Microstructure Evolution and Durability of Advanced Environmental Barrier Coating Systems for SiC/SiC Ceramic Matrix Composites

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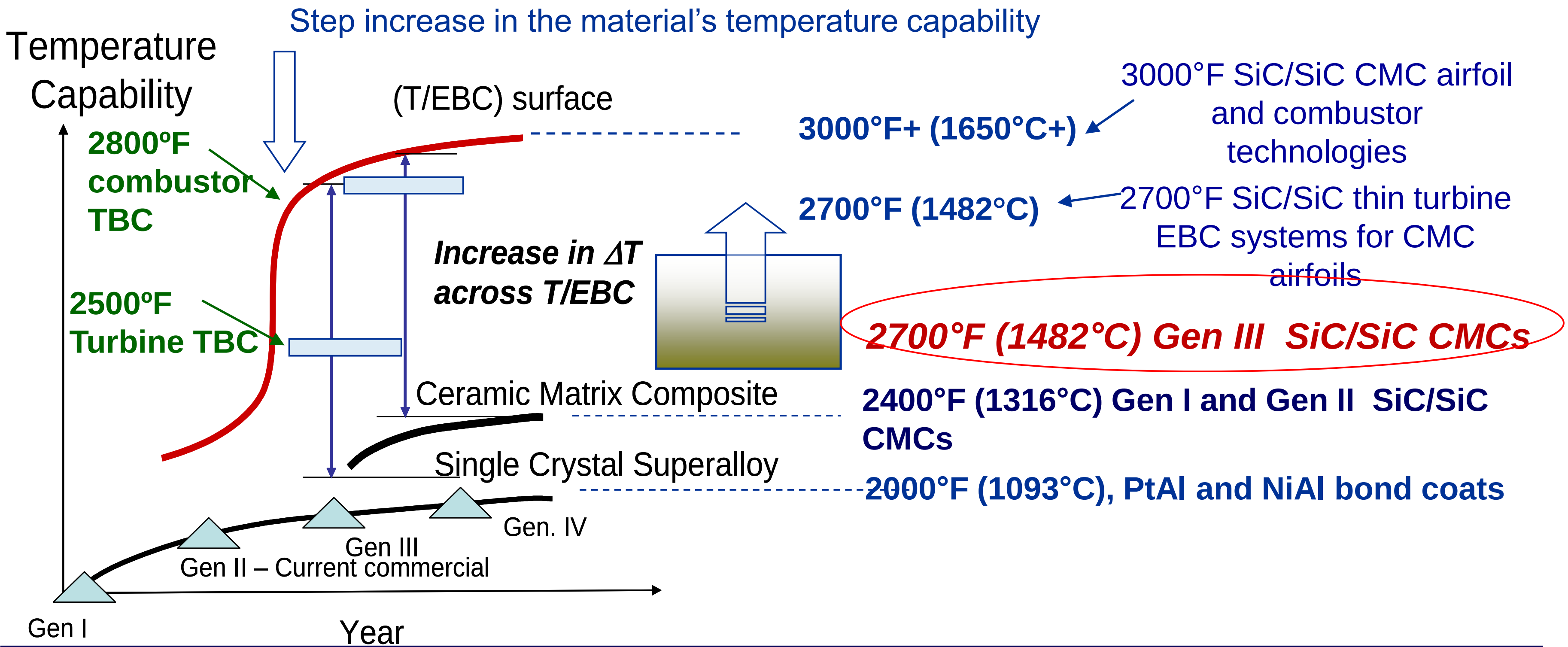
NASA EBC and CMC System Development

– **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



NASA Advanced Environmental Barrier Coating Technology Development

- **Development Objective:** Develop advanced 2700°F+ capable bond coat and EBC systems with high strength
- **Approaches:**

- Fundamental studies of environmental barrier coating materials and coating systems, stability, temperature limits and failure mechanisms
- Focus on high performance high stability patented cluster HfO_2 and ZrO_2 -RE_2O_3-SiO_2/$RE_2Si_{2-x}O_{7-2x}$ environmental barrier systems
  - Controlled silica content and transition element and rare earth dopants to improve EBC stability and toughness
  - Significantly reduce diffusion, grain growth, mechanical strength and toughness with multicomponent systems
  - Develop HfO_2-Si based + X (dopants)
  - Develop prime-reliant Rare Earth Si alloys and composites for integrated EBC-bond coat systems
- Develop advanced NASA high toughness, compositions and processing
  - Achieving high toughness and erosion resistance
  - Achieving high stability and recession resistance
  - Improving the resistance to CMAS and Volcano ash deposits

Outline

- **Advanced EBC and Rare Earth – Silicon based 2700°F+ capable bond coat developments**
  - Development approaches
  - Oxidation resistance
  - Cyclic and thermomecahnical durability

- **Microstructural and phase composition evolution of an environmental barrier coating (EBC) system**
  - Consisting of a multicomponent rare earth silicate EBC, along with YbGdSi 2700°F (1482°C) capable bond coat
  - Tested in high heat flux tensile rupture, fluxture fatigue, and furnace cyclic tests up to 500 hours at 2700°F (1482°C)
  - Examine Microstructure changes after thermomechanical and furnace cyclic testing
  - EDS - WDS Composition analysis Comparisons

- **Summary and conclusion**

Development Strategy for 2700°F EBC Systems

(US Patent Zhu and Miller, US 7740960; US Patent Application: Zhu & Hurst, LEW 18949, 2012; PCT/US13/46946, 2013)

— Modify silicon with rare earth, zirconium, hafnium dopants to increase its melting point and developing slower growing protective scales and refractory silicates
- Control oxygen content and EBC-CMC interface oxygen partial pressure for improved protection and stability

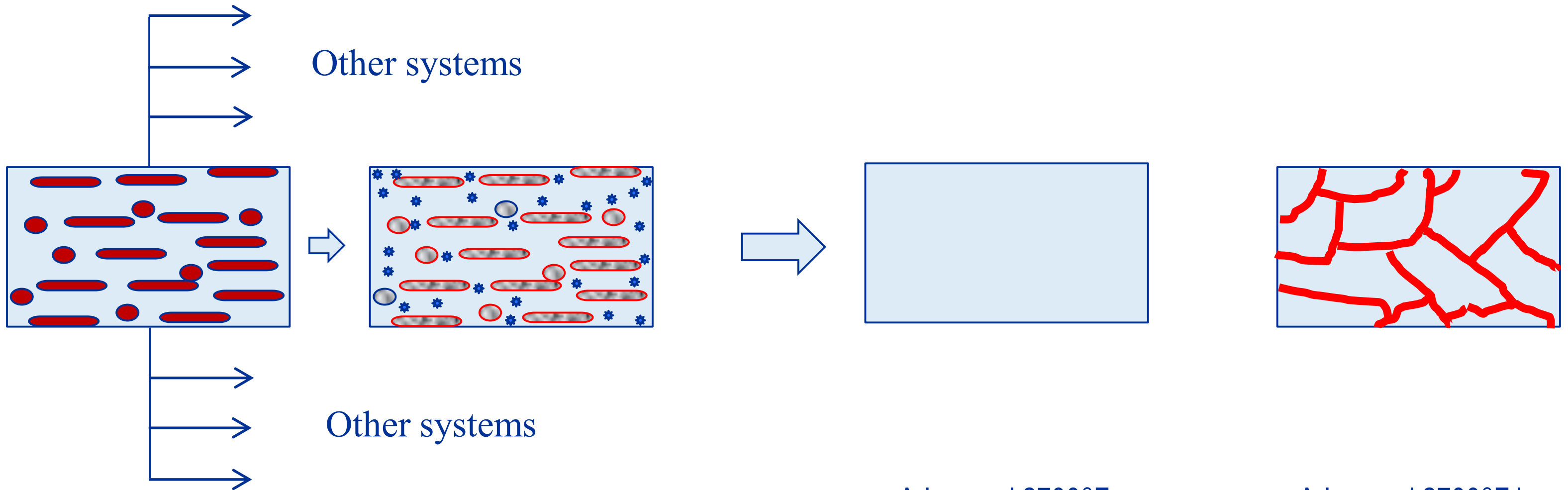
— Composite bond coat systems with refractory oxides and silicates to reinforce silicon containing bond coat matrix

— Composite bond coat systems with refractory oxide or silicate matrix, with silicon containing bond coat inter-phases

— Develop rare earth metal -, zirconium -, hafnium – silicon systems and the silicide containing systems for bond coats with engineered grain boundary phases

Advanced High Temperature and 2700°F+ Bond Coat Development

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



High strength, high stability reinforced composites: HfO_2-Si and a series of Oxide-Si systems

HfO_2-Si based and minor alloyed systems for improved strength and stability

Advanced 2700°F bond coat systems: RE-Si based systems

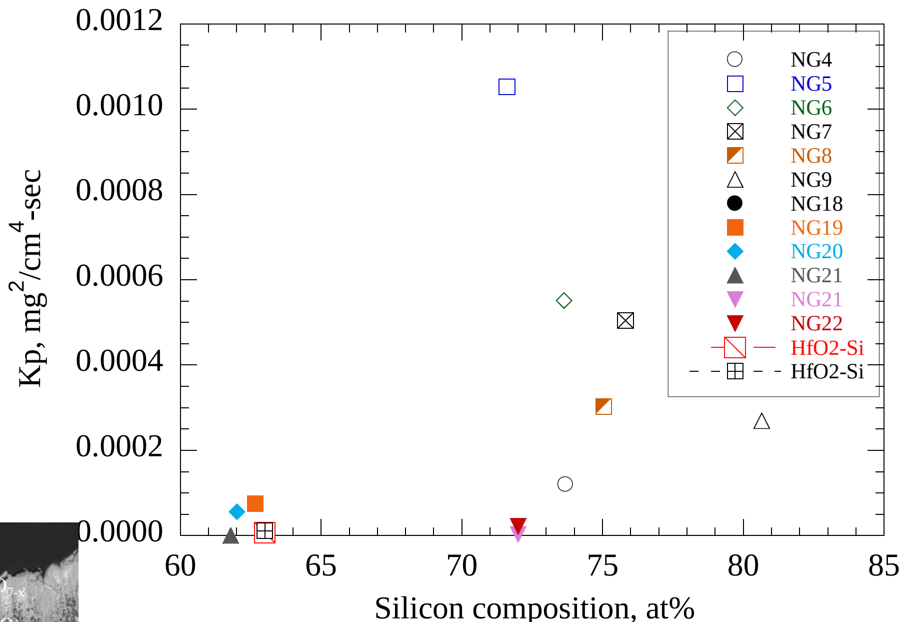
Advanced 2700°F bond coat systems: RE-Si based Systems, grain boundary engineering designs and/or composite systems -

HfO_2-Si systems

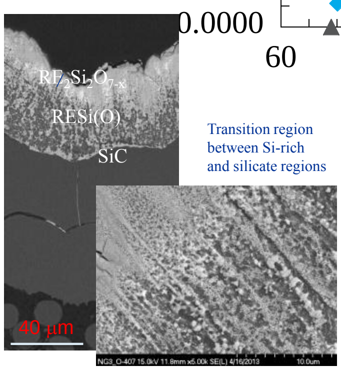
Advanced 2700°F+ Rare Earth - Bond Coat systems

Furnace Cycle Test Results of Selected RESi and ZrSi + Dopant Bond Coats - Testing in Air at 1500°C, 1 hr cycles

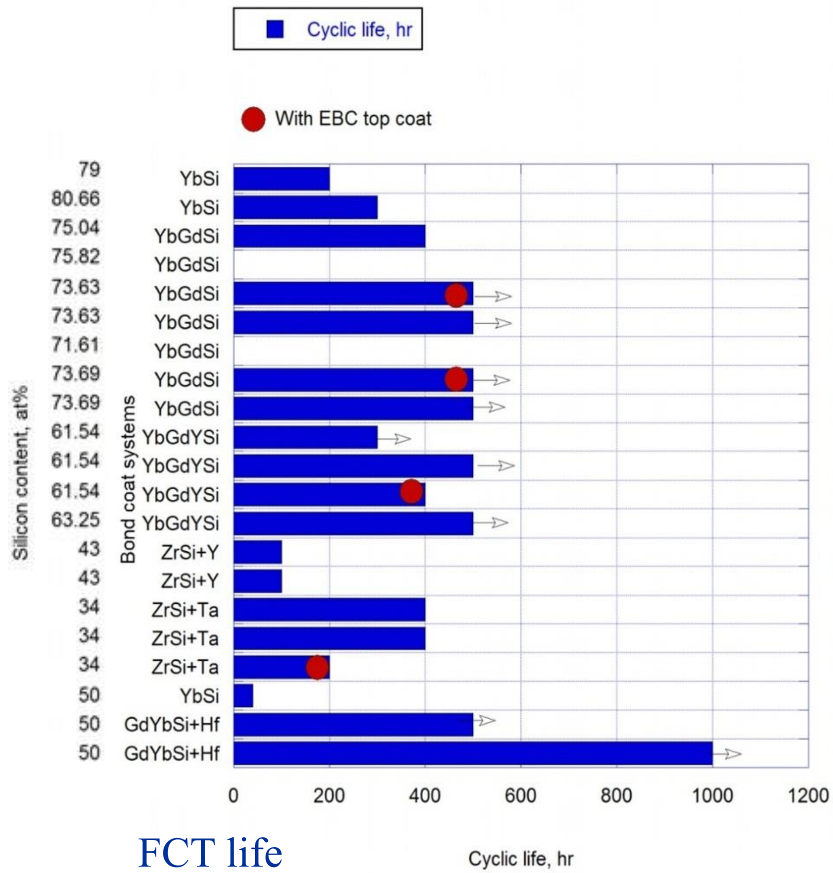
- Some initial multi-component systems showed excellent furnace cyclic durability at 1500°C
- FCT and steam tests also performed for RESiO-Hf systems
- Generally good correlation between FCT and oxidation resistance



Oxidation kinetics



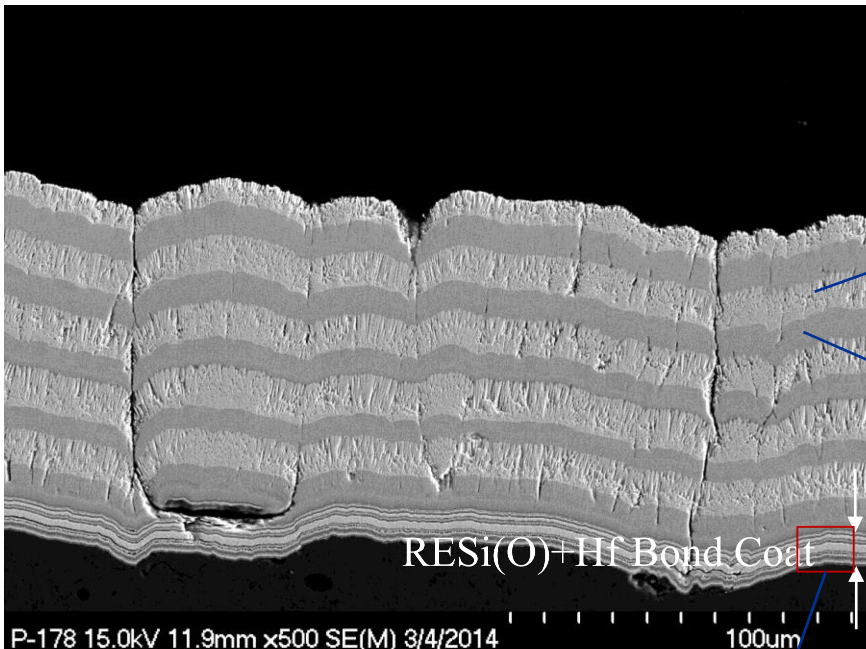
An example of cross-section TGA tested specimen

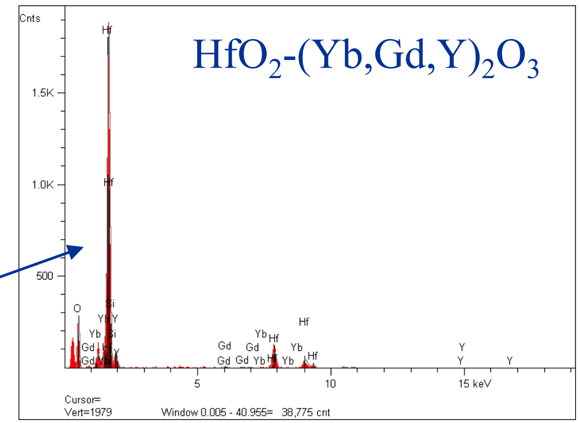


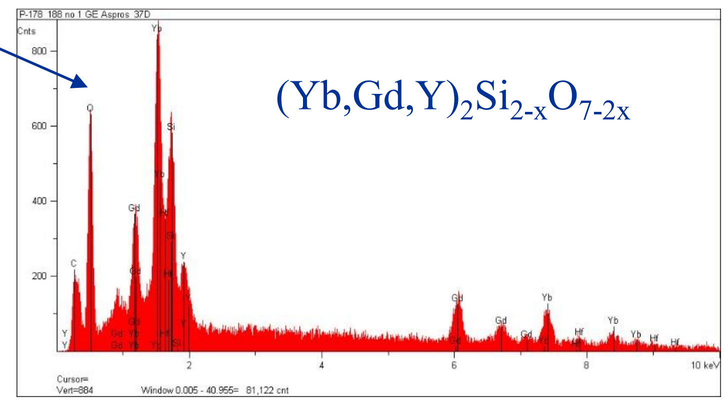
FCT life

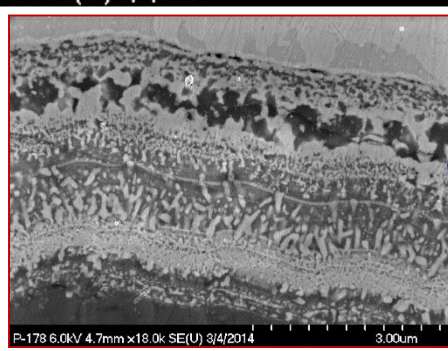
The Environmental Barrier Coating System

- Alternating layered HfO_2-Rare Earth silicate EBC for fundamental stability studies
- 2700F capable Yb-YbO based bond coat
- Coated onto SiC/SiC CMC substrates using EB-PVD





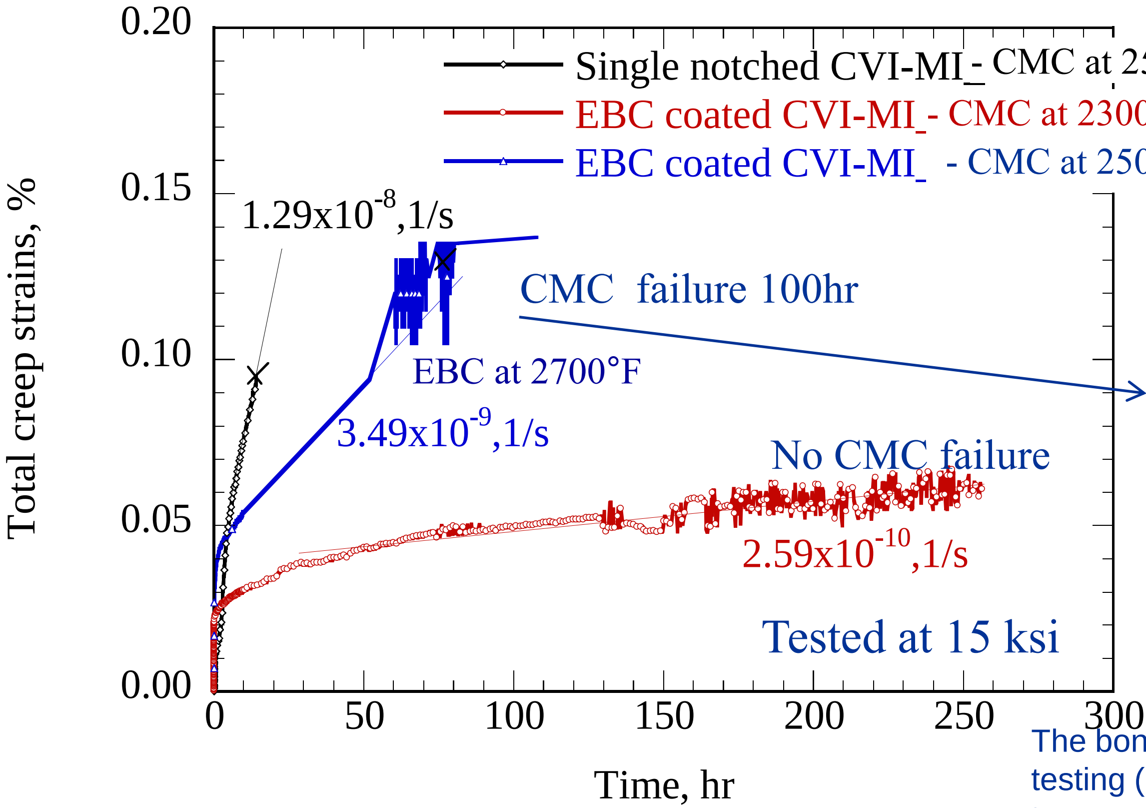


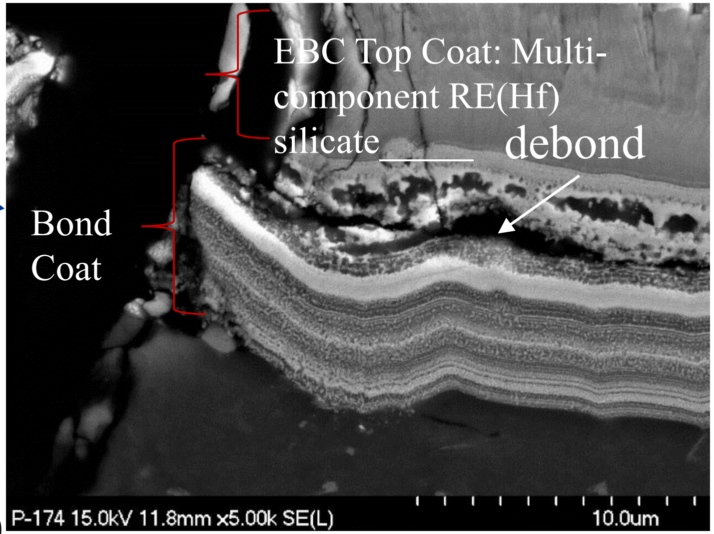


The bond coat region

Environmental Barrier Coating System

- YbGdSi(O) (+Hf) Bond Coat + multi-component EBC Top Coat on woven SiC/SiC CVI-MI SiC/SiC CMC
- Creep testing conducted with 15 ksi load and laser thermal gradient at 0.15% total creep strain, bond coat at up to 2700°F (1482°C)



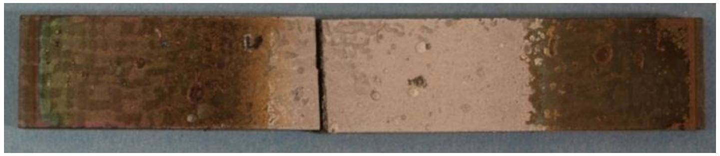


The bond coat remains mostly intact after 100 hr creep testing (CMC fracture) with 2700°F coating surface temperature, except some debond near the top coat/bond coat region due to high Si segregation or processing defective regions

The Flexural Fatigue Tested Environmental Barrier Coating 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

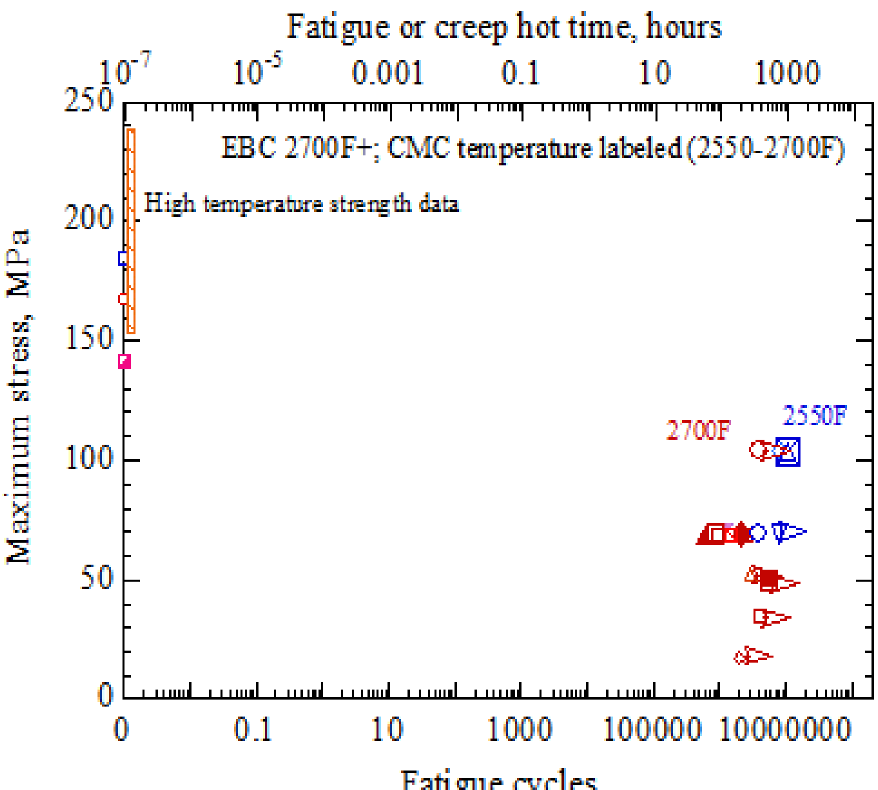
- Flexural fatigue tests with 15 Ksi (138 MPa) stress amplitude loading



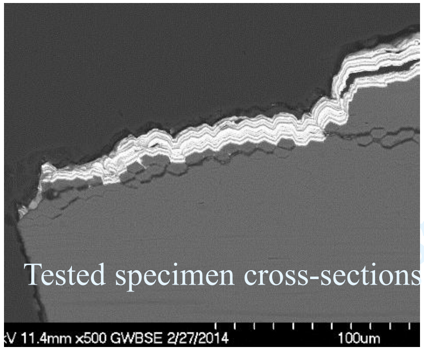
Tested, SA Tyrannohex with bond coat only

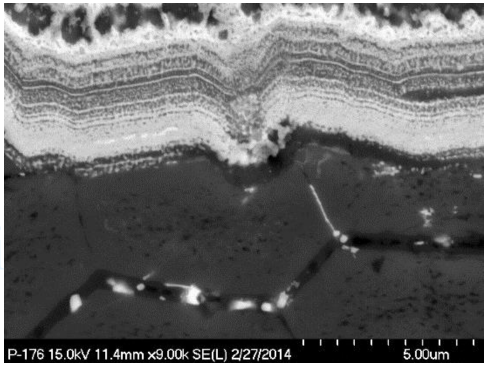
Tested, SA Tyrannohex with EBC system 188

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



Creep-fatigue durability tests

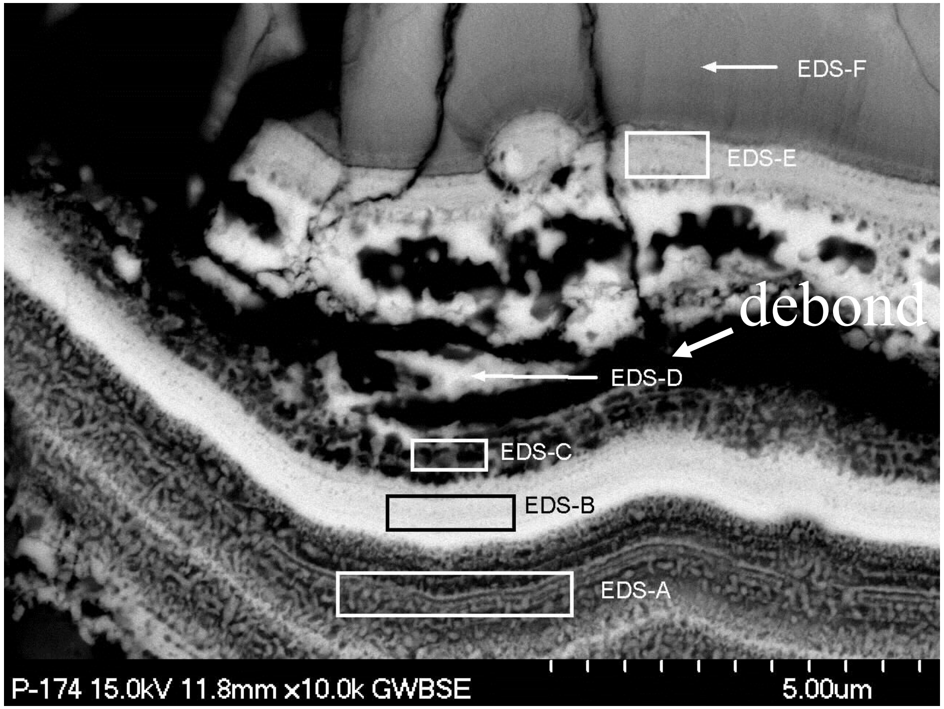




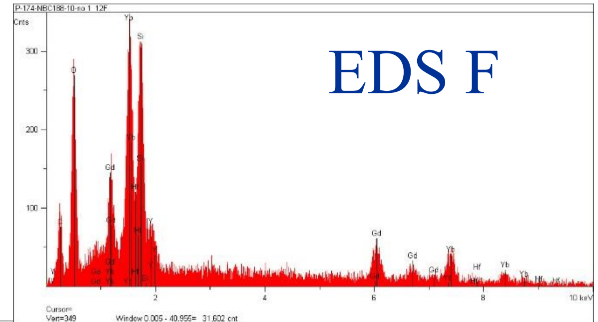
Examples of fatigue test EBC systems on Tyrannohex SA SiC composites (Ube Industries, Inc,)

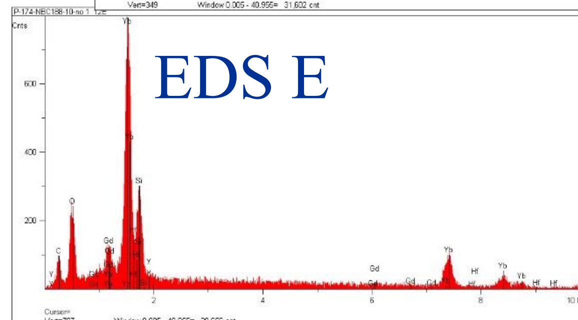
SEM – EDS Analysis of the Tensile Rupture Tested Environmental Barrier Coatings System

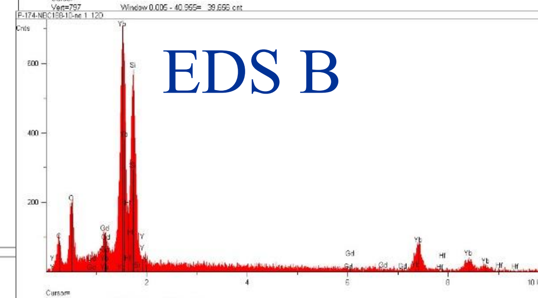
- YbGdSi(O) (+Hf) Bond Coat region



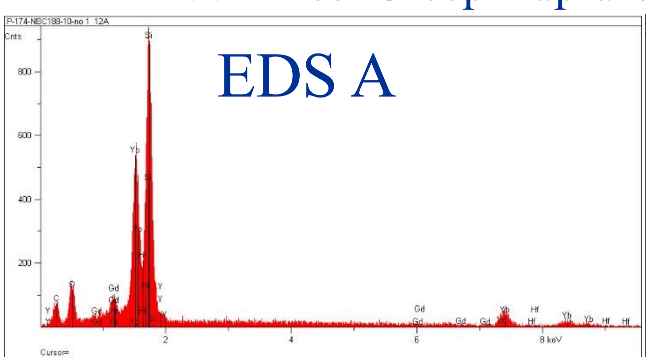
100 hr test Creep Rupture Test

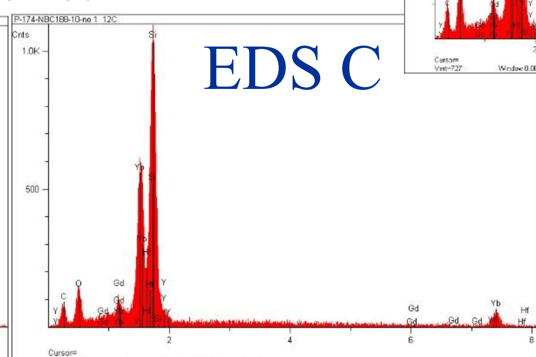


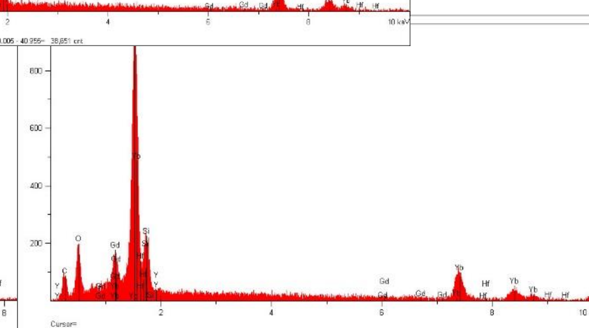




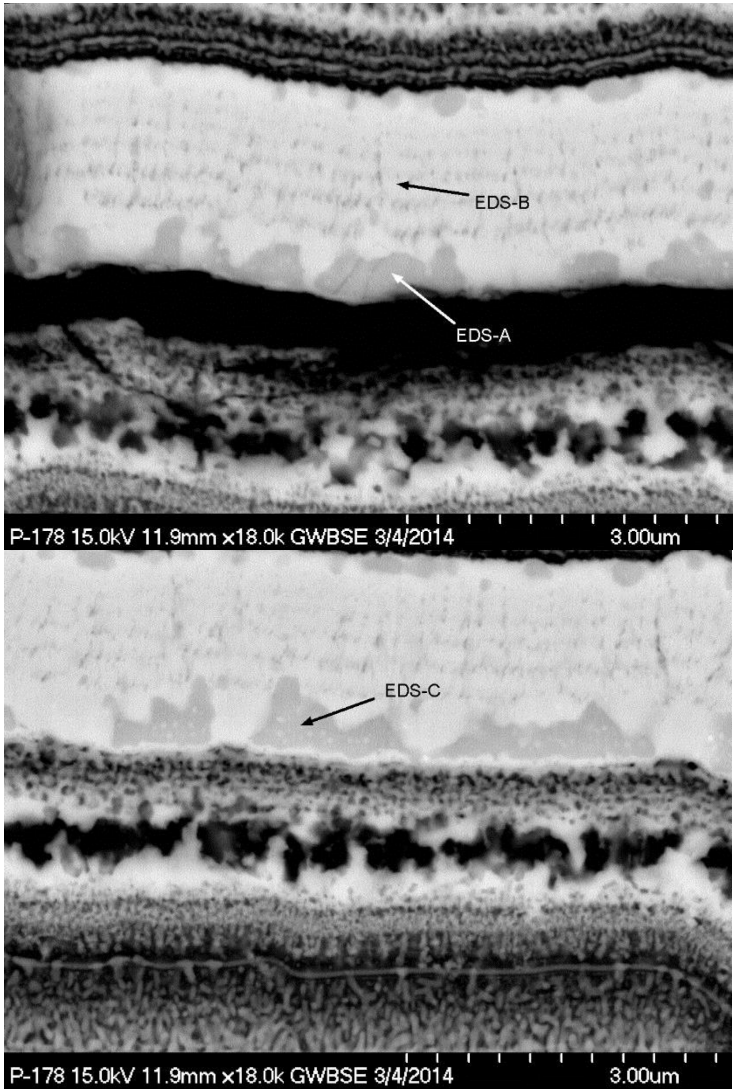
Oxygen content increases



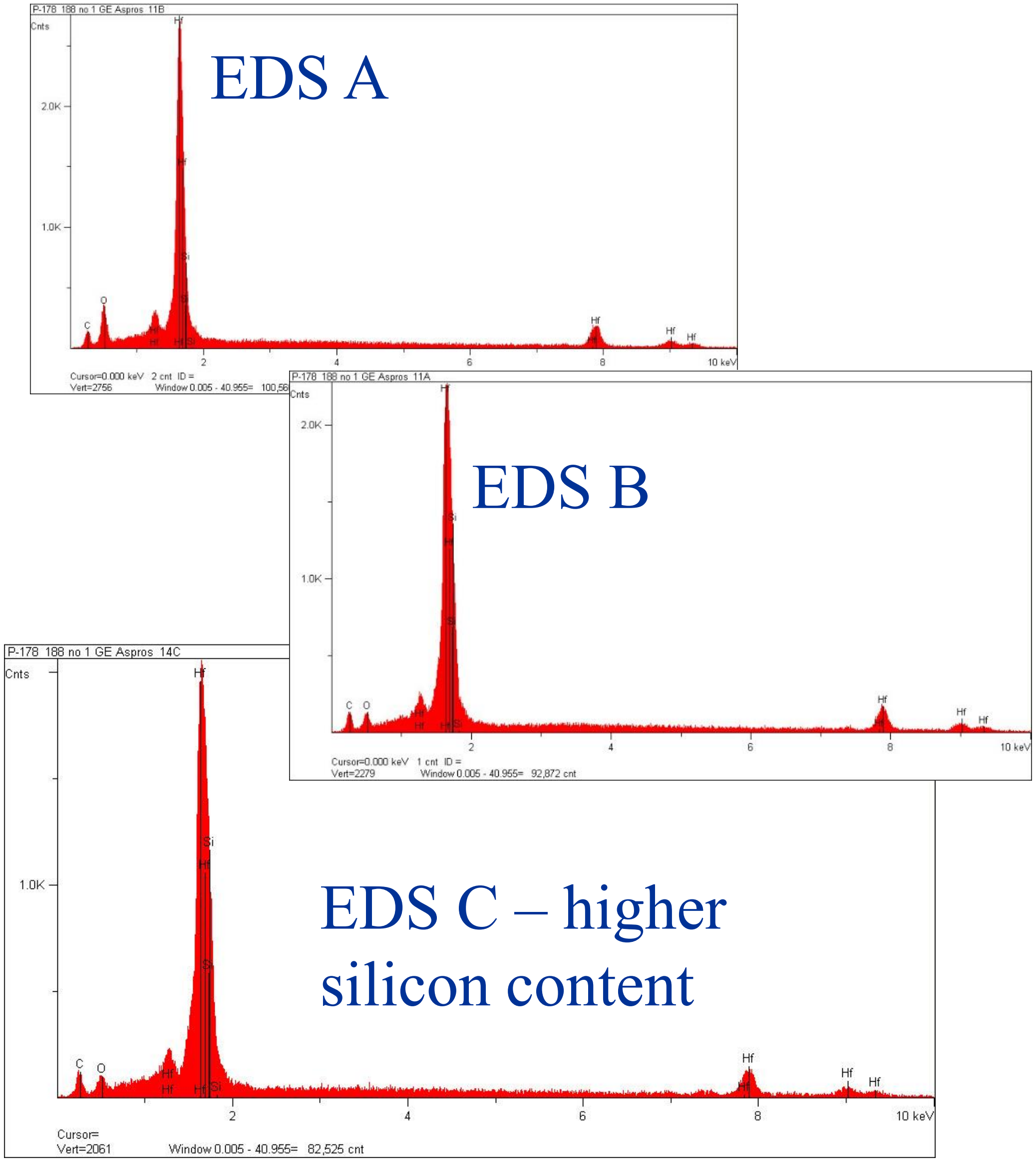




SEM – EDS Analysis of the Tensile Ruptured Tested Environmental Barrier Coating System - Continued

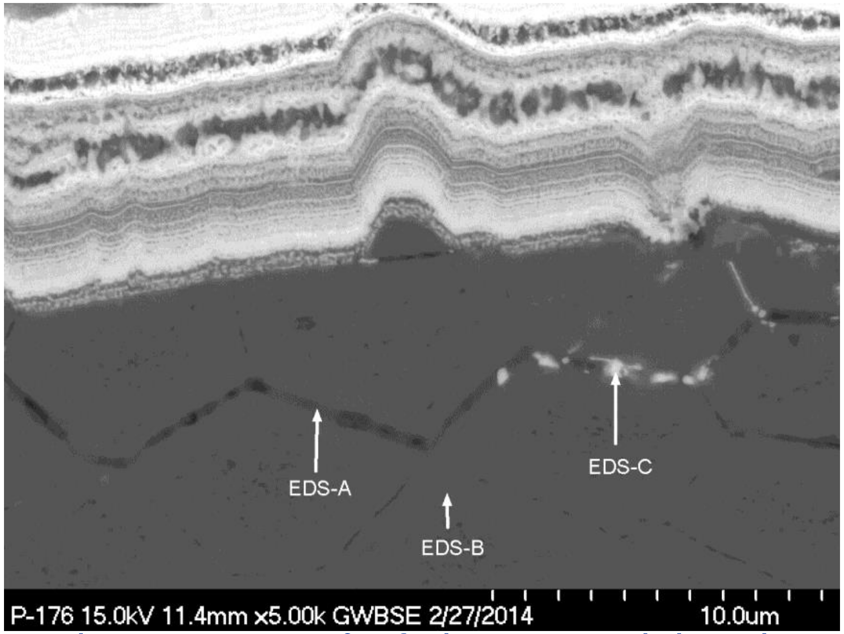


$Hf(O)-HfSi_2(O)$ bond coat region, 100hr

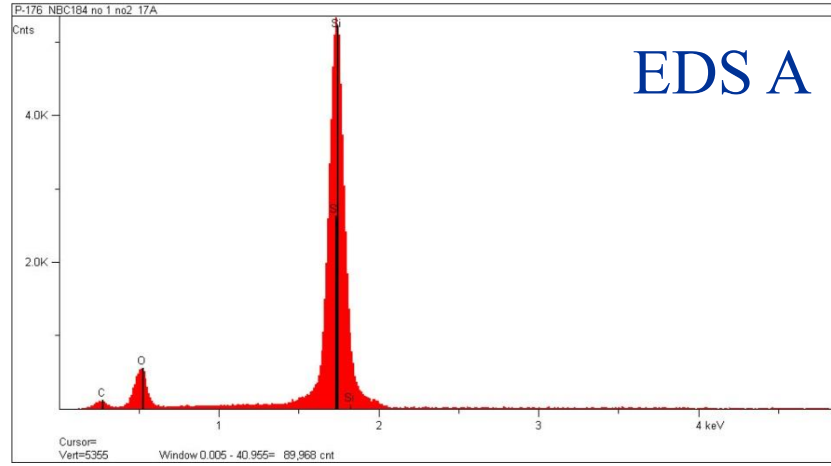


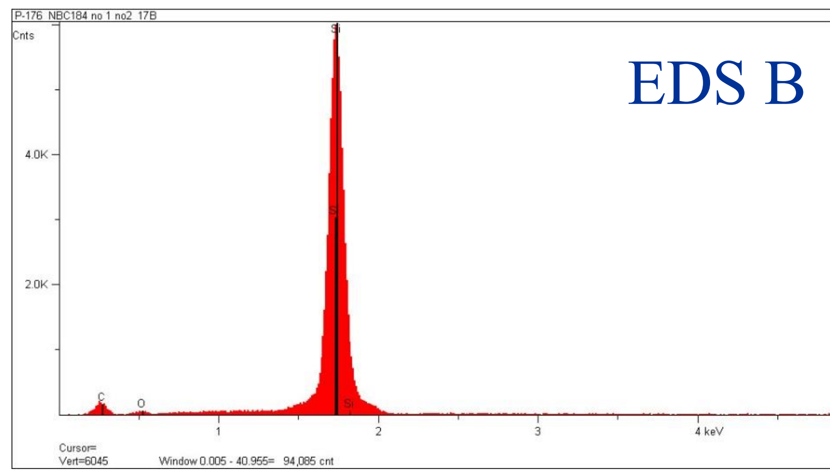
The Flexural Fatigue Tested Environmental Barrier Coating System

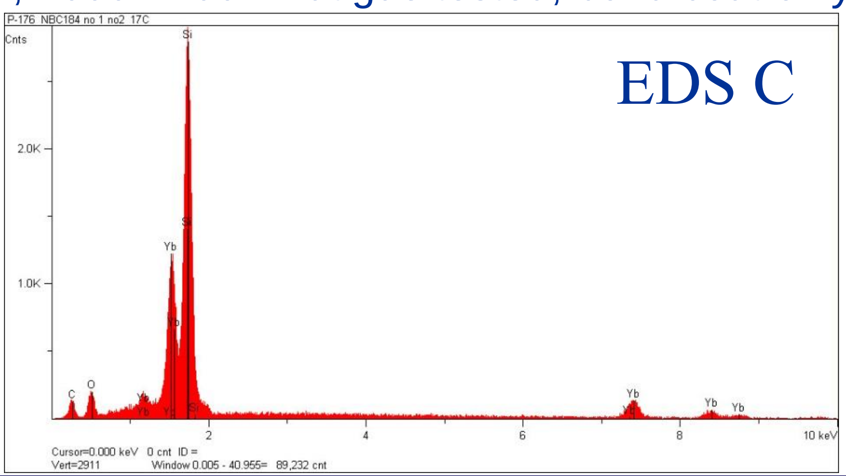
- Ytterbium containing bond coat help self-healing the composite fatigue cracking



460hr, 2600-2700°F fatigue tested, bond coat only

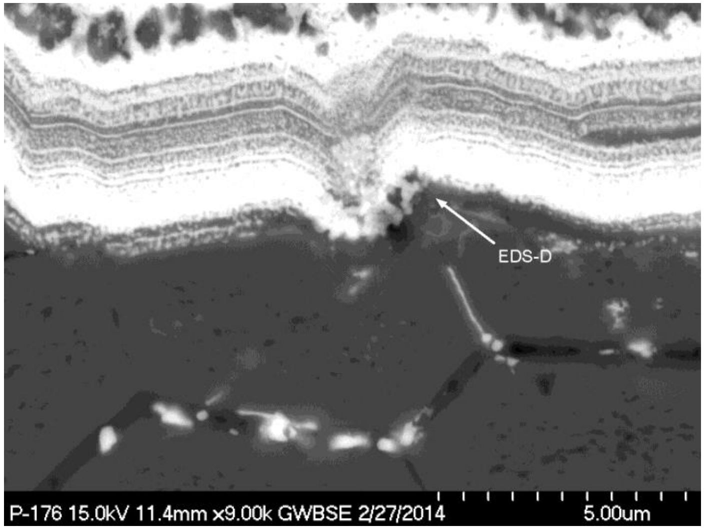


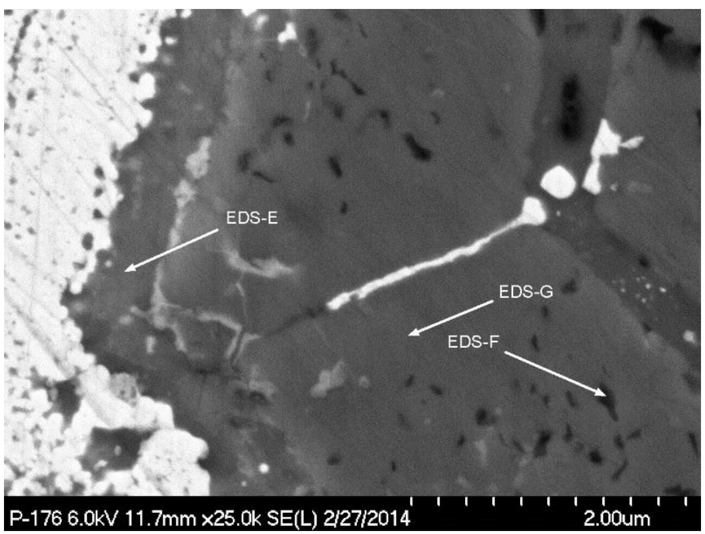




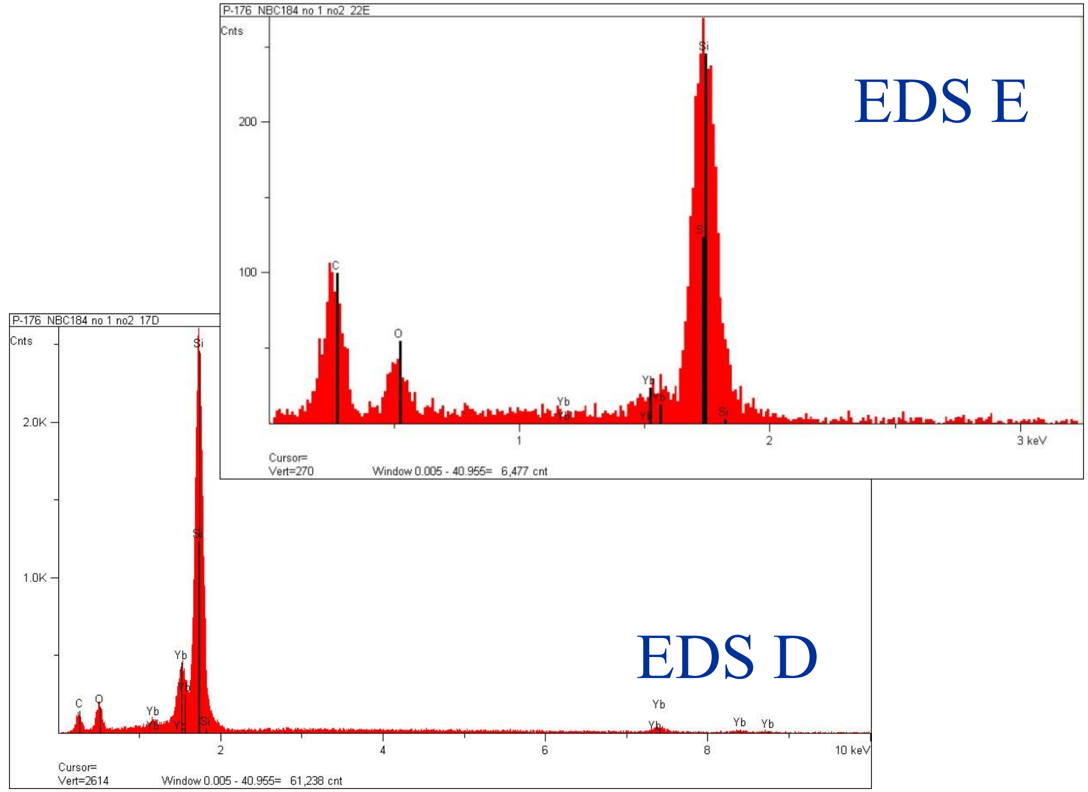
The Flexural Fatigue Tested Environmental Barrier Coating System - Continued

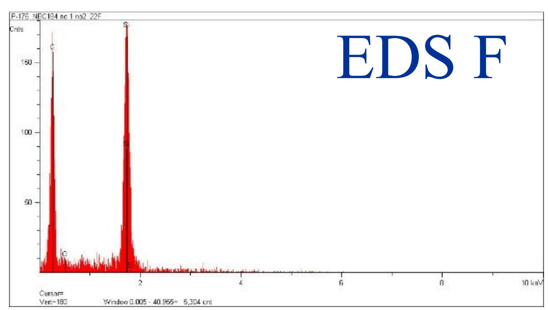
- Ytterbium containing bond coat help self-healing the composite fatigue cracking

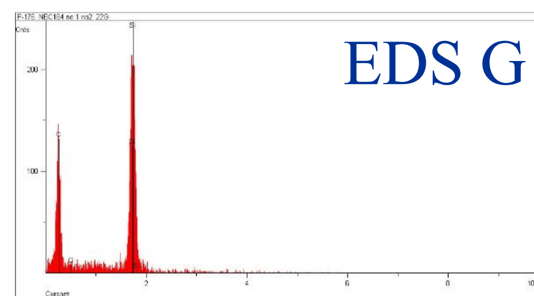




460hr, 2600-2700F fatigue tested

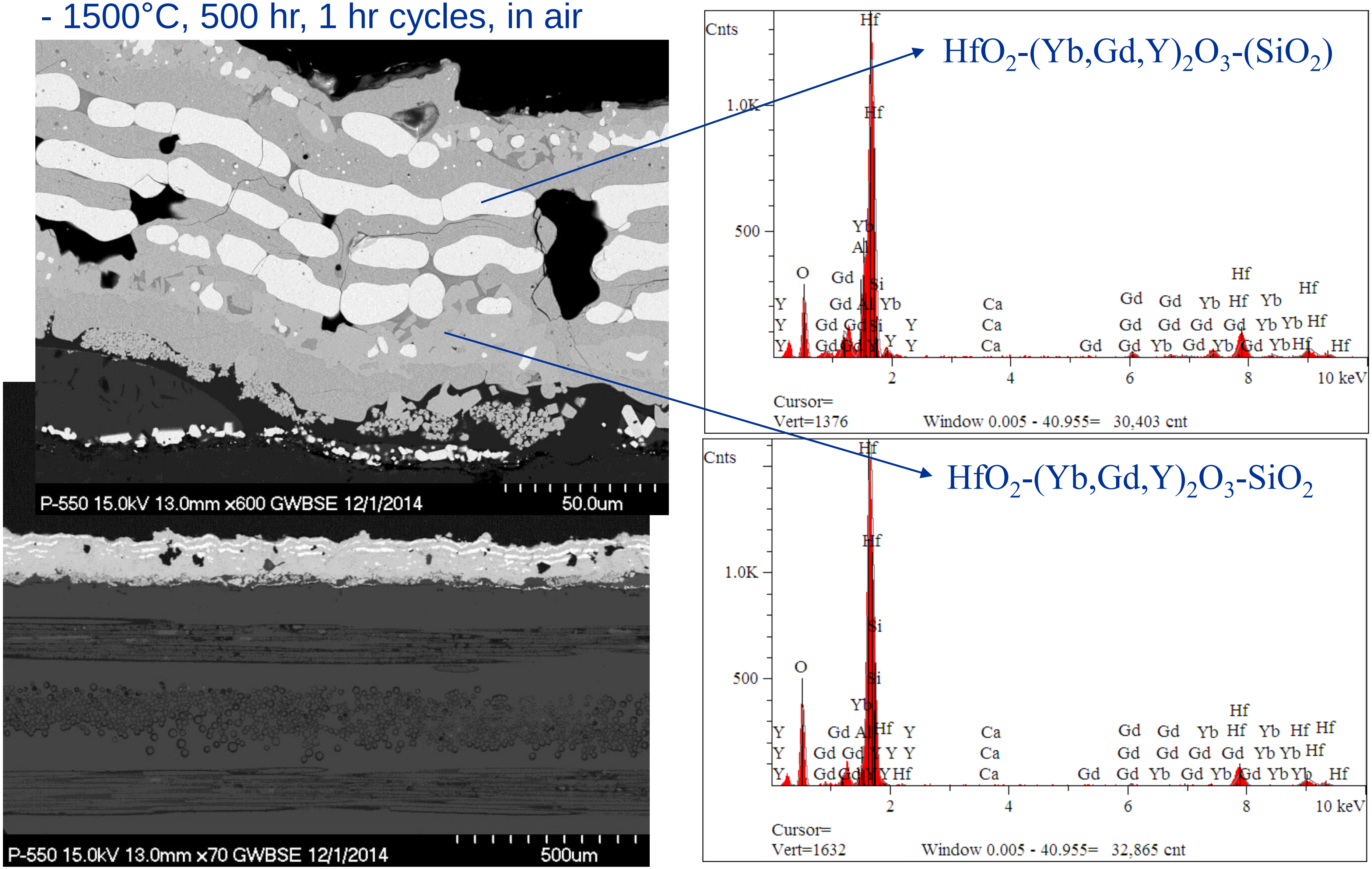






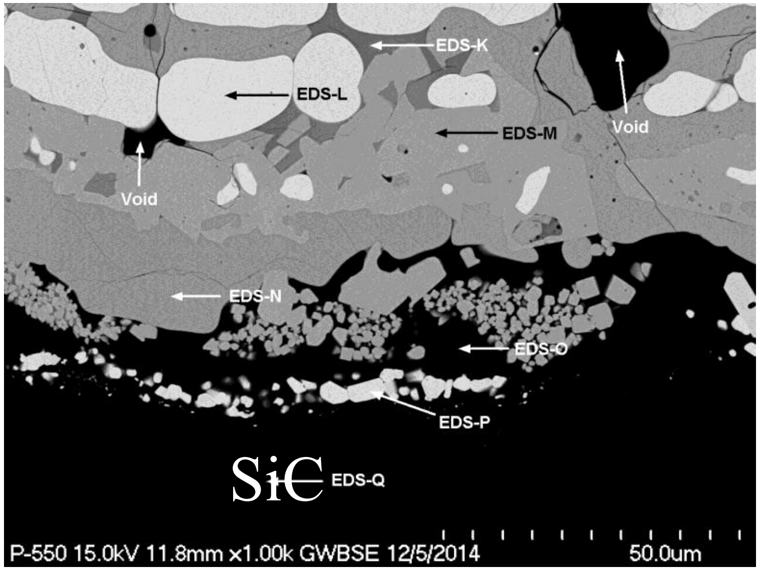
The Long-Term Furnace Cyclic Tested Environmental Barrier Coating System: Rare Earth doped HfO_2 and Rare Earth Silicates Showed Compatibility and Stability

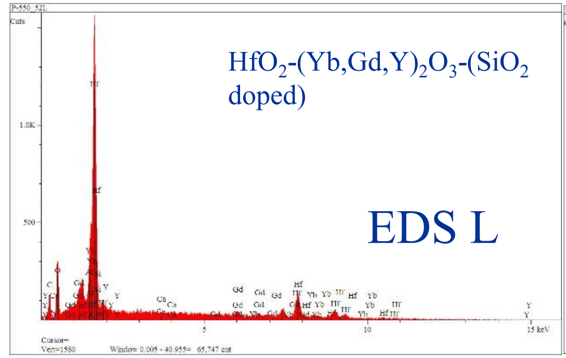
- 1500°C, 500 hr, 1 hr cycles, in air

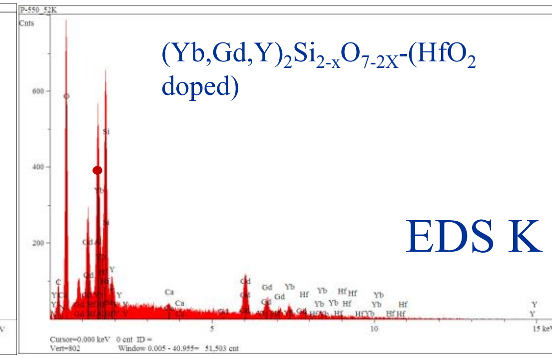


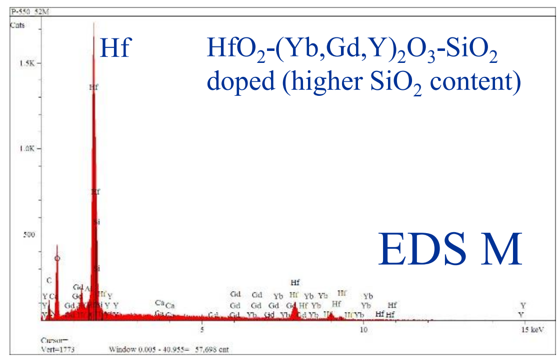
The Long-Term Furnace Cyclic Tested Environmental Barrier Coating System: Rare Earth doped HfO_2 and Rare Earth Silicates Showed Compatibility and Stability - Continued

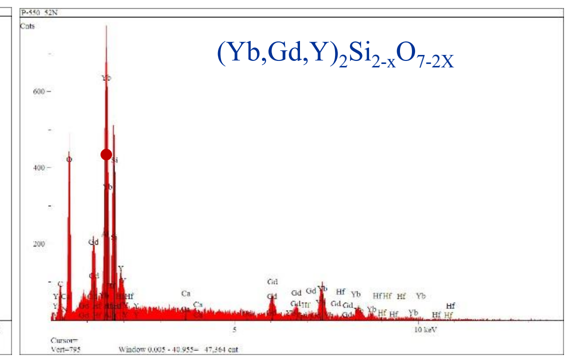
- 1500°C, 500 hr, 1 hr cycles, in air

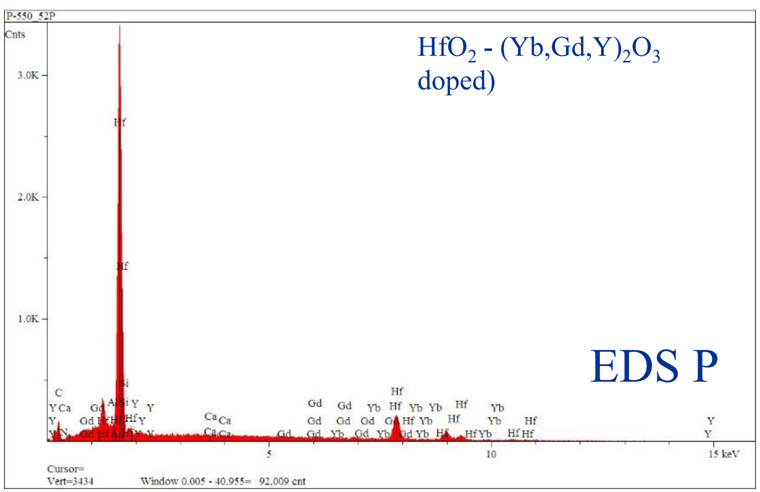


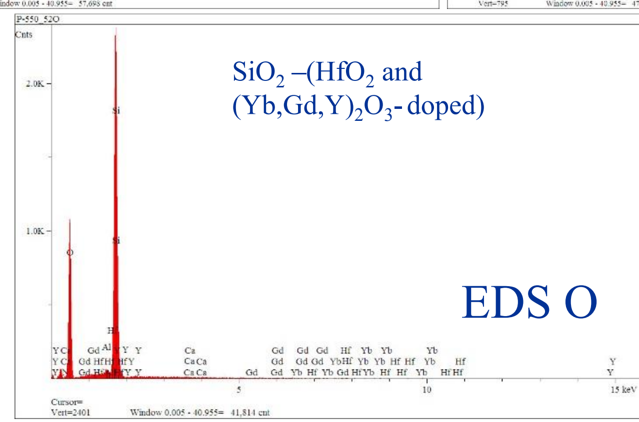






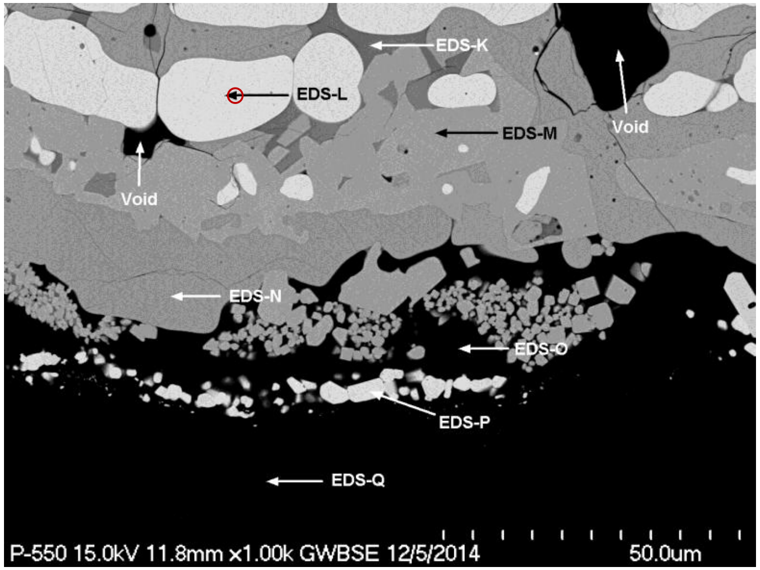


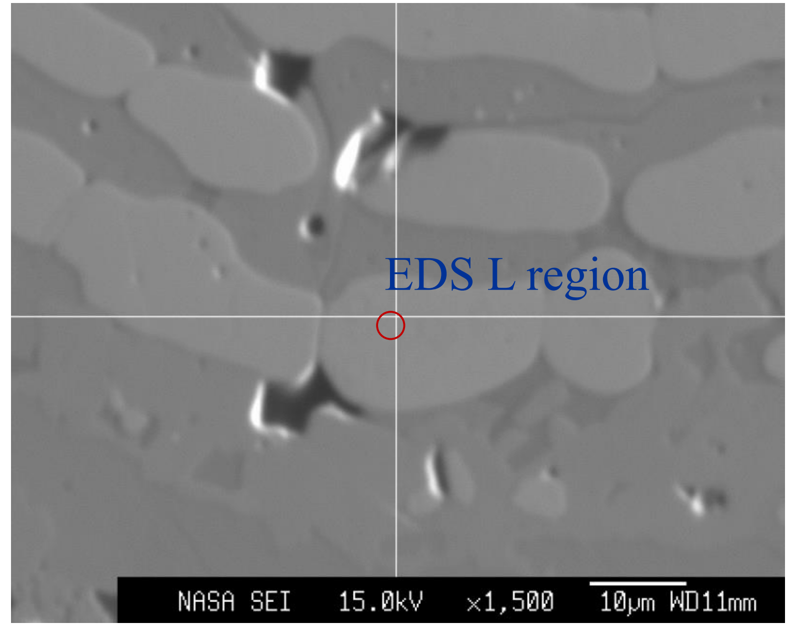




EDS (Si Drift Detector) and WDS Comparisons Showed Good Agreements in the Composition Analysis

- 1500°C, 500 hr, 1 hr cycles, in air





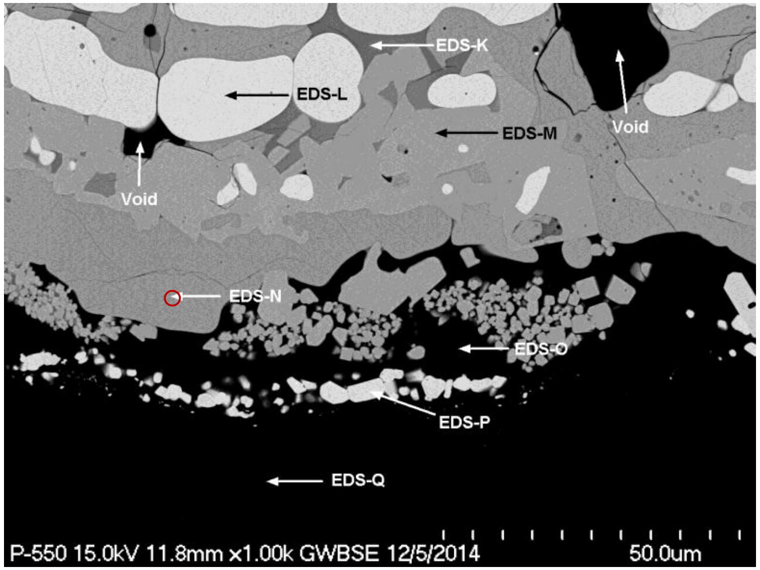
WDS 10 points to obtain the average composition of the L region

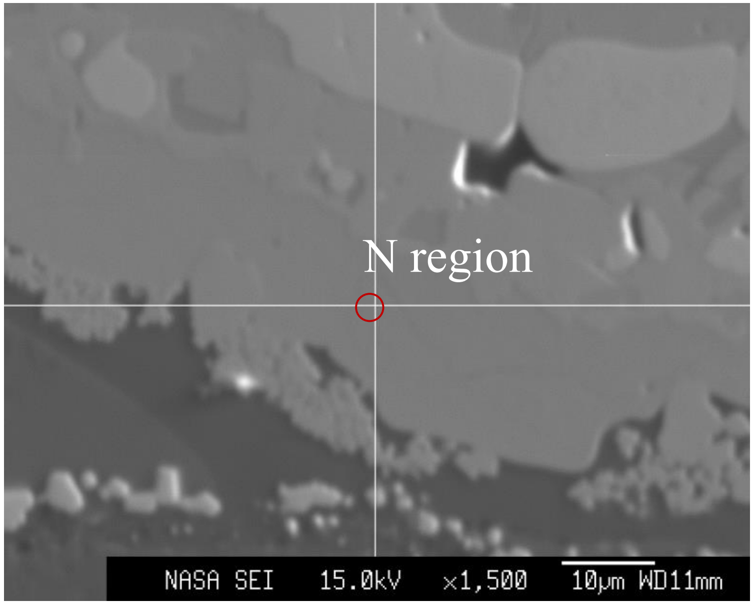
Elt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units
O	Ka	40.77	2.065	14.484	**wt.%**
Si	Ka	0.00	1.554	0.004	**wt.%**
Y	La	4.34	1.641	1.054	**wt.%**
Gd	La	6.01	1.312	6.290	**wt.%**
Yb	La	10.20	1.349	19.181	**wt.%**
Hf	La	25.25	1.730	58.987	**wt.%**
Total				**100.000**	**wt.%**

IMG52-L	**PROBE DATA-average 10pts**					
Elt.	Line	Spec-Xtal	Conc, wt	Units	Conc	Units
O	Ka	4-LDE1	13.24	wt.%	62.4	at%
Si	Ka	2-PETJ	0.036	wt.%	0.098	at%
Y	La	2-PETJ	2.093	wt.%	1.78	at%
Gd	La	5-LIFH	4.9	wt.%	2.35	at%
Yb	La	5-LIFH	15.59	wt.%	6.8	at%
Hf	Ma	2-PETJ	62.796	wt.%	26.57	at%
Total			**98.66**	**wt.%**	**100**	**at%**

EDS (Si Drifting Detector) and WDS Comparisons Showed Good Agreements in the Composition Analysis - Continued

- 1500°C, 500 hr, 1 hr cycles, in air





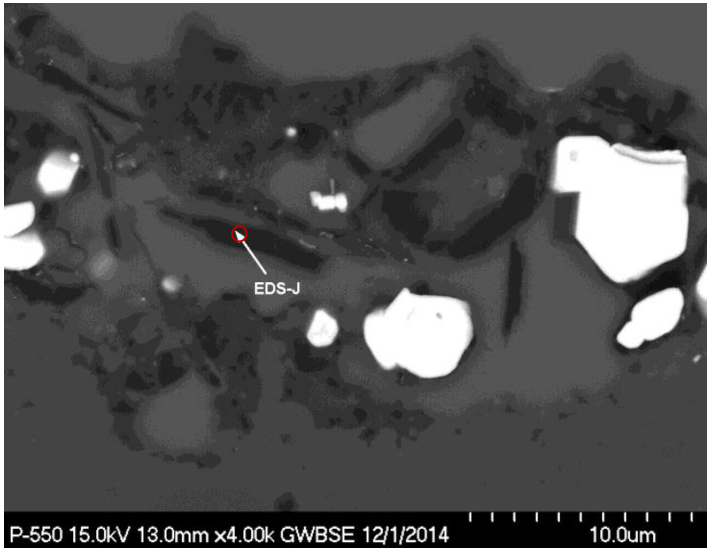
WDS 10 points to obtain the average composition of the N region

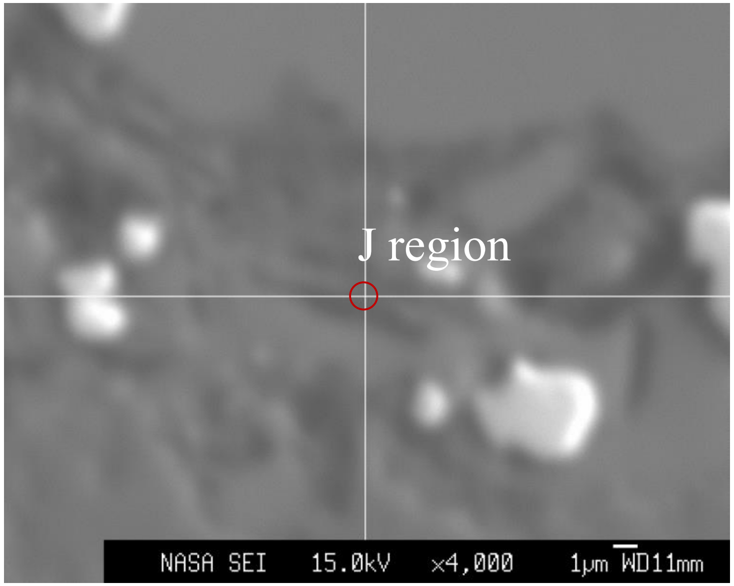
Elt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units
O	Ka	62.15	2.382	19.238	wt.%
Si	Ka	82.63	2.975	7.027	wt.%
Y	La	14.54	1.749	5.614	wt.%
Gd	La	12.38	1.364	19.333	wt.%
Yb	La	17.14	1.480	48.788	wt.%
Hf	La	0.00	0.831	0.000	wt.%
Total				100.000	wt.%

IMG52-N		PROBE DATA-average 10pts				
Elt.	Line	Spec-Xtal	Conc	Units	Conc	Units
O	Ka	4-LDE1	21.67	wt.%	60.25	at%
Si	Ka	2-PETJ	13.25	wt.%	20.997	at%
Y	La	2-PETJ	6.2	wt.%	3.11	at%
Gd	La	5-LIFH	15.37	wt.%	4.35	at%
Yb	La	5-LIFH	42.019	wt.%	10.81	at%
Hf	Ma	2-PETJ	0.893	wt.%	0.223	at%
Total			99.46	wt.%	100	at%

EDS (Si Drifting Detector) and WDS Comparisons Showed Good Agreements in the Composition Analysis - Continued

- 1500°C, 500 hr, 1 hr cycles, in air





WDS 4 points to obtain the average composition of the N region

Elt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units
B	Ka	19.68	1.340	0.300	**wt.%**
C	Ka	2.70	0.848	0.264	**wt.%**
N	Ka	31.68	1.669	21.438	**wt.%**
O	Ka	1.33	0.646	44.318	**wt.%**
Si	Ka	295.83	4.950	25.893	**wt.%**
Y	La	0.00	0.824	0.000	**wt.%**
Gd	La	0.14	0.417	0.415	**wt.%**
Yb	La	0.40	0.383	4.435	**wt.%**
Hf	La	0.41	0.393	2.938	**wt.%**
Total				**100.000**	**wt.%**

IMG45-J	**PROBE DATA-average 4pts**					
Elt.	Line	Spec-Xtal	Conc	Units	Conc	Units
B	Ka	1-LDE2	30.46	wt.%	43.34	at%
C	Ka	1-LDE2	0.015	wt.%	0.018	at%
N	Ka	1-LDE2	24.47	wt.%	27.01	at%
O	Ka	4-LDE1	13.74	wt.%	13.72	at%
Si	Ka	2-PETJ	27.77	wt.%	15.59	at%
Y	La	2-PETJ	0.01	wt.%	0.0019	at%
Gd	La	5-LIFH	0.009	wt.%	0.0009	at%
Yb	La	5-LIFH	0.0015	wt.%	0.0001	at%
Hf	Ma	2-PETJ	3.33	wt.%	0.33	at%
Total			**99.8**	**wt.%**	**100**	**at%**

Summary and Conclusions

- Environmental barrier coatings with YbGd-HfSi(O) based bond coat, and HfO_2 – multicomponent Rare Earth silicate top coat were tested on SiC/SiC ceramic matrix composites for initial durability studies
- The coatings showed excellent oxidation resistance in O_2 and air testing environments , adhesion and good protection for SiC/SiC CMCs
- The initial silicon content range of the Rare Earth-Silicon coatings was down-selected, multicomponent systems designed and demonstrated for further improved stability
- The rare earth – silicon based coatings showed 2700°F or 1500°C operating temperature viability and durability on SiC/SiC ceramic matrix composites, the EBC-CMC system microstructure and phase changes were investigated
- The rare earths, hafnium and silica showed wide range solubility, and composition ranges of EBC materials are being optimized for coating stability and performance
- The extensive studies of the EDS and WDS composition analyses of the EBC system showed good agreements
    - WDS may be more sensitive to light elements;
    - Field emission gun SEM Silicon drift detector EDS has spatial resolution advantages

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