Integrated TBC/EBC for SiC Fiber Reinforced SiC Matrix Composites for Next Generation Gas Turbines

DoE UTSR DEFE0031281 (10/2017 – 09/2020)
Progress Review Meeting
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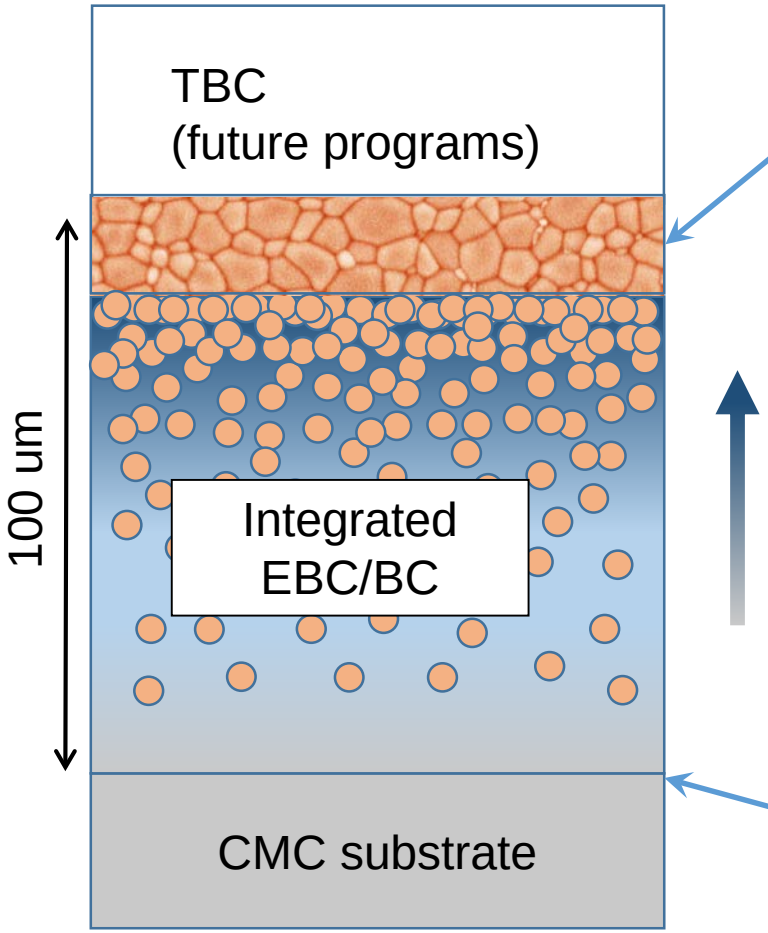
In Collaboration with GE Power Team led by John Delvaux

Outlines

1. The concept of integrated TBC/EBC/BC
2. Overall Goals
3. Objectives
4. Project Tasks
5. Project Progress
6. Project Short Term Plans

1. The concept of integrated TBC/EBC/BC



- Dense Y_2O_3 or Yb_2O_3 top layer ensures low oxygen diffusion and volatilization rates under high temperature high velocity steam environment.
- Graded composition allows smooth transition from SiC to SiBCNO with increasing amount of embedded Y_2O_3 particles.
  - Graded structure avoids sharp CTE mismatch
  - Tolerant to oxidation; further increase TBC lifetime
- PDC SiC bond coat/SiC substrate interface provides excellent adhesion

2. Overall Goals

- Develop an integrated and graded EBC/BC that is:
  - Good bonding with CMC;
  - Graded compositions without sharp interfaces to mitigate thermal stresses from CTE mismatch;
  - Low oxygen transport rate, low oxidation rate and low volatility in high temperature, high velocity steam environment;
  - Tolerant to certain degree of oxidation thereby preventing catastrophic failure;
  - Chemically stable and compatible with CMC and TBC

- Create a strong collaborative team with complementary expertise and state-of-the-art facilities
  - The Clemson University team of Drs. Bordia and Peng.
  - The GE team, led by John Delvaux

3. Objectives

- Investigate the effect of composite stoichiometry (*i.e.* Si/B/C/N ratio in the precursor and the ratio of the Si-based precursor to yttrium oxide (Y_2O_3) (or ytterbium oxide (Yb_2O_3)) particle filler and processing conditions on the size of the resultant phases and nanostructure of the composite ceramics.

- Investigate the effect of the composition and nanostructure on the thermal properties and oxidation and volatilization behavior in oxidizing and high velocity steam environments. The control parameters are the stoichiometry of the precursor (*e.g.* Si/B/C/N ratio) and the volume fraction of the oxide particles Y_2O_3 (or Yb_2O_3) and range of microstructures produced as part of the first objective

3. Objectives (contd.)

- Process the graded Y_2O_3 (or Yb_2O_3) particulate /silicon boron carbon nitride (SiBCN) matrix composite coating and investigate the phase and microstructure stability during high velocity steam exposure at temperatures up to 1500ºC.

- Develop a method to create Y_2O_3 (or Yb_2O_3) and SiBCN powders with predetermined compositions suitable for atmospheric plasma spraying (APS). The powders will be provided to the industrial collaborators for the fabrication of integrated environmental barrier coating/bond coating (EBC/BC) using APS.

- Evaluate the performance of integrated BC/EBCs from APS under high velocity steam environments at temperatures up to 1500ºC.

4. Project Tasks

- **Task 1:** Project management and planning
- **Task 2**: Processing and stability of Y_2O_3-Si-B-C-N and Yb_2O_3-Si-B-C-N composites
- **Task 3:** Thermal and oxidation response of Y_2O_3-Si-B-C-N and Yb_2O_3-Si-B-C-N composites
- **Task 4:** Processing and performance of graded coatings processed using cold spray and pyrolysis
- **Task 5:** Processing and performance of graded coatings processed using atmospheric plasma spraying (APS)

5. Project Progress-Task 1

Task 1.0: Project management and planning

- Kickoff meeting 10/27/17
- A poster at the 2017 UTSR review meeting
- Recruitment of UG students and post doc to work on the project
- Coordination with GE Team including scheduling review meetings
- Regular review meetings with DoE Program Manager and GE team
- A talk and a poster at the 2018 UTSR review meeting

5. Project Progress-Task 2

Task 2: Processing and stability of Y_2O_3-Si-B-C, Yb_2O_3-Si-B-C, Y_2O_3-Si-B-C-N and Yb_2O_3-Si-B-C-N composites

Completed:

- Acquired raw materials (Y_2O_3, Yb_2O_3, preceramic precursors, and *etc.*)
- Developed the processing procedure, and characterization plan
- Sintered and characterized dense Y_2O_3 ceramics to be applied as the top layer
- Fabricated Y_2O_3-Si-C-N and Y_2O_3-Si-C-B composite ceramic powders and achieved submicron particle sizes
- Studied the processing of composites in the Y_2O_3-Si-C-B and the Y_2O_3-Si-C-N system. Investigated the effect of composition and processing temperature on density, porosity, phase, and composition

Current Focus:

- Study synthesis atmosphere and heat-treatment effects on Y_2O_3-Si-C-B and the Y_2O_3-Si-C-N microstructure and composition
- Process and characterize Yb_2O_3-Si-C-B and Yb_2O_3-Si-C-N composites

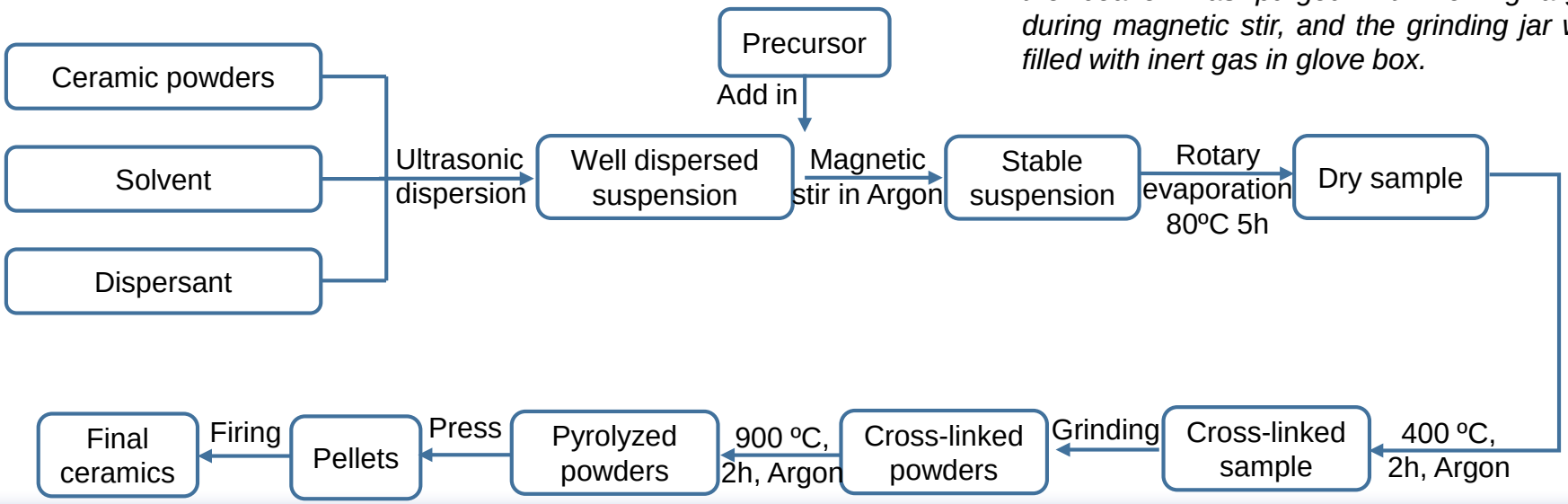
5. Project Progress-Task 2

Raw materials:

Raw materials	Specifications	Supplier	Function in the system
Y_2O_3	Purity: 99.9%; APS: 0.5~1 μm	American Elements (USA)	Ceramic filler
Yb_2O_3	Purity: 99.9%; APS: 3~5 μm	American Elements (USA)	Ceramic filler
Durazane 1800	Polysilazane	Merck KGaA (Germany)	Precursor for SiCN ceramic
SMP10	Polycarbosilane	Stafire (USA)	Precursor for SiC ceramic
Decaborane	Purity: 98%	Alfa Aesar (USA)	Boron source
Disperbyk-2070		BYK (Germany)	Dispersant
Dicumyl peroxide (DCP)	Purity: 99%	Acros Organics (USA)	Cross-link agent
Cyclohexane	Purity: 99%	Alfa Aesar (USA)	Solvent for SMP10
Di-n-butyl ether (DNB)	Purity: 99%	Acros Organics (USA)	Solvent for Durazane 1800

Processing procedure:

In order to eliminate the oxygen and moisture, the beaker was purged with flowing argon during magnetic stir, and the grinding jar was filled with inert gas in glove box.



5. Project Progress-Task 2

Processing Protocol for $SiCN/Y_2O_3$ composite

Composition effect

Sample Id	Composition		Processing temperature (ºC)	Dwell time (h)	Processing atmosphere	Processing method
	Y_2O_3 (vol.%)	Durazane 1800 (vol.%)				
D10:90-1500	10	90	1500	2	Argon	Pressureless
D30:70-1500	30	70	1500	2	Argon	Pressureless
D50:50-1500	50	50	1500	2	Argon	Pressureless
D70:30-1500	70	30	1500	2	Argon	Pressureless
Dd90:10-1500	90	10	1500	2	Argon	Pressureless

Processing temperature effect

Sample Id	Composition		Processing temperature (ºC)	Dwell time (h)	Processing atmosphere	Processing method
	Y_2O_3 (vol.%)	Durazane 1800 (vol.%)				
D30:70-1300	30	70	1300	2	Argon	Pressureless
D30:70-1400	30	70	1400	2	Argon	Pressureless
D30:70-1500	30	70	1500	2	Argon	Pressureless
D30:70-1600	30	70	1600	2	Argon	Pressureless
D30:70-1650	30	70	1650	2	Argon	Pressureless

Processing atmosphere effect

Sample Id	Composition		Processing temperature (ºC)	Dwell time (h)	Processing atmosphere	Processing method
	Y_2O_3 (vol.%)	Durazane 1800 (vol.%)				
D30:70-1500-a	10	90	1500	2	Air, Nitrogen	Pressureless
D30:70-1500-a	30	70	1500	2	Air, Nitrogen	Pressureless
D30:70-1500-a	50	50	1500	2	Air, Nitrogen	Pressureless
D30:70-1500-a	70	30	1500	2	Air, Nitrogen	Pressureless
D30:70-1500-a	90	10	1500	2	Air, Nitrogen	Pressureless

Processing method effect

Sample Id	Composition		Processing temperature (ºC)	Dwell time (h)	Processing atmosphere	Processing method
	Y_2O_3 (vol.%)	Durazane 1800 (vol.%)				
D10:90-1500-h	10	90	1500	2	Argon	Hot press
D30:70-1500-h	30	70	1500	2	Argon	Hot press
D50:50-1500-h	50	50	1500	2	Argon	Hot press
D70:30-1500-h	70	30	1500	2	Argon	Hot press
D90:10-1500-h	90	10	1500	2	Argon	Hot press

Same protocol for $SiCN/Yb_2O_3$, $SiC(B)/Y_2O_3$ and $SiC(B)/Yb_2O_3$ composite

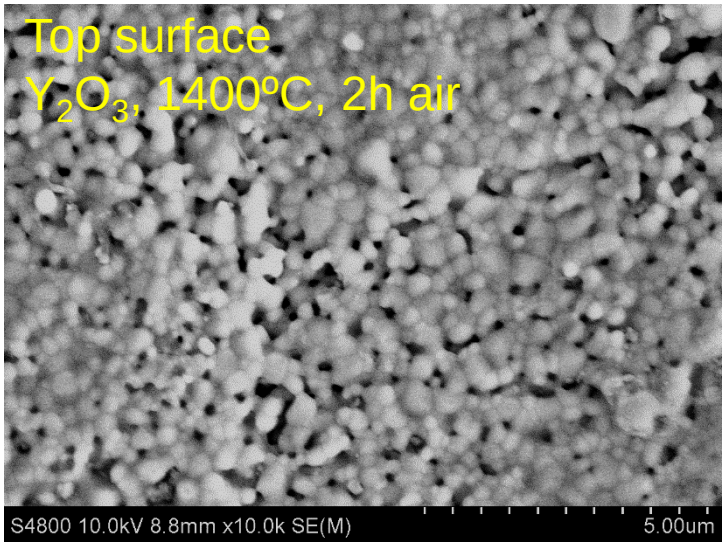
5. Project Progress-Task 2

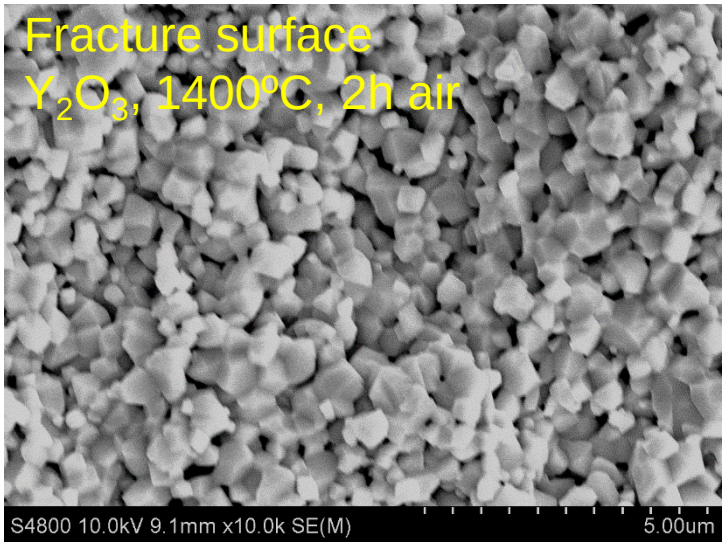
Composite Characterization

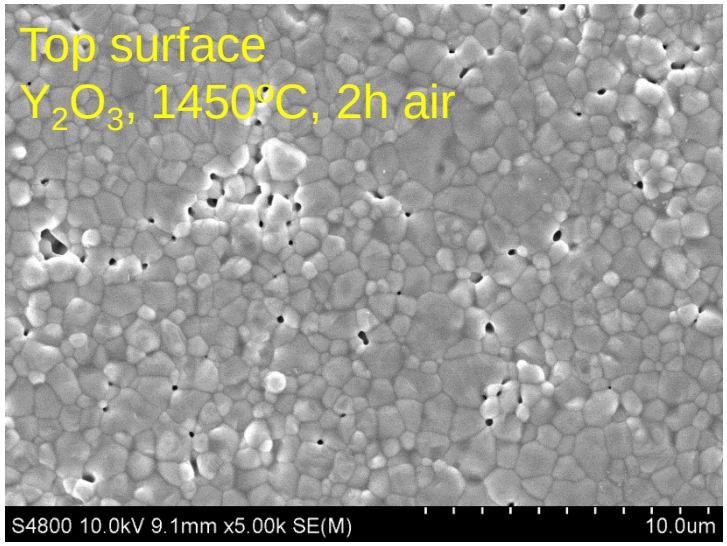
- TGA-DTA: cross-linked powders, weight loss and thermal behavior
- Density and porosity test: ceramic samples, density and porosity changes
- XRD: ceramic samples, phase conversion processes and crystalline phase compositions
- Raman spectrum: ceramic samples, phase compositions
- SEM: ceramic samples, surface microstructure
- TEM: ceramic samples, composition and microstructure
- Thermal expansion test: ceramic samples, coefficient of thermal expansion
- TMA test: ceramic samples, elastic modulus
- Thermal conductivity test: ceramic samples, thermal conductivity

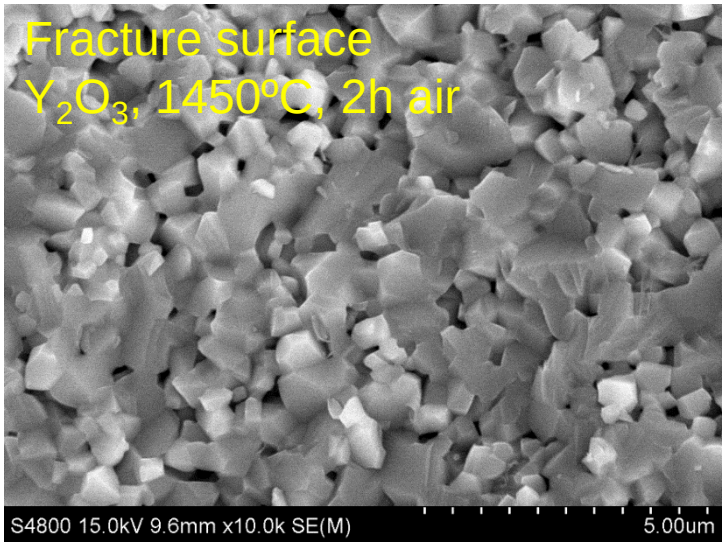
5. Task 2-Sintering of Y_2O_3 Top Coat

Y_2O_3 ceramic pellets were fired at 1400, 1450, 1500ºC for 2h in air



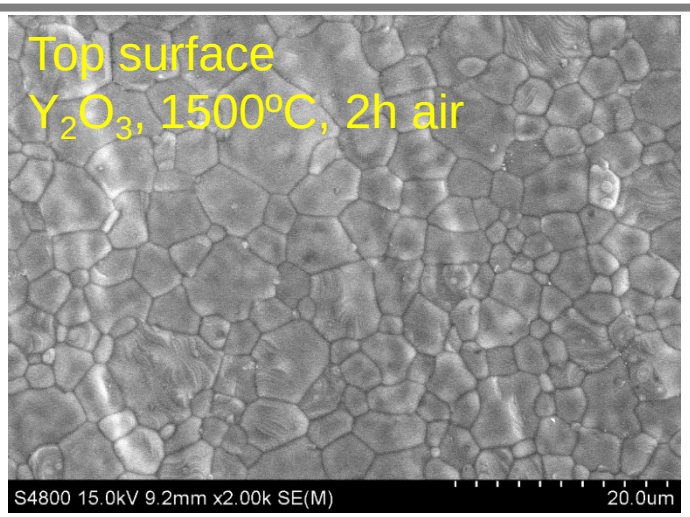


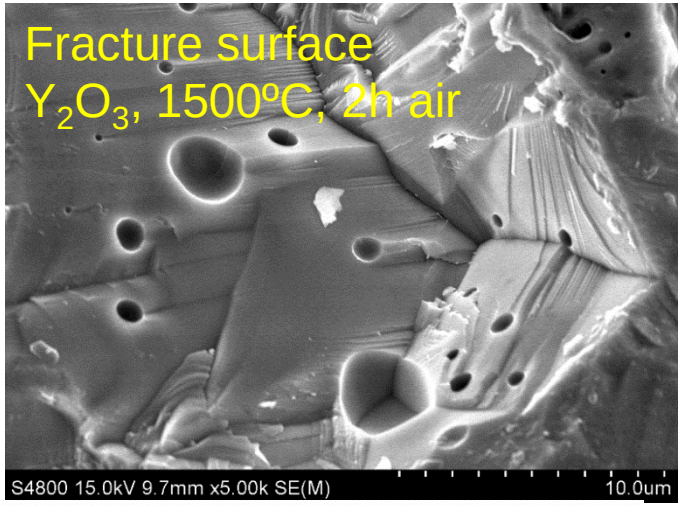


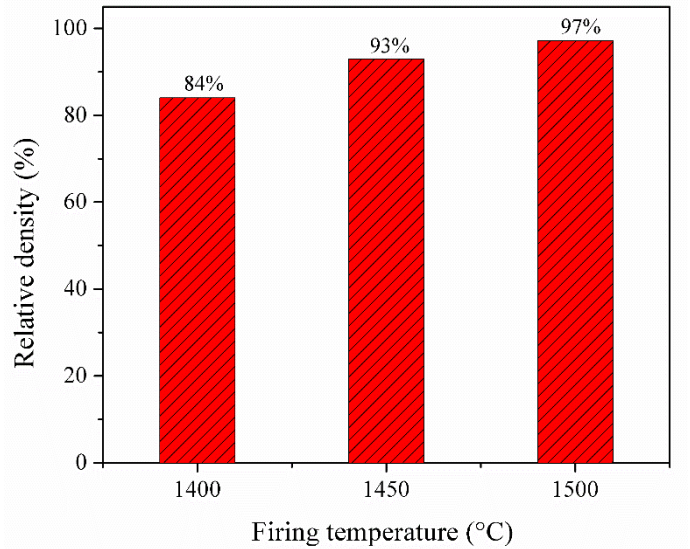


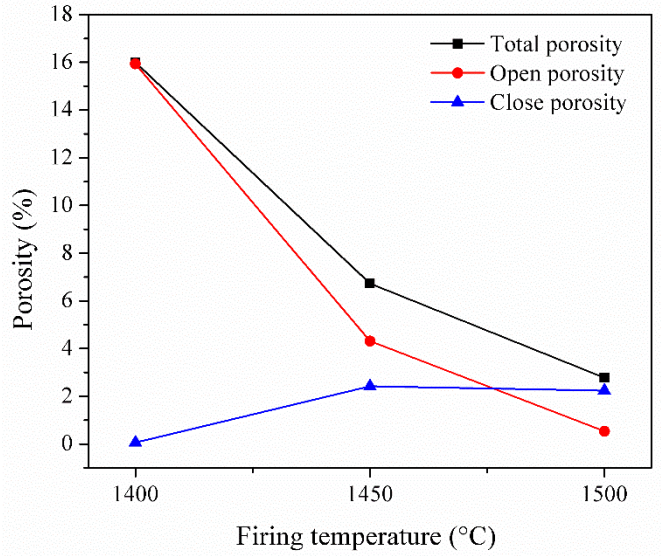
5. Task 2-Sintering of Y_2O_3 Top Coat (contd.)

Y_2O_3









- Density increases and porosity decreases with increasing processing temperature
- At 1500ºC, the relative density reaches 97% with only 0.5% of open porosity
- Some closed pores in the inside of sample. Increase firing time may reduce more pores
- Y_2O_3 fabricated at 1500ºC can be used at top EBC coating

5. Task 2-Composite Ceramic Powder

The Y_2O_3/SiCN and Y_2O_3/SiC(B) ceramic powders were made. In order to get better sintering behavior, these powders were ground to fine particle.

Y_2O_3/SiCN composite

Sample Id	Composition	
	Y_2O_3 (vol.%)	PDC from durazane 1800 (vol.%)
D10:90-1500	10	90
D30:70-1500	30	70
D50:50-1500	50	50
D70:30-1500	70	30
D90:10-1500	90	10

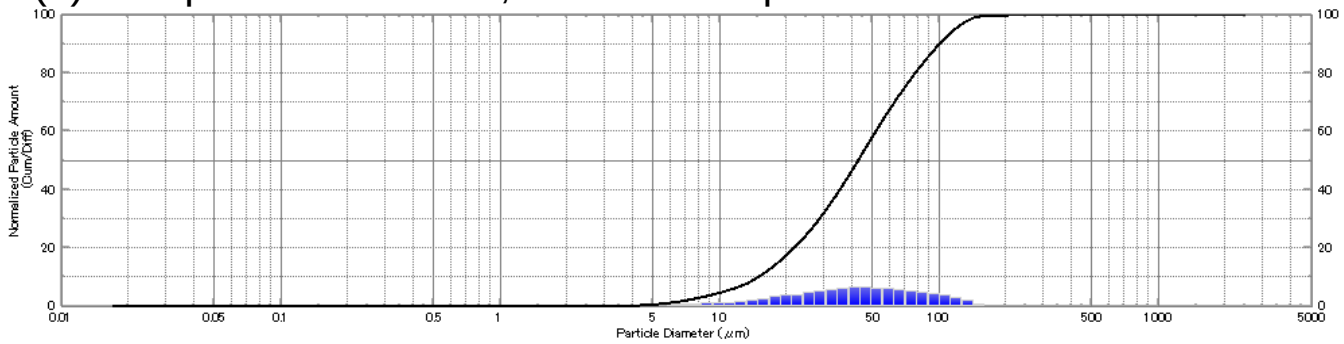
Y_2O_3/SiC(B) composite

Sample Id	Composition	
	Y_2O_3 (vol.%)	PDC from SMP10 (vol.%)
S10:90-1500	10	90
S30:70-1500	30	70
S50:50-1500	50	50
S70:30-1500	70	30
S90:10-1500	90	10

5. Task 2-Composite Ceramic Powder

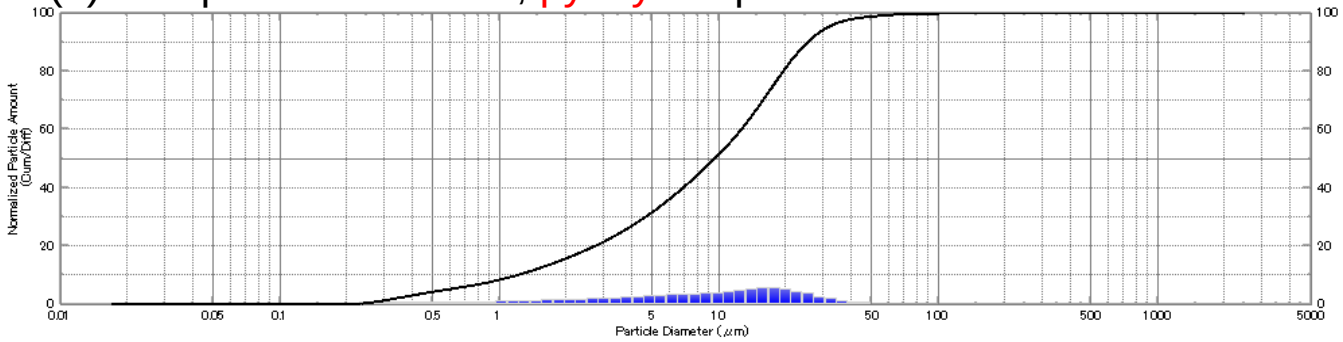
Spex milling (1 hour) to reduce particle size reduction of crosslinked and pyrolyzed powders

(1) Sample D70:30-1500, cross-linked powders



Median (μm)	42.4
Mean	39.7
D25	24.8
D50	42.4
D75	69.1
D90	100.4

(2) Sample D30:70-1500, pyrolyzed powders



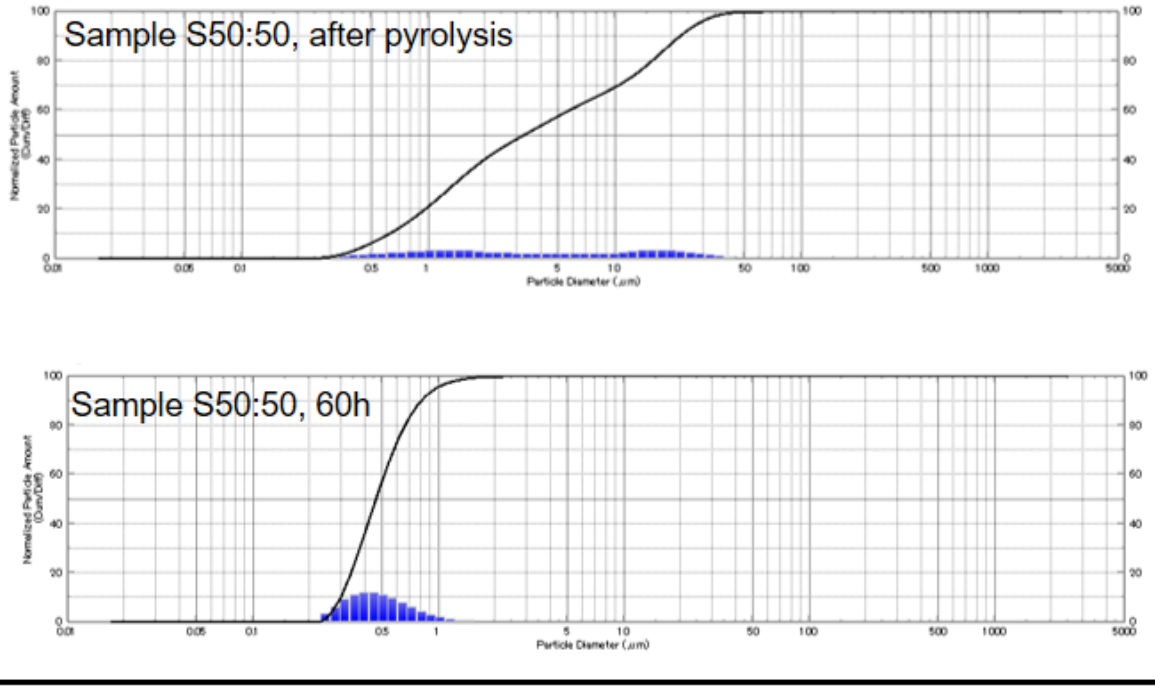
Median (μm)	9.5
Mean	7.1
D25	3.6
D50	9.5
D75	17.5
D90	25.4

- As expected, significant smaller particle size of the pyrolyzed ground powders than the cross-linked powder since the pyrolyzed ceramic is brittle.
- However, particle size still too large. Target particle size is sub-micron.

5. Task 2-Composite Ceramic Powders

- Several different milling approaches were evaluated.
- Optimized milling approach: 1 hour Spex mill for crosslinked powder; 60 hours planetary ball mill for pyrolyzed powders

Y_2O_3-Si-C-B system



Median (µm)	3.23
Mean	3.57
D25	1.14
D50	3.23
D75	12.99
D90	22.31

Median (µm)	0.46
Mean	0.35
D25	0.53
D50	0.78
D75	0.61
D90	0.81

After grinding for 60h, the ceramic powders have sub-micron particle size distribution.

5. Task 2-Composite Ceramic Powders

Particle size reduction-Summary

$SiCN/Y_2O_3$ composite

Sample Id	Composition		Synthesis temperature (°C)	Grinding Time (h)	Average particle size (μm)
	Y_2O_3 (vol.%)	Durazane 1800 (vol.%)			
D10:90	10	90	900	36	0.84
D30:70	30	70	900	36	0.75
D50:50	50	50	900	36	0.84
D70:30	70	30	900	36	0.78
D90:10	90	10	900	36	0.57

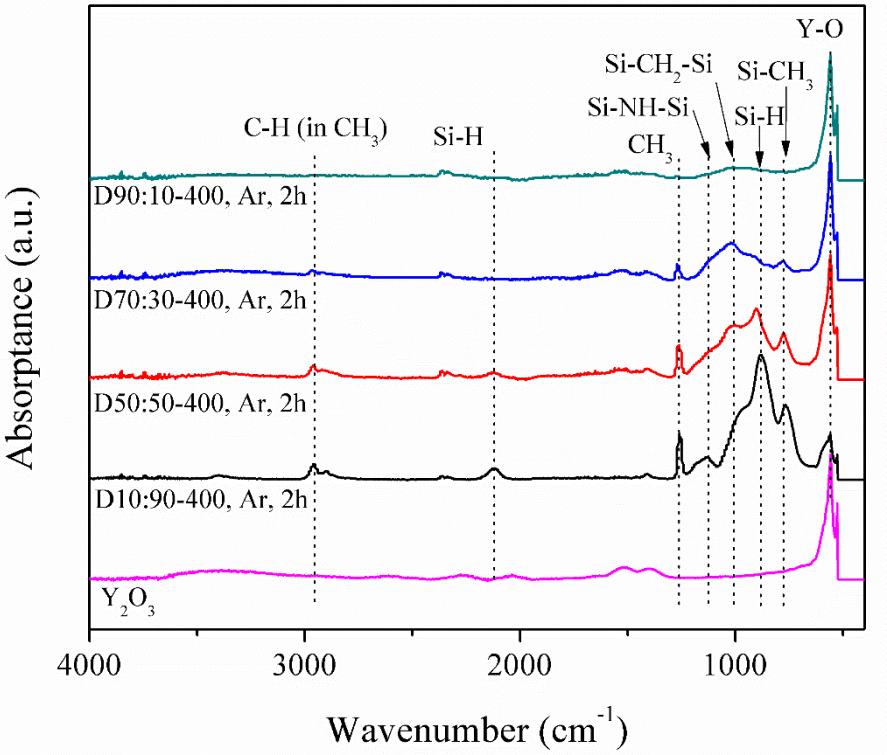
$SiC(B)/Y_2O_3$ composite

Sample Id	Composition		Synthesis temperature (°C)	Grinding Time (h)	Average particle size (μm)
	Y_2O_3 (vol.%)	Durazane 1800 (vol.%)			
S10:90	10	90	900	60	0.60
S30:70	30	70	900	60	0.77
S50:50	50	50	900	60	0.35
S70:30	70	30	900	60	0.55
S90:10	90	10	900	60	0.53

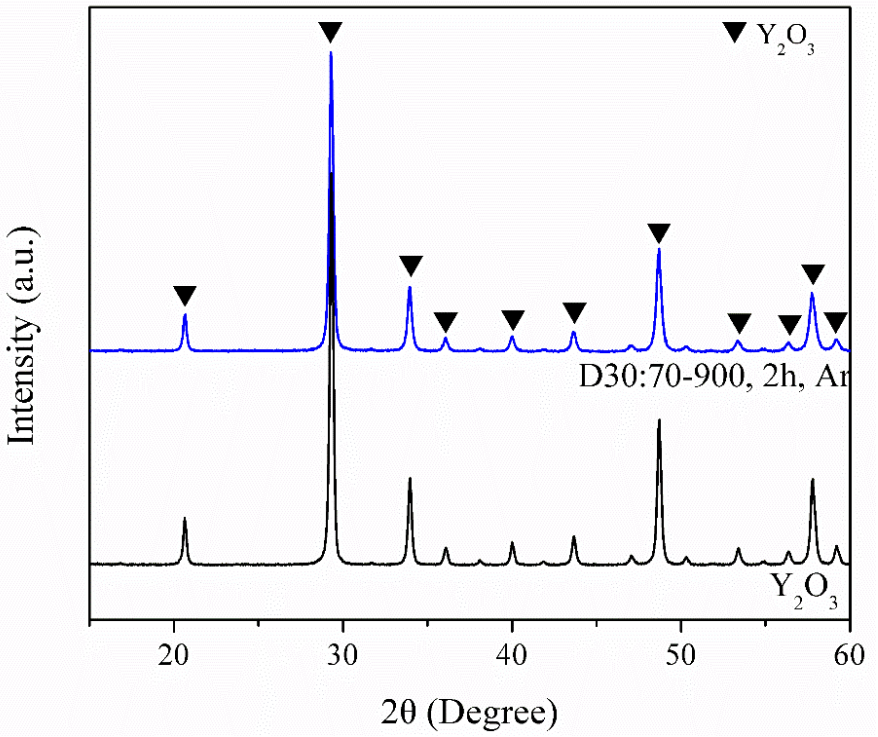
Using the optimized grinding procedure, all the powders can be ground to an average particle size smaller than 1 μm.

5. Task 2-Y_2O_3/SiCN Composite Ceramic

Powder characterization-FTIR and XRD



FTIR of cross-linked Y_2O_3/SiCN sample



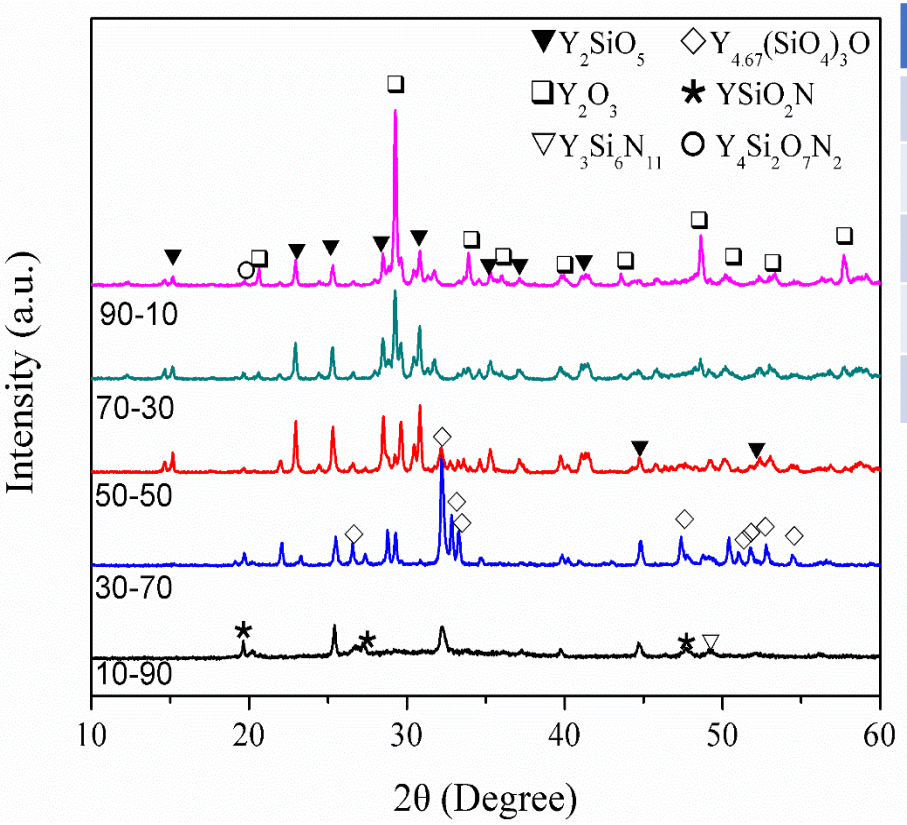
XRD of Y_2O_3 and sample after pyrolysis at 900ºC

- For Y_2O_3-Durazane system, Si-H, Si-CH_3, Si-NH-Si, Si-CH_2-Si from cross-linked Durazane, while Y-O from Y_2O_3.
- For Y_2O_3-SMP10 system, Si-H, Si-CH_3, and Si-CH_2-Si from cross-linked SMP10, while Y-O from Y_2O_3.
- After pyrolysis at 900ºC, only Y_2O_3 phases are shown in the XRD curves. This is because SiCN ceramic is amorphous after pyrolysis

5. Task 2-Y_2O_3/SiCN Composite Ceramic

Y_2O_3/SiCN pellets were fired at 1400, 1500 and 1600ºC under a flowing argon. The density, open porosity and microstructure were characterized

Y_2O_3/SiCN ceramic pellets (1400ºC) characterization-Phase composition



Sample	Phase compositions
10-90	$YSiO_2N$, Y_2SiO_5, $Y_3Si_6N_{11}$, $Y_{4.67}(SiO_4)_3O$
30-70	$Y_{4.67}(SiO_4)_3O$, Y_2SiO_5 Y_2O_3
50-50	$Y_{4.67}(SiO_4)_3O$, Y_2SiO_5 Y_2O_3
70-30	Y_2O_3, Y_2SiO_5,
90-10	Y_2O_3, Y_2SiO_5

$$Y_2O_3(s) + SiO_2(s) = Y_2SiO_5(s)$$

$$Y_2O_3(s) + Si_2N_2O(s) = 2YSiO_2N\ (s)$$

$$4Y_2O_3(s) + Si_3N_4(s) + SiO_2(s) = 2Y_4Si_2O_7N_2$$

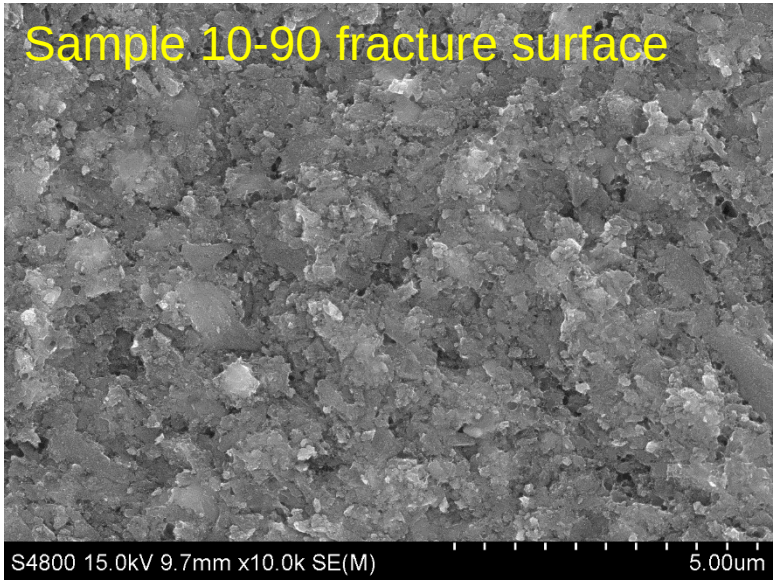
$$2.335Y_2O_3(s) + 3SiO_2(s) = Y_{4.67}(SiO_4)_3O(s)$$

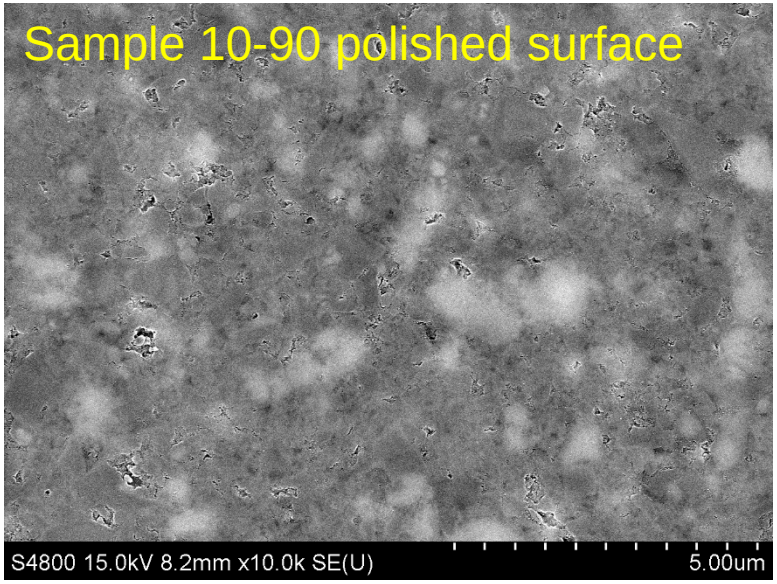
$$2/3Y_{4.67}(SiO_4)_3O(s) + 4/9Y_2O_3 = 2Y_2SiO_5$$

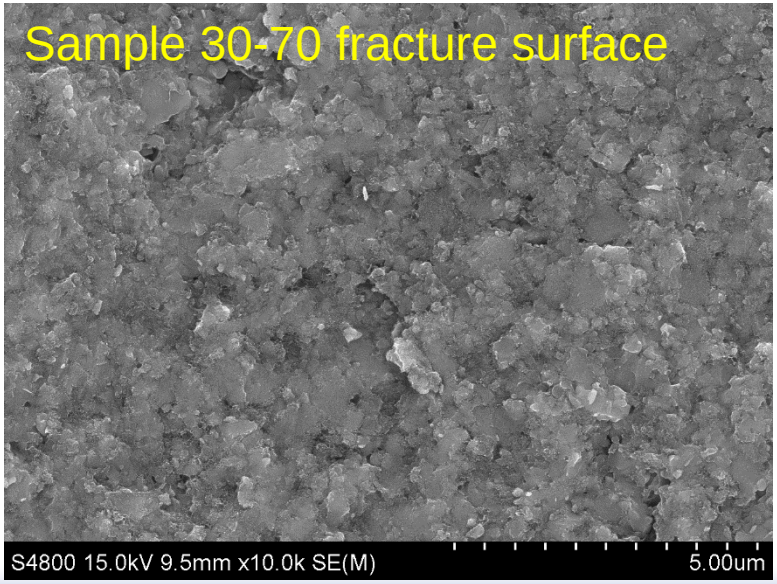
- No Si_3N_4 or SiC phases are detected in the samples, mainly because the amorphous SiCN is stable up to 1500 ºC

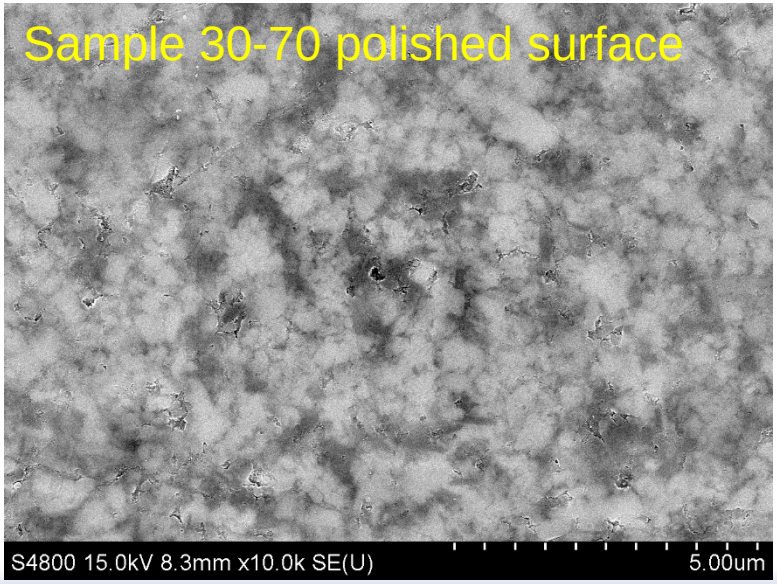
5. Task 2-Y_2O_3/SiCN Composite Ceramic

Y_2O_3/SiCN ceramic composites (1400ºC) characterization-Microstructure



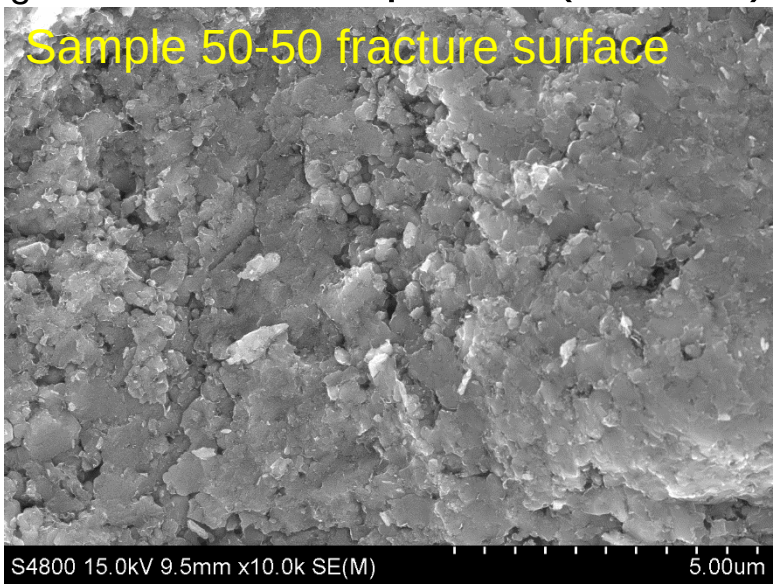


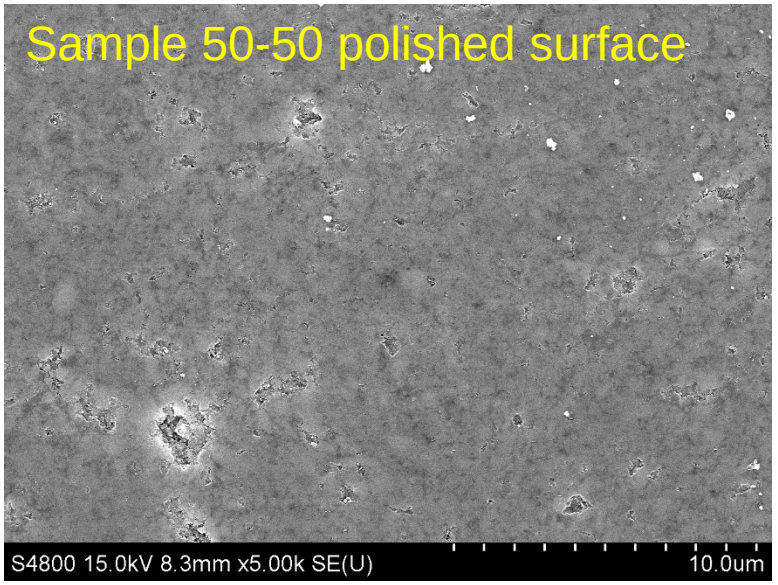


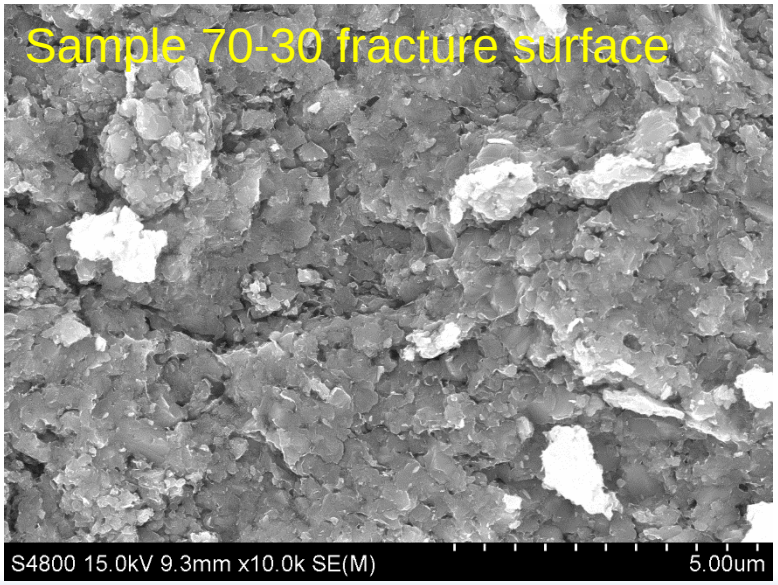


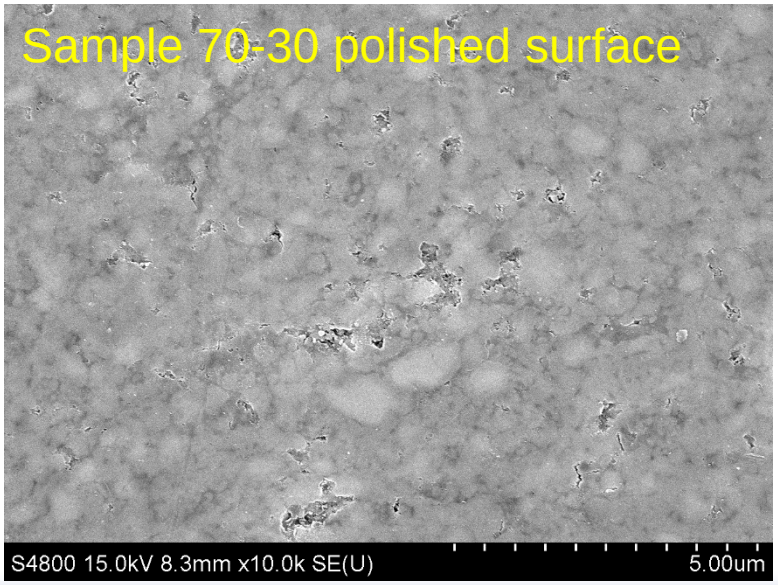
5. Task 2-Y_2O_3/SiCN Composite Ceramic

Y_2O_3/SiCN ceramic pellets (1400ºC) characterization-Microstructure



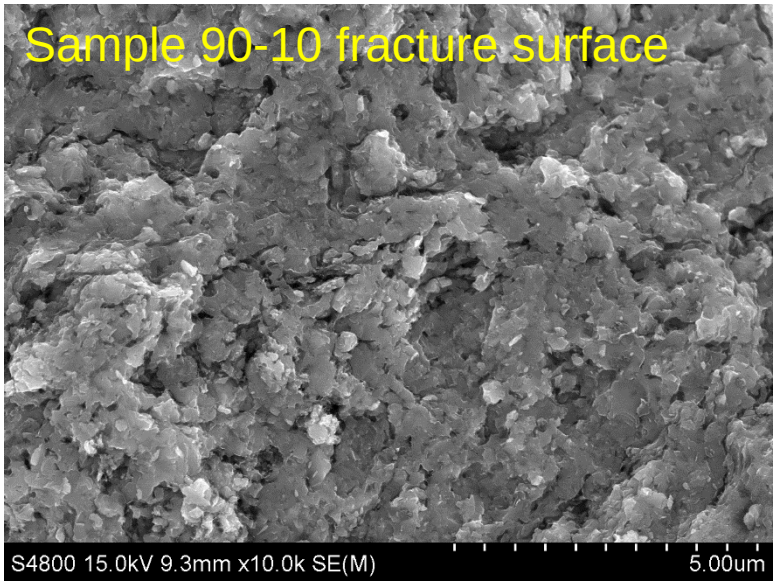


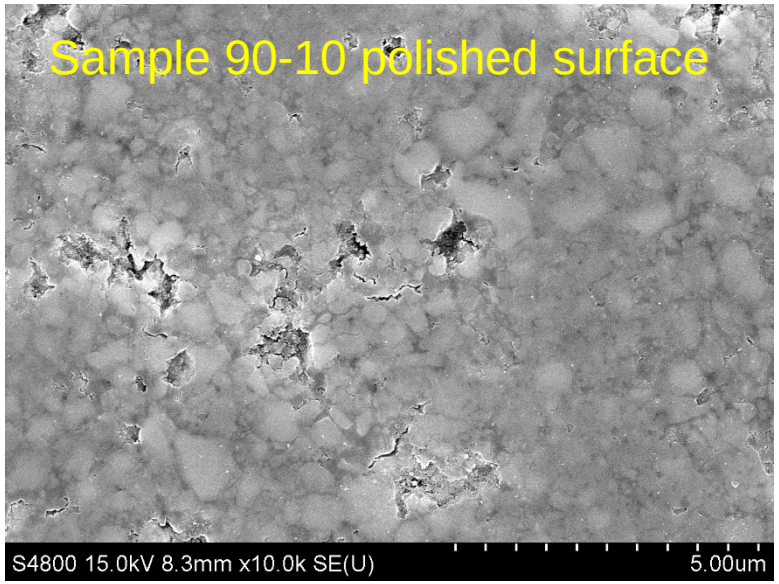




5. Task 2-Y_2O_3/SiCN Composite Ceramic

Y_2O_3/SiCN ceramic pellets (1400ºC) characterization-Microstructure





Density characterizations:

1. Green density (geometric):

2. The bulk densities (ρ_b) and open porosities (P_o) of fired pellets were obtained from Archimedes' method according to the ASTM standard

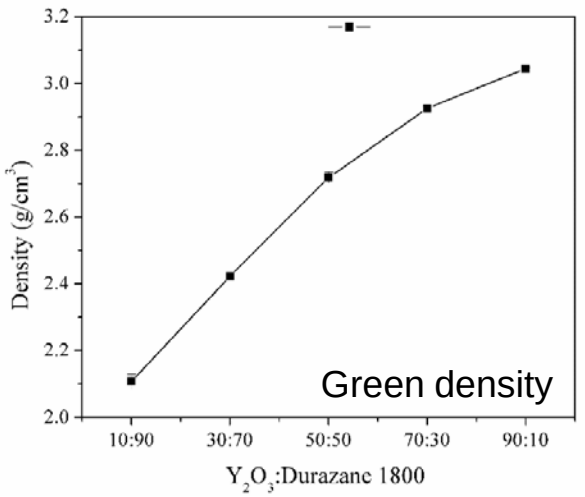
3. The skeletal densities (ρ_s) of fired pellets were obtained through helium pycnometer test.

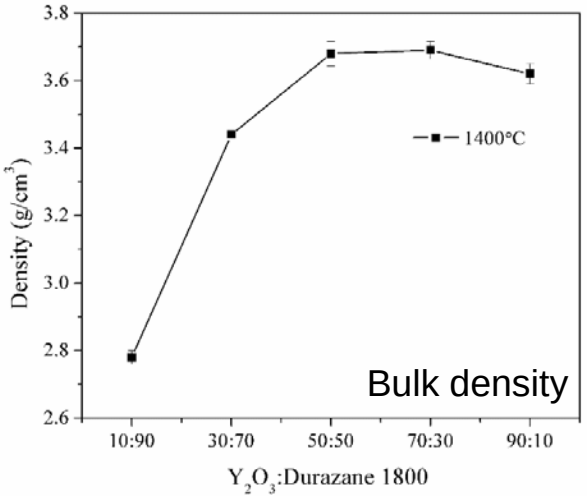
The relative density (ρ_r) and total porosity (P_t) of fired pellets were obtained from the following equations:

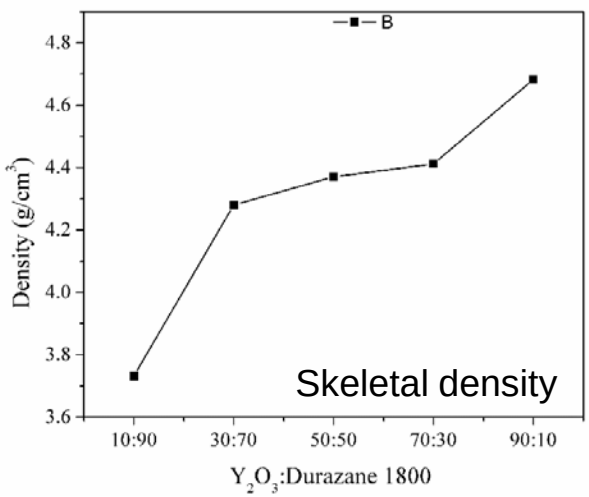
$$\boldsymbol{\rho_r = \frac{\rho_b}{\rho_s} \times 100} \qquad \boldsymbol{P_t = (1 - \frac{\rho_b}{\rho_s}) \times 100}$$

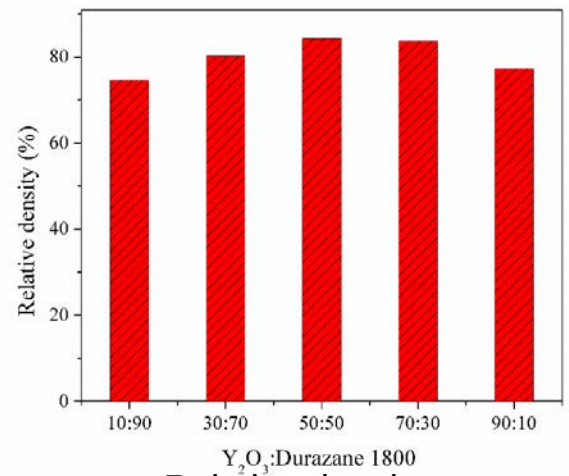
5. Task 2-Y_2O_3/SiCN Composite Ceramic

Y_2O_3/SiCN ceramic composites (1400ºC) characterization-Density and Porosity







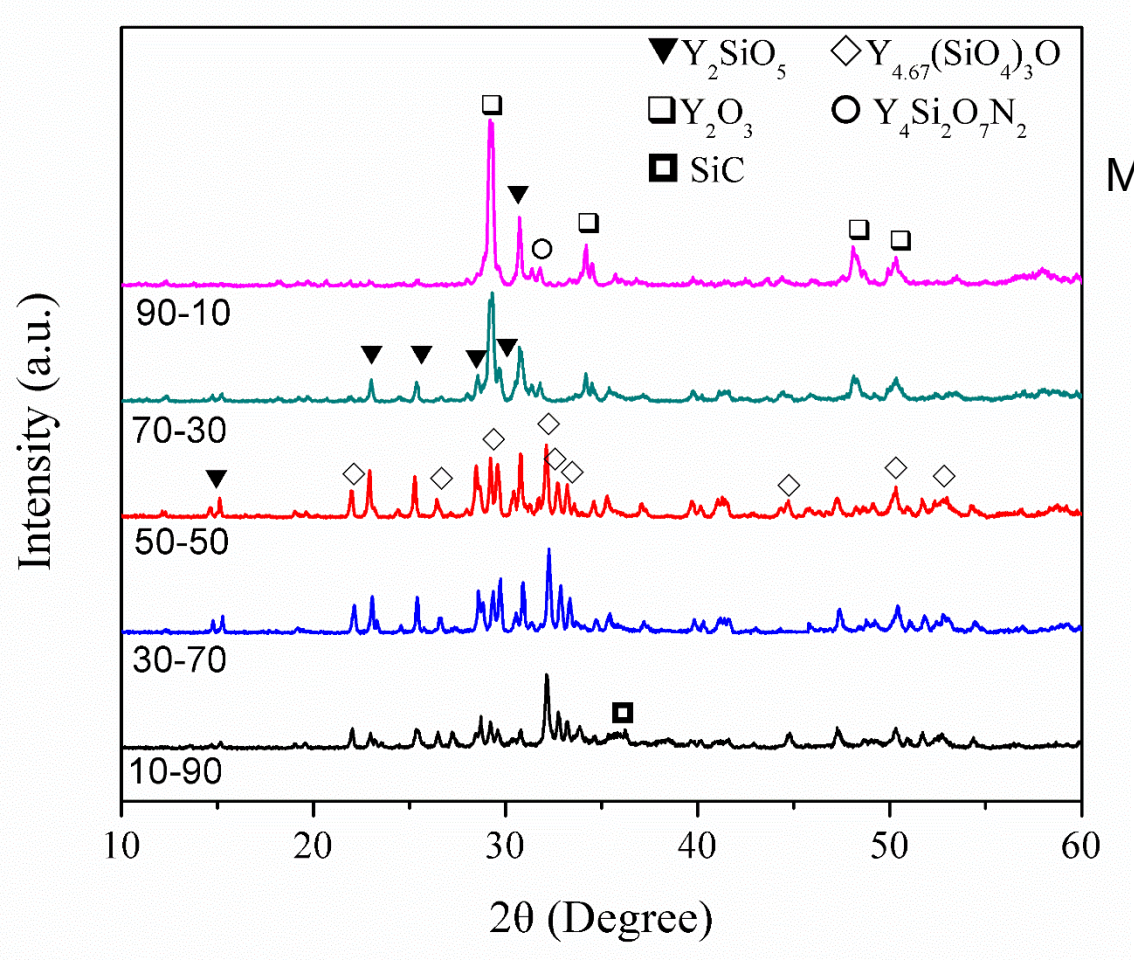


Relative density

- The green densities, bulk densities and skeletal densities of samples show increasing trend with increasing Y_2O_3 volume. Density of Y_2O_3 (5.01 g/cm^3) > Density of PDC-SiCN
- The highest relative density is 84%.

5. Task 2-Y_2O_3/SiCN Composite Ceramic

Y_2O_3/SiCN ceramic composites (1600ºC) characterization-Phase composition



Main phases:

Y_2O_3, Y_2SiO_5

Y_2O_3, Y_2SiO_5

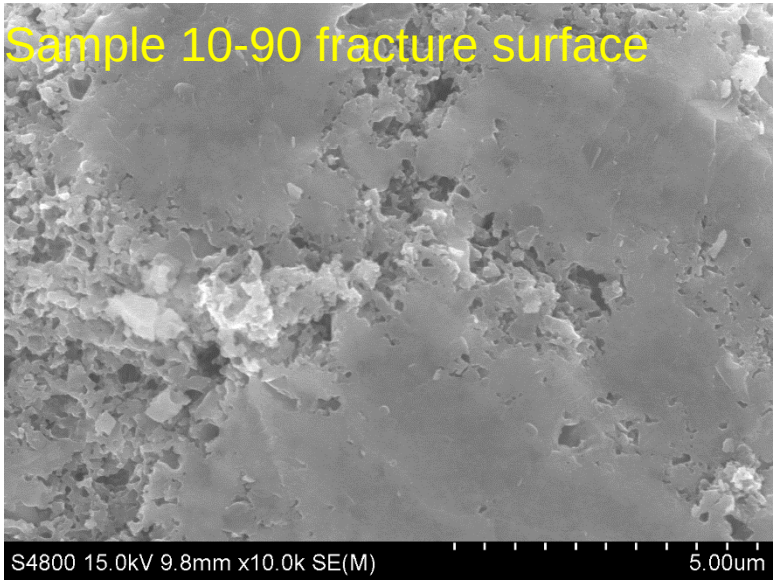
$Y_{4.67}(SiO_4)_3O$, Y_2SiO_5

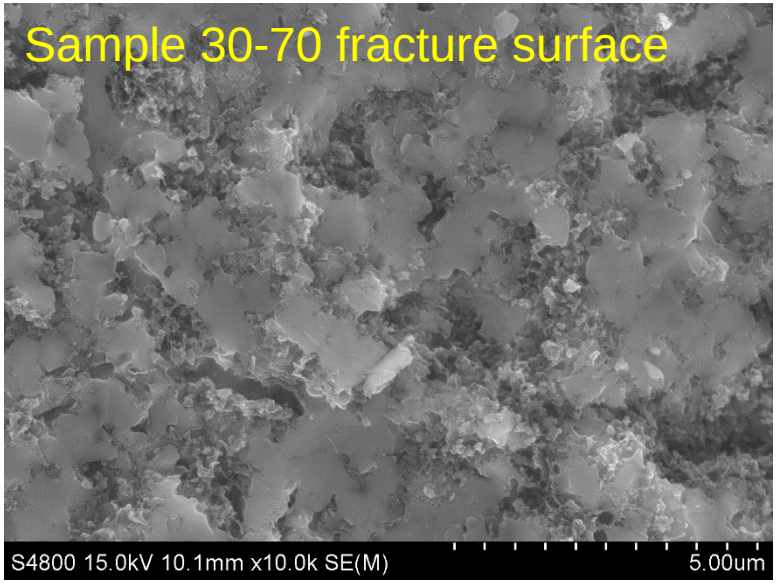
$Y_{4.67}(SiO_4)_3O$, Y_2SiO_5

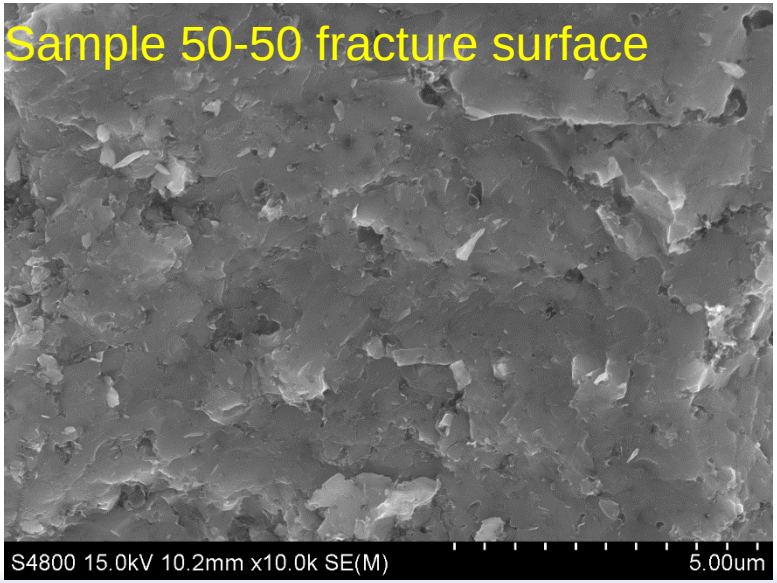
$Y_{4.67}(SiO_4)_3O$, Y_2SiO_5

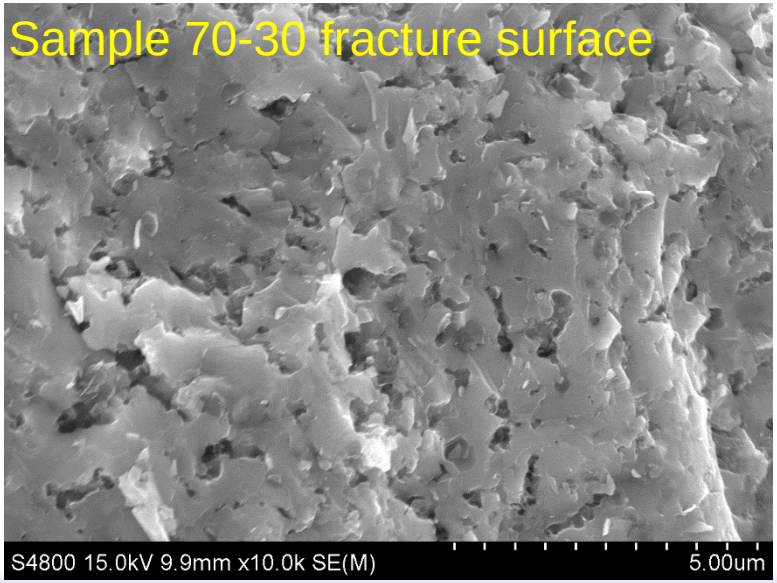
5. Task 2-Y_2O_3/SiCN Composite Ceramic

Y_2O_3/SiCN ceramic composites (1600ºC) characterization-Microstructure



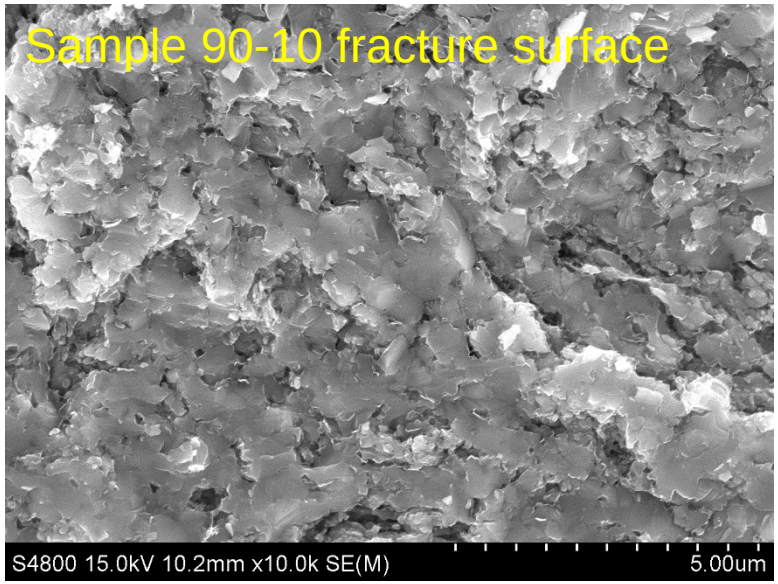






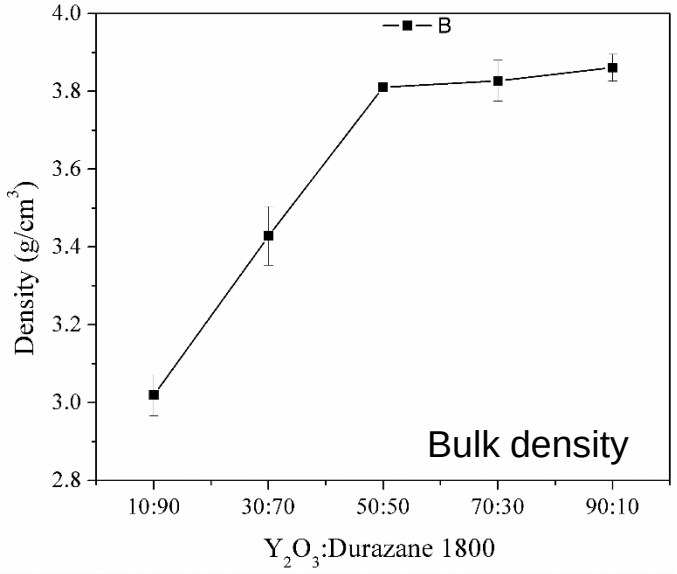
5. Task 2-Y_2O_3/SiCN Composite Ceramic

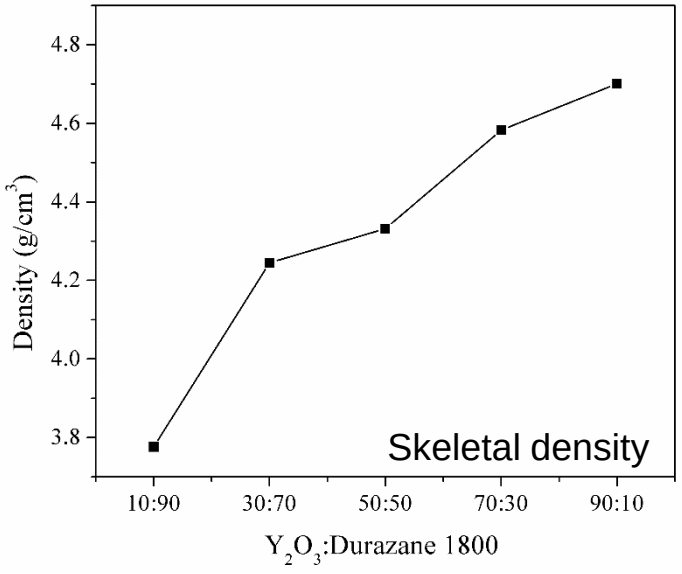
3. Y_2O_3/SiCN ceramic composites (1600ºC) characterization-Microstructure

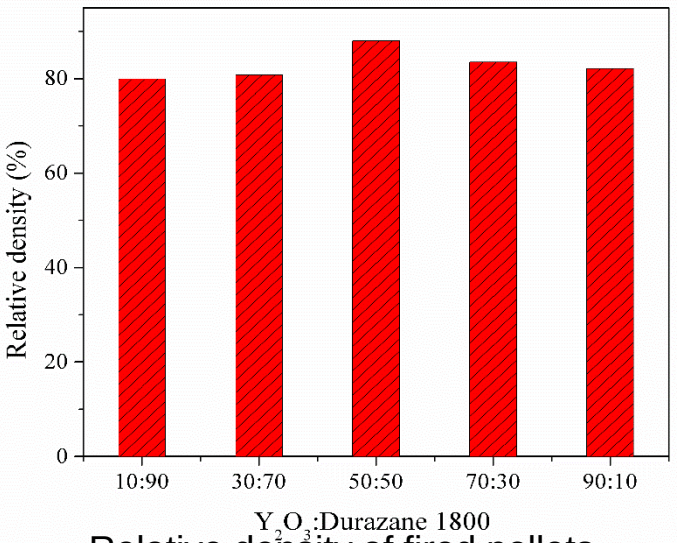


5. Task 2-Y_2O_3/SiCN Composite Ceramic

3. Y_2O_3/SiCN ceramic pellets (1600ºC) characterization-Microstructure





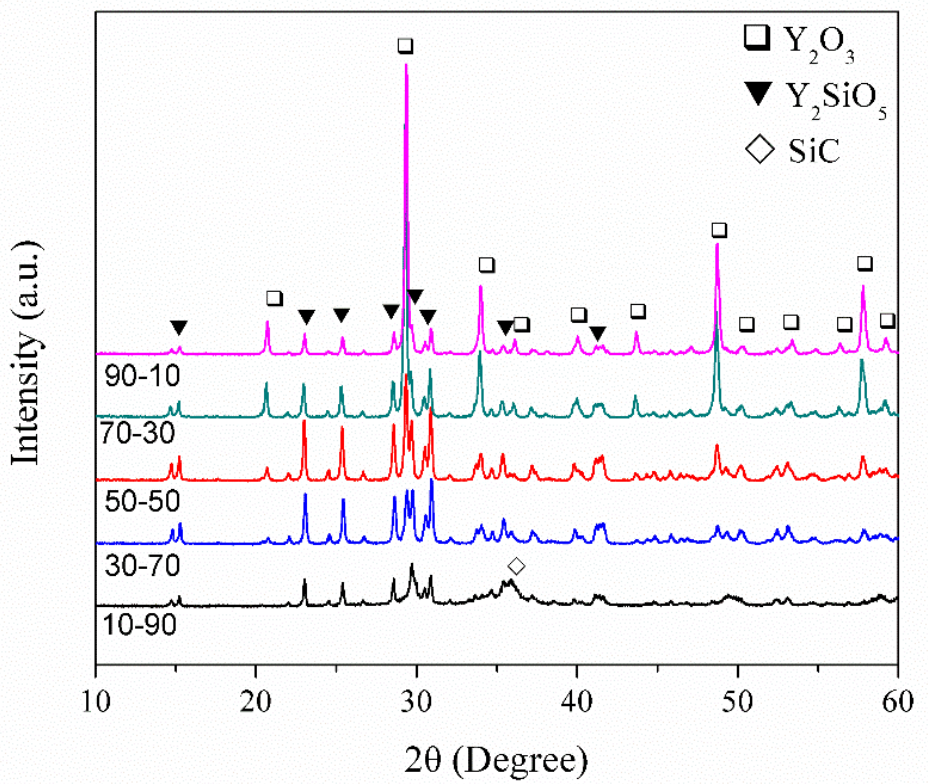


Relative density of fired pellets

- When firing temperature increases to 1600ºC, all the relative densities increase. The highest relative density is 88%.

5. Task 2-Y_2O_3/SiC(B) Composite Ceramic

Y_2O_3/SiC(B) ceramic composites (1500ºC) characterization-Phase composition

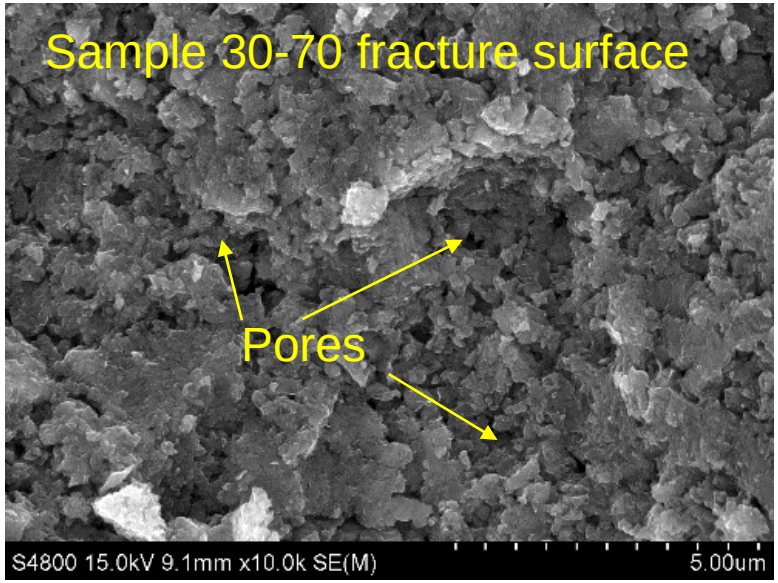


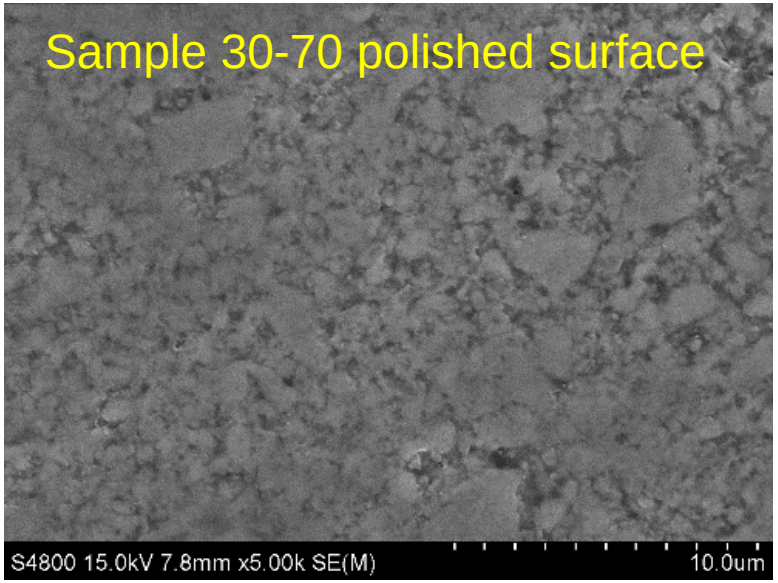
$$Y_2O_3(s) + SiO_2(s) = Y_2SiO_5(s)$$

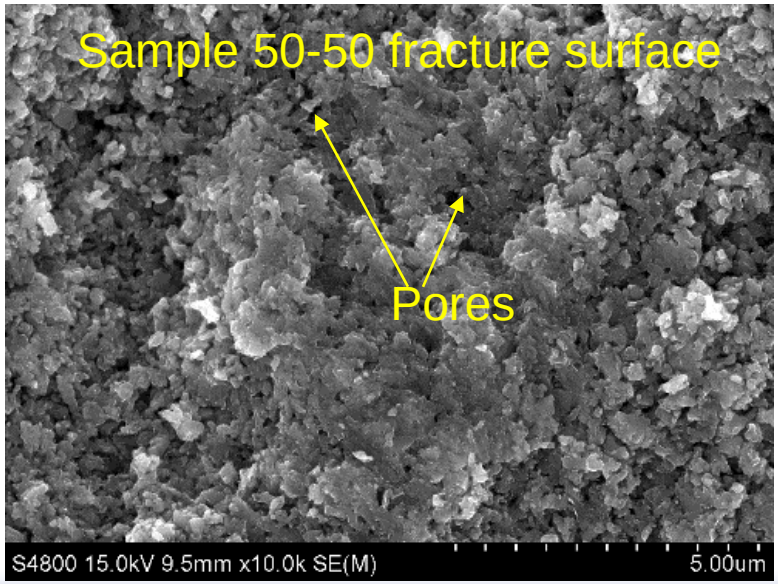
- The main crystallized phases are Y_2O_3 and Y_2SiO_5

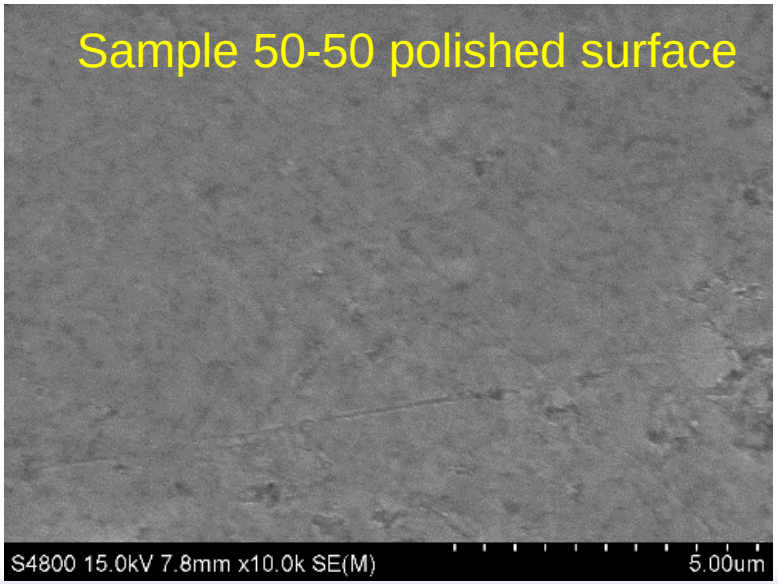
5. Task 2-Y_2O_3/SiC(B) Composite Ceramic

Y_2O_3/SiC(B) ceramic composites (1500ºC) characterization-Microstructure



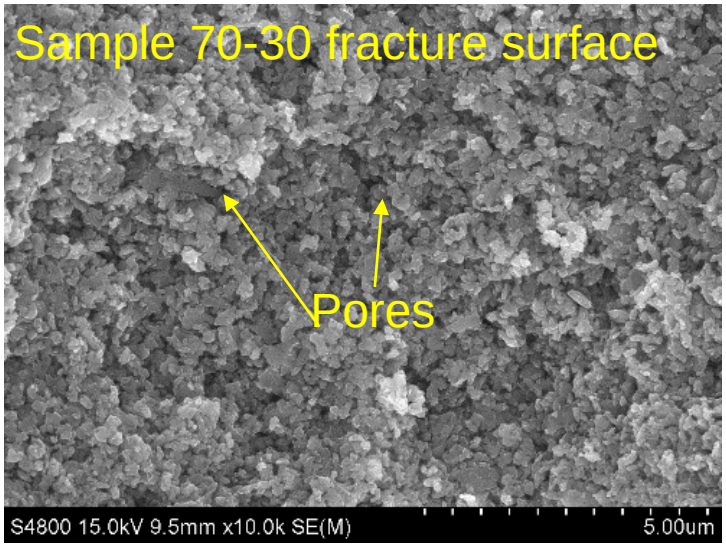


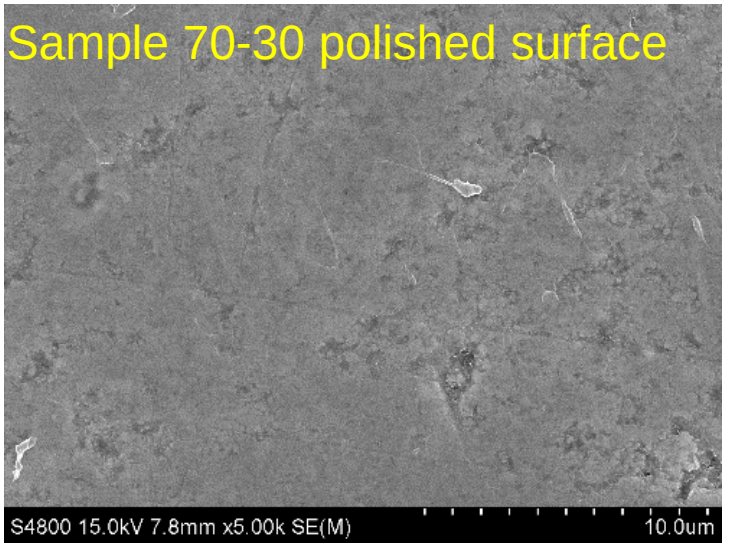


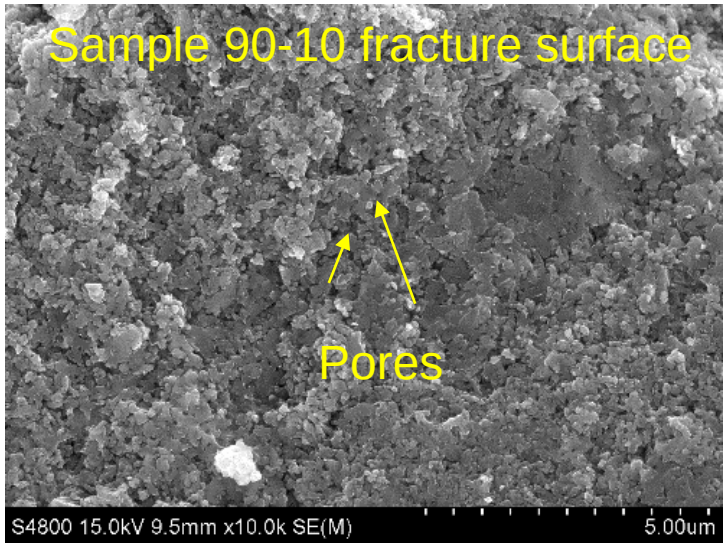


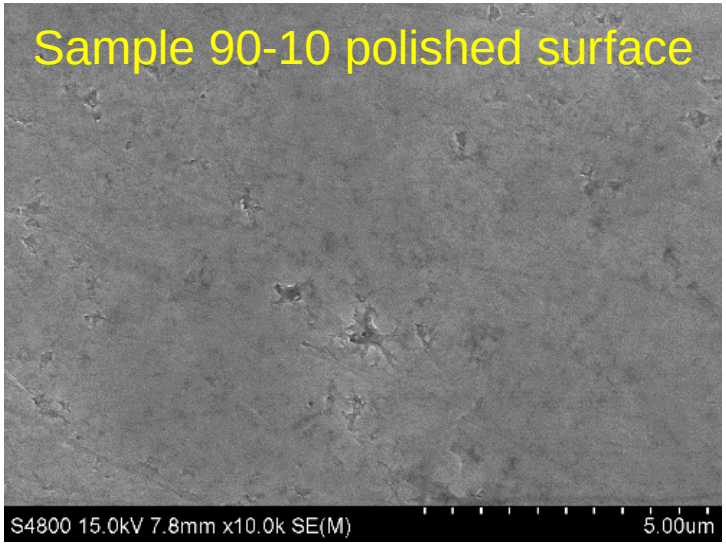
5. Task 2-Y_2O_3/SiC(B) Composite Ceramic

Y_2O_3/SiC(B) ceramic composites(1500ºC) characterization-Microstructure





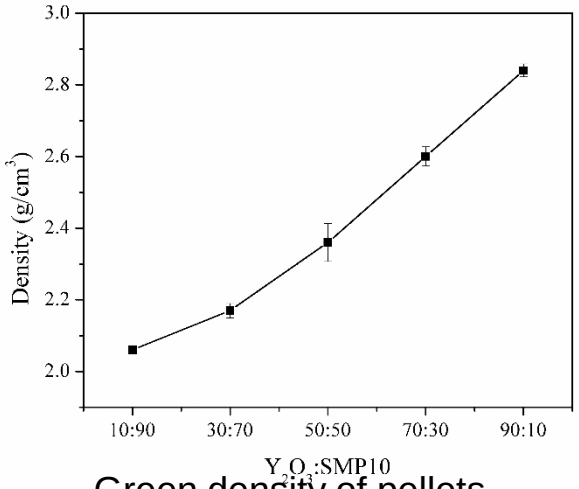




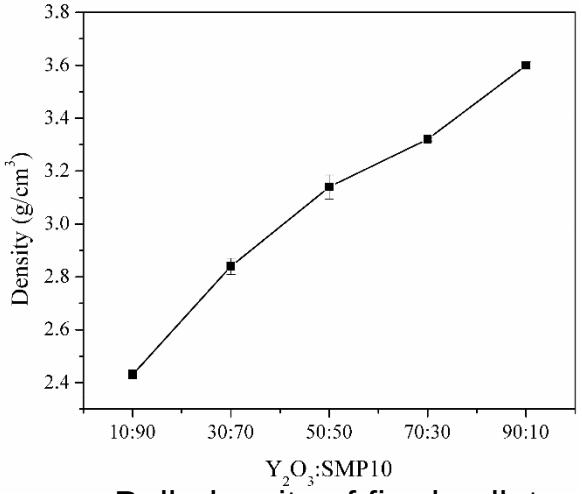
The surface after polishing becomes smoother when the volume of Y_2O_3 is greater than 30%.

5. Task 2-Y_2O_3/SiC(B) Composite Ceramic

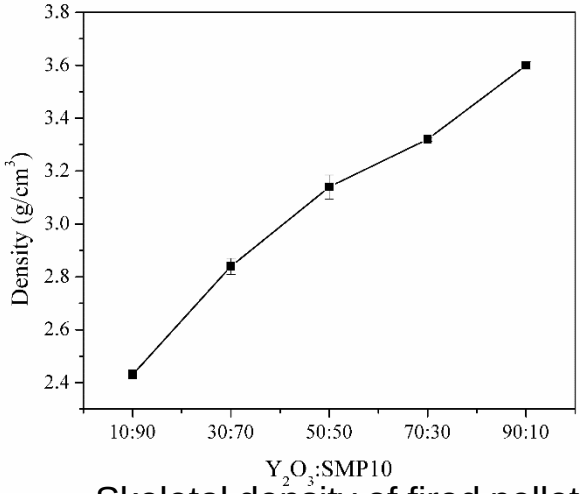
1. Y_2O_3/SiC(B) ceramic pellets (1500ºC) characterization-Density and porosity



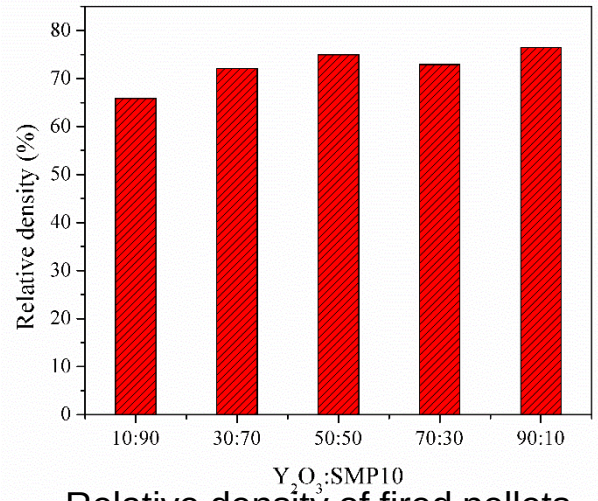
Green density of pellets



Bulk density of fired pellets



Skeletal density of fired pellets



Relative density of fired pellets

- The densities of samples increase with increasing Y_2O_3 volume.
- The highest relative density is 76%.

5. Project Progress-Task 2

Summary of Progress on Processing and stability of Y_2O_3-Si-B-C, Yb_2O_3-Si-B-C, Y_2O_3-Si-B-C-N and Yb_2O_3-Si-B-C-N composites

- High density top coat processed
- Composite powders synthesized over a broad range of compositions
- Milling procedure optimized
- Effect of processing temperature on the density and microstructure in some systems investigated and quantified (Y_2O_3-Si-B-C, and Y_2O_3-Si-B-C-N)
- The densities of the intermediate layers are in the acceptable range.

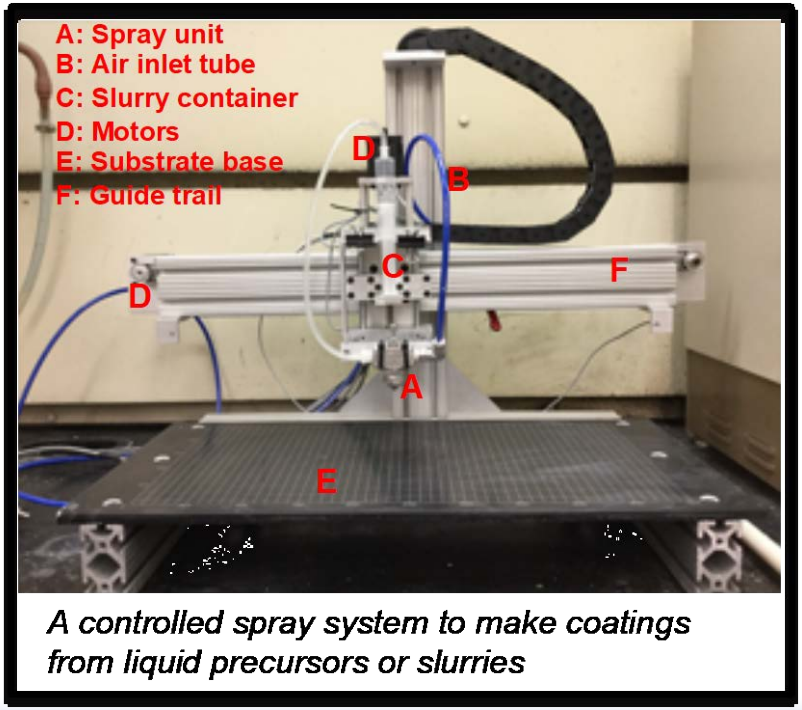
Ongoing work

- Complete the effect of processing temperature on the density and microstructure
- Effect of processing atmosphere

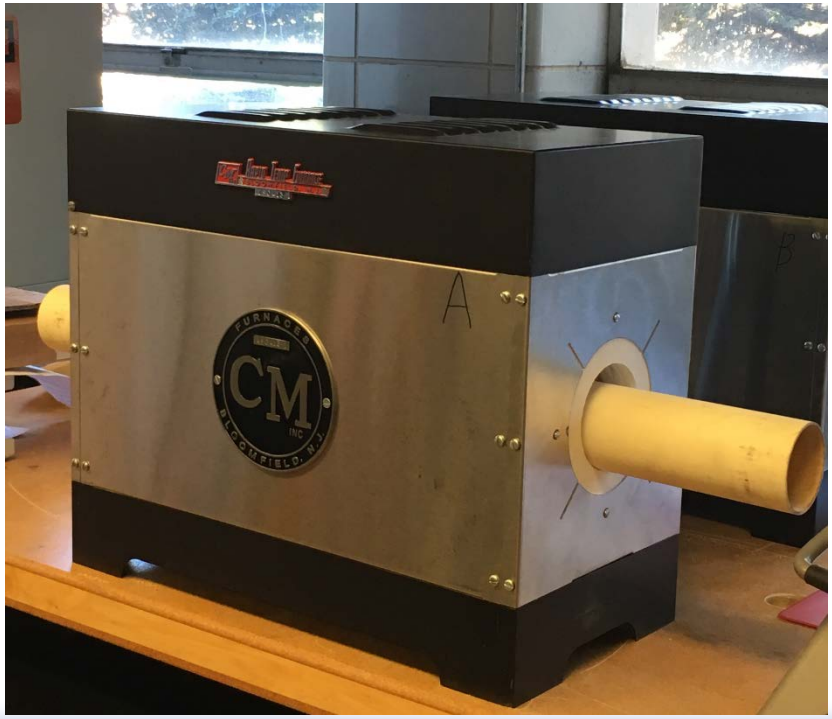
5. Project Progress-Task 4

Task 4: Processing and performance of graded coatings processed using cold spray and pyrolysis

- The cold spray system to make coatings has been assembled (100% completion)
- Purchased the tube furnace for the investigation of oxidation response of the composites (100% completion)
- Designing and setting up the steam jet oxidation furnace (60% completion)



A controlled spray system to make coatings from liquid precursors or slurries



6. Project Short Term Plans

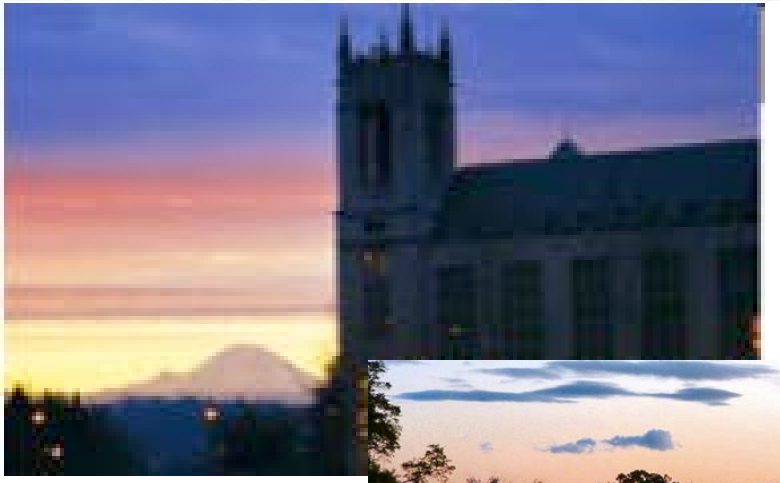
In the next few months work work will focus on

Task 2.0: Processing and stability of Y_2O_3-Si-B-C-N and Yb_2O_3-Si-B-C-N composites

- Studies on the processing of composites in the Y_2O_3-Si-C-B and the Y_2O_3-Si-C-N systems – effect of synthesis atmosphere and synthesis method on density, porosity and phase composition

Task 3: Thermal and oxidation response of Y_2O_3-Si-B-C-N and Yb_2O_3-Si-B-C-N composites

- Complete the experimental setup to investigate the oxidation response of the composites (under high velocity steam) and begin these studies.



Thank you very much for your attention and support