Advanced Reaction Systems (ARS) FWP1022405

Task 4: Advanced Manufacturing and Materials Technologies for Gasification

September 2, 2020

Jinichiro Nakano[1,2], Anna Nakano[1,2], Hugh Thomas[1], and Ömer Doğan[1]

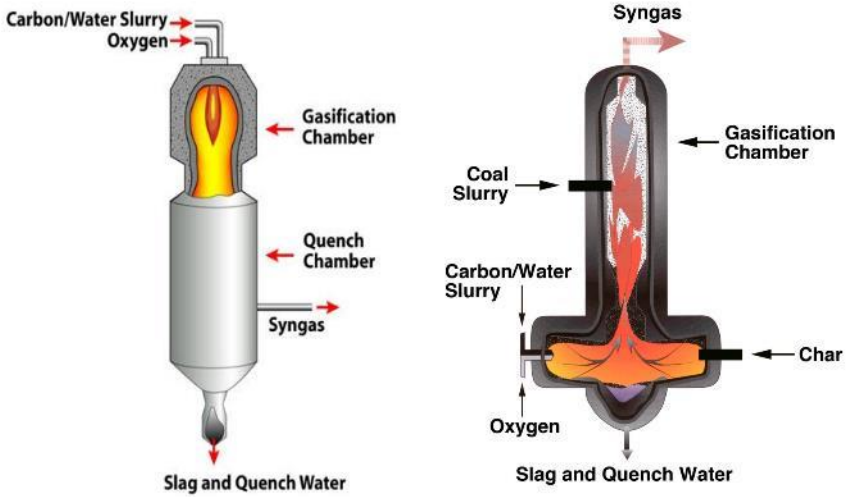
[1]U.S. Department of Energy National Energy Technology Laboratory, 1450 Queen Avenue SW, Albany, OR 97321, USA.
[2]Leidos Research Support Team, 1450 Queen Avenue SW, Albany, OR 97321, USA.

Task objectives

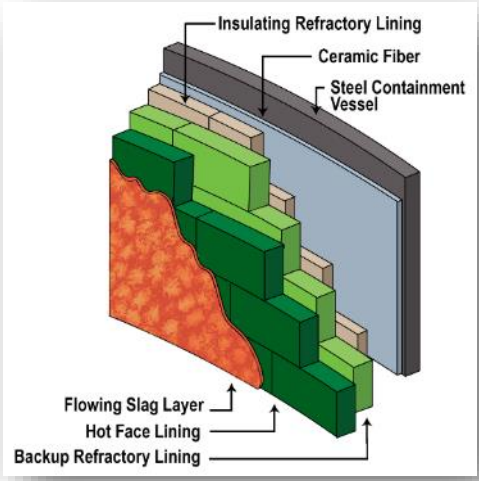
Task 4: Advanced Manufacturing and Materials Technologies for Gasification

- **The objective of this effort is to identify materials of construction and the manufacturing technologies to build small-scale computer modeled ARS gasification modules that will meet the system performance requirement in laboratory studies (temperatures up to 1200°C, coal as the primary carbon feedstock, an initial targeted material throughput of one ton/hour, and an initial service life of 500 hours).**

Commercial Gasifier for Power Generation



Some Current Gasifier Designs



Refractory lining

Traditional Gasifier Liner Removal/Rebuild

EY20 Work Plan

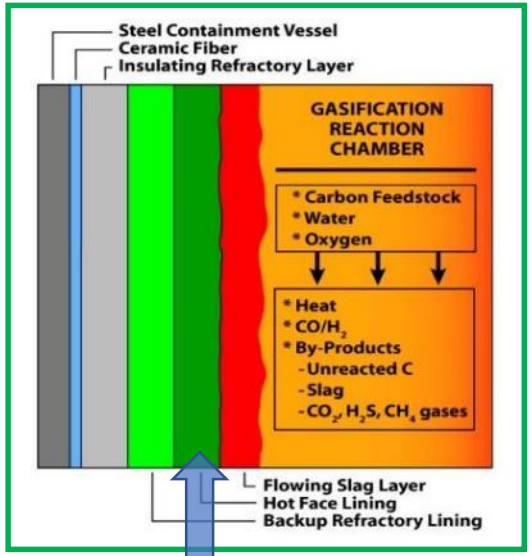
Refractory investigation

Goals:

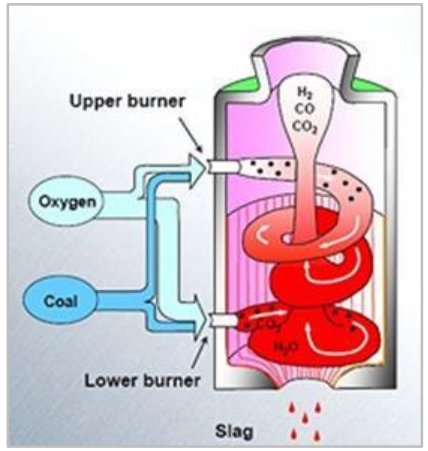
Examine chemically bonded refractory materials that withstand **coal ash + up to 20 wt.% biomass ash** environments at up to 1200 °C. (The test will also identify highest non-slagging temperature of the ashes for longer performance.)

Benefits:

Development of cost effective high performance refractory materials aids designing of small scale gasifier unit operation at lower cost. A choice of chemically bonded refractory will accommodate a small reactor design (1t/hr), which would be otherwise challenging with common lining bricks. If successfully proven with biomass addition in EY20, it will broaden up reactor designing.



Hot face liner



Milestones

Identifier	Type[1]	Expected Completion Date	Description (What, How, Who, Where)
4.A	Go/No-Go	10/30/2019	A Go/No-Go decision will be made on the viability of using chemical bonded refractory materials for hot face lining applications over metal support structures in ARS gasifier module applications up to 1,200°C. **Completed**.
4.B	Major	6/30/2020*	List appropriate material or combination of chemically bonded materials for the spectrum of the Radically Engineered Modular Systems (REMS)/ARS reaction chambers and the feasibility of using those materials to manufacture targeted reaction system designs. (note this now targets Usibelli coal). **Delayed.**
4.C	Major	3/31/2021	Determine the performance of at least two chemically bonded materials against coal ash chemistry with up to 20 wt.% biomass in simulated gasifier environments at temperature up to 1,200 °C. **On track.**
4.D	Major	3/31/2022	Recommend at least one appropriate chemically bonded material and application technique to be used in the targeted ARS reaction chamber design. **On track.**

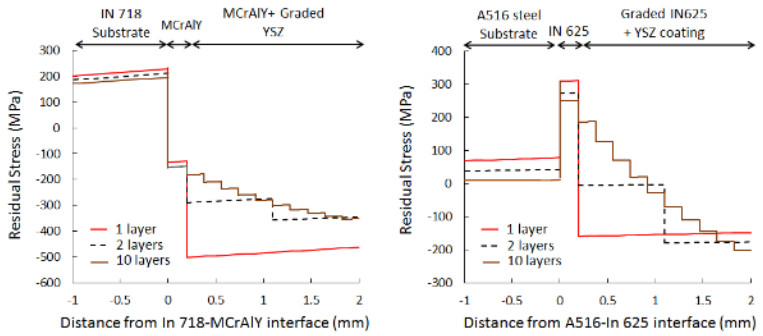
Deliverables

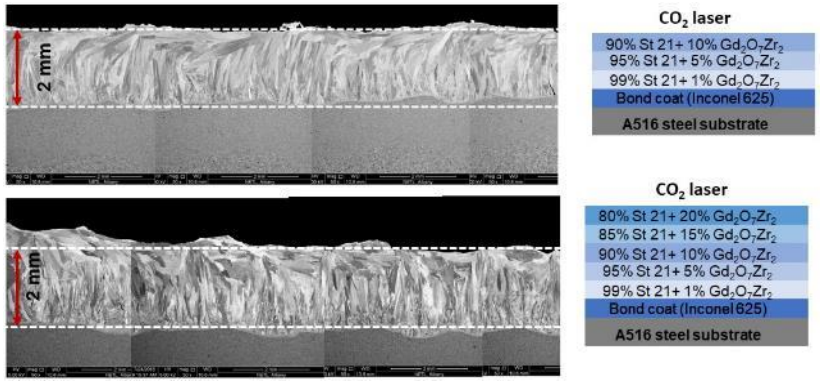
Number	Deliverable Title	Expected Completion Date	Description
1	Test Plan/Decision Point Flowsheet	07/31/2019	Construct a flowsheet illustrating a test plan and decision points to identify appropriate manufacturing processes (AM, conventional, and/or hybrid) and materials of construction (metals, cermets, refractories, and/or chemically bonded ceramics) with potential for use over a variety of gasification chamber process conditions using coal as a carbon feedstock. **Completed.**
2	Chemically Bonded Refractory Liner – 1,200°C Applications	5/31/2020	Identify and produce at least two different test coupons of potential chemically bonded refractory liner materials on metal surfaces for evaluation in the first-generation ARS gasification module. These coupons will have been evaluated for at least 50 hours in a simulated gasification environment and shown little to no wear/corrosion. The coupons will be ready for longer term exposure in the NETL prototype gasifier, where it will encounter commercial gasification temperature and syngas exposures at temperatures up to 1,200°C. (note this now targets Usibelli coal). **Delayed.**
3	AM Metal/Ceramic Liner Performance – 800°C Applications	6/30/2020	Identify and produce at least two different test coupons of potential AM ceramic and metal structures for evaluation in the first-generation ARS gasification module. These coupons will have been evaluated for at least 50 hours in a simulated gasification environment and shown little to no wear/corrosion. The coupons will be ready for longer term exposure in the NETL prototype gasifier, where it will encounter commercial gasification temperature and syngas exposures at temperatures up to 800°C. (note this now targets Usibelli coal). **Delayed.**
4	Chemically Bonded Refractory Liners in gasification environment with up to 20 wt.% biomass additions to coal	3/31/2021	Evaluation of at least two different test coupons of chemically bonded refractory liner materials and identify challenges and potential improvements to be used for the first-generation ARS gasification module. These coupons will have been tested for at least 50 hours in a simulated gasification environment with up to 20 wt.% biomass additions to coal and shown little to no wear/corrosion. If successful, the coupons will be ready for longer term exposure in the NETL prototype gasifier, where it will encounter commercial gasification temperature and syngas exposures at temperatures up to 1,200°C. **On track.**

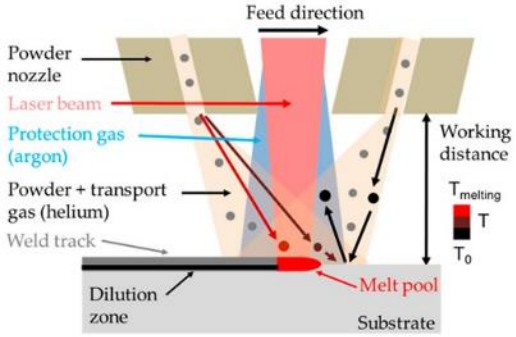
EY19: Ceramic liner by additive manufacturing

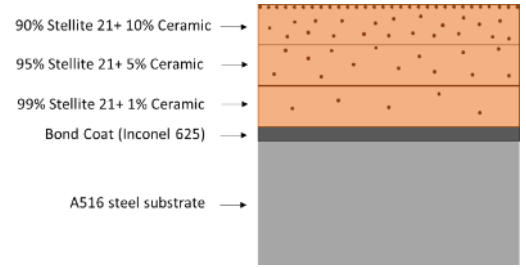
Industrial partner: DM3D

Effect of functional grading on residual stress

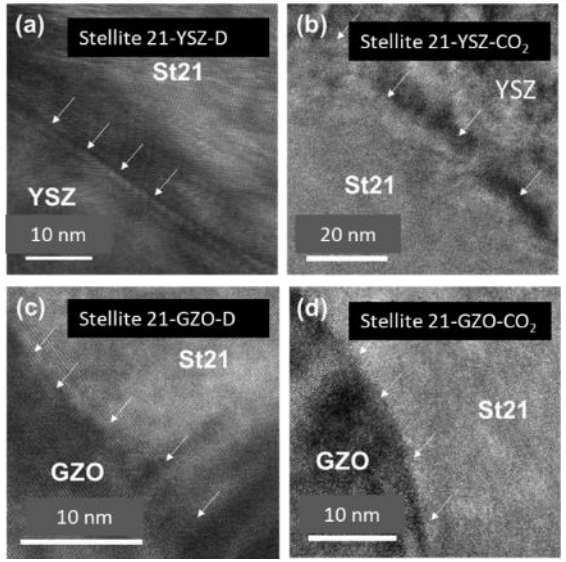


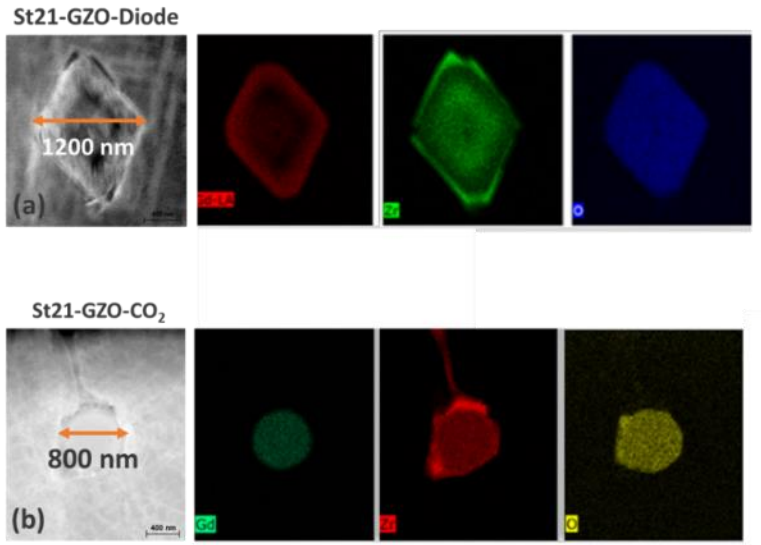






Particle coherency in functionally graded layers





Publications (2019 – present)

Journal

1. H. Rao, I. Jayasekara, B. Dutta, D. Maurice, Segregation phenomena during deposition of functionally graded zirconia-based ceramics with Stellite 21 on a steel substrate, Surface & Coatings Technology, 383 (2020) 125270.
2. H. Rao, R.P. Oleksak, K. Favara, A. Harooni, B. Dutta, D. Maurice, Behavior of YSZ during laser direct energy deposition of an Inconel 625-YSZ cermet, Additive Manufacturing, 31 (2020) 100932.
3. A. Bhattacharyya and D. Maurice, Residual Stresses in Functionally Graded Thermal Barrier Coatings, Mechanics of Materials, 2019. 129: p. 50-56

Book chapter

1. A. Nakano, J. Nakano, J. Bennett, 'In situ investigation of Pt-Rh thermocouple degradation by P-bearing gases,' a book chapter, Advanced Real Time Imaging II – Cutting-edge technologies for materials science, edited by J. Nakano. et al., Springer, 2019, pp. 143-150.

Conference proceedings

1. A. Nakano, J. Nakano, J. Bennett, 'Real time evolutions of individual industrial coal particles in varied oxygen partial pressure environments,' MOLTEN 2021, Seoul, South Korea, February 2021 - proceedings accepted.
2. C. Ortiz, J. Nakano, A. Nakano, J. P. Bennett, 'An investigation of the impact experimental equipment parameters have on synthetic slag behaviors in an oxidative environment using a confocal laser microscope,' proceedings of the TMS 2020, San Diego, CA, February 2020.
3. J. Bennett, A. Nakano, J. Nakano, H. Thomas, 'Aluminum Phosphate Phase Changes Driven by Environmental Exposure Conditions,' Unified International Technical Conference on Refractories UNITECR 2019, Yokohama, Japan, October 2019.
4. J. Bennett, D. Maurice, J. Nakano, 'Material and Construction Considerations in the Development of Novel Coal Reactors', proceedings of the Clearwater Clean Energy Conference, 44th International Technical Conference on Clean Energy, Clearwater, FL, June 2019.
5. J. Bennett, A. Nakano, J. Nakano, J. Widmer, 'Phase Changes in Aluminum Phosphates Caused by Refractory Fabrication and Service,' 55th Annual St. Louis Section / Refractory Ceramics Division Symposium on Refractories., St. Louis, MO, USA, March 2019.

Publications (2019 – present) continued

Conference presentations

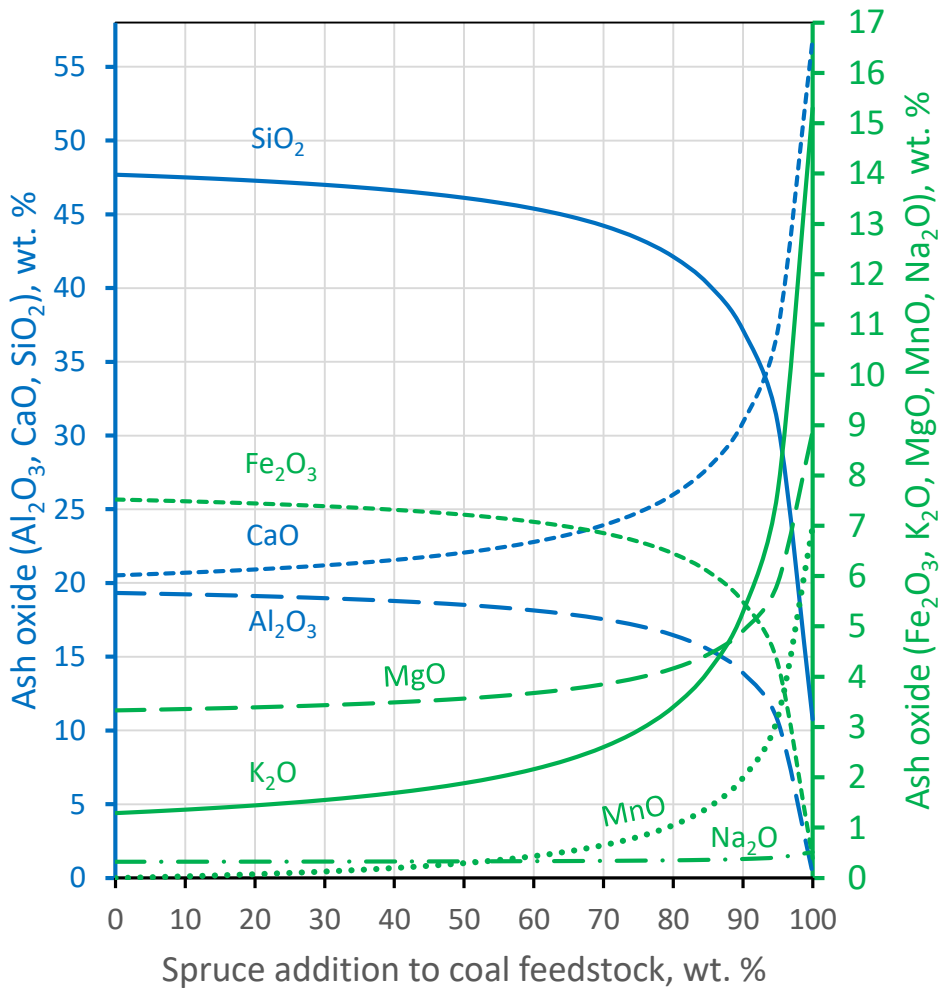
1. J.P. Bennett, J. Nakano, A. Nakano, and H. Thomas, 'The Role of Phosphates in Chrome Oxide Gasifier Refractories,' CIMTEC 2021, Montecatini Terme, Italy, June 2021 – abstract accepted
2. J. Nakano, A. Nakano, Ömer Doğan, 'In-operando investigations of refractory materials interacting with ash/slag from mixed feedstock gasification,' TMS 2021, Orlando, FL, March 2021 – abstract accepted
3. A. Nakano, J. Nakano, J. P. Bennett, 'Real time evolutions of individual industrial coal particles in varied oxygen partial pressure environments,' MOLTEN 2021, Seoul, South Korea, February 2021 – abstract accepted.
4. C. Ortiz, J. Nakano, A. Nakano, J. P. Bennett, 'An investigation of the impact experimental equipment parameters have on synthetic slag behaviors in an oxidative environment using a confocal laser microscope,' TMS 2020, San Diego, CA, February 2020.
5. J. Nakano, J. Bennett, A. Nakano, H. Thomas, 'Aluminum Phosphate Phase Changes Driven by Environmental Exposure Conditions,' Unified International Technical Conference on Refractories UNITECR 2019, Yokohama, Japan, October 2019.
6. K. Collins, A. Nakano, J. Nakano, 'Element peak shift in WDX ', poster, Microscopy & Microanalysis 2019 Meeting, Portland, OR, August 2019.
7. J. Nakano, A. Nakano, J. P. Bennett, 'Conversion of waste from gasification facilities, refineries, and steelmaking plants to H_2 and/or CO,' Clearwater Clean Energy Conference, the 44th International Technical Conference on Clean Energy, Clearwater, FL, June 2019.
8. J. Bennett, D. Maurice, J. Nakano, 'Material and Construction Considerations in the Development of Novel Coal Reactors', Clearwater Clean Energy Conference, 44th International Technical Conference on Clean Energy, Clearwater, FL, June 2019.
9. D. Maurice, J. Nakano, J. Bennett, 'Material Development for Advanced Manufacturing of Gasification Systems,' poster, 2019 Annual Cross-Cutting Review Meeting, Pittsburgh, PA, April 2019.
10. J. Bennett, J. Nakano, A. Nakano, 'Slag Management of Carbon Feedstock Used in Gasification," poster, 2019 Annual Cross-Cutting Review Meeting, Pittsburgh, PA, April 2019.
11. J. Bennett, A. Nakano, J. Nakano, J. Widmer, 'Phase Changes in Aluminum Phosphates Caused by Refractory Fabrication and Service,' 55th Annual St. Louis Section / Refractory Ceramics Division Symposium on Refractories, St. Louis, MO, March 2019.
12. A. Nakano, J. Nakano, J. Bennett, 'In situ investigation of Pt-Rh thermocouple degradation by P-bearing gases,' TMS 2019, San Antonio, TX, March 2019.

EY20: Result thus far

Direct firing tests (furnace and confocal)

Ash chemistry

(wt.%)	100% Coal	100% Spruce	10% spruce – 90 % coal	20% spruce – 80% coal
Ash contents	7	0.31		
SiO2	47.69	10.76	47.51	47.29
Al2O3	19.33	0.31	19.24	19.12
Fe2O3	7.52	0.39	7.49	7.44
CaO	20.52	56.88	20.70	20.92
MgO	3.33	8.87	3.36	3.39
K2O	1.29	15.3	1.36	1.44
Na2O	0.32	0.51	0.32	0.32
MnO		6.98	0.03	0.08
Total	100.00	100.00	100.00	100.00



2015, Usibelli coal data sheet, Usibelli Coal Mine

Refractory materials identified for coal/biomass ash

Industrial partner: Allied Mineral Products

(1) V-CAST

	wt.%
Al2O3	70.9
SiC + C	18.1
SiO2	7.5
TiO2	1.4

Alumina based

(2)TUFF-FLO

	wt.%
Al2O3	60.3
SiO2	28.4
SiC	4.4
TiO2	2.0
CaO	1.9
ZrO2	1.3
Fe2O3	0.9
others	0.8

Mullite based

(3) TUFFCRETE

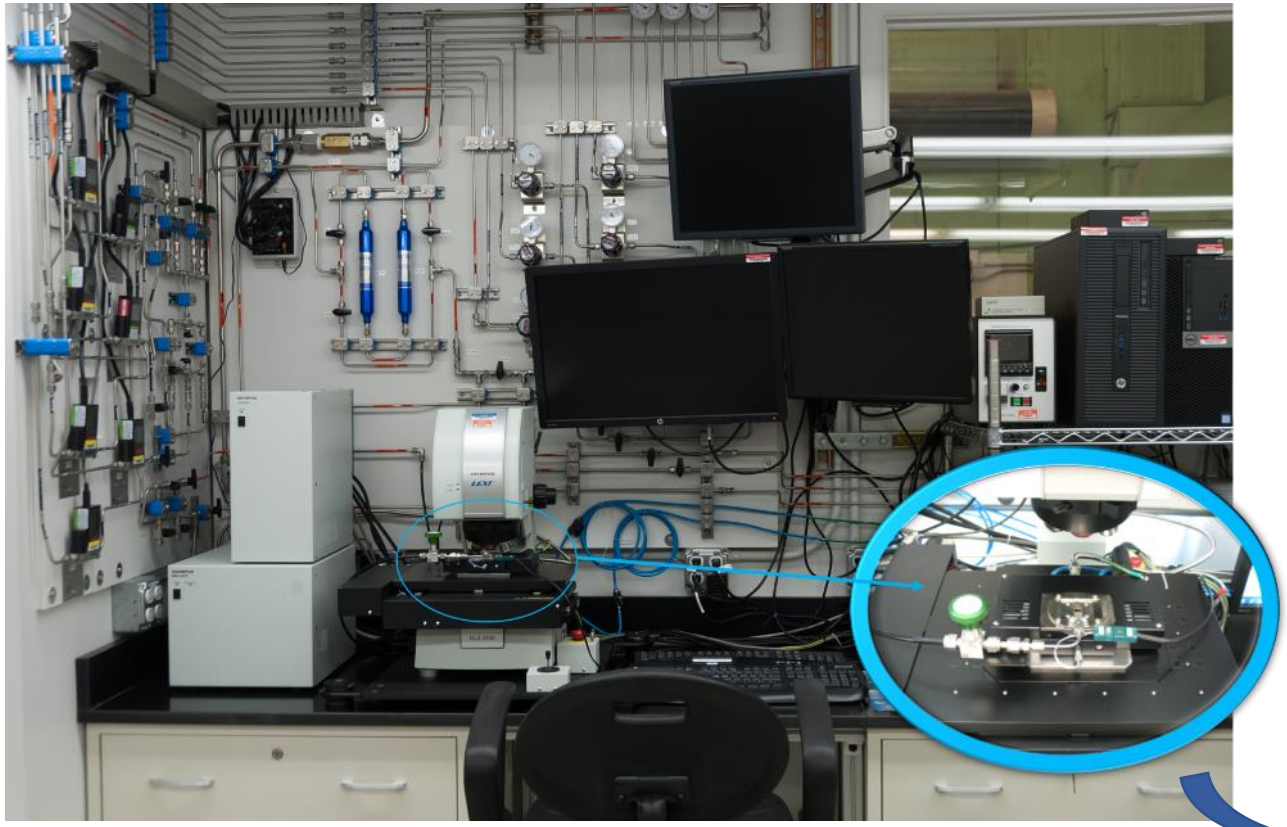
	wt.%
Al2O3	42.0
SiO2	21.2
CaO	1.9
TiO2	0.1
Fe2O3	0.2
SiC	5.3
ZrO2	27.7
others	1.6

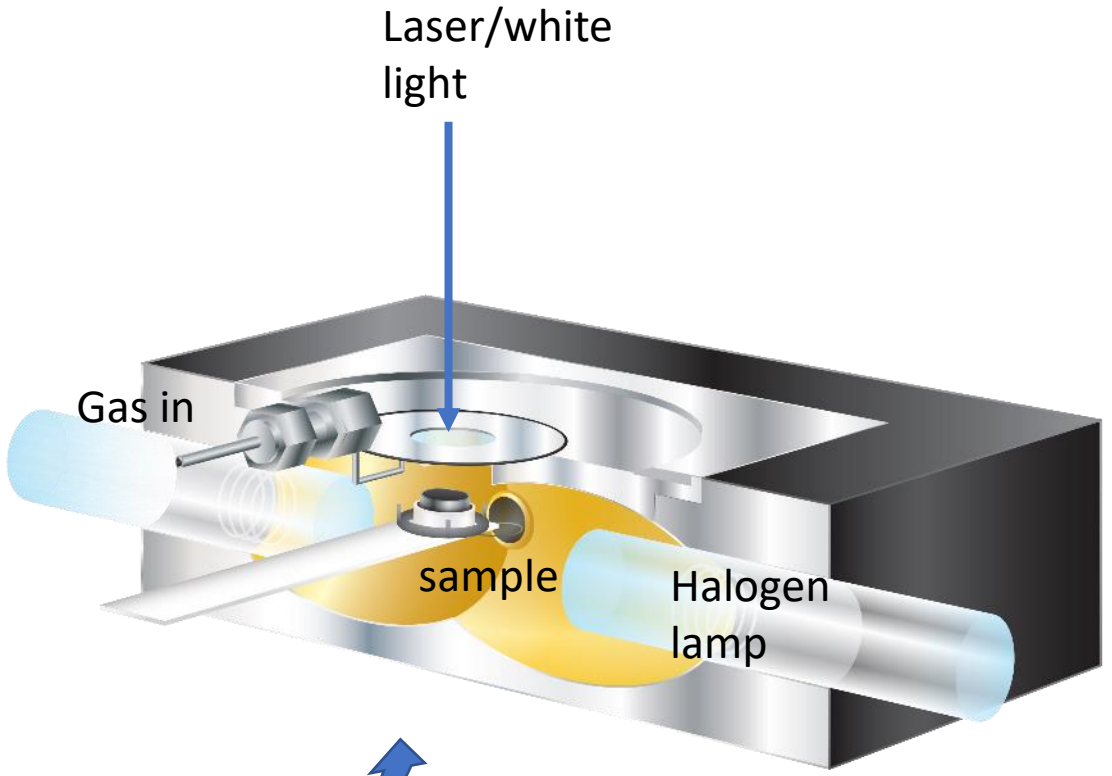
Alumina-zirconia-silica based

Materials supplied by Allied Mineral Products

Firing tests with confocal microscope

High temperature environmental confocal scanning laser microscope



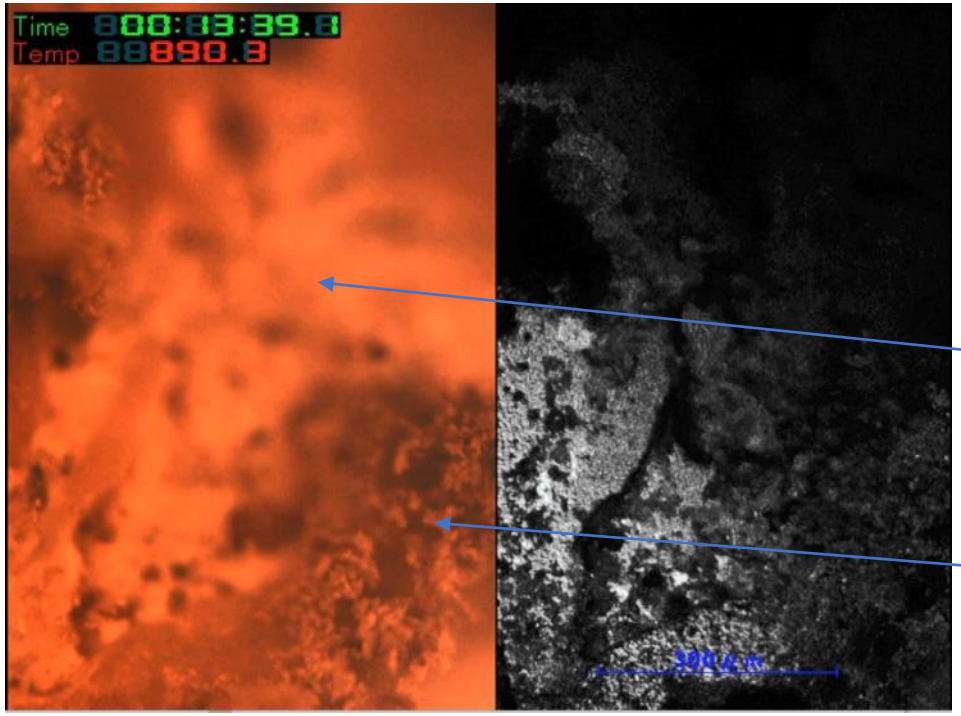


Ash preheat treated at 800 °C, 800 °C/1200 °C, 64%CO-36%CO2, 1 hr exposure

CSLM real-time observation (100% coal ash)

Movie clips at 800 °C and 1200 °C

TUFF-FLO at 800 °C

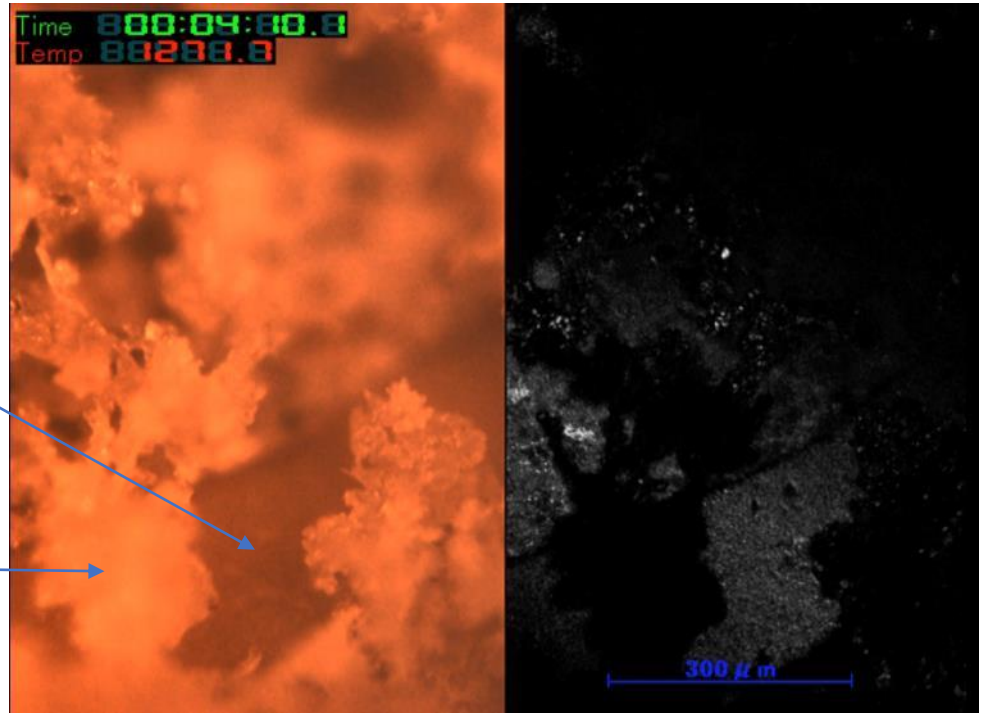


White light | Laser

Refractory surface

Ash

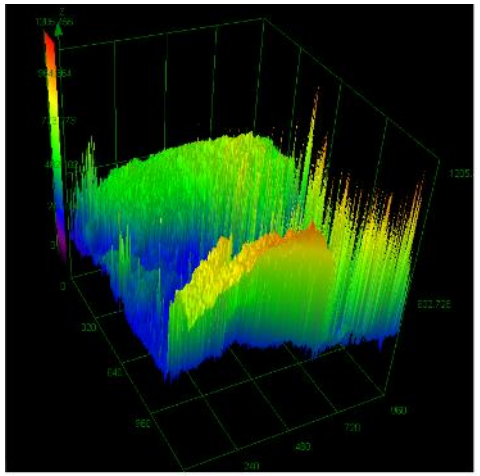
TUFF-FLO at 1200 °C



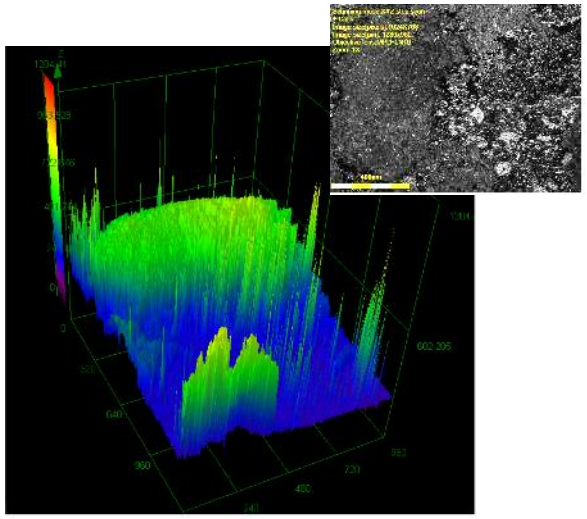
White light | Laser

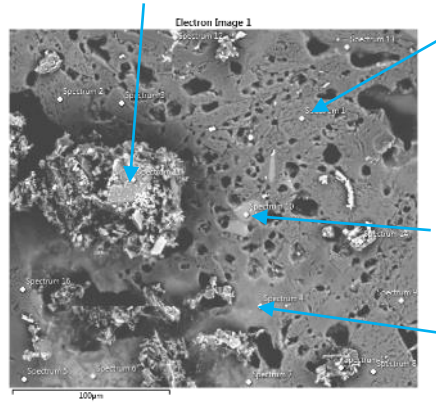
V-CAST (CSLM)

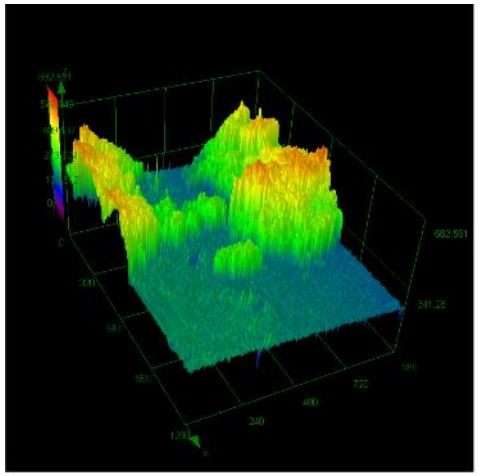
64%CO-36%CO2, 1 hr exposure



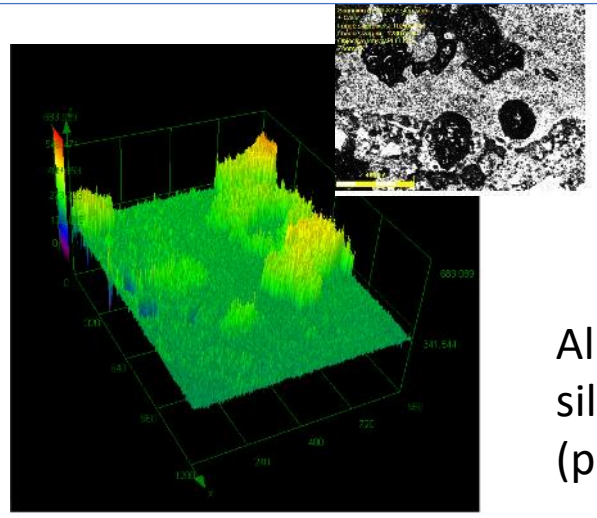
800 °C

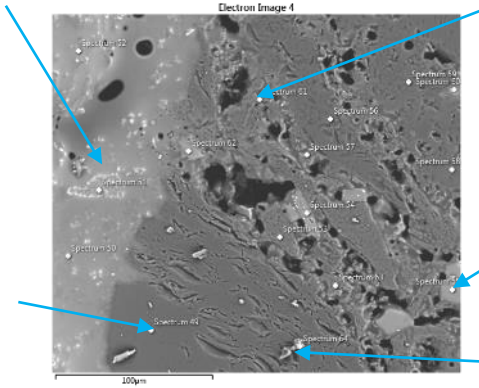






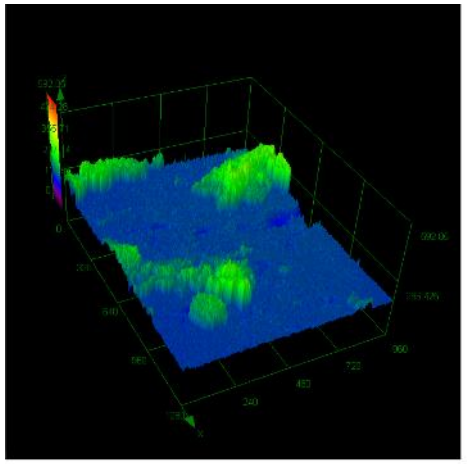
1200 °C



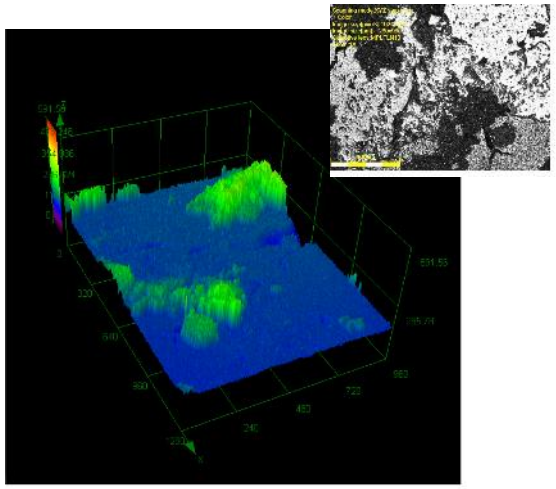


TUFF-FLO (CSLM)

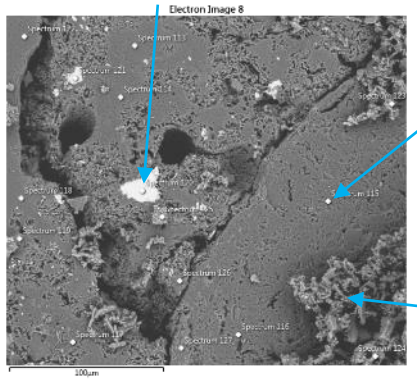
64%CO-36%CO2, 1 hr exposure



800 °C

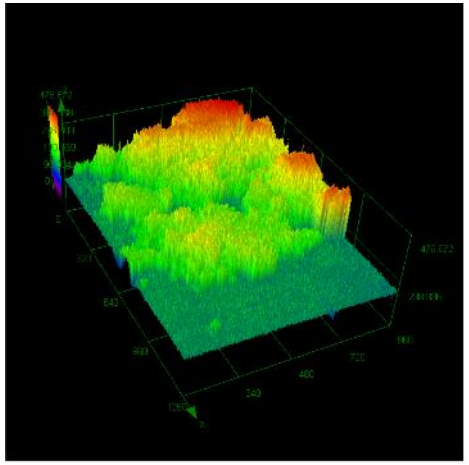


Zirconia (refractory)

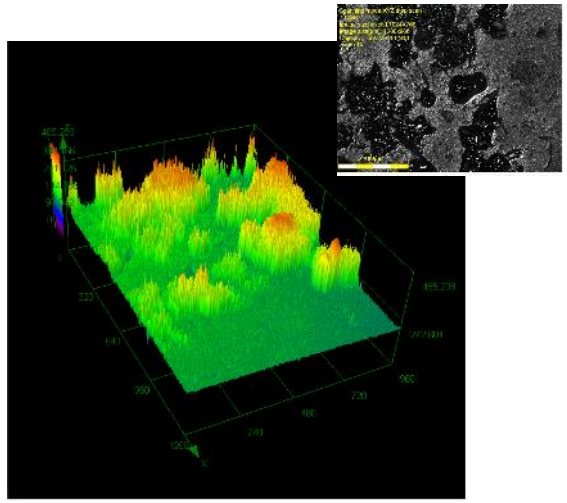


Aluminum silicate (refractory)

Calcium silicate (ash)



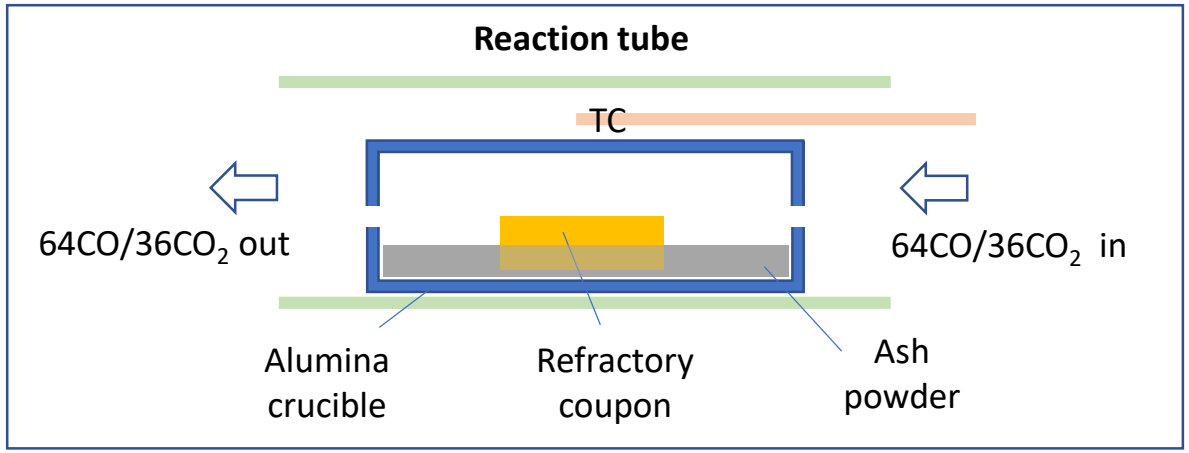
1200 °C

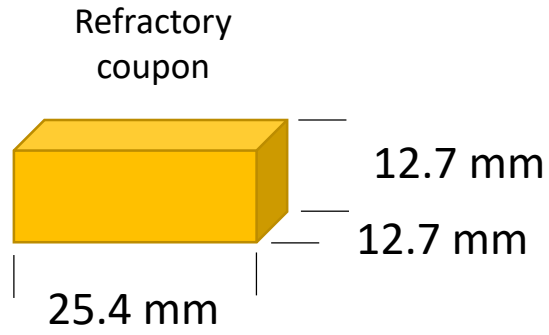


SEM charging issue…

EY20: Direct firing test (on-going)

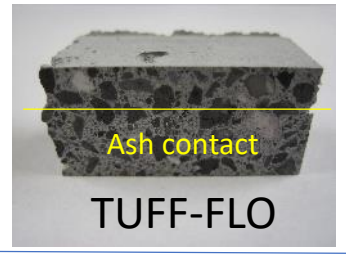
50 hrs at 800 °C/1200 °C in 64%CO-36%CO2





100% coal ash 800 °C

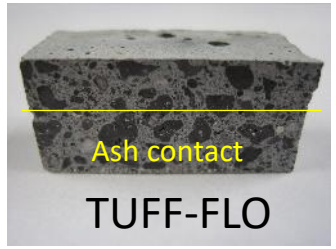
50 hrs



No apparent degradation

80% coal ash – 20% spruce ash 800 °C

50 hrs

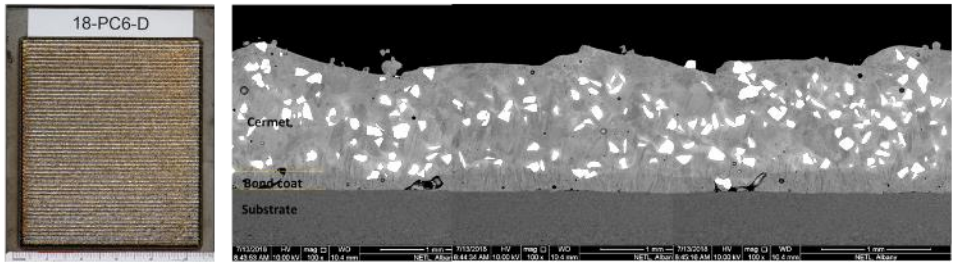


No apparent degradation

EY20: AM liner exposure test (on-going)

Corrosion Performance of Additively Manufactured ARS Liners

Substrate : A516 steel (1.5 cm thick), Bond coat : Inconel 625, Cermet : Inconel 625 (80 Wt.%) + Tungsten Carbide/ WC (20 Wt.%)



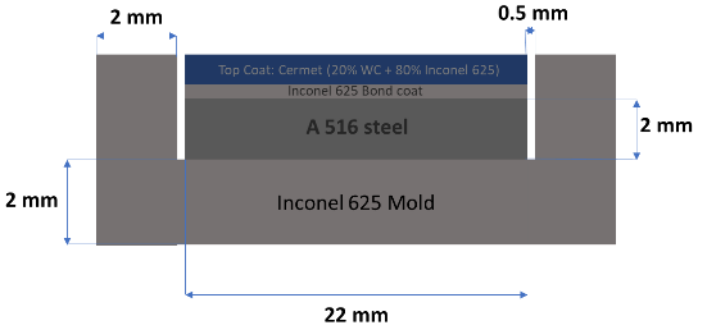
80% IN625+20%WC cermet top coat
Diode laser
Un-glazed

80% IN625+20%WC cermet top coat
Diode laser
Glazed

Test Specimens

Produced by AM Diode LDED

- 80% In 625+20% WC Glazed
- 80% In 625+20% WC Un-glazed
- 100% In 625 Glazed
- 100% In 625 Un-glazed



<u>High-Temperature Corrosion Tests</u>

Temperature: 800 ˚C

Moisture and O_2 free reducing environment

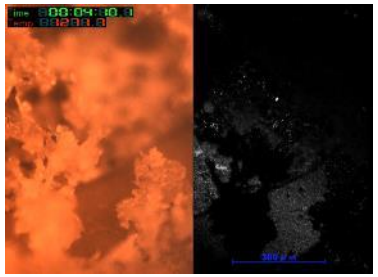
Gas mixture: 38% H_2, 16% CO_2, 36% CO and 10% CH_4

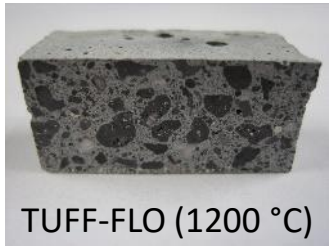
Flow high purity N_2 gas during heating and cooling

Test duration: 500 h

Conclusions

- 3 refractory materials identified potentially used in coal-biomass ash environments in a gasifier. (alumina, mullite based)
- Real-time high temperature microscopic observations indicated coal ash starts to melt if heated above 1200 °C and changes interaction with refractory. Ash transformed to calcium silicate.
- After 50 hrs exposure, V-CAST and TUFF-FLO exhibited no apparent degradation to 100% coal ash and 20% spruce-80% coal ash.





Future work

- **TUFFCRETE will be added to study**
- **Cross-sectional analysis of the fired materials**
- **100% biomass exposure test at 800 °C and 1200 °C**
- **500-hrs exposure test of AM samples at 800 °C**

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Acknowledgement and disclaimer

Acknowledgement

This work was performed in support of the US Department of Energy's Fossil Energy Advanced Reaction Systems. The Research was executed through the NETL Research and Innovation Center's Advanced Reaction Systems Field Work Proposal. Research performed by Leidos Research Support Team staff was conducted under the RSS contract 89243318CFE000003.

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