materials testing and analysis.

  Merrill Wilson

  Design development, manufacturing support.

- **University of Florida:**

  Darryl Butt

  Environmental resistance testing, analysis and improvement.

- **University of Wisconsin:**

  Reid Cooper

  Geomimetic coating composition selection.

Ceramatec, Inc.: Corporate experience

- Founded in 1976
- Through 1990's, Ceramatec spun-off successfully several product companies, and was a subsidiary of Elkem A.S.
- In 2000, Ceramatec became a minority owned small business focused on developing novel ceramic technologies and products.
- R&D is focused on commercializing advanced ceramic technologies
- Specialized expertise in electrochemical technologies
  - ionically transmitting membranes (O_2/syngas generation, solid electrolyte O_2 sensors)
  - solid oxide fuel cells
- New business programs
  - Advanced turbine materials, pre-ceramic polymer derived coatings, fiber optics, proton/sodium conductors, microchannel devices, ozone generation, water purification, drug delivery, ceramic armor, NO_x sensors.

Ceramatec's Strategy for EBC Development

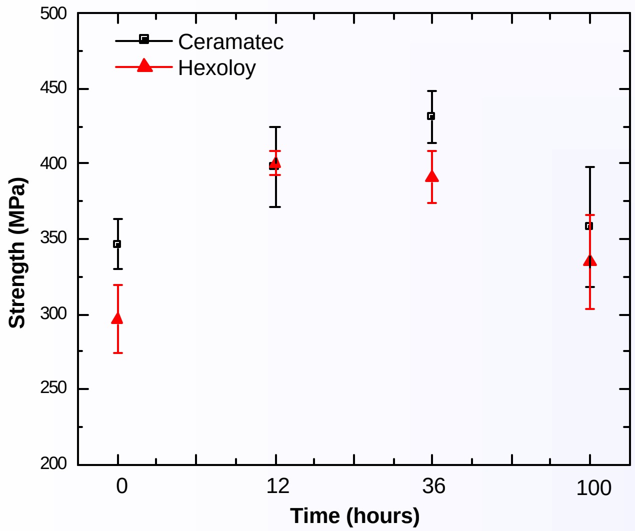
- Collaborate with advanced turbine manufacturers, materials suppliers, government agencies and strategic partners to leverage our materials technology portfolio to develop new functional EBC systems.

Related R&D at Ceramatec

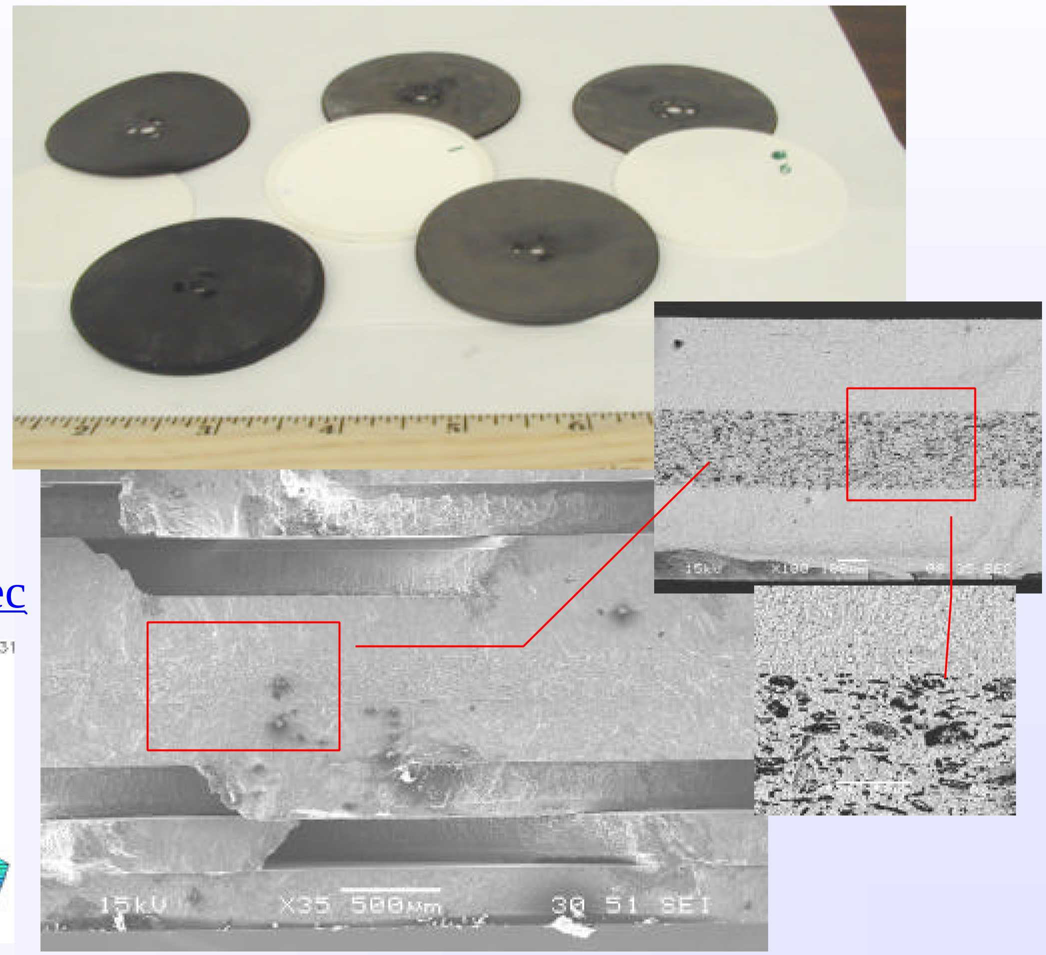
- Materials development for hydrothermal corrosion environments
  - SOFC seals from pre-ceramic polymers (DOE SBIR)
  - Geomimetic compositions for ceramic composite matrices (Air Force STTR)
  - High temperature SiC heat exchanger development (DOE SBIR)
  - Corrosion resistant oxide coatings for SOFC interconnects (DOE SECA)
  - Corrosion resistant oxide coatings for hot gas corrosion in the chemical process industry (IR&D program)
  - New IR&D program on turbine coatings development

SiC heat exchanger – materials and engineering development

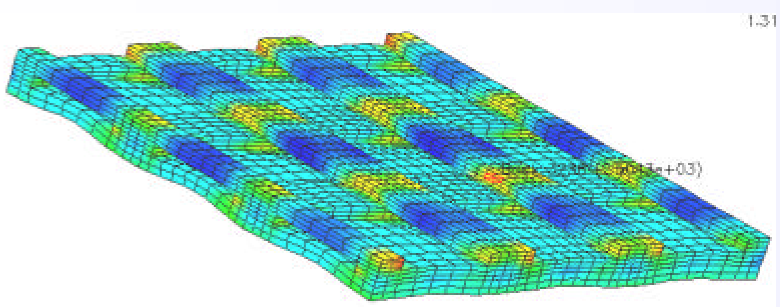
SiC Corrosion – U of F Darryl Butt



Heat Exchanger Fabrication – Ceramatec Inc



Thermo-Mechanical Design – Ceramatec



Coating Requirements

- **Coating lifetime target: 15, 000 h between overhauls, 45, 000 h lifetime.**
- **Inlet temperatures of more than 1000°C under conditions of pressure, water vapor content, and gas velocity equivalent to current turbine designs.**
- ***Low-cost***
- ***Non line-of sight coating methods***
- ***Benign coating technique: No surface degradation***
- **CTE matching to lower residual stresses**
- **Phase and dimensional stability**

Materials for advanced turbines

Materials

Si_3N_4

Si_3N_4-$MoSi_2$

Si_3N_4-SiC

SiC

$SiO_xN_yB_z$

Others

Coatings

Mullite

Alumina

Zirconia

Ta_2O_5

CMZP*

Geomimetic

Si-B-C-N

None/Others

Turbine/ Component

*$(Ca_{0.6}Mg_{0.4})Zr(PO_4)_6$

SiO_2 volatility limits material lifetime

- In mixed oxidizing/reducing gases the silica scale can be reduced to form volatile SiO(g):

$$SiO_2 + H_2(g) = SiO(g) + H_2O(g)$$
$$SiO_2 + CO(g) = SiO(g) + CO_2(g)$$

Opila E.J., Jacobson N.S., "SiO(g) Formation from SiC in Mixed Oxidizing-Reducing Gases," *Oxid. Met.*, **44** [5/6] 527-544 (1995).

- In environments containing water vapor volatile hydroxides or oxyhydroxides can form:

$$SiO_2 + H_2O(g) = SiO(OH)_2(g)$$
$$SiO_2 + 2H_2O(g) = SiO(OH)_4(g)$$
$$SiO_2 + ½H_2O(g) = SiO(OH)(g) + ¼\ O_2(g)$$

Opila E.J., Smialek J.L.., Robinson R.C., Fox D.S., Jacobson N.S., "SiC Recession Caused by SiO_2 Scale Volatility under Combustion Conditions: II, Thermodynamics and Gaseous-Diffusion Model," *J. Am. Ceram. Soc..*, **82** [7] 1826-1834 (1999).

Candidate coatings for improving properties

- Materials with low silica activity, possessing reduced oxidation rates and attractive, high temperature mechanical properties are under development at Ceramatec, Inc.:
  - Si-B-C-N
  - Geomimetic coatings: eg. BAS/alumina
  - Composite coatings: polymer-derived base, oxidation resistant fillers.

Si-B-C-N ceramics: novel materials for high temperature applications

- Addition of B to Si-C-N ceramics resulted in a material with better thermal stability.
  - Improves the resistance to crystallization at high temperature: ceramic remains amorphous up to 1700˚C.
  - Increases the resistance to high temperature oxidation: withstand temperatures up to 2000ºC for several hours without degradation.
- Excellent high temperature properties are attributed to the formation of B containing phases.
  - Stabilizes the amorphous state at higher temperature.
  - Reduces C activity by incorporating it into B-containing phases.
  - Shifts Si_3N_4 and SiC degradation reactions to higher temperatures by increasing the local N_2 pressure.

Si-B-C-N ceramics: understanding of oxidation behavior is required

- Si-B-C-N ceramics have attractive properties for high temperature applications environments, yet they have unknown behavior in environments relevant to microturbines.
- To fully exploit the use of Si-B-C-N ceramics in high temperature applications, it is important to predict the behavior of this material to potential working environments. Thus, further studies are required in the following areas:
  - The oxidation behavior in different gaseous environment.
  - The hydrothermal oxidation behavior at medium and high pressures.
  - Characterization of the involved oxidation kinetics and mechanisms.

Si-B-C-N coatings

- Recent efforts have led to organic precursors that can be pyrolysed to form non-oxide ceramics with high yields and low shrinkage.
- Compositions containing Si, B, C, and N exhibited good high temperature properties:
  - Creep rates, at T>1550ºC, two orders of magnitude lower than CVD or RB SiC.
  - Oxidation resistance equivalent or superior to conventional Si_3N_4

  (Riedel et al 1995, Jacobson et al 2001, Butchereit 2001).
- Hardness values up to 16 GPa, elastic modulus ˜120 GPa, fracture toughness = 2.5 MPa-$m^{1/2}$ => impact resistance.

  (Galusek D., et al. 2001).
- Properties can be tailored using composite "Active filler control". For example, the addition of $MoSi_2$ exhibited a creep rate of 10^{-7} s^{-1} at 1500ºC and 100 MPa.

  (Greil , 1995).

Advantages of Si-B-C-N ceramics obtained from polymer precursors

- Obtain materials with “tailor-made” properties.
  Properties can be “designed” at the molecular level based on the composition of the polymeric compounds.
- The material has a more homogeneous distribution of elements.
  The structural unit and stoichiometry of the resulting ceramic is very close to those of the polymer precursor.
- Ceramic can be processed in a relatively simple manner at relatively low temperatures.
- No sintering additives are required during fabrication processes.
  Formation of detrimental grain boundary phases is avoided, thus high temperature mechanical stability is maintained.

UNIVERSITY OF FLORIDA

Benefits of coating with preceramic polymers

- Allows liquid and polymeric processing methods – dip coating, spray coating, spin coating, etc.
- Non line-of-sight process.
- Potentially benign coating technique (compatible materials, relatively lower processing temperature ~ 1000°C).
- Precursors wet and adhere to a variety of substrates (ceramics, composites and metals).
- Leads to formation of amorphous, non-oxide materials with enhanced mechanical properties than alternative materials.

Benefits of coating with preceramic polymers (Cont.)

- Can obtain uniform coatings by controlling precursor rheology.
- Graded and multi-layer coatings easily obtainable.
- Can tailor CTE by filler additions.
- Potential for repair.

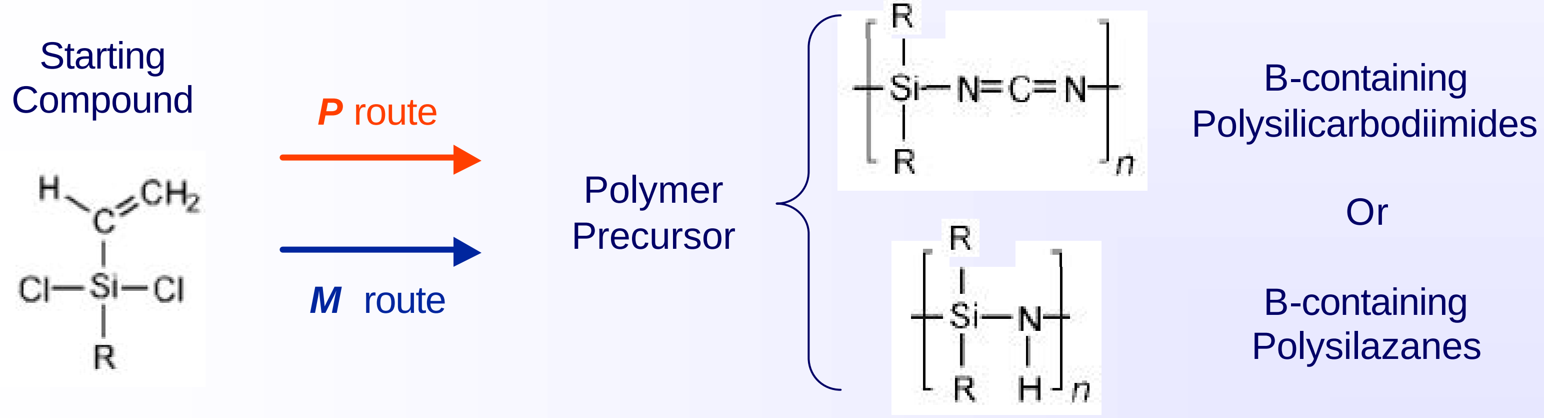
Methods of tailoring Si-B-C-N coatings

- Fillers
  - Inert fillers reduce initial polymer volume, accommodate shrinkage.
  - Active fillers modify thermal expansion, oxidation, erosion resistance, etc..

- Chemical synthesis
  - incorporation of elements that form oxidation resistant products: Yb, Ba, Sr, etc.

Si-B-C-N ceramic processing

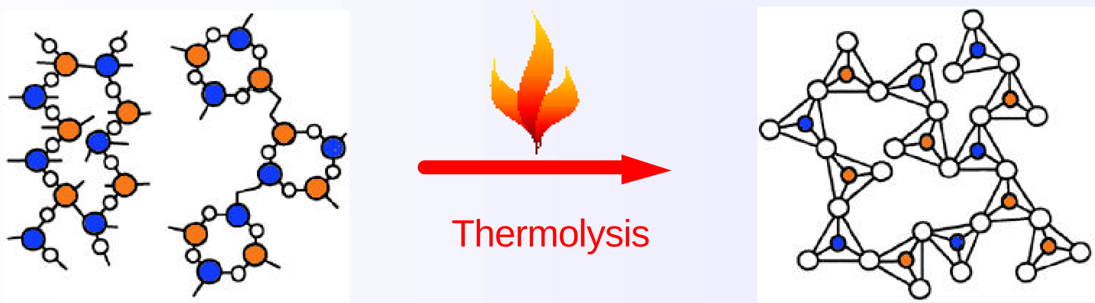
- **Two methods for synthesizing the polymer.**
  Polymer route (*P*): Chemical modification of Si-based polymers with B containing compounds
  Monomer route (*M*): Synthesis from B-based monomers
- **Modified polysilazanes or polysilylcarbodiimides are the more common compounds for polymer precursors.**



Si-B-C-N Ceramic Processing

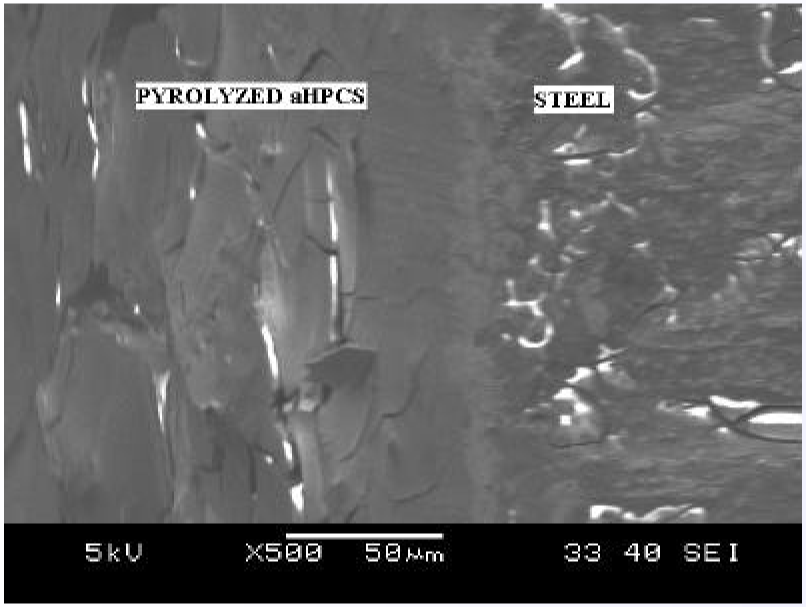
- Ceramic obtained by thermolysis of the polymer precursors in an Ar environment from 500°C to 1800°C.
- Polymer to amorphous ceramic transformation: 500°C≤T≤1050°C
  - Amorphous C/BN domains embedded in a Si-C-N matrix
- Amorphous to crystalline transformation: T≥1700°C
  - SiC and Si_3N_4 nanocrsystals embedded in a layered B-N-C matrix

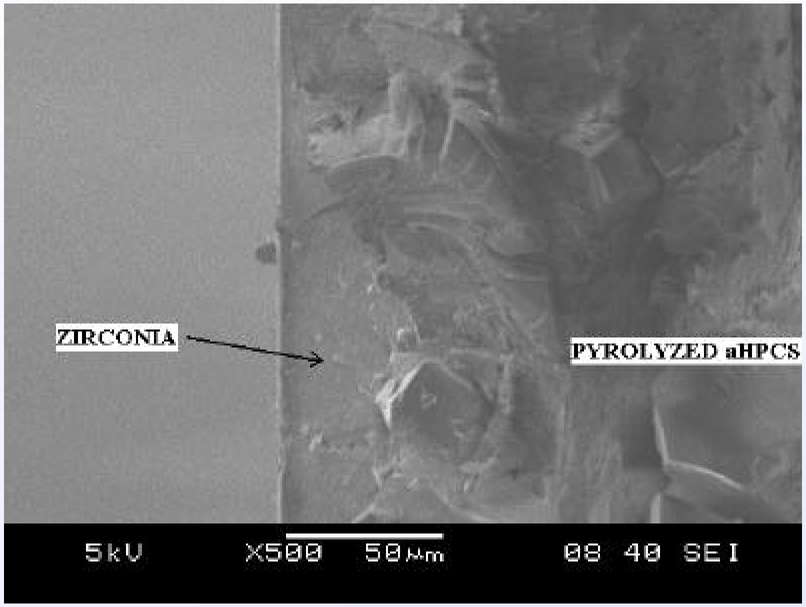
Polymeric Precursor



Ceramic

Examples of wetting with preceramic polymers





- ***Pyrolyzed aHPCS bonds to metals and ceramics.***

Preceramic polymer Coating Methodology

- Mix precursors, fillers, solvents, etc.
- Coating application (Dip coating, spray coating, painting etc.).
- Cure or crosslink – thermal, chemical, UV
- Pyrolyze – slow heating to avoid entrapment of volatile hydrocarbons and to avoid shrinkage stresses at elevated temperatures.

Geomimetic coatings

- Approach is based on hydrothermal phase stability studies of aluminosilicates in the geology literature.

- Data is available for phase stability of naturally occurring aluminosilicates under high water partial pressures (few GPa) at high temperatures.

Strategy for Selecting Stable Coating Compositions

- Systematic selection of stable compositions from geology literature data.
- Potential compositions investigated for secondary criteria such as CTE match or reactivity with substrates (if data is available)
- Preliminary screening study
- Adhesion, processing, cost issues etc.

Benefits of the Geomimetic Selection Strategy

- Materials selection will be carried out from an application standpoint: hydrothermal corrosion environment.
- Materials will be selected that are expected to have high performance under expected operating conditions.
- This will promote timely and cost-effective development of coatings and materials that practical for use in advanced turbine applications.

Case Study - Geomimetic approach to coating selection: why not mullite?

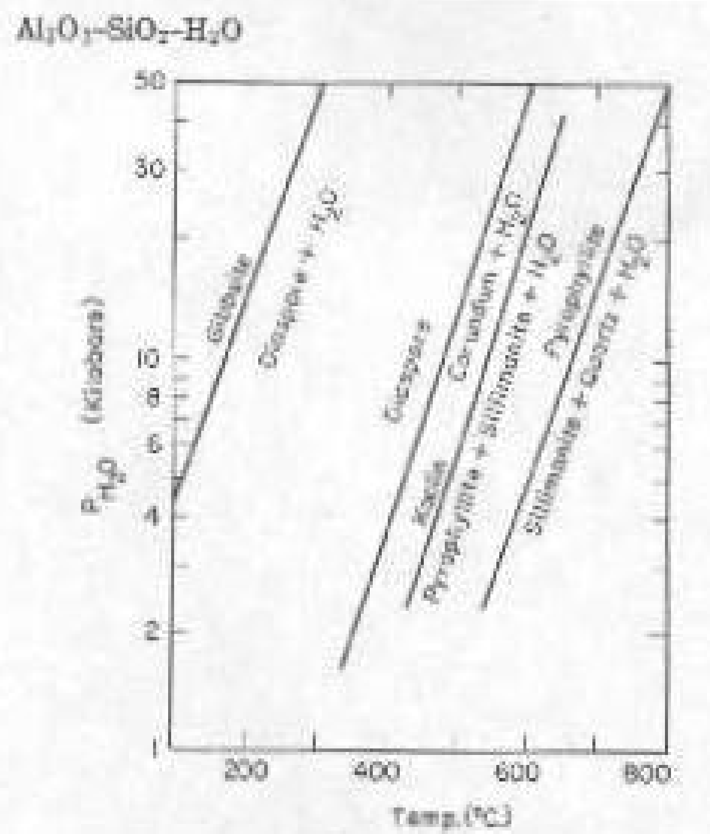


FIG. 2009.—System Al_2O_3–SiO_2–H_2O; v.p. of reactions. G. C. Kennedy, Am. J. Sci., 257, 570 (1959).

- Expected Turbine operating conditions: $P_{H2O} \approx$ 0.1-1 atm (10^{-3}-10^{-2} kbar).
- While this is off the graph, the linear behavior of the plots allows some logical deductions.
- Mullite has no phase stable regime under hydrothermal conditions
- The probable phases at high-T, turbine conditions are sillimanite + Quartz + H_2O
- The quartz formation is not good due to silica volatilization.
- So, mullite was not a good choice!

Case Study – BAS Stability

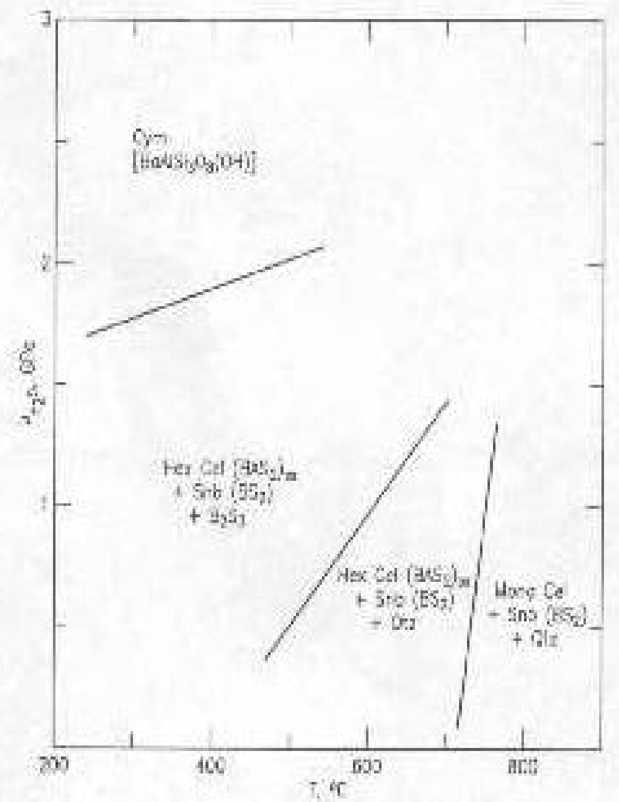


Fig. 7974—System BaO-Al_2O_3-SiO_2-H_2O. Qtz = quartz; Hex = hexagonal; Mono = monoclinic; B = BaO; A = Al_2O_3; S = SiO_2; Cel = celsian ($BaAl_2Si_2O_8$); Sob = sanbornite ($BaSi_2O_5$); Cym = cymrite [$BaAlSi_3O_8(OH)$].
Y. Seki and G. C. Kennedy, *Am. Mineral.*, 49, 1407-1426 (1964).

- Monocelsian + quartz forms under static pressure
- Silica volatalization in flowing gas makes this undesirable
- Mono-celsian (BAS) should be stable if we batch for excess of alumina as opposed to silica.
- Studies at University of Wisconsin have shown that celsian forms as a stable end-product due to reaction of barium-micas with water

King et al (2000)

Other Considerations for BAS

- Which Celsian phase is optimal for hydrothermal oxidation resistance?
- Geomimetics suggests that the high-T, High P_{H2O} phase is mono-celsian.
- Barium addition to form barium strontium aluminosilicate (BSAS) is common
- However, very little is known about the BSAS phase diagram – the phase diagram on the right is the only one available but its accuracy is questionable
- There is a good deal of data that suggests monocelsian stability over a wider composition/temperature range in the BSAS diagram

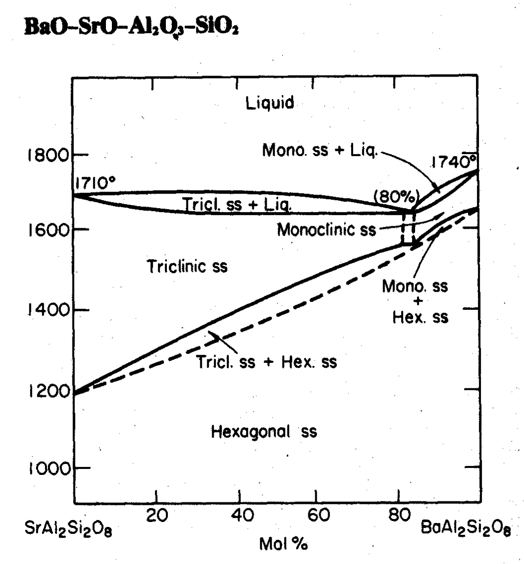


FIG. 5462.—System $SrAl_2Si_2O_8$–$BaAl_2Si_2O_8$.
N. A. Sirazhiddinov, P. A. Arifov, and R. G. Grebenshchikov, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **8** [5] 870 (1972); *Inorg. Mater. (Engl. Transl.)*, **8** [5] 756 (1972).

Geomimetic Coating Methodology

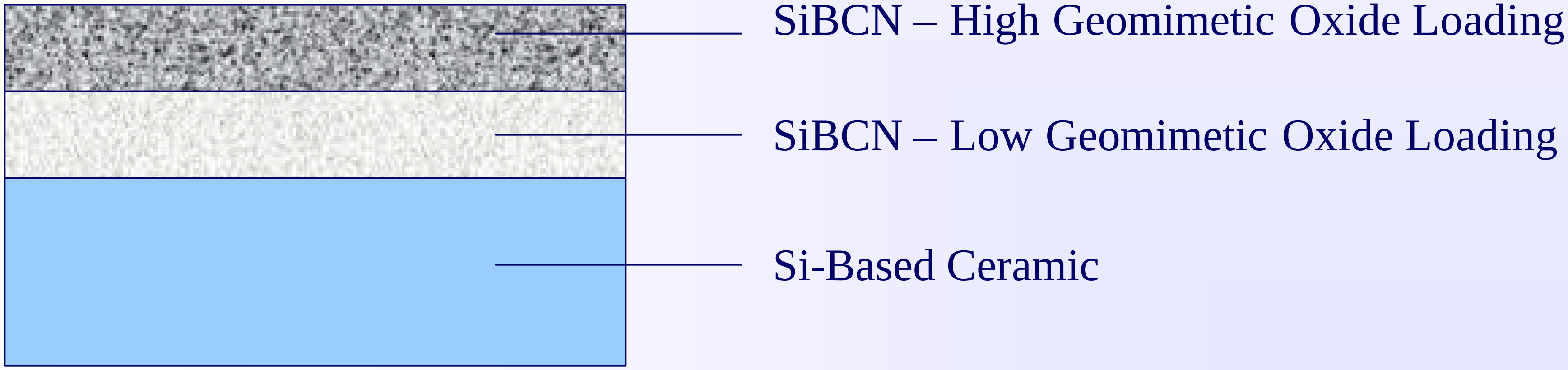
- Powder batching
- Geometic oxide powder processing
- Milling
- Slip/Slurry Preparation
- Coating application (dip coating, spray coating)
- Sintering
- Reinfiltration (if-required)
- Second firing

Coating Design

- ***Graded Coatings***
- ***Composite Coatings***
- ***Bond Coats***
- ***"Base coating" = SiBCN preceramic polymer***
- ***Low Si activity oxide phase (e.g. geomimetic fillers)***

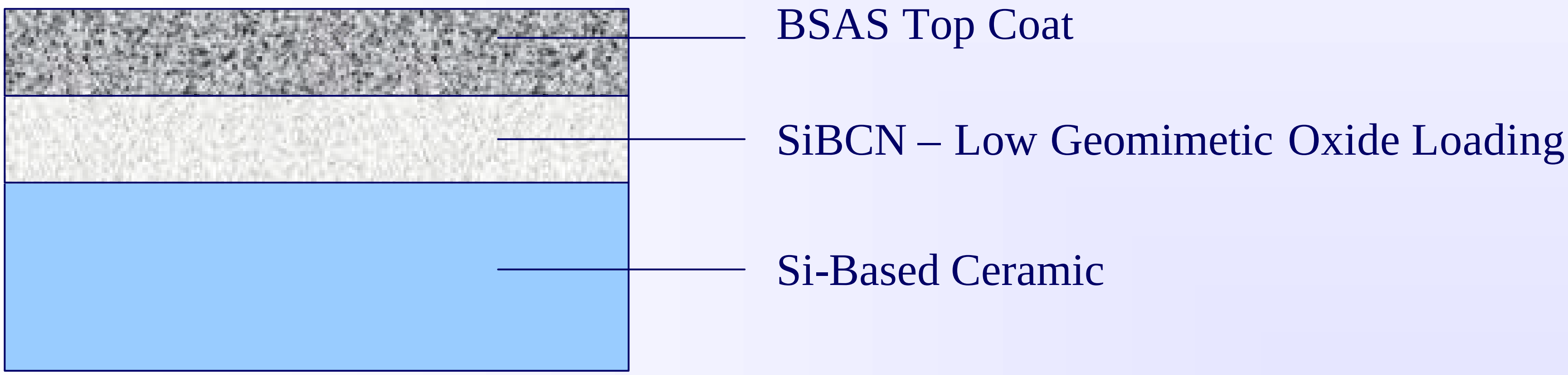
Graded/Functional EBC Coatings

- The SiBCN/geomimetic materials system can be designed so that properties can be graded across the interface
- CTE,corrosion resistance can be textured for functionality

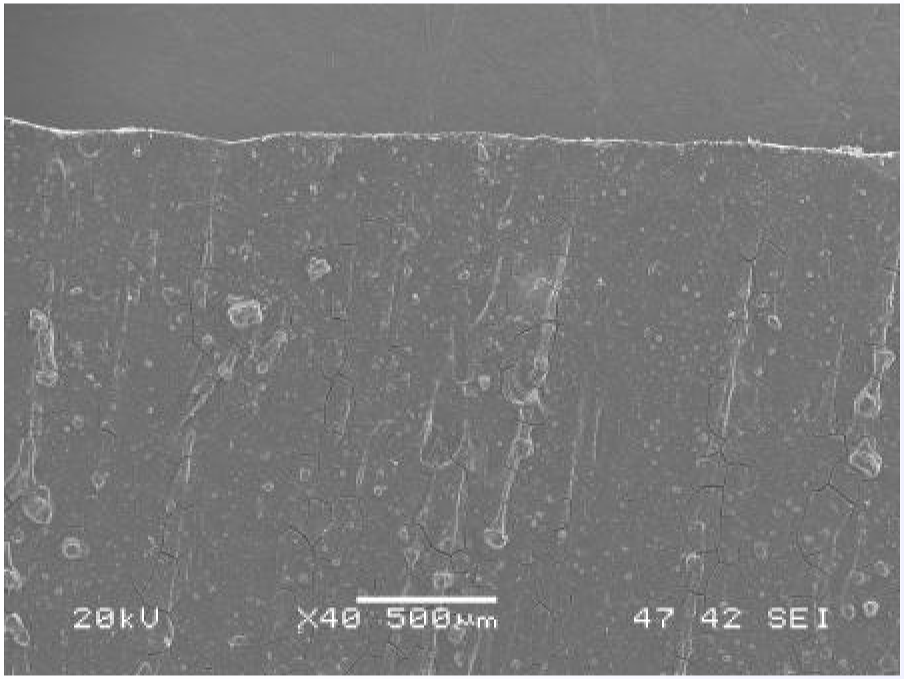


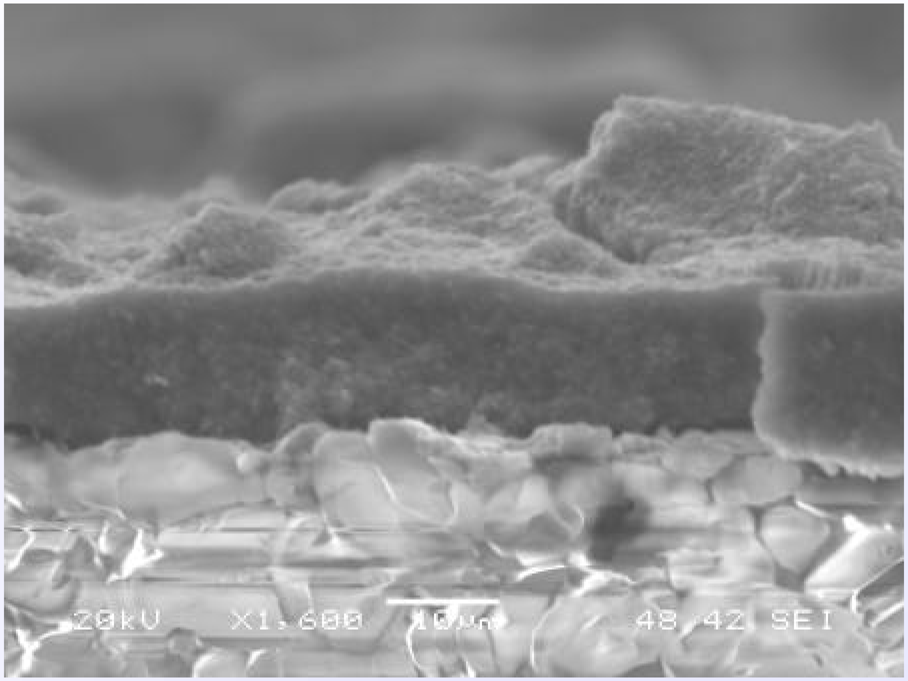
Composite Coating as a Bond Coat

- For BSAS coatings, the key issue seems to be adhesion with the ceramic substrate
- The polymer derived ceramic/geomimetic material can be a composite that facilitates adhesion between a BSAS top coat and the SiC/Si_3N_4 substrate



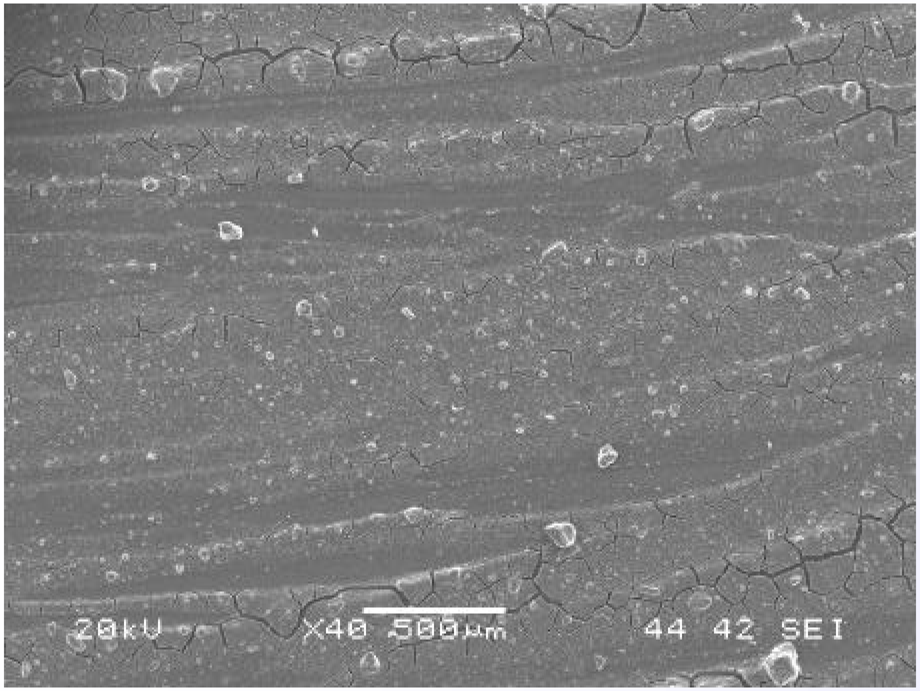
Composite coatings

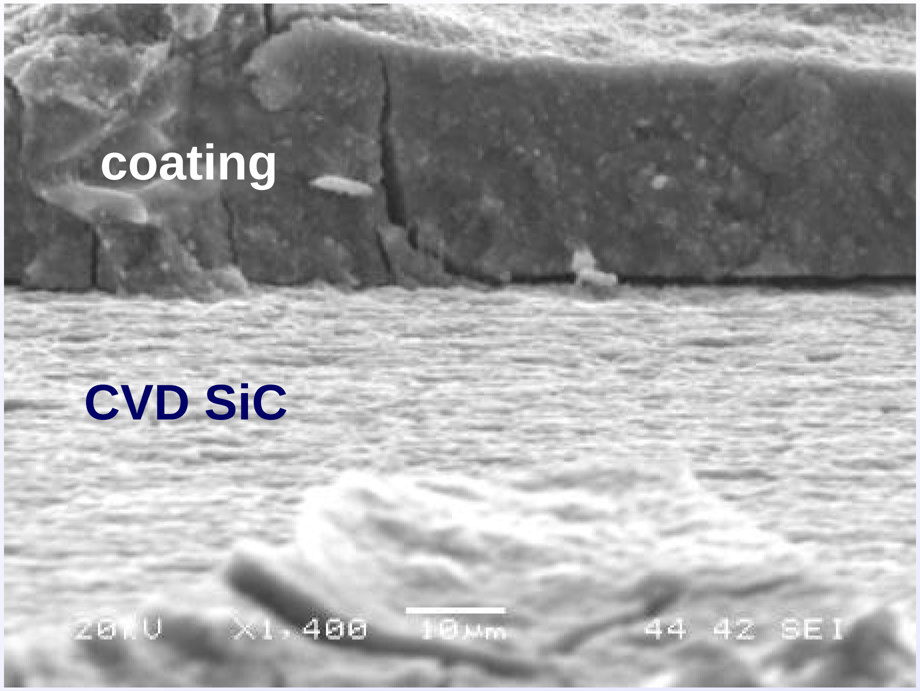




- ***"Base coating" = aHPCs + submicron SiC powder***
- ***Geomimetic powder added to improve oxidation resistance***
- ***Coating applied by hand on alumina substrate***

Composite coatings





- ***"Base coating" = aHPCs + submicron SiC powder***
- ***Geomimetic powder added to improve oxidation resistance***
- ***Coating applied by hand on CVD SiC substrate***

Summary

- The introduction of ceramic materials in gas turbine hot section components is limited by environmental degradation.
- Methods for obtaining EBCs with low silica activity – polymer pyrolysis and geomimetic coatings - appear promising.
- Ceramatec, and its collaborators, have identified tasks required for additional coating development.
- Ceramatec has resources to develop new coatings materials and processing methods.

Supplemental information

Ceramatec Capabilities

Ceramatec facilities: processing

- Powder Processing: Ball Mills, Attrition Mills, Rolling Mills
- Consolidation/Forming: Hot press, isostatic press, production tape caster, laboratory tape caster, laser cutter
- Variety of high-T furnaces with and without environmental control

Ceramatec facilities: testing and characterization

X-ray Diffraction

TGA/DTA

SEM/EDS

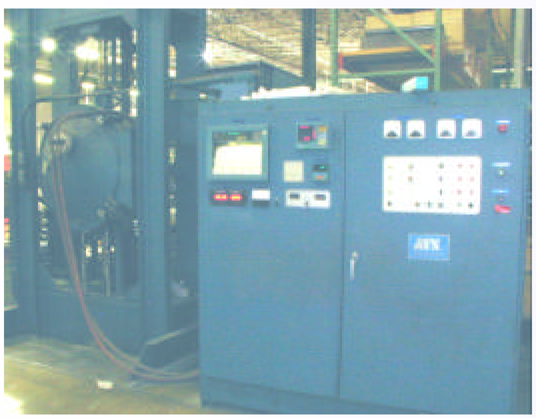
Dilatometry

Mechanical Testing

Surface Area Analysis

Ceramatec processing capabilities

Proven scale-up of viable manufacturing process at Ceramatec, Inc.:
Flexible Microchannel Designs and Processes.



Fabrication Method

Tape Cast
(Solvent Based)

Features/Slots
(Laser Cut)

Lamination
(Heat/Pressure/Solvent)

Sinter

Key business alliances

- Air Products and Chemicals
  - Oxygen generation and purification
  - Partial oxidation chemical synthesis
- McDermott Int. (SOFCo)
  - Small SOFC's for POU applications
  - Large SOFC's for low cost power generation.
- Alltrista (Microlin)
  - Controlled, "micro release" technologies
  - Batteries

Current R&D Partners

- Sandia National Laboratory
- Pacific Northwest National Laboratory (PNNL)
- Idaho National Engineering Laboratory (INEEL)
- University of Utah
- University of Florida
- University of Wisconsin-Madison
- New Mexico Institute of Technology
- University of Nevada-Reno
- Washington University at St. Louis
- Tulane University
- The Pennsylvania State University
- Colorado School of Mines