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

DoE UTSR DEFE0031281 (10/2017 – 09/2021)
Annual Review Meeting
Program Manager: Matthew Adams

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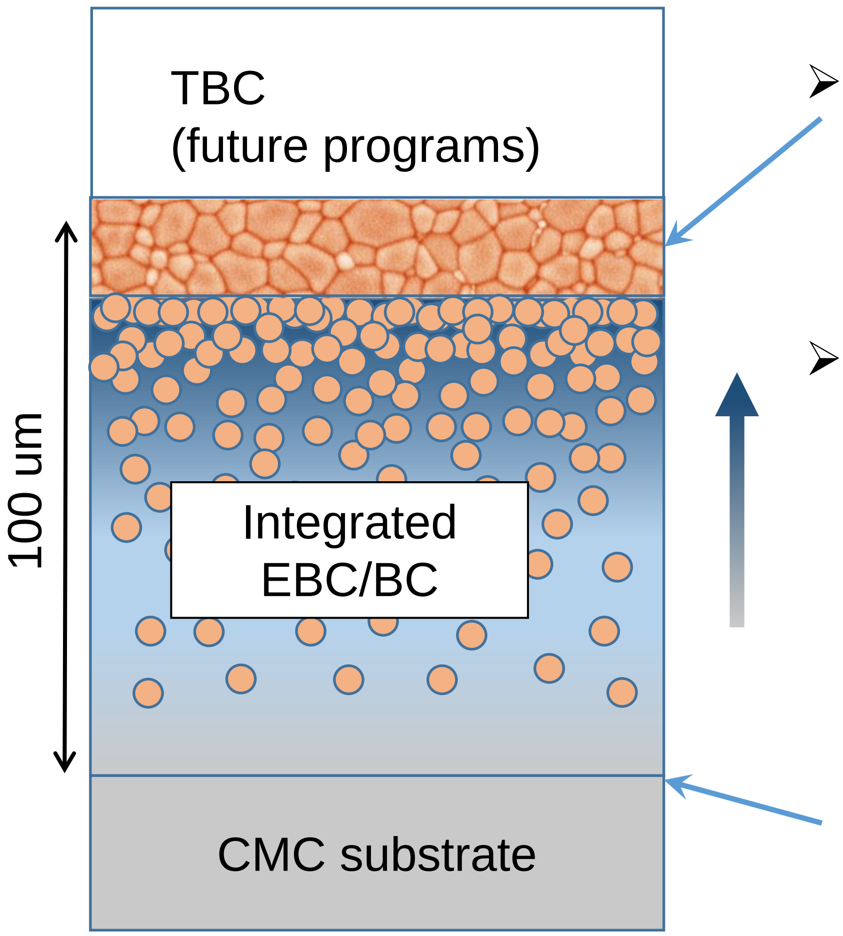
In Collaboration with GE Power Team led by John Delvaux

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-C-N and Yb_2O_3-Si-C-N composites
- **Task 3:** Thermal and oxidation response of Y_2O_3-Si-C-N and Yb_2O_3-Si-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
- A talk and a poster at the 2018 UTSR review meeting
- A talk at 2019 UTSR review meeting.
- Request for a one year no-cost extension (approved)
- Regular periodic review meetings with DoE Program Manager and GE team throughout the project

5. Project Progress - Task 2:

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

Sub-task 2.1: Determine the effect of composition and processing temperature on the phase and microstructure of composites

Part of this task (~ 20%) completed in year 1 and rest of the part is completed in year 2

Sub-task 2.2: Investigate the effect of temperatures on the phase stability phase and microstructure of composites during oxidation at temperatures up to 1600ºC.

Completed in year 2.

5. Project Progress - Task 3

Task 3: Thermal and oxidation response of Y_2O_3-Si-C-N and Yb_2O_3-Si-C-N composites (90% complete)

Sub-task 3.1: Determine the effect of composition and microstructure of composites on thermal expansion coefficient, elastic modulus and thermal conductivity (80 % completed)

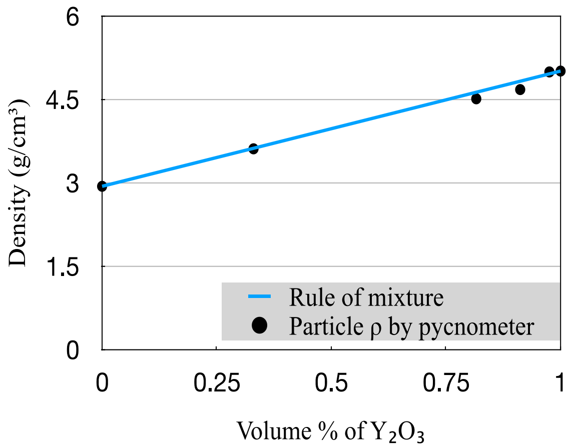
In year 2, we have completed this sub-task around 40 %. Accomplished the following:

- Measured the heat capacity and thermal conductivity of the Y_2O_3-SiO_2 composites
- Developed and validated a technique for high temperature elastic modulus of ceramics

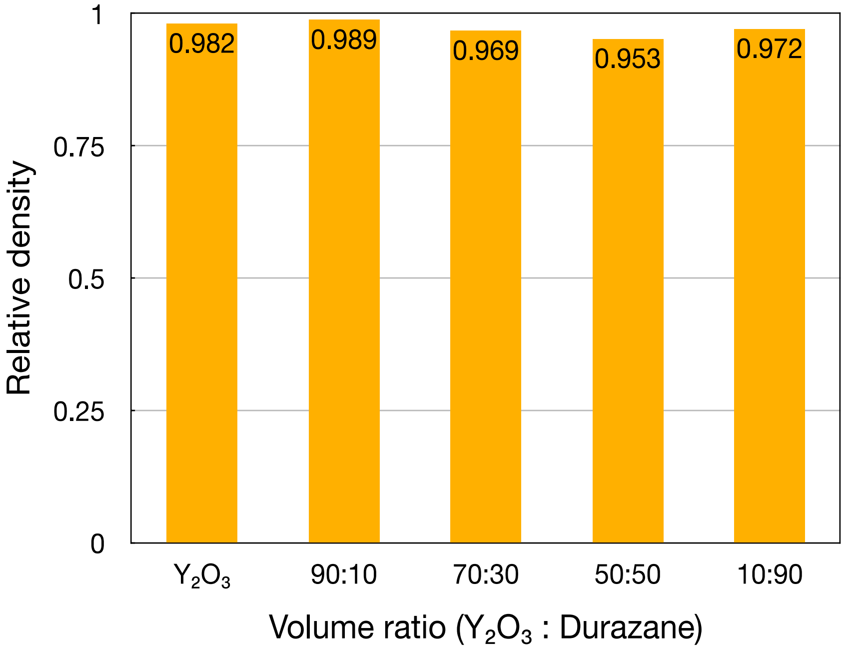
In year 3, we have completed 80 % of the sub-task. Accomplished the following:

- Made high density Y_2O_3-SiCN composites using field assisted sintering (FAST)
- Measured the coefficients of thermal expansion for Y_2O_3-SiCN, Y_2O_3-SiO_2, and Yb_2O_3-SiO_2 composites
- Measured the elastic modulus of Y_2O_3-SiCN composites as a function of temperature
- Measured the heat capacity of Yb_2O_3-SiO_2 composites

5. Task 3 - High Density Y_2O_3-SiCN Composites



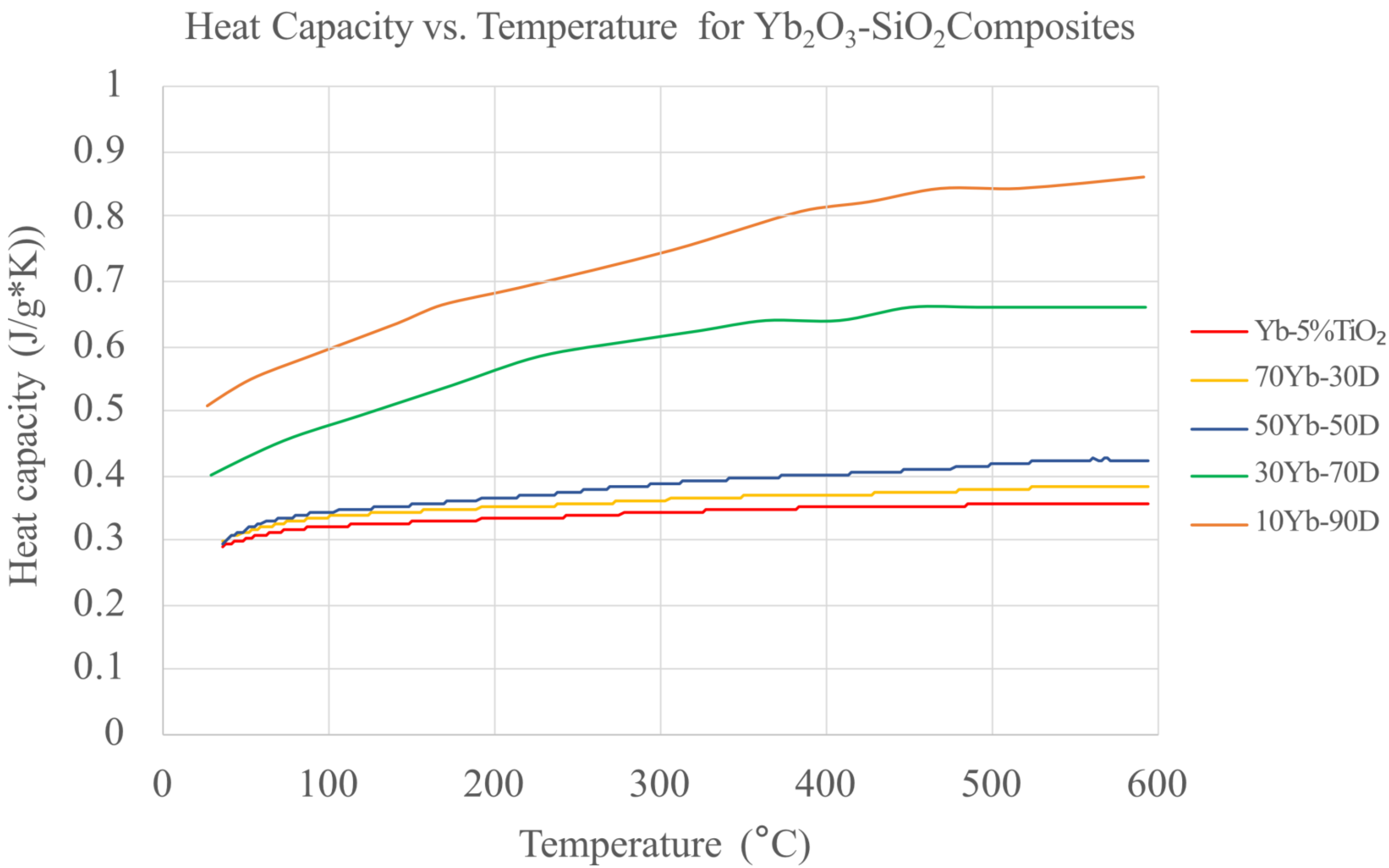
	After heat treatment	
Sample	Volume % of Y_2O_3	Volume % of SiCN
Y_2O_3	100	0
9Y-1D	98	2
7Y-3D	91	9
5Y-5D	82	18
1Y-9D	33	67
Durazane	0.00	100



Relative density of FAST samples processed at 1350°C for 5 mins under vacuum

Processing protocols to make high density Y_2O_3-SiCN compositions using FAST (needed for thermomechanical property measurement

5. Task 3 - Heat Capacity of Yb_2O_3-SiO_2 Composites

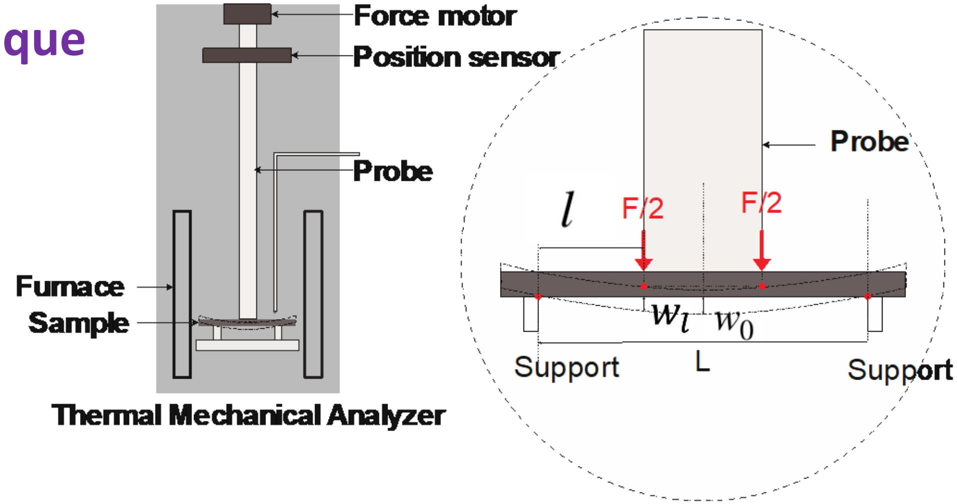


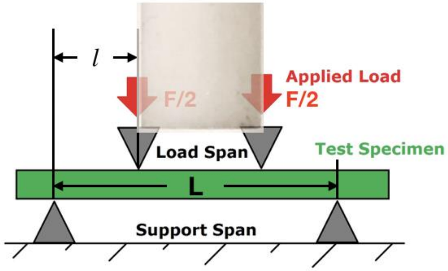
As expected, the higher Yb_2O_3 content, the lower heat capacity.

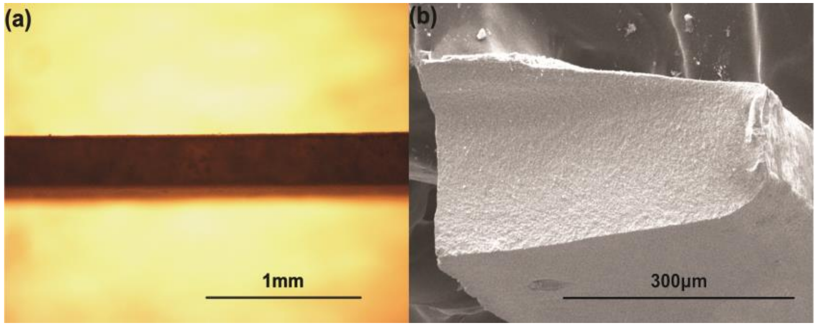
5. Task 3 - Elastic Modulus of Y_2O_3-SiCN Composites

Thermo Mechanical Analyzer (SS6000)

Developed Technique

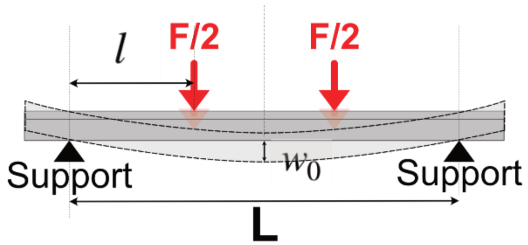




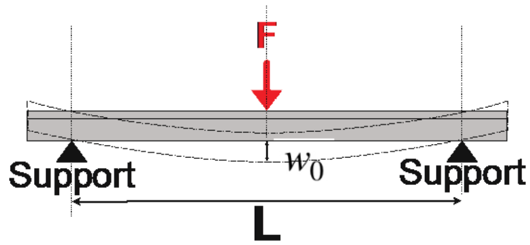


- Sample fabricated using laser machining
- Analysis uses the tapered sample cross-section

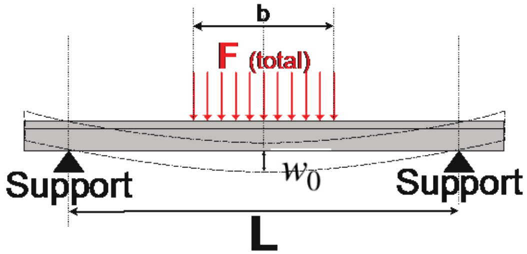
5. Task 3 – Elastic Modulus Technique Development



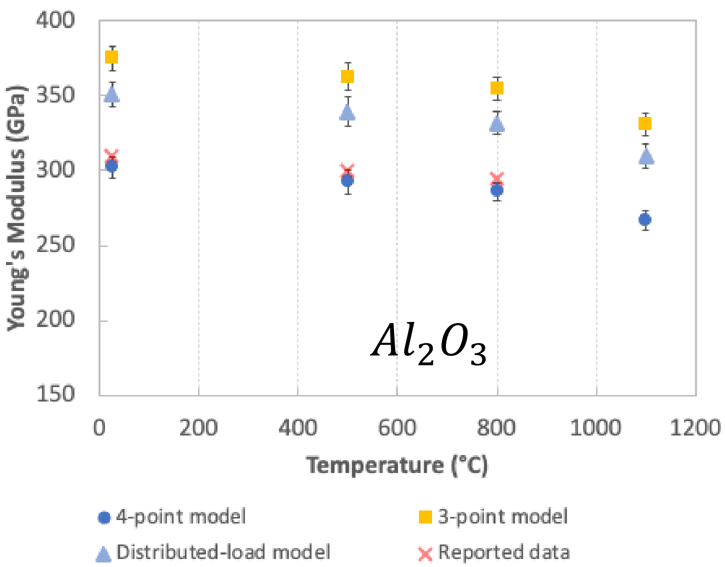
$$E = \frac{Fl(3L^2 - 4l^2)}{48Iw}$$

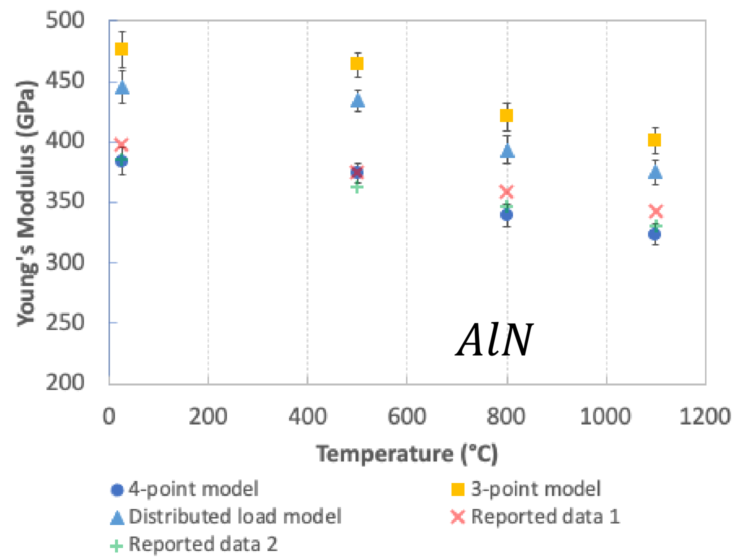


$$E = \frac{FL^3}{48Iw}$$



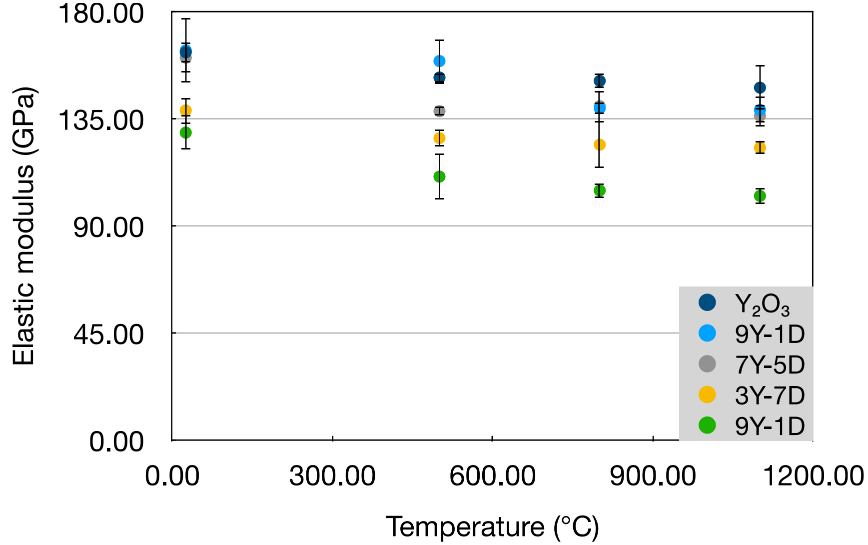
$$E = \frac{F(8L^3 - 4b^2L + b^3)}{384Iw}$$

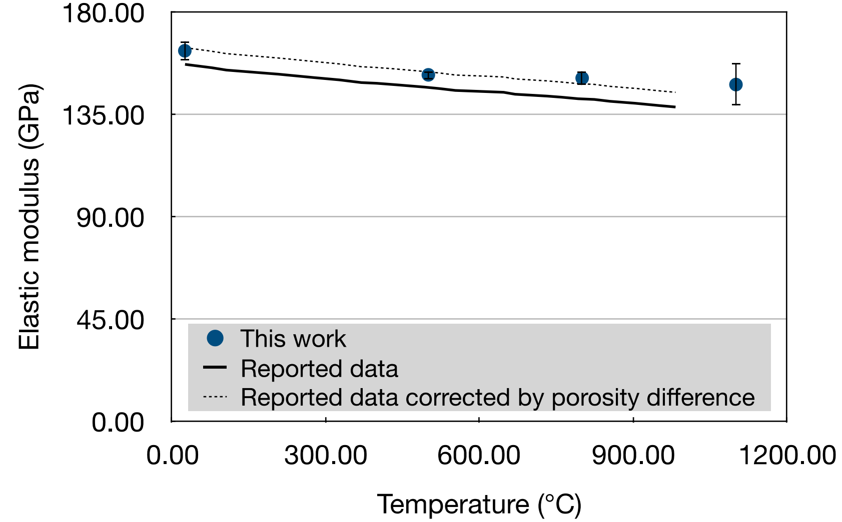




- 4-point model best since the modulus is measured at the start of the unloading process.
- The measured results match value the reported values for Al_2O_3 and AlN

5. Task 3 - Elastic Modulus of Y_2O_3-SiCN Composites





- Elastic modulus of Y_2O_3-SiNC composites decreased with temperature and the content of amorphous silicate phase.
- The temperature dependence of pure Y_2O_3 samples matches well with reported results.

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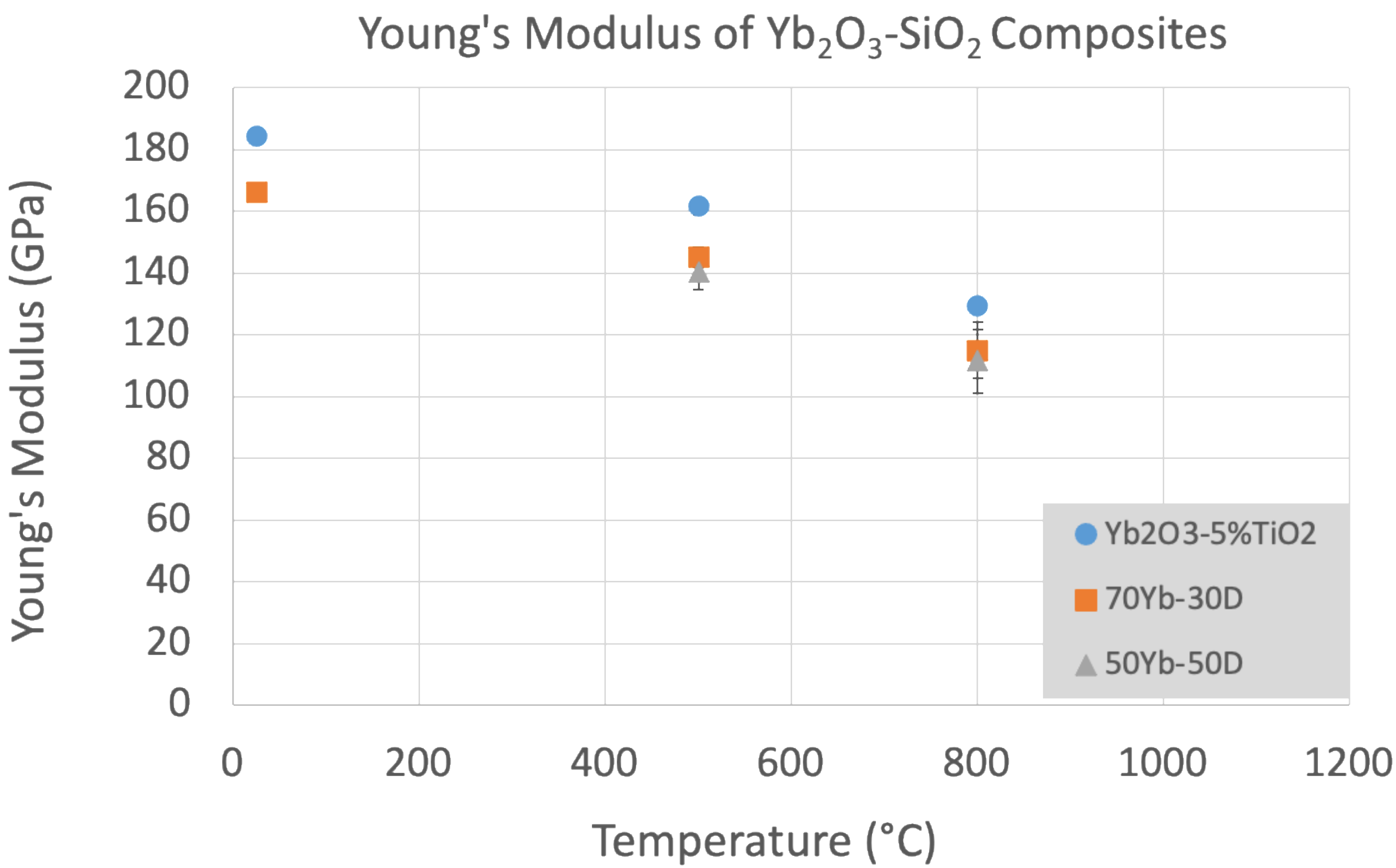
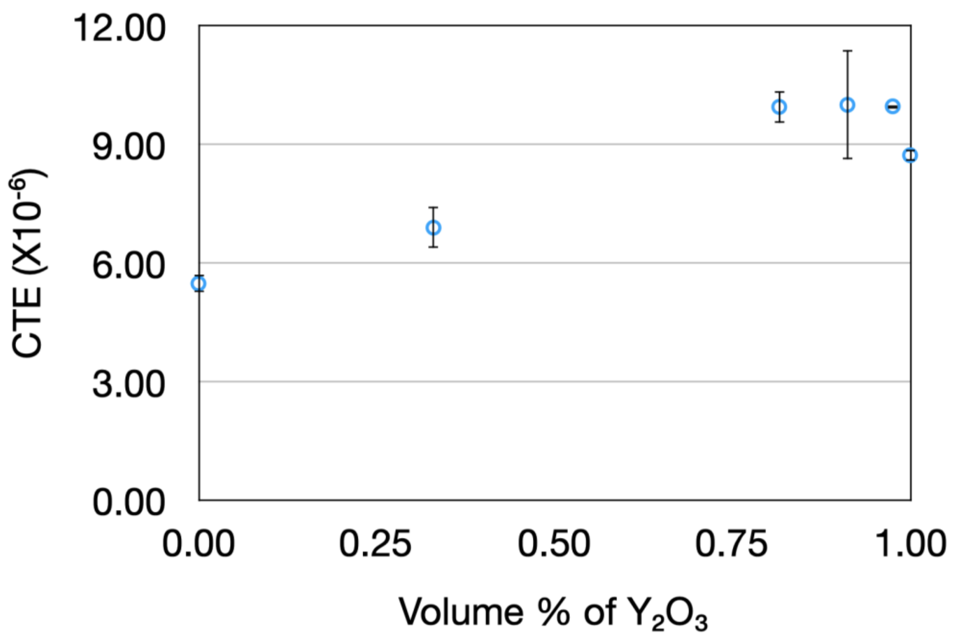
5. Task 3 - Elastic Modulus of Y_2O_3-SiO_2 composites



❖ Elastic modulus of Y_2O_3-SiO_2 composites decreased with temperature and SiO_2 content.

5. Task 3 - Coefficient of Thermal Expansion of Y_2O_3-SiCN Composites

	CTE ($\times 10^{-6}$/°C)
Y_2O_3	8.73
90Y-10D	9.97
70Y-30D	10
50Y-50D	9.95
10Y-90D	6.9
Durazane	5.49



- Pure Durazane derived ceramics have the lowest value
- Y_2O_3 value similar to reported data.
- The higher values for some composites maybe be due to oxidation during the CTE measurement.

5. Task 3 - Coefficient of Thermal Expansion of Y_2O_3-SiO_2 and Yb_2O_3-SiO_2 Composites

	CTE (×10^{-6}/°C)
Y_2O_3-5TiO_2	8.46
90Y-10D	8.24
70Y-30D	7.67
50Y-50D	6.89
30Y-70D	4.64
10Y-90D	

	CTE (×10^{-6}/°C)
Yb_2O_3-5TiO_2	8.07
90Yb-10D	8.14
70Yb-30D	8.11
50Yb-50D	7.66
30Yb-70D	5.80
10Yb-90D	3.26

- The CTEs of Y_2O_3-SiO_2 composites and Yb_2O_3-SiO_2 composites both decrease as the content of SiO_2 increases.

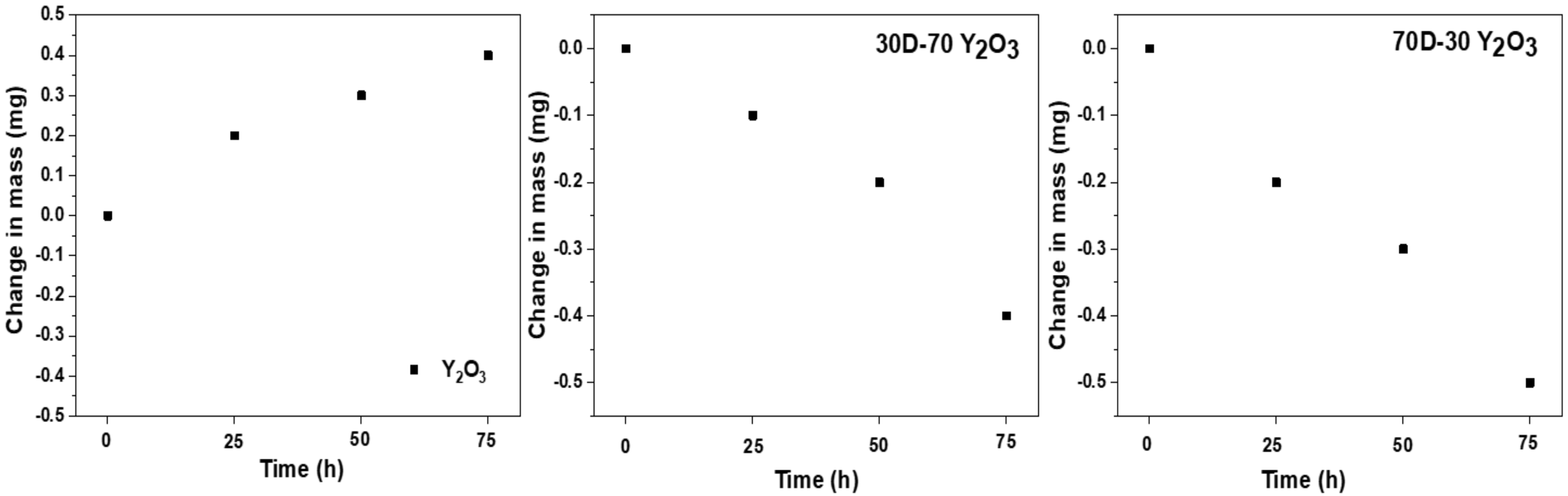
5. Project Progress - Task 3

Sub-task 3.2: Determine the effect of composition and microstructure of composites on oxidation and volatilization during exposure to high velocity steam at temperatures up to 1350ºC.

- Significant work has been done and analysed in year 1 and 2.
- In the year 3, we have modified our steam oxidation set up by introducing zirconia holder and sapphire tube instead of alumina holder and tube to reduce the contamination
- In addition, we have modified the set up to introduce flushing inert gas to reduce contamination
- In consultation with GE, it was decided to focus only on Y_2O_3 and its composites.

This sub-task is 100 % complete

5. Task 3 - Steam oxidation behavior of Y_2O_3 and its composite



- ❖ Small increase in mass with time for the Y_2O_3 sample - due to the deposition of alumina contamination
- ❖ Composite material shows linear mass loss with time
- ❖ 70D-30 Y_2O_3 composite material shows higher mass loss compared to 30D-70 Y_2O_3 due to the presence of higher amount of silica-rich phase.

As postulated in the proposal, Y_2O_3 and high Y_2O_3 low SiO_2 composites are more resistant to high velocity stream oxidation and volatilization

5. Project Progress - Task 4

Task 4: Graded composition coatings using cold spray followed by heat treatment (30 % completed)

- **Sub-task 4.1**: Design and processing of the optimized composition graded coatings (60 % completed)

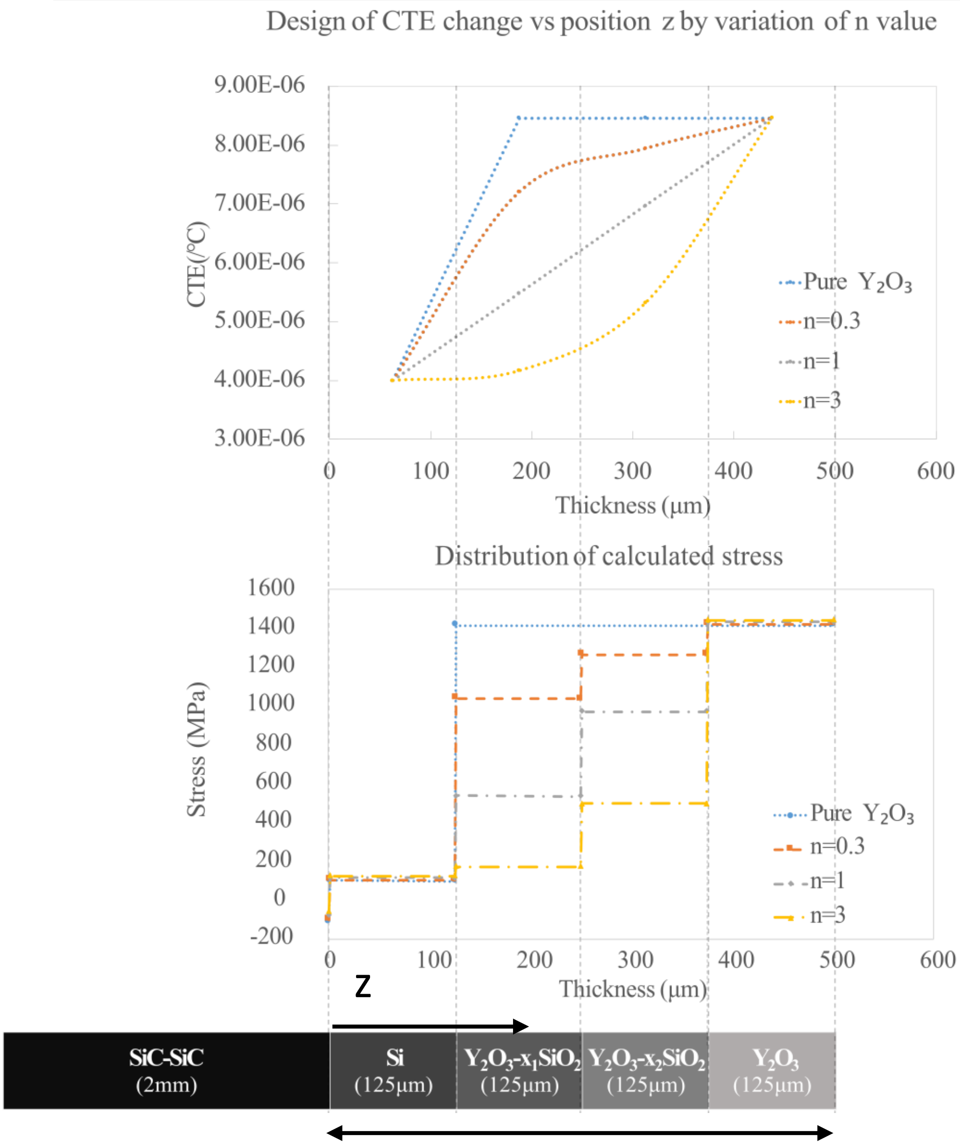
In the year 2, we have completed the following goals:

- The cold spray system to make coatings has been assembled
- Developed the protocol of the Y_2O_3-SiCN submicrometer suspension
- Studied the microstructure uniformity of Y_2O_3-SiCN composite film from dip-coating

In this year 3, we have focused on the following aspects:

- Determined the optimal composition profile for the graded coatings through COMSOL simulation

5. Task 4 - Optimal Composition Profile for the Graded Coatings



h=500um

Assume CTE of the composites follows the rule of mixture.

- The thermal stress in the top coating remains almost constant.
- The thermal stress in the intermediate layers have the lowest thermal stress with the compositional profile when n=3 (CTE1=5.32×10⁻⁶/℃, CTE2=4.16×10⁻⁶/℃).

$$V_{Y_2O_3}(z) = \left(\frac{z}{h}\right)^n$$

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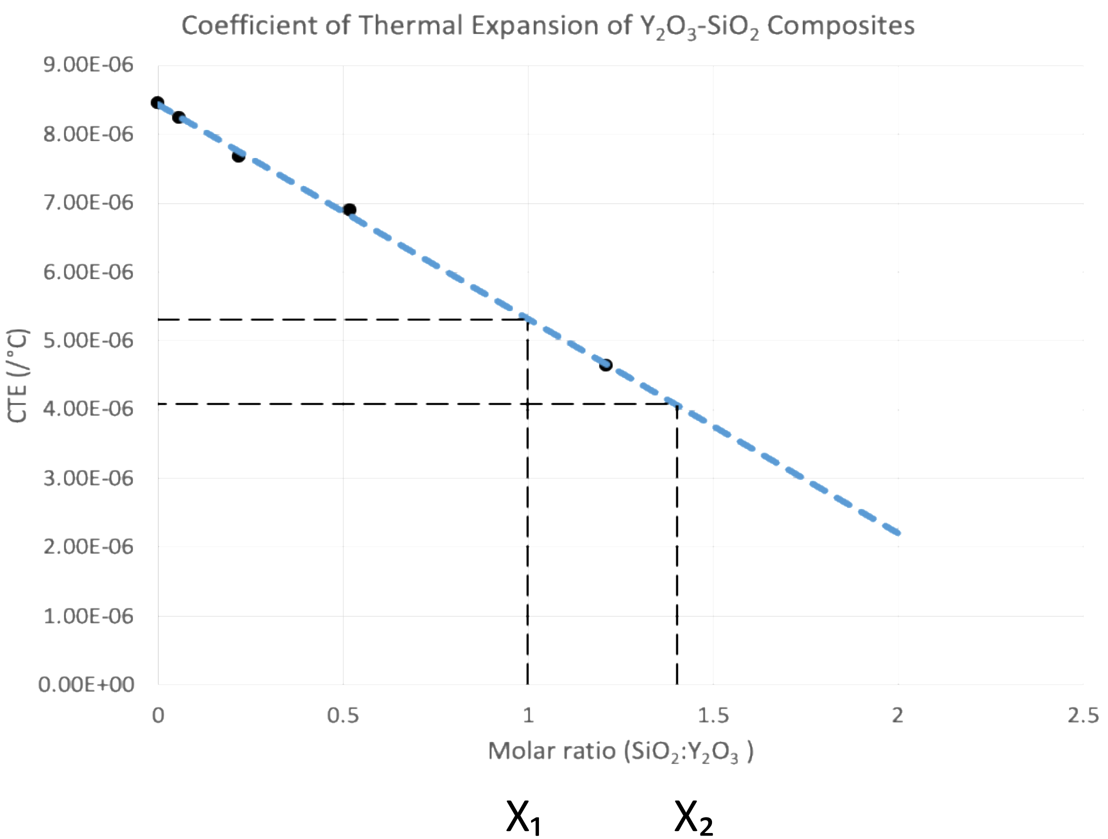
5. Task 4 - Optimal Composition Profile for the Graded Coatings (Contd.)

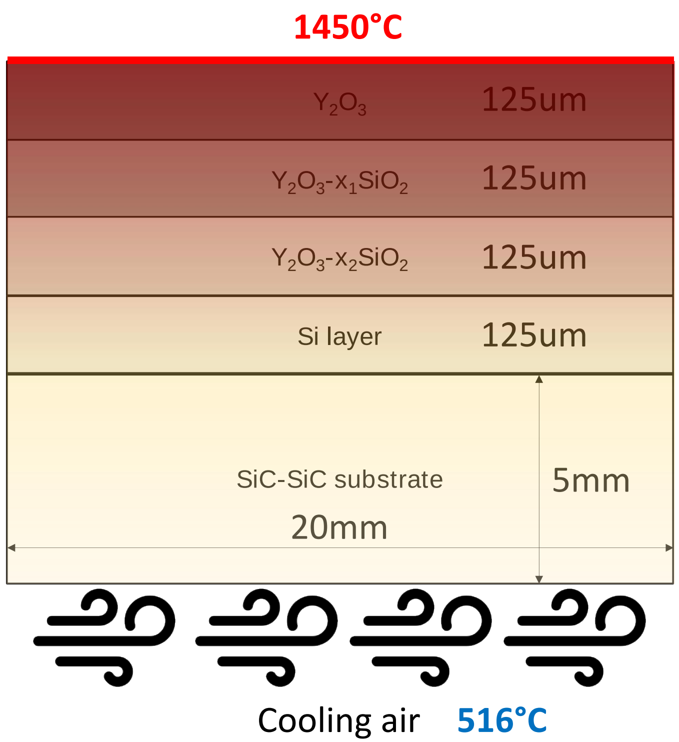
CTE=5.32×10^{-6}/℃

CTE=4.16×10^{-6}/℃



- Based on the required CTE values (5.32E-6 and 4.16E-6) when n=3, we can determine the required compositions of the intermediate layers (x_1, x_2)

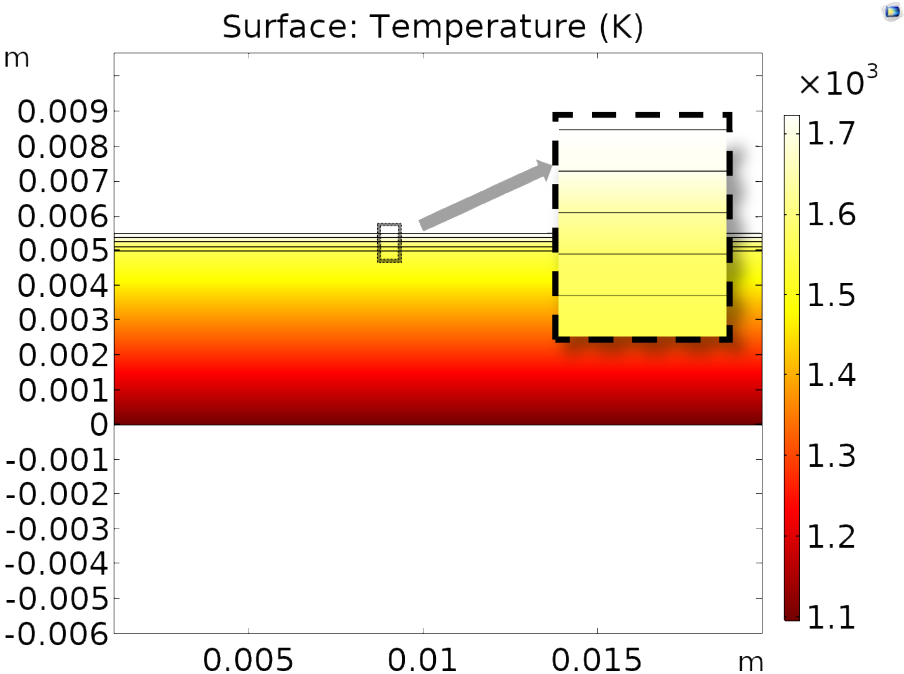
5. Task 4 - Temperature Profile Simulation Set Up



Parameter	Value
Thermal conductivity (Y_2O_3)	7 W/(m·K)
Thermal conductivity (Y_2O_3-x_1SiO_2)[1]	1.4 W/(m·K)
Thermal conductivity (Y_2O_3-x_2SiO_2)	2 W/(m·K)
Thermal conductivity (Si)[2]	25 W/(m·K)
Thermal conductivity (SiC/SiC)[3]	15 W/(m·K)
Heat transfer coefficient (cooling air)[4]	3000 $W/(m^2 \cdot K)$
Temperature (Top surface of Y_2O_3 layer)	1450° C
Temperature (Cooling air)[4]	516° C

Boundary conditions in consultation with GE

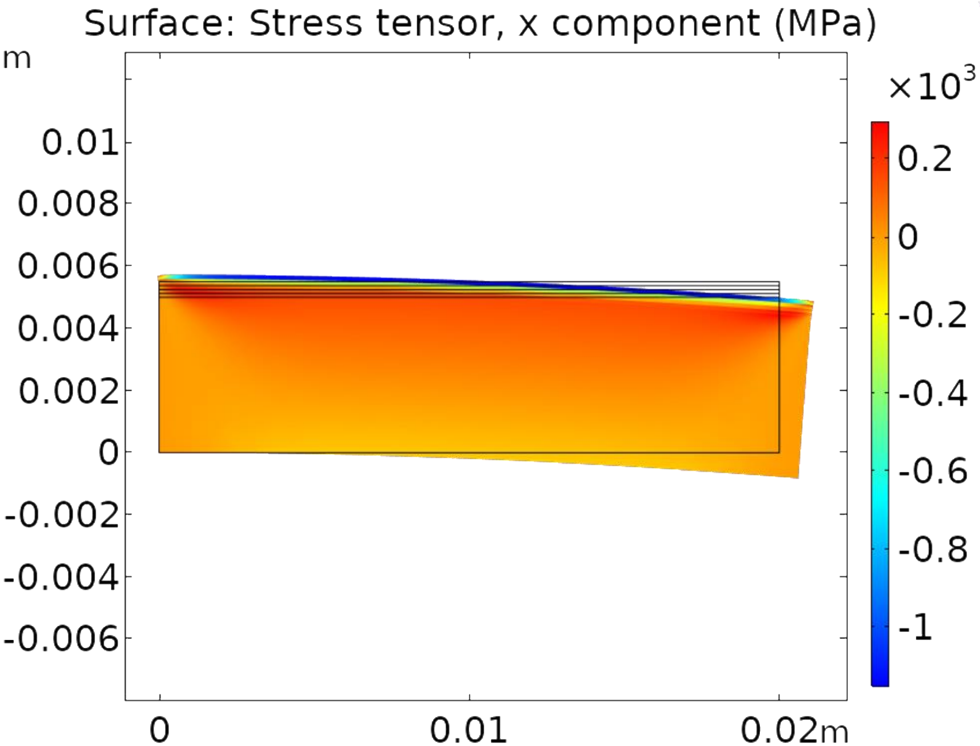
5. Task 4 - Simulated Temperature Profile by COMSOL (on changing gas temperature from 25℃ to 1450℃)

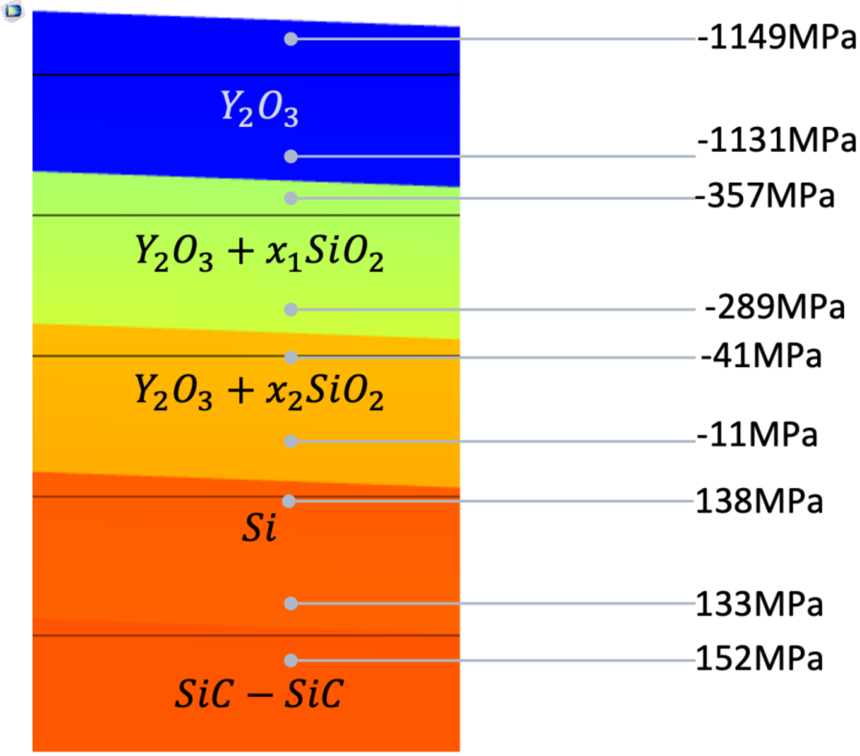


Location	Initial T (℃)	Final T (℃)
Top surface of Y_2O_3 layer	25	1450
Y_2O_3 and Y_2O_3-x_1SiO_2 interface	25	1419
Y_2O_3-x_1SiO_2 and Y_2O_3-x_2SiO_2 interface	25	1337
Y_2O_3-x_2SiO_2 and Si interface	25	**1266**
Si and SiC/SiC interface	25	1261
Bottom surface of SiC/SiC	25	891

❖ Steady state temperatures obtained in each layer

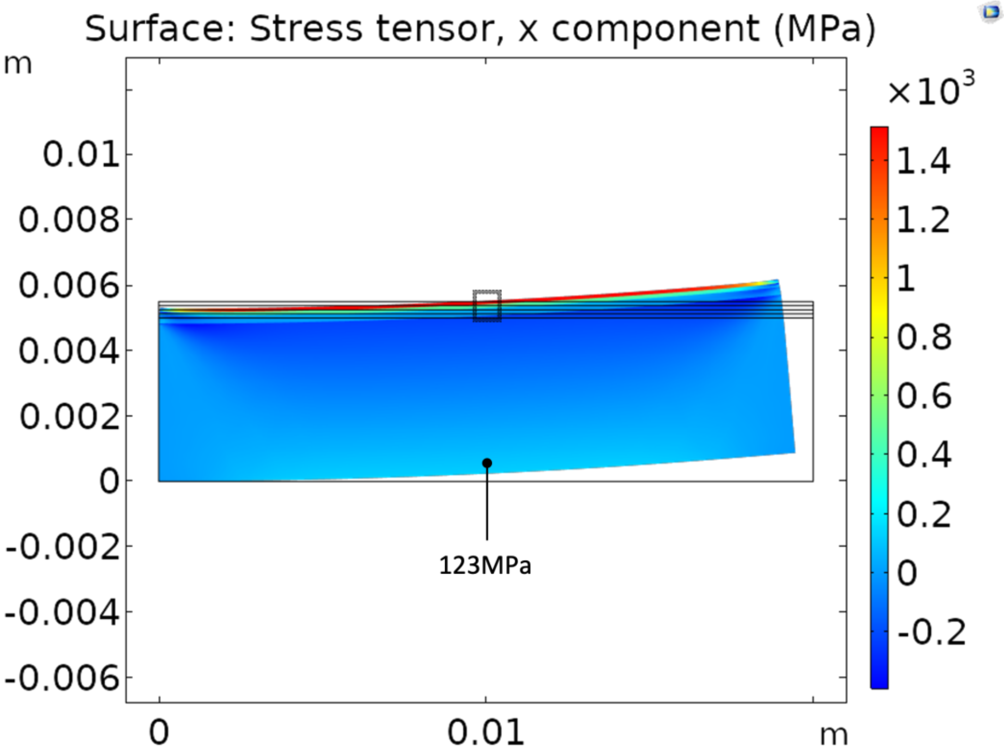
5. Task 4 - Simulated Thermal Stress Profile 25℃ (stress free)→ 1450℃

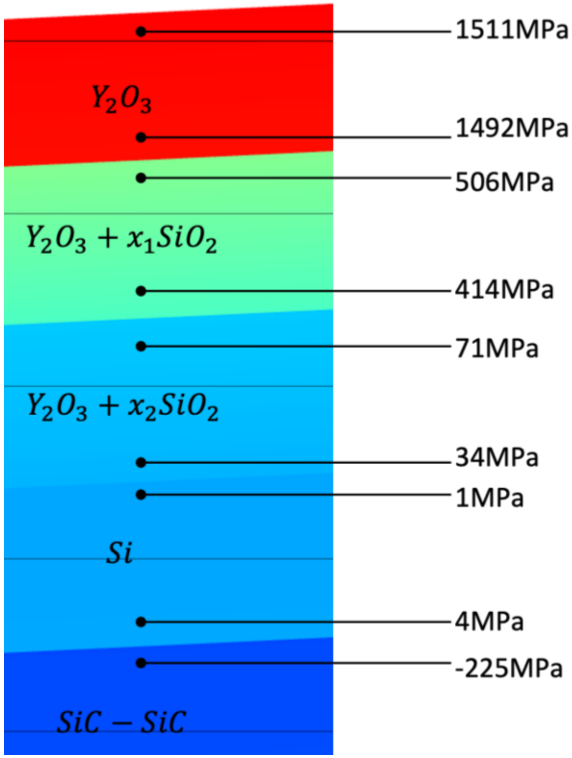




- EBC layers are under tension. The stress in the top layer (Y_2O_3) is high due to significant CTE mismatch.
- The stresses in the intermediate layers are much lower – advantage of graded coating

5. Task 4 - Simulated Thermal Stress Profile 1450℃ (stress free)→ 25℃





- EBC layers are under compression. The stress in the top layer (Y_2O_3) is high due to significant CTE mismatch.
- The stresses in the intermediate layers are much lower – advantage of graded coating

5. Project Progress - Task 4

- **Sub-task 4.2**: Characterization of the oxidation and volatilization during exposure to high velocity steam at temperatures up to 1500ºC and performance in burner rig. (20 % completed)

In the year 2 and 3, we have developed the steam oxidation set up for coated samples.

- **Sub-task 4.3:** Thermal cycling investigation of the coatings

We have not started sub-task

5. Project Progress - Task 5

Task 5: Processing and performance of graded coatings processed using atmospheric plasma spraying (APS) (50% completed)

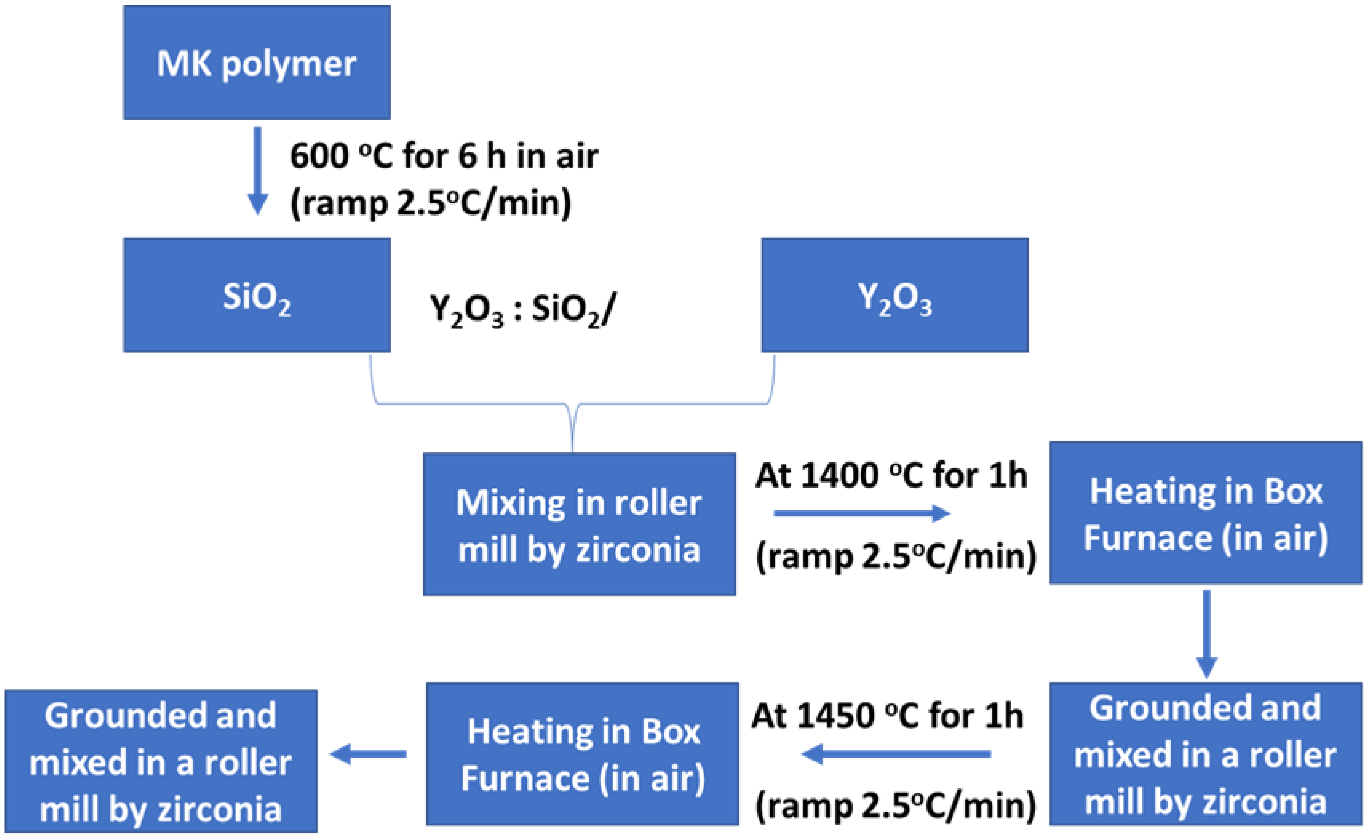
- **Sub-task 5.1**: Processing of powders suitable for APS (100% completed)

We initiated this sub-task in year 2 (about 10%).

In this year, we have done significant work and completed this sub-task.

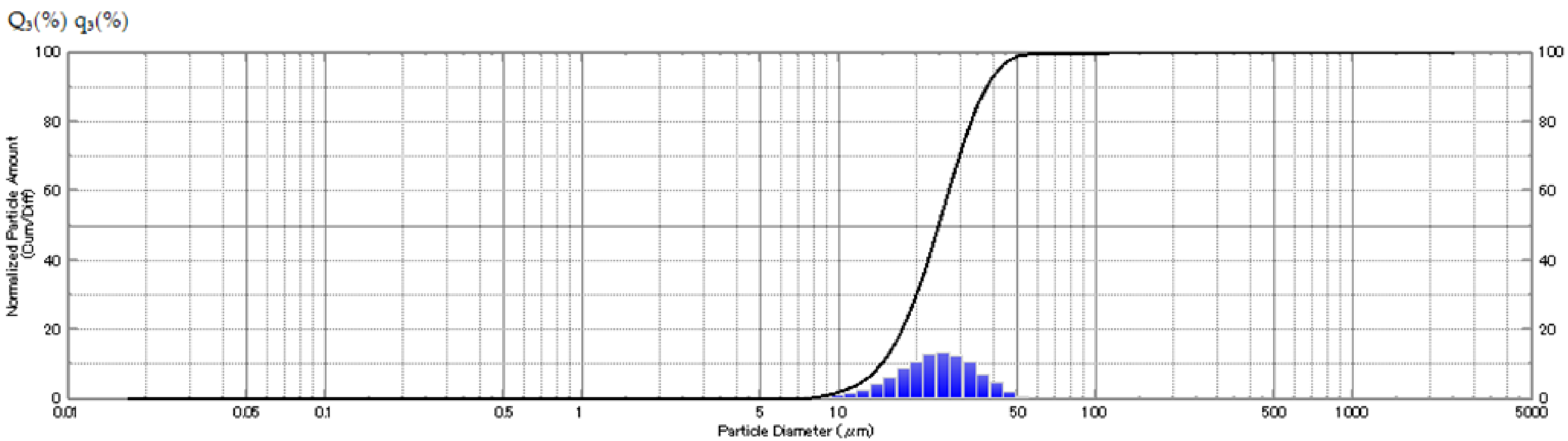
1. Determined the optimal composition for graded coating through COMSOL simulation.
2. Subsequently, we have synthesized large quantity of optimized composite sample (~6.5 lb)
3. Analyze the particle size suitable for APS.
4. We have sent composite sample along with pure Y_2O_3 sample to GE

5. Task 5 - Processing of Powders Suitable for APS



Complete protocol for large scale synthesis of composite powders

5. Task 5: Particle size analysis



❖ Average particle size of the composite powder ~ 24 micron

5. Project Progress - Task 5

- **Sub-task 5.2**: Processing of graded coatings using APS

This sub-task will be done by GE in Quarter 13

- **Sub-task 5.3**: Characterization of the oxidation and volatilization of APS coatings during exposure to high velocity steam at temperatures up to 1500ºC and performance in burner rig.

This sub-task will start in Quarter 14

- **Sub-task 5.4:** Thermal cycling investigation of the APS coatings.

This sub-task will start in Quarter 14

6. Project Short Term Plans

- Complete sub-task 3.1 (10% remaining)
- Fabricate graded coating using the cold spray method and characterize the microstructure (sub-Task 4.1).
- Steam oxidation behavior of coated sample (sub-tasks 4.2 and 4.3)

Milestones

The milestones remained the same as in the original Statement of Work. Due to the one-year no-cost extension, the completion date was modified and approved by DoE.

Year 1

- M1: Selection of polymers and acquisition of the needed materials. Planned completion: end of Q1 (12/17) (Status: Completed).
- M2: Establish the effect of composition and processing temperature on the phase and microstructure of Y_2O_3-Si-B-C-N and Yb_2O_3-Si-B-C-N composites Planned completion: end of Q3 (6/18) (Status: Completed).
- M3: Design and fabrication of the cold spray processing of coatings and high velocity steam oxidation equipment Planned completion: end of Q3 (6/18) (Status: Completed).
- M4: Establish the effect of temperatures on the phase stability during oxidation at temperatures up to 1500ºC. Planned completion: end of Q4 (9/18) (Status: Completed).

Milestones (Contd.)

Year 2

No Milestones planned for completion in Year 2

Year 3

- M5: Determine thermal expansion coefficient, elastic modulus and thermal conductivity for select composite coating compositions Planned completion: end of Q12 (9/20) (Status: 90 % Completed)
- M6: Determine the effect of composition on oxidation and volatilization during exposure to high velocity steam at temperatures up to 1500°C. Planned completion: end of Q12 (9/20) (Status: 100% completed).

Milestones (Contd.)

Year 4

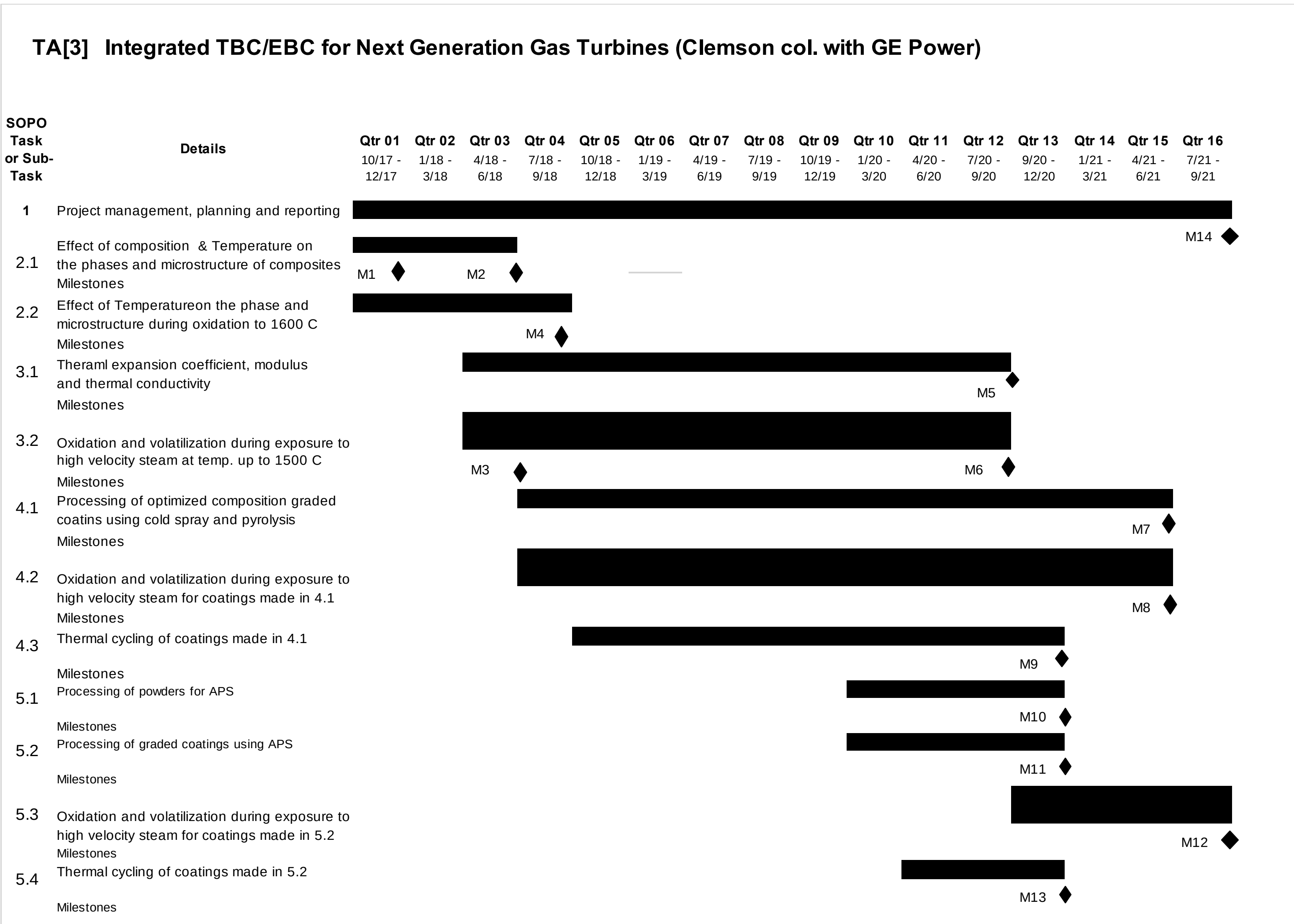
- M7: Processing of composition graded coatings using cold-spray and pyrolysis. Planned completion: end of Q15 (6/21) (Status: 50% completed).
- M8: Determine the effect of exposure to high velocity steam at temperatures up to 1500°C on graded coatings made using cold spray and pyrolysis Planned completion: end of Q15 (6/21) (Status: 0 % complete)
- M9: Investigate the effect of thermal cycling and steam oxidation on graded coatings made using cold spray and pyrolysis Planned completion: end of Q13 (12/20) (Status: 0 % complete) .
- M10: Supply powders for APS to GE Power (Clemson) Planned completion end of Q13 (12/20) (Status: 100 % Completed)

Milestones (Contd.)

Year 4 (Contd.)

- M11: Complete Fabrication of graded coatings using APS Planned completion: end of Q13 (12/20) (Status: 0 % completed)
- M12: Establish the effect of exposure to high velocity steam at temperatures up to 1500°C on graded coatings made by APS Planned completion: end of Q16 (9/21) (Status: 0 % completed)
- M13: Investigate the effect of thermal cycling on graded coatings made by APS Planned completion: end of Q13 (12/20) (Status: 0 % completed)
- M14: Phase 1 completion including final report Planned completion: end of Q16 (9/21) Status: Ongoing

Current Version of Timeline



Thank you very much for your attention and support