Development and Property Evaluation of Selected HfO_2-Silicon and Rare Earth-Silicon Based Bond Coats and Environmental Barrier Coating Systems for SiC/SiC Ceramic Matrix Composites

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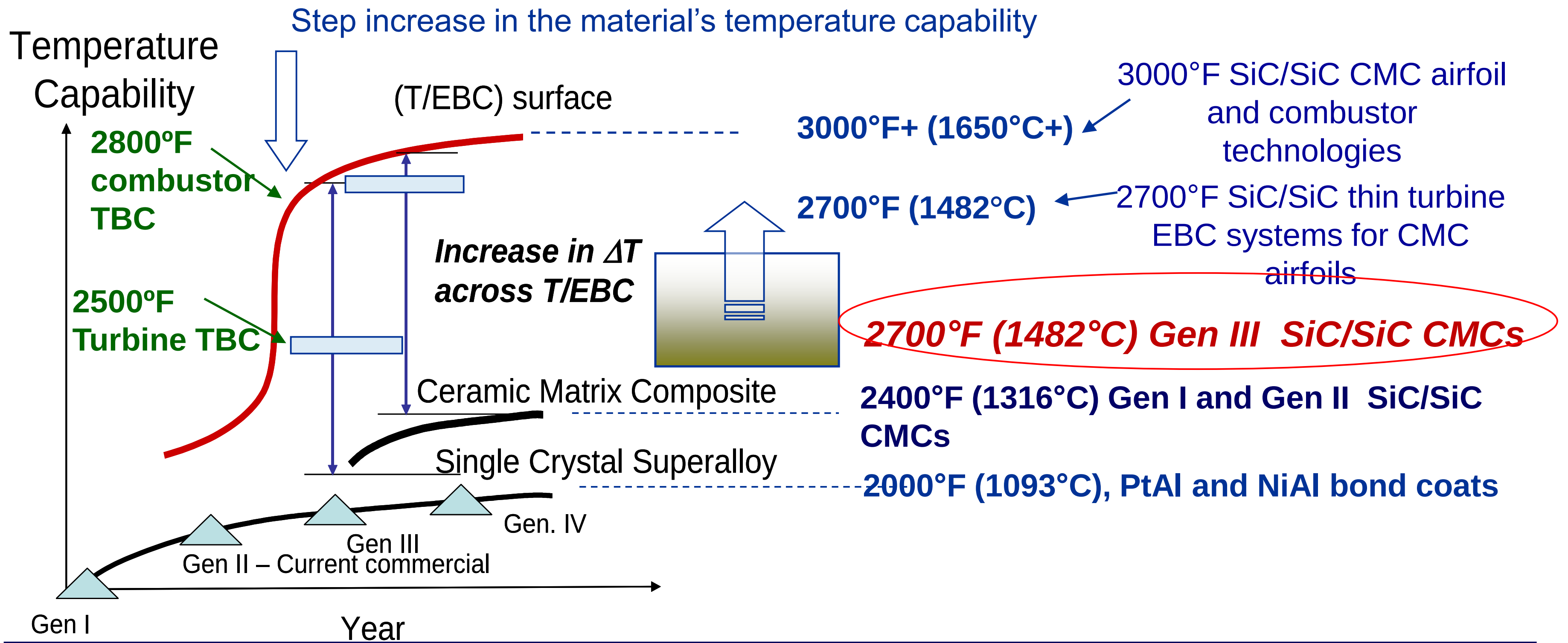
NASA EBC and CMC System Development

- **Emphasize temperature capability, performance and *long-term* durability**
  - Highly loaded EBC-CMCs
  - 2700-3000°F (1482-1650°C) turbine and CMC combustor coatings
  - 2700°F (1482°C) EBC bond coat technology for supporting next generation
    - Recession: <5 mg/cm^2 per 1000 h
    - Coating and component strength requirements: 15-30 ksi, or 100- 207 MPa



Outline

- **Environmental barrier coating (EBC) system development: needs and challenges**

- **Advanced bond coat development approaches, NASA HfO_2-Si bond coat systems**
  - Focused on oxidation resistance, high temperature strength, toughness and creep properties

- **Advanced Rare Earth – Silicon based 2700°F+ capable bond coat developments**

– Development approaches

– Oxidation resistance

– Furnace and thermomecahnical durability

- **Summary**

NASA EBC and CMC System Development

– Current EBCs limited in their temperature capability, water vapor stability and long-term durability, especially for advanced high pressure, high bypass turbine engines

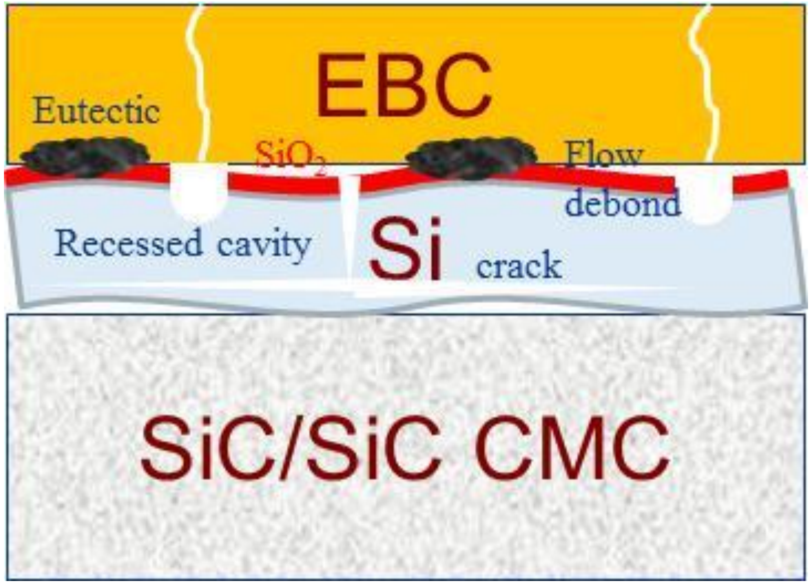
– Advanced EBCs also require high strength and toughness
  - Resistance to heat-flux, high pressure combustion environment, creep-fatigue loading interactions
  - Bond coat cyclic oxidation resistance

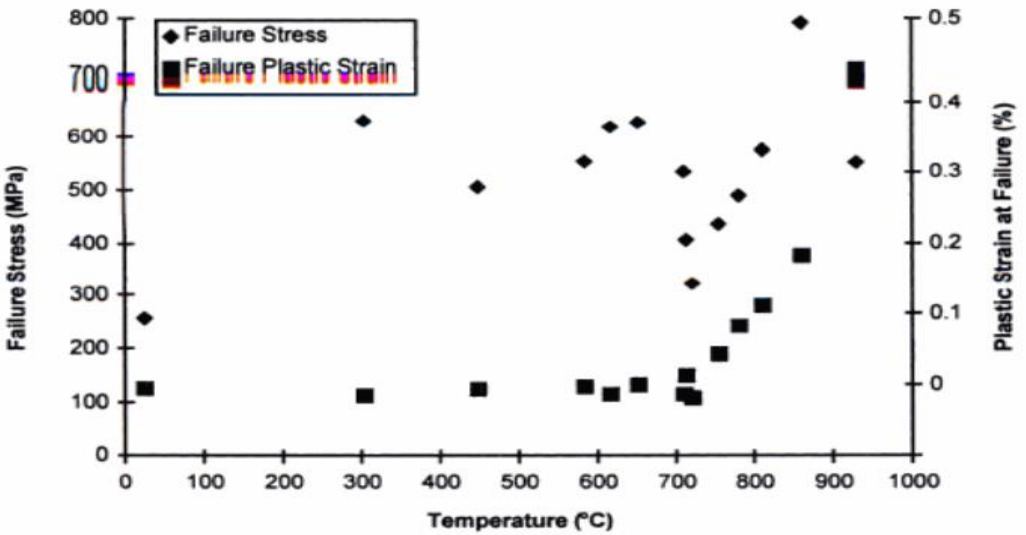
– EBCs need improved erosion, impact and calcium-magnesium-alumino-silicate (CMAS) resistance and interface stability
  - Critical to reduce the EBC system Si/SiO_2 reactivity and their concentration tolerance

– EBC-CMC systems need advanced and affordable processing
  - Using existing infrastructure and alternative coating production processing systems, including Plasma Spray, EB-PVD and Directed Vapor EB-PVD, and/or emerging Plasma Spray - Physical Vapor Deposition
  - Affordable and safe, suitable for various engine components

Degradation Mechanisms for Si Bond Coat

- Silicon bond coat melts at 1410°C (melting point)
- Fast oxidation rates (forming SiO_2) and high volatility at high temperature
- Low toughness at room temperature (0.8-0.9 MPa $m^{1/2}$; Brittle to Ductile Transition Temperature about 750°C)
- Low strength and high creep rates at high temperatures, leading to coating delamination
- Interface reactions leading to low melting phases
  - A more significant issue when sand deposit Calcium- Magnesium –Alumino-Siliacte (CMAS) is present
- Si and SiO_2 volatility at high temperature (with and without moisture)





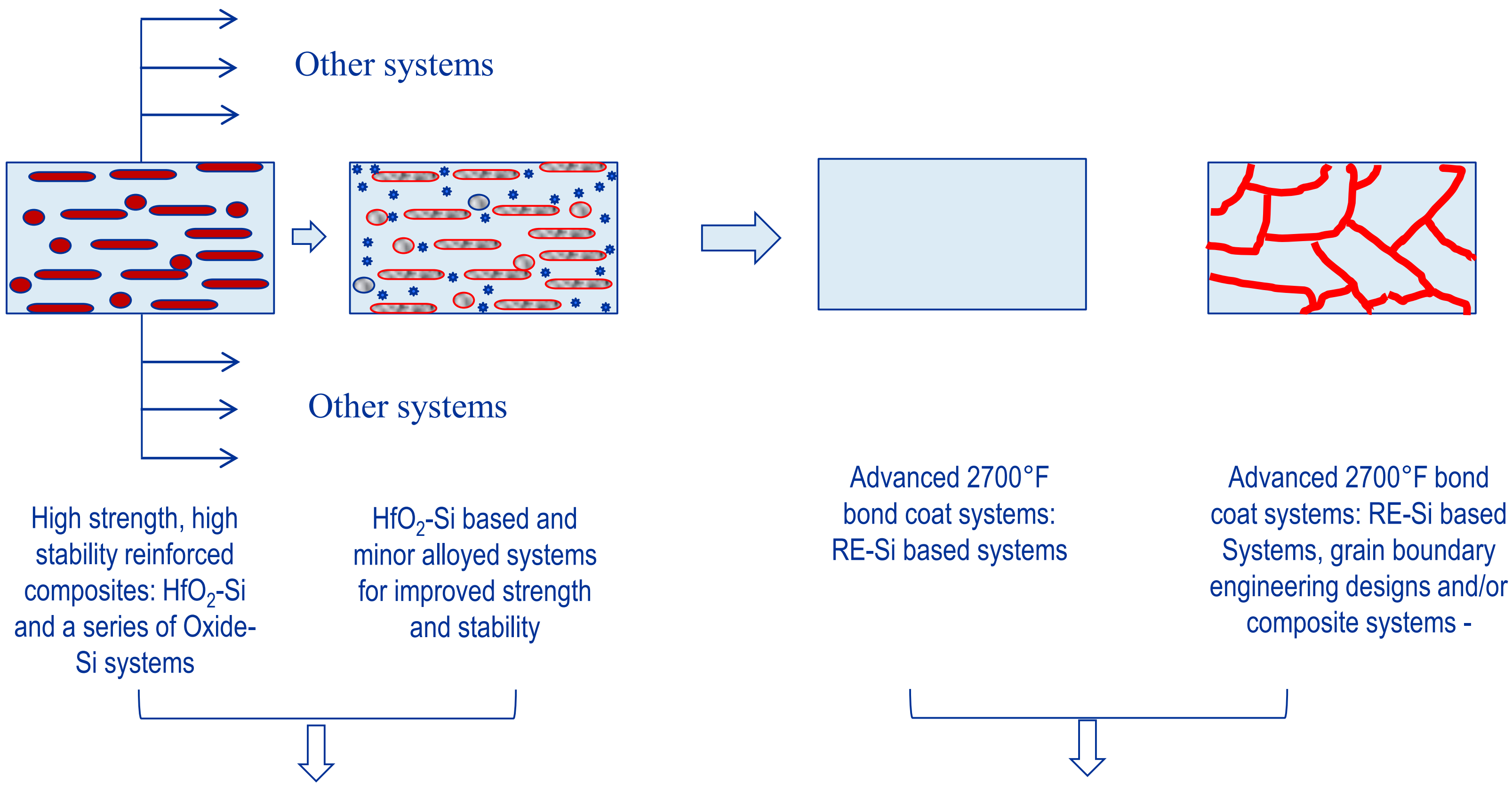
Brittle to Ductile transition in polycrystalline Si

Design Requirements for 2700°F Bond Coat Systems

- High melting point and thermal stability
- Develop slow growing, adherent protective scales
  - High strength and low thermal expansion coefficient scales, and minimum element depletion in the bond coat due to the scale formation essential
- Provide oxidation and environment protection for SiC/SiC CMC substrate
  - Oxidation resistance in all operating temperature range, up to 1600°C, no pesting
- High creep strength and excellent fatigue resistance
  - High resistance to impact, erosion, and CMAS, and environment induced degradations
- Excellent bond strengths (important to provide strong bond for the EBC to the substrate!)
- Thermal expansion coefficient matching to the CMC substrate
- Thermal chemical and thermal mechanical compatibility with EBC and CMC
- Improved bond coat – CMC interface architecture and integration
- Ensure low oxygen activity at the bond coat – CMC interfaces
  - Preferably kinetics controlled and dynamic bond coat systems for durability

Advanced High Temperature and 2700°F+ Bond Coat Development

– Development approach:
- Advanced compositions ensuring high strength, high stability, high toughness
- Bond coat systems for prime reliant EBCs; capable of self-healing

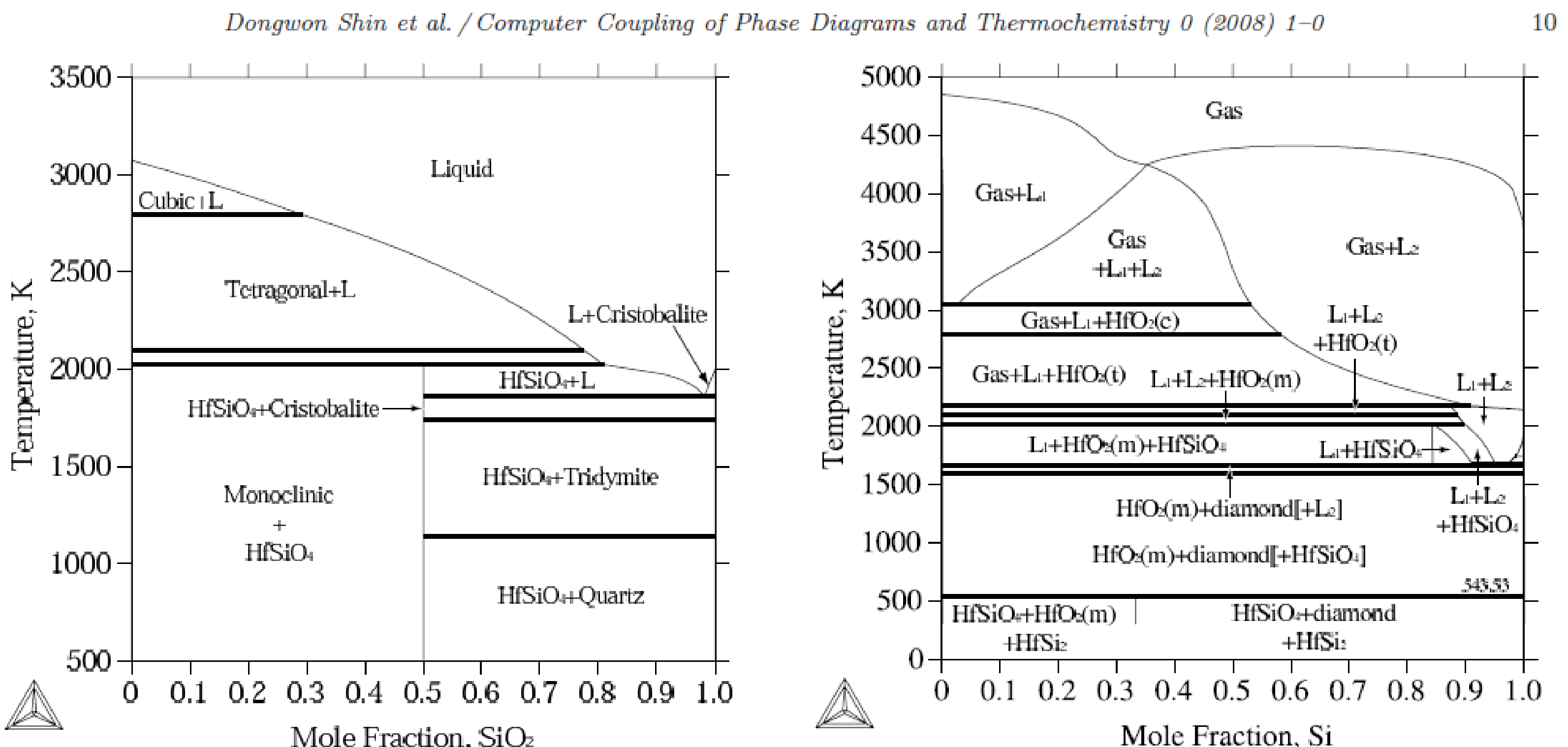


HfO_2-Si systems

Advanced 2700°F+ Bond Coat systems

HfO_2-Si Bond Coats for Improved Temperature Capability, and High Temperature Strength

- A relatively low cost bond coat system, APS and EB-PVD processing capable
- Excellent oxidation resistance, also ensuring low oxygen activities at the EBC-CMC interface
- Upper use temperature 1400°C and can be up to 1482°C
- SiO_2-$HfSiO_4$-HfO_2 phase system at very high temperature
- Thermal expansion coefficient ~ 5.5 $\times 10^{-6}$ /K
- Rare earth metal or other dopants added for improved stability



Hf-Si-O system

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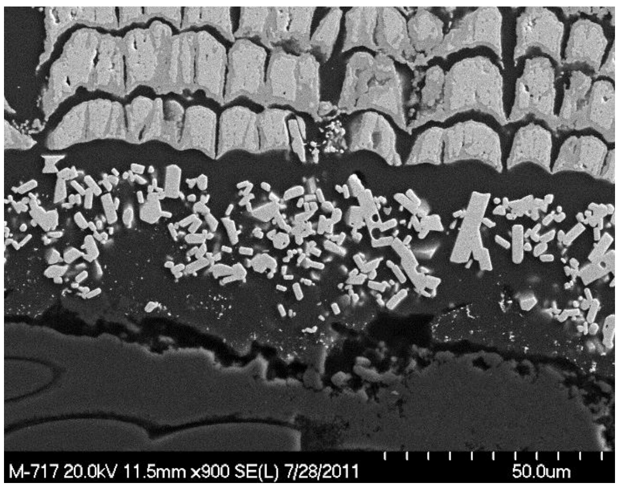
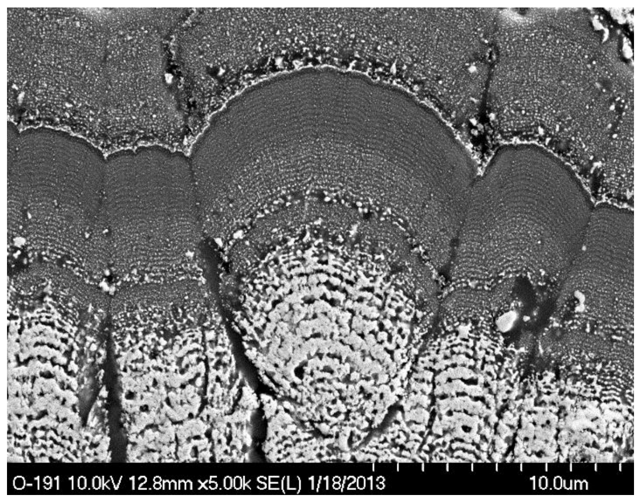
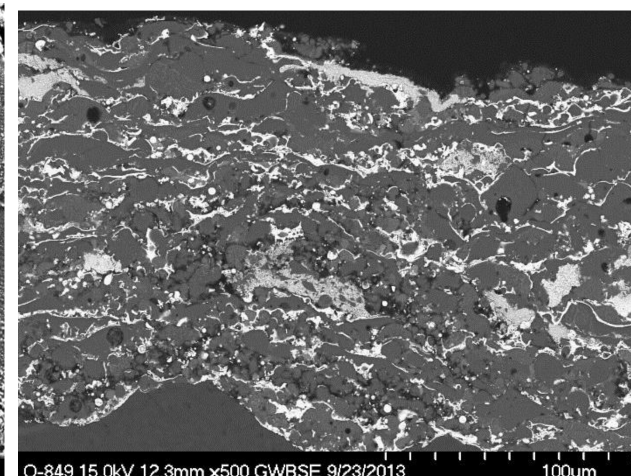






HfO_2-Si and alloyed EBC bond coats using EB-PVD processing: achieving higher temperature capability

Plasma sprayed HfO_2-Si EBC bond coat

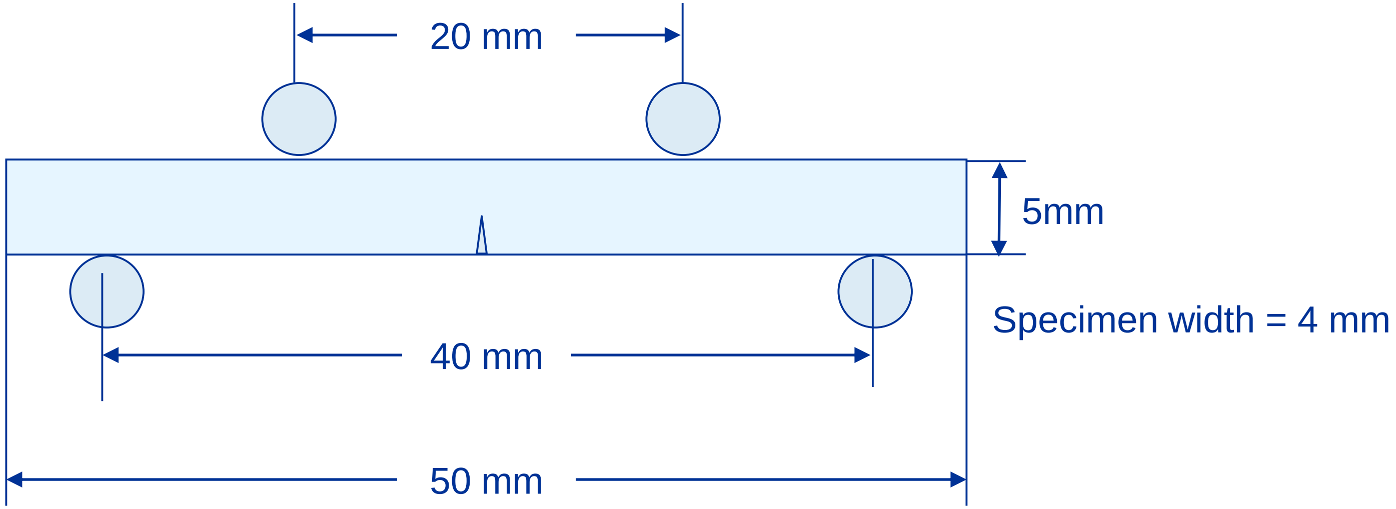
Experimental: Mechanical Specimen Configurations

— Flexural specimens with dimensions 4x5x50 mm, machined from hot-pressed air plasma spray (APS) HfO_2-Si powders (billets size 75mmx50mmx10mm); test spans 20 and 40 mm
  - Using ASTM standards 1161 and 1211
  - Si concentration range from 25 to 70wt% in the HfO_2-Si systems

— The non-notched bar specimens used for strength, and creep testing

— Single edge V-notched beam (SEVNB) specimens used for toughness tests

— Test temperature range room temperature, 1200 up to 1500°C



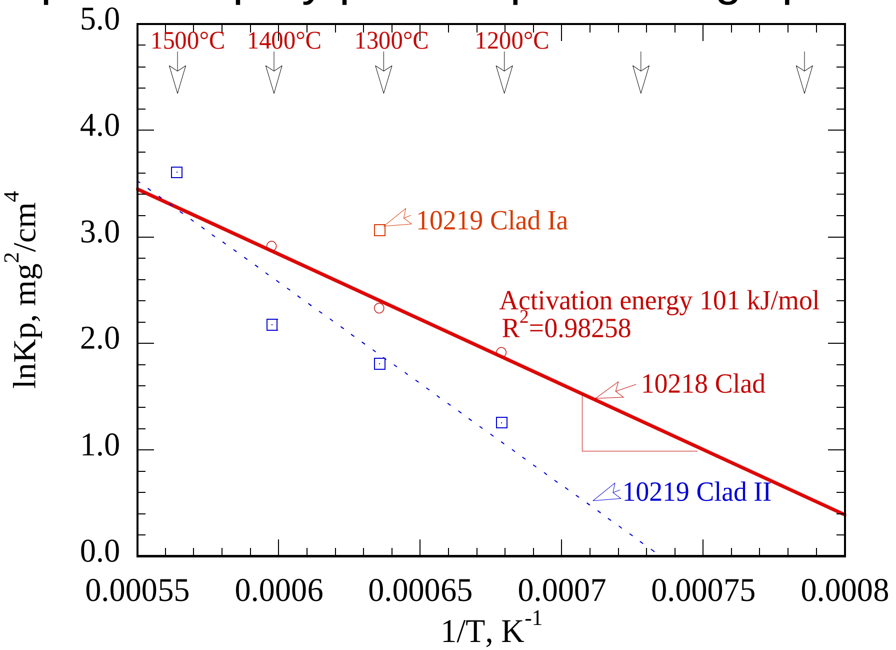
Experimental: Oxidation and Durability Tests

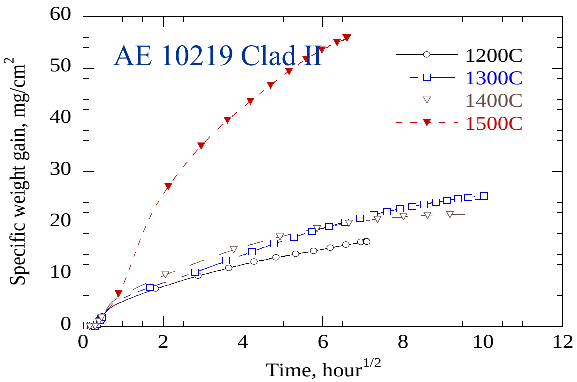
- Test specimens with dimensions 25 mm diameter disc specimens for oxidation, laser heat flux and furnace cyclic test (FCT)
- Test specimens with dimensions 152x12.7 mm dog-bone, and 76x12.7mm for tensile creep rupture and fatigue tests

- Tests were also conducted including
  - Thermogravimetric analysis (TGA)
  - FCT test
  - Laser + steam/CMAS water vapor cyclic test
  - Thermomechanical creep and fatigue

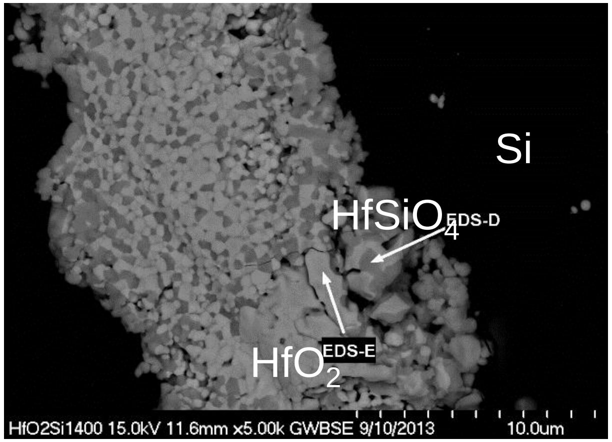
Oxidation Resistance of HfO_2-Si

- TGA weight change measurements in flowing O_2
- Parabolic oxidation kinetics generally observed
- Solid-state reaction is also involved with the systems, and more complex behavior at 1400 and 1500°C
- Excellent oxidation resistance and improved oxidation resistance through APS plasma spray powder processing optimization





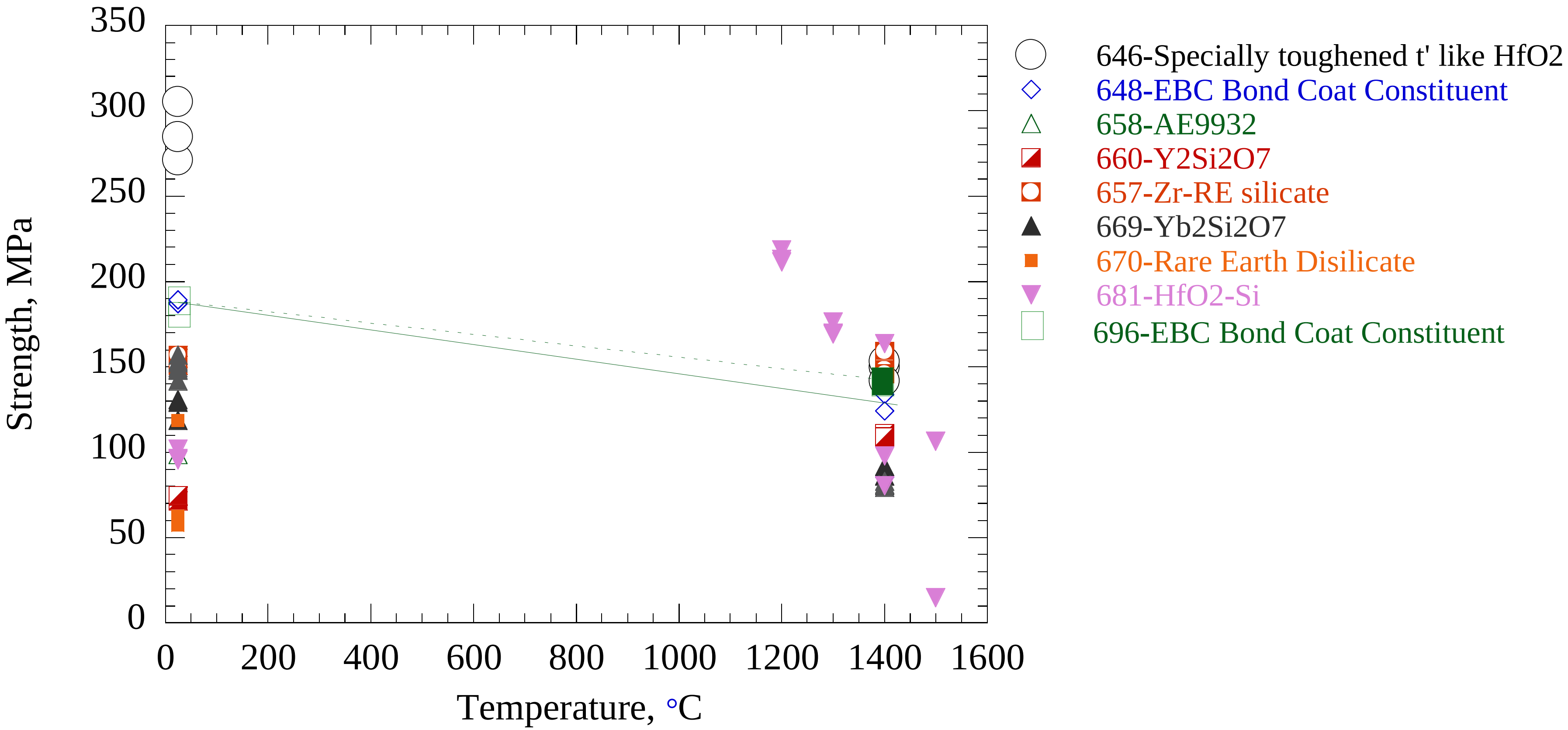
- TGA weight change measurements at various temperatures
- AE 10219 is first Generation HfO_2-30wt%Si composite APS powders used in NASA ERA liner component demonstrations
- AE 10218 is HfO_2-30wt%Si composite APS powders used in NASA ERA liner component demonstrations.
- AE 10219 Clad II is second Generation HfO_2-30wt%Si composite APS powders



Polished specimen microstructure after 1400°C test

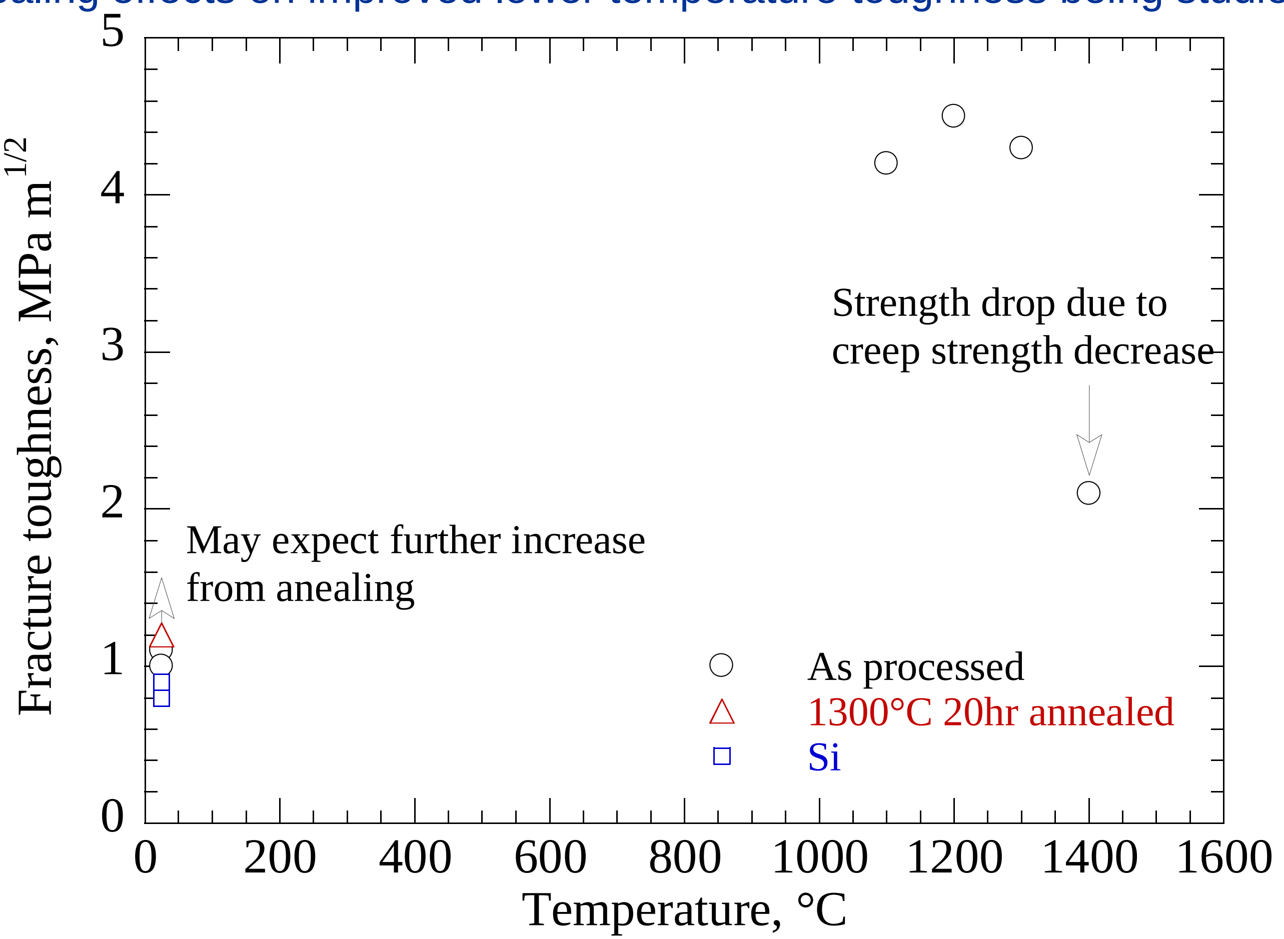
High Strength EBC and Bond Coat Composition Development

- Bond coats and bond coat constituents designed with high strength to achieve the ultimate coating durability, compared with EBCs' strengths
- HfO_2-Si based systems showed high strength and high toughness



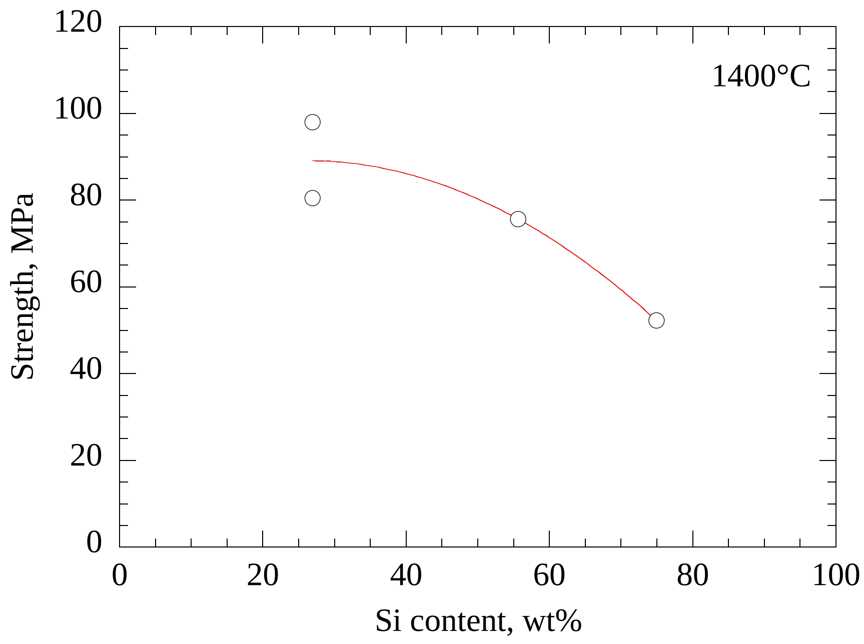
High Toughness HfO_2-Si Bond Coat Composition Development

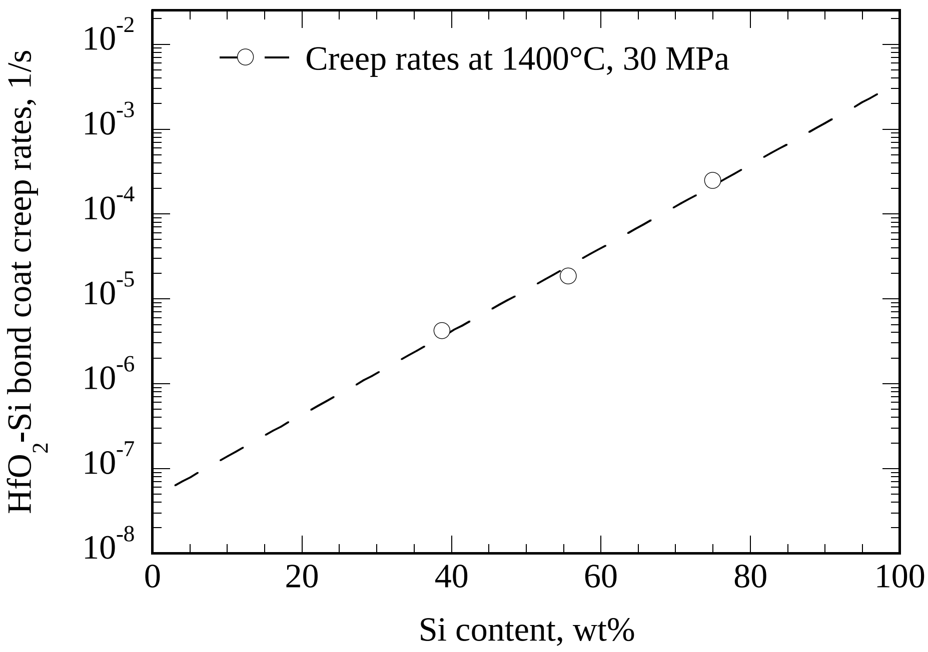
– HfO_2-Si Bond coats showed high toughness
  - Toughness >4-5 MPa $m^{1/2}$ achieved
  - Emphasis on improving the lower temperature toughness
  - Annealing effects on improved lower temperature toughness being studied



Effects of Compositions on HfO_2-Si Strength and Creep Rates

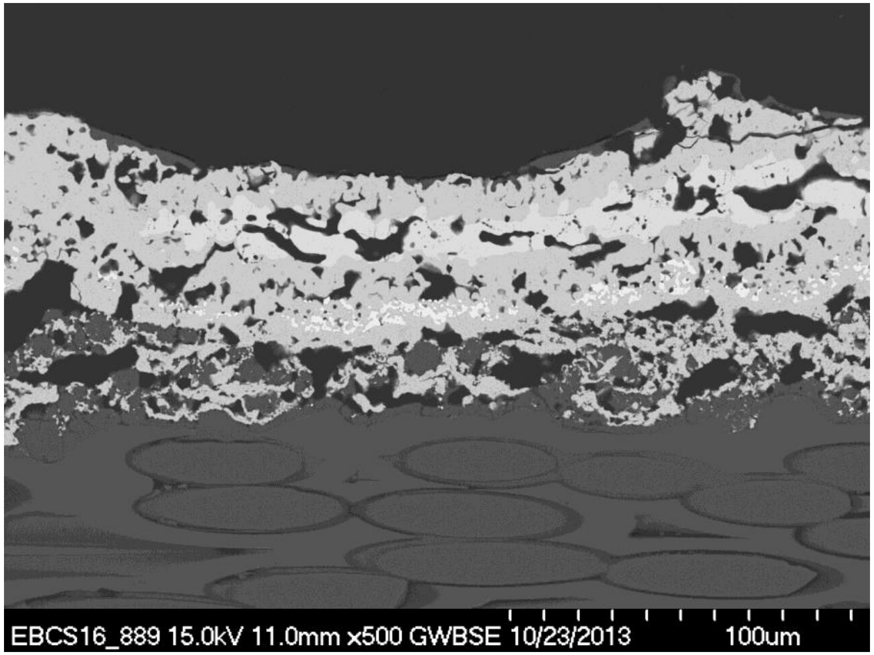
- The composites coatings have improved creep strength, and creep resistance at high temperatures
- *Increased HfO_2-$HfSiO_4$ contents improve high temperature strength and creep resistance*

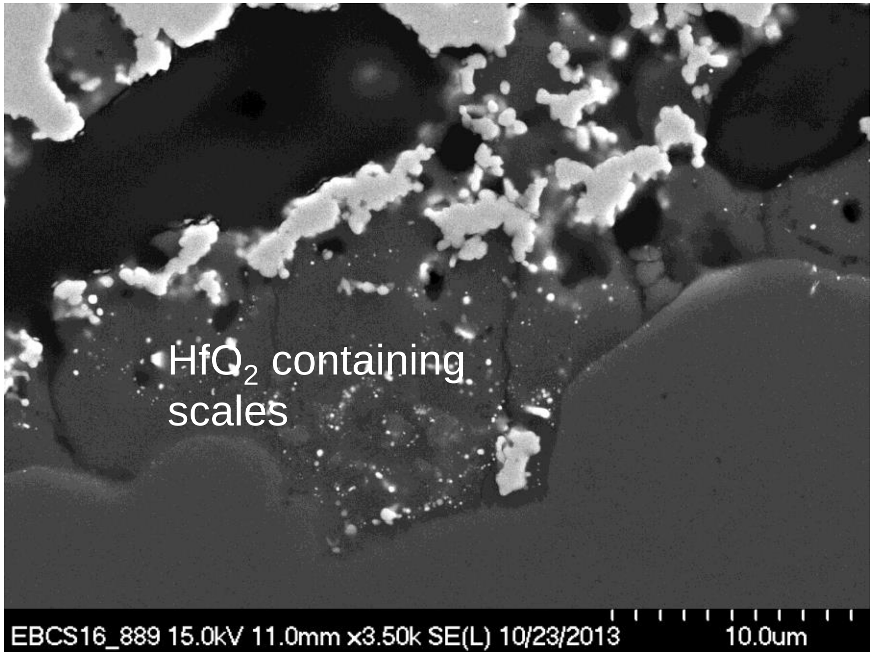




HfO_2-Si/Ytterbium Silicate EBC System Furnace Cyclic Durability Test at 1500°C

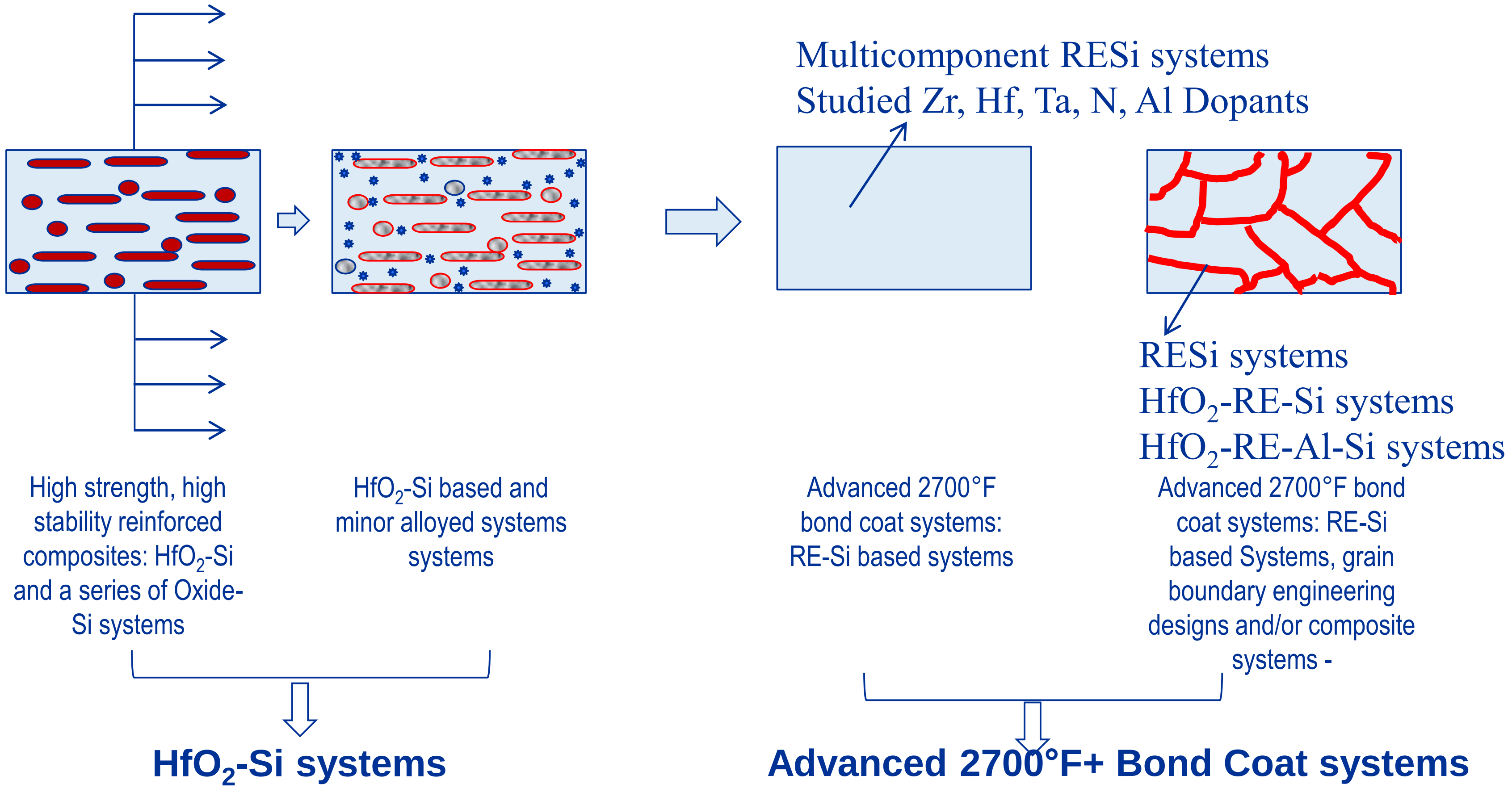
- Coating processed using Triplex Pro plasma spray processing, not necessarily fully optimized
- Long-term furnace cyclic durability tested 1500°C for 500 hr in air
- EBC with HfO_2-Si bond coat adherent (no any spallation) after testing
- Excellent oxidation resistance in protecting SiC/SiC
- SiO_2 loss in ytterbium silicate EBC (some area became ytterbia), and in the HfO_2-Si bond coat
- Some HfO_2 containing scales may be stable





Advanced 2700°F+ Bond Coats (Beyond HfO_2-Si)

– Development approach:
- Advanced compositions ensuring high strength, high stability, high toughness
- Bond coat systems for prime reliant EBCs; capable of self-healing



2700°F+ Advanced EBC Bond Coat Developments: Rare Earth Silicon Systems and Effect of Dopants

– Ytterbium, Yttrium and Gadolinium – Silicon or Silicide systems

- **Controlled silicon compositions and oxygen activities** to achieve good thermal expansion match with SiC/SiC CMCs and EBCs, and high melting points and stability
- **Focusing on multicomponent high temperature based systems** to ensure high temperature capability, oxidation resistance and durability
- **Emphasizing chemically and mechanically compatibility** with SiC/SiC CMCs and various environmental barrier coatings, *no free-standing silicon phases in composition designs*
- **Low temperature oxidation resistance and pesting issues** are also addressed in the developments

NASA Advanced 2700°F Silicide Based Bond Coats – System Processing for Various Component Applications

- Advanced systems developed and processed to improve Technology Readiness Levels (TRL)
- Composition ranges studied mostly from 50 – 80 atomic% silicon
  - PVD-CVD processing, for composition downselects - also helping potentially develop a low cost CVD or laser CVD approach
  - Compositions initially downselected for selected EB-PVD and APS coating composition processing
  - Viable EB-PVD and APS systems downselected and tested; development new PVD-CVD approaches

PVD-CVD

YSi	YbGdYSi	GdYSi
ZrSi+Y	YbGdYSi	GdYSi
ZrSi+Y	YbGdYSi	GdYSi
ZrSi+Ta	YbGdYSi	GdYSi
ZrSi+Ta	YbGdSi	GdYSi-X
HfSi + Si	YbGdSi	GdYSi-X
HfSi + YSi	YbGdSi	
HfSi+Ysi+Si	YbGdSi	
YbSi	YbGdSi	
	YbSi	
HfSi + YbSi		
GdYbSi(Hf)		
YYbGdSi(Hf)	YbYSi	
	YbHfSi	
	YbHfSi	
	YbHfSi	
	YbHfSi	
	YbHfSi	
	YbSi	

Process and composition transitions

EB-PVD

HfO2-Si;
REHfSi
GdYSi
GdYbSi
GdYb-LuSi
NdYSi

APS*

HfO2-Si YSi+RESilicate	
YSi+Hf-RESilicate	
Hf-RESilicate	Used in ERA components as part of bond coat system
Hf-RE-Al-Silicate	Used also in ERA components Used in ERA components as part of bond coat system

FurnaceLaser/CVD/PVD

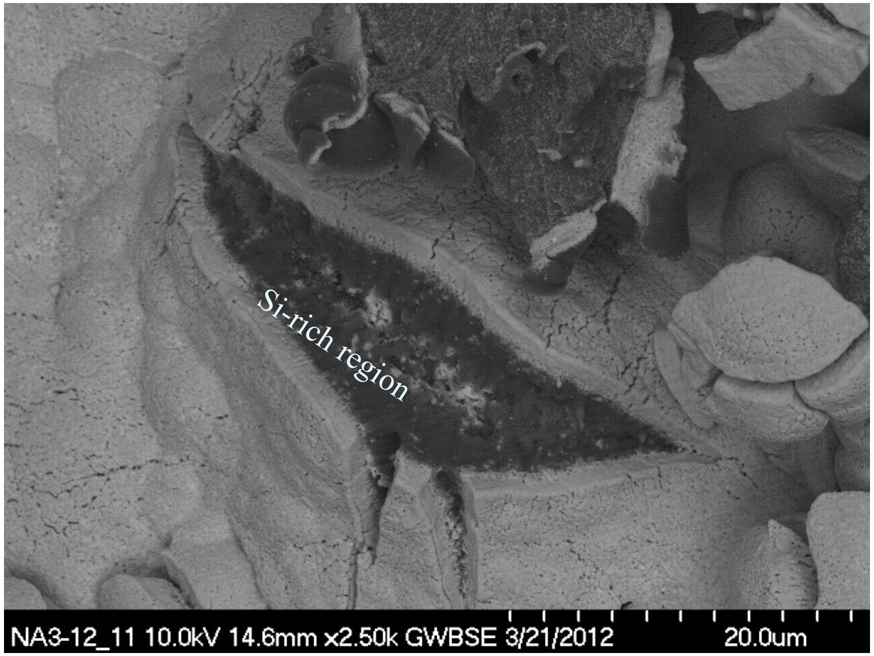
REHfSi

APS*: or plasma spray related processing methods

US Patent Application S/N: 13/923,450 (LEW 18949-1), US Provisional Patent Serial No.: 62/329,500 (LEW 18949-1), LEW 19435-1

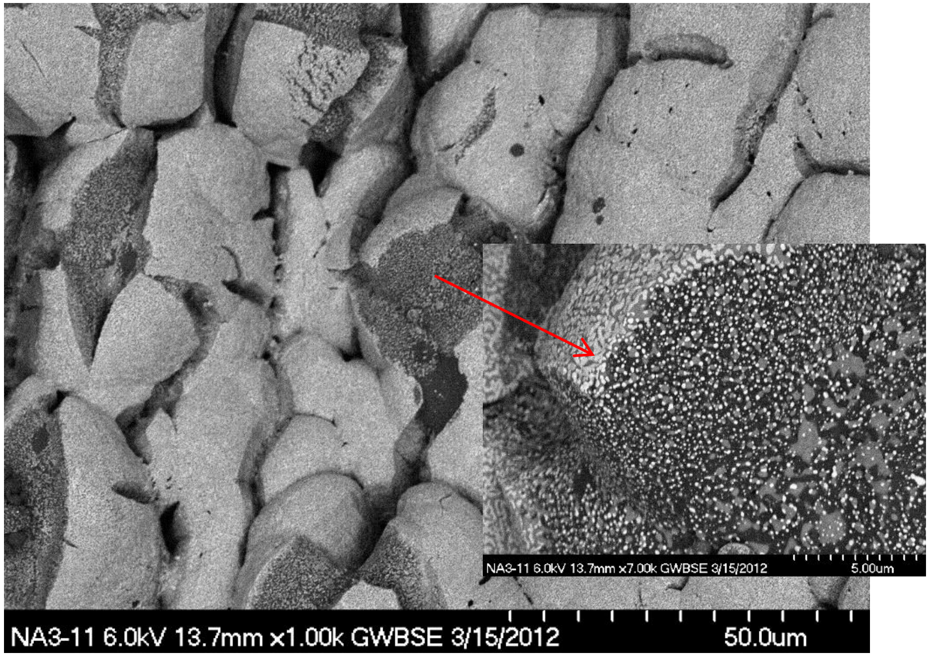
Rare Earth Silicon Systems and Multi-Dopants for Stability

- Silicon-rich phase separations can limit high temperature stability
- Further thermal stability and mechanical strength can be improved by:
  - Composition controls (e.g. optimize silicon contents and addition of dopants)
  - Multi-dopant composition designs for reduced Si/SiO_2 activity



$YbSi_x$ (no additional dopant)
Exposed to 1100°C for 20 h

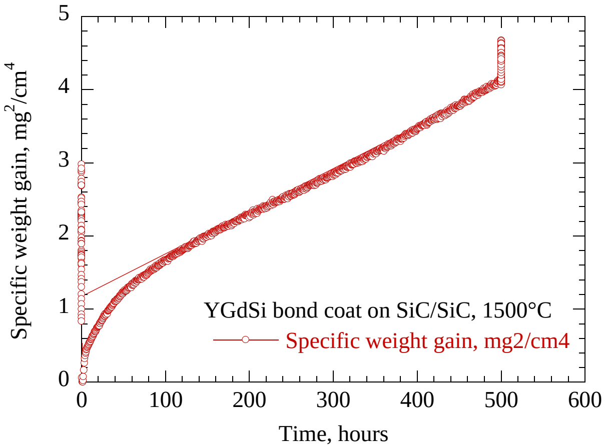
Undoped material: shows separation of Si-rich/silica-rich phase



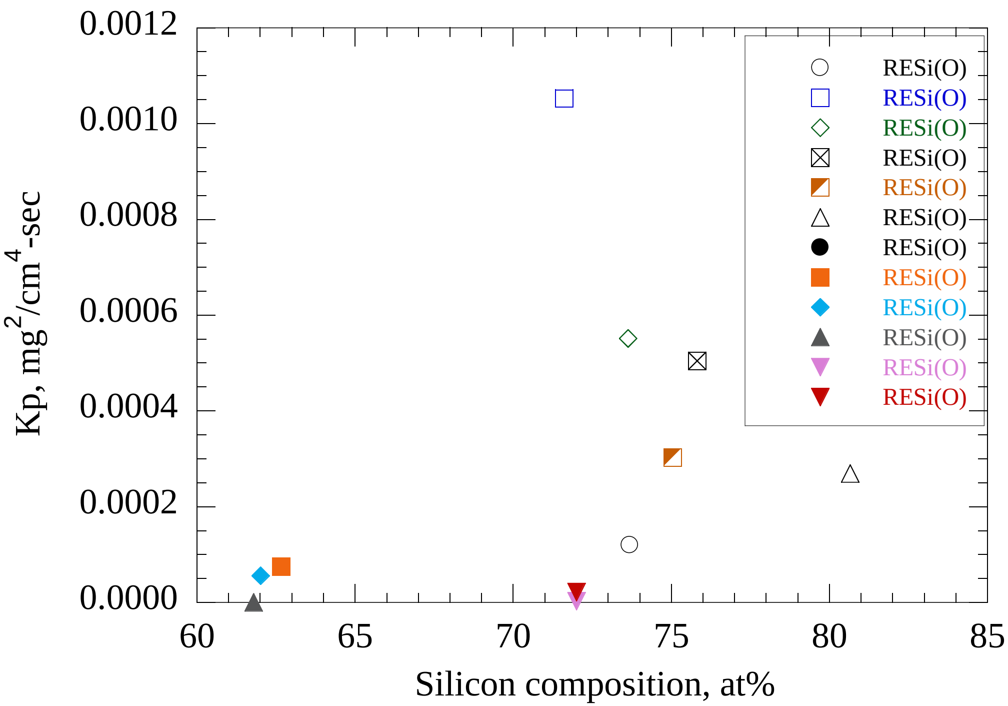
$(Y,Hf)Si_x$
1100°C for 20 h
When dopant included: The Si-rich/silica-rich phases converted to more stable HfO_2 - Hafnium silicate, and yttrium silicate containing phases

Advanced Bond Coats for Turbine EBCs – Oxidation Resistance

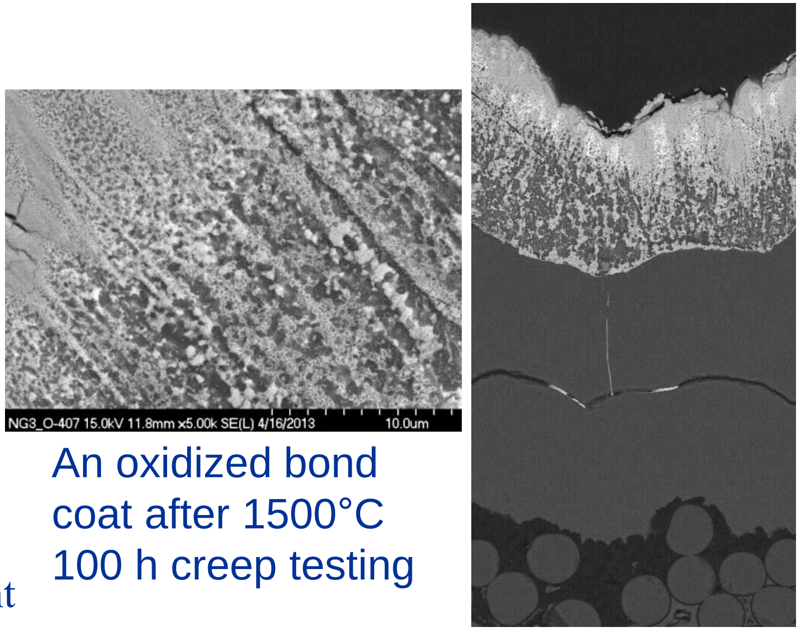
- 1500°C (2732°F) capable RESiO+X series EBC bond coat compositions and related composite coatings developed for combustor and turbine airfoil applications
- Oxidation kinetics studied using TGA in flowing O_2
- Parabolic or pseudo-parabolic oxidation behavior observed



Oxidation kinetics of a YbGdSi(O) bond coat



Parabolic rate constant Kp as a function of silicon content

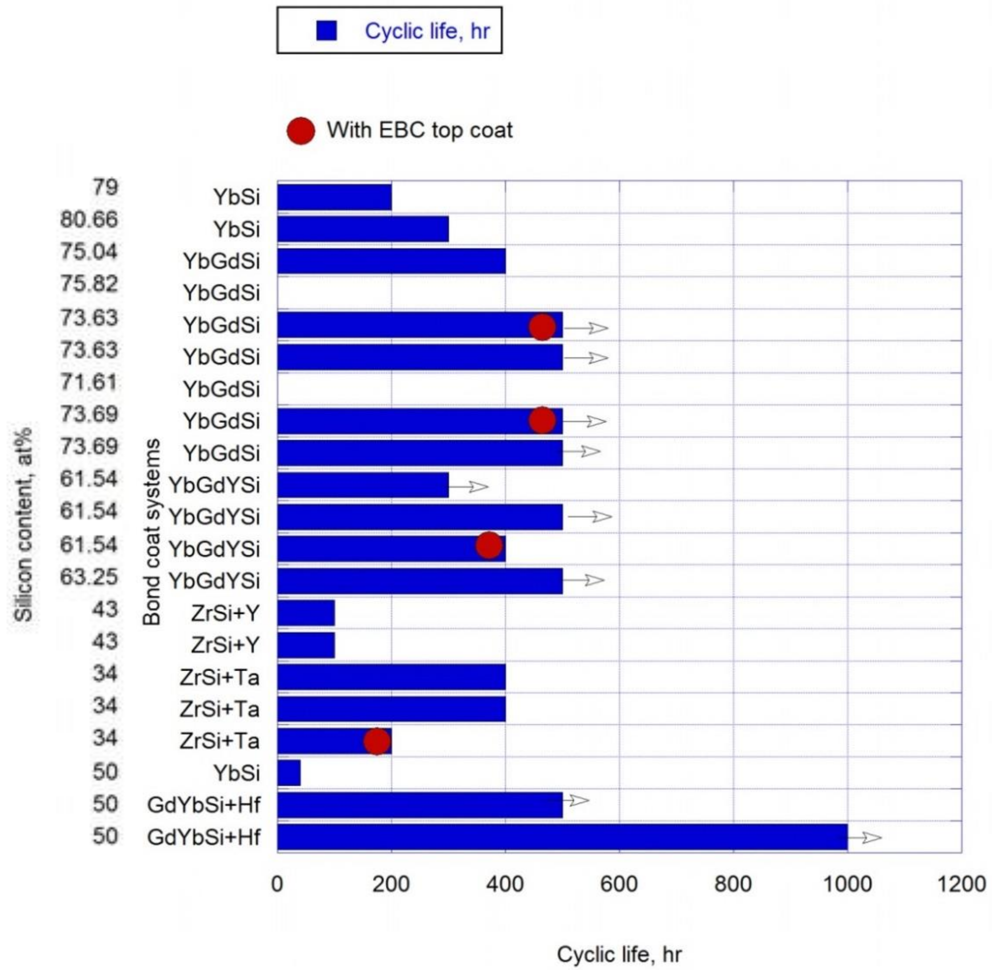


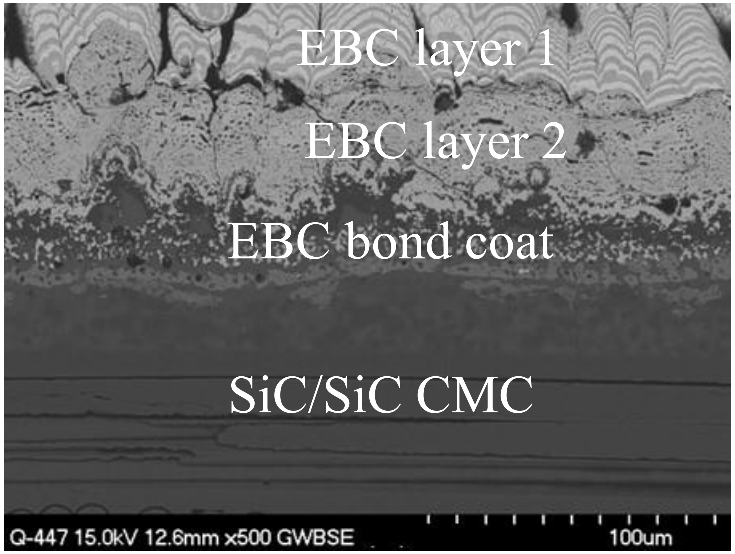
An oxidized bond coat after 1500°C 100 h creep testing

Furnace Cycle Test Results of Selected RESi and ZrSi + Dopant Bond Coats

- Testing in Air at 1500°C, 1 hr cycles

– Multi-component systems showed excellent furnace cyclic durability at 1500°C

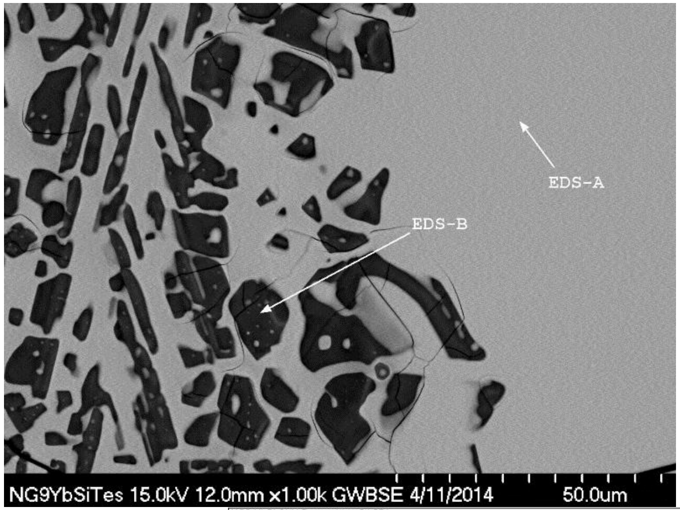


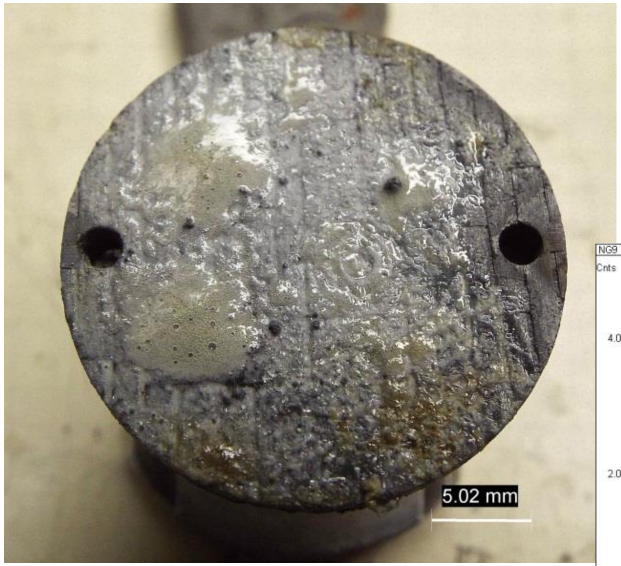


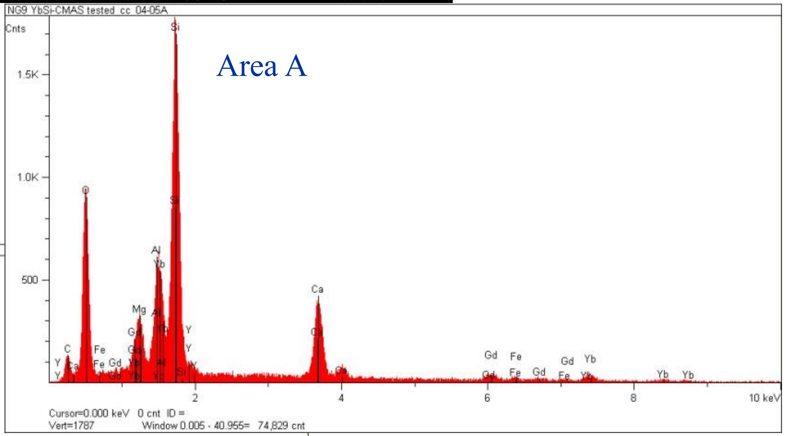
Cross-section micrograph tested at 1500°C, 300hr

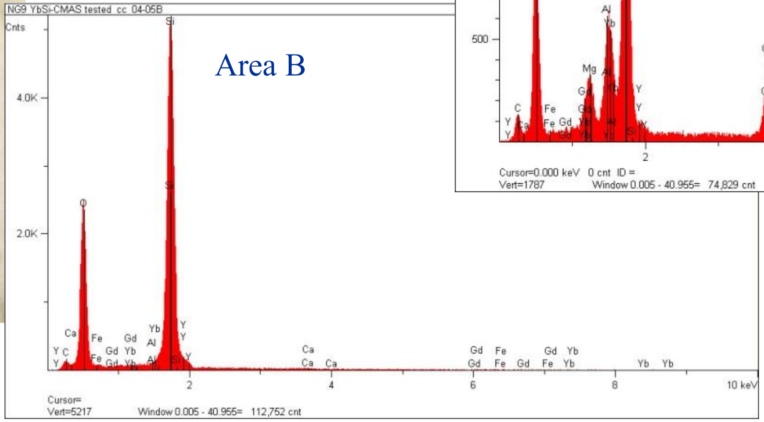
High Stability and CMAS Resistance Observed from the Rare Earth Silicon High Melting Point Coating Compositions

– Demonstrated CMAS resistance of RESi at 1500°C, 100 hr



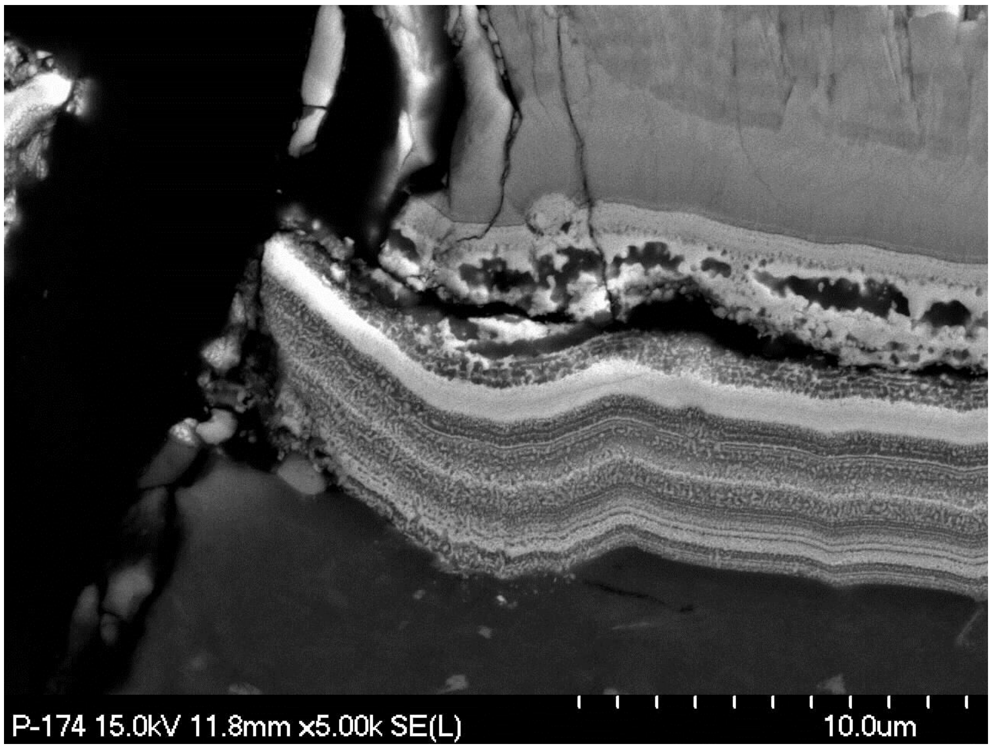






Processing Advancements and Improvements for RE Si Bond Coats in EBC Systems

- Selected EBC system processed by EB-PVD and plasma Spray: Doped RE Si (+Hf) Bond Coat + advanced multi-component EBC Top Coat on woven SiC/SiC CVI-SMI CMC
- Creep testing conducted with 15 ksi load and laser thermal gradient



RE(Hf) silicate
EBC Top Coat

RESi Composite Bond Coat System: Striations indicate EB-PVD layers with compositional variations

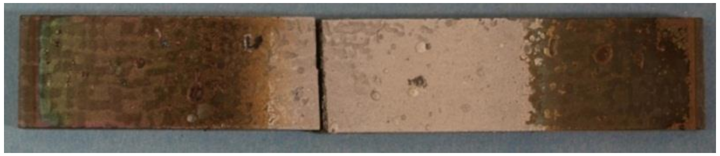
Excellent compatibility

EBC System after 100 hr creep testing with 2700°F coating surface temperature and 2500°F CMC back temperature

Bond coat remains generally well-adhered to CMC substrate after the CMC failure, except some top bond coat composition segregation or processing defective regions

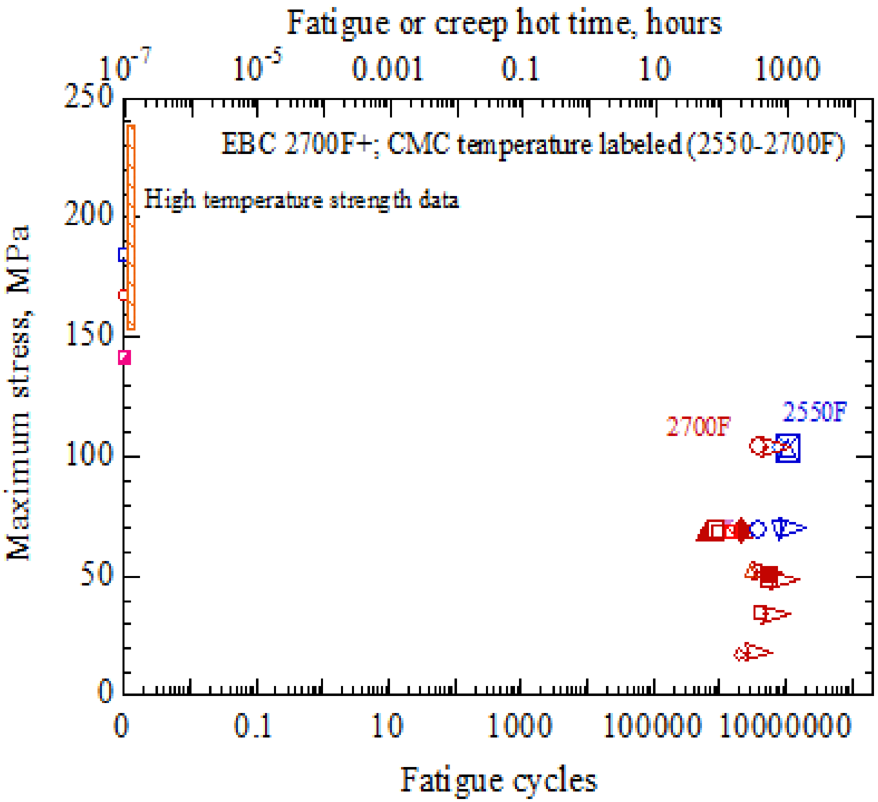
Fatigue Tests of Advanced Bond Coats and EBC Systems

- Strength and Fatigue cycles in laser heat flux rigs in tension, compression and bending
- Fatigue tests at 3 Hz, 2600-2700°F, stress ratio 0.05, surface tension-tension cycles
- Early fatigue-CMAS durability demonstrated

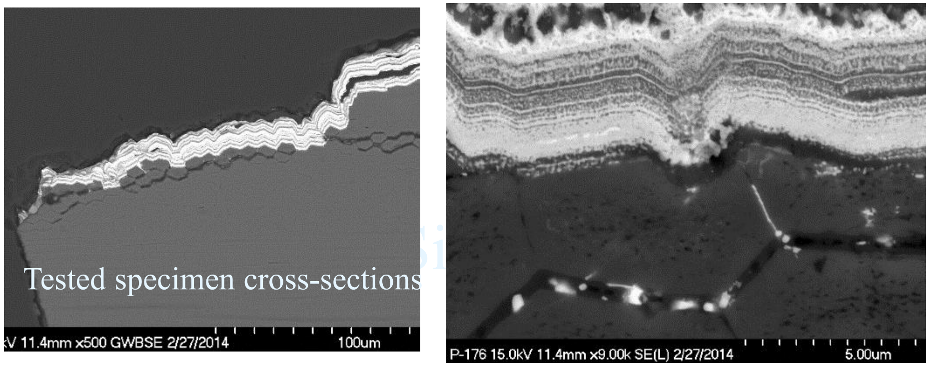

Tested, SA Tyrannohex with bond coat only


Tested, SA Tyrannohex with EBC system 188

Achieved long-term fatigue lives (near 500 hr) with EBC at 2700°F



Creep-fatigue durability test summary



Example of fatigue test EBC systems on Tyrannohex SiC composites

Summary

- Advanced HfO_2-Si and Rare Earth - Silicon based bond coat compositions developed
- The coatings showed excellent oxidation resistance and protection for CMCs
- HfO_2-Si showed excellent strength, fracture toughness, its upper use temperature may be limited to 1400°C due to higher silica activity, in particular in the CMAS environments
- The initial silicon content range of the Rare Earth-Silicon coatings was down-selected, multicomponent systems designed for further improved stability
- The rare earth – silicon based coatings showed 1500°C operating temperature viability and durability on SiC/SiC ceramic matrix composites
- The rare earth – silicon based coatings compositions will be down-selected; and further processing optimization planned

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