# RCC Coating Pack Cementation Kinetics

Oliver Hoppe, Kali Robson, Ryan Sanchez, Kaleb Shaw, Bo Sodnombayar
Mentors: Mike Beerman, Li Li, Hanson Fong, Alex Gray

## Introduction

### Reinforced Carbon-Carbon (RCC)

- Blue Origin mission statement: "we envision a future where millions of people will live and work in space"
- RCC heat shields insulate spacecraft from high temp, low pressure atmospheric re-entry environment
- Problem: Carbon oxidized at high temperatures
- RCC needs an oxidation resistant coating

### SiC Oxidation-Resistant Coating & Pack Cementation

- Silicon carbide (SiC) is inert and has high melting point
- Si vapor diffuses into RCC via **pack cementation** process to convert C/C surface to SiC
- Parts placed in a powder bed and heated to 1650 °C
- Thermodynamics and kinetics largely unknown – **opportunity to improve** the pack cementation process

## Design Objective

Design a process to characterize and quantify reaction kinetics of two blended powders provided by Blue at a temperatures up to 1650 °C, and leverage these findings to develop a comprehensive kinetic framework that enables predictive understanding and process optimization

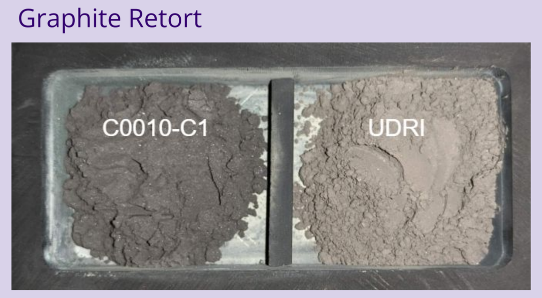
## Design Criteria

The scope of this team's project is focused on the comprehensive analysis and characterization of the powder blend reactions and driving kinetics. The reaction kinetics of the two blended powders were studied at elevated temperatures.

## Methods

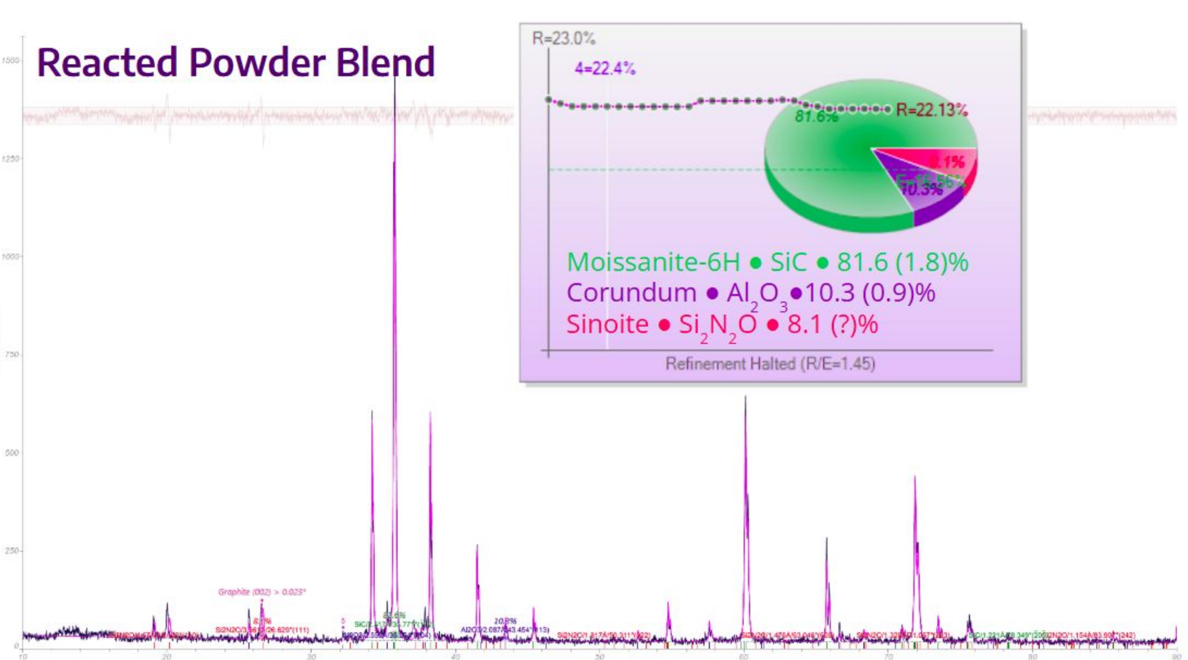
- Differential Scanning Calorimetry (DSC)
- Differential Thermal Analysis (DTA)
- Energy Dispersive Spectroscopy (EDS)
- Graphite Retort
- Laser Particle Size Analysis (LPSA)
- Scanning Electron Microscope (SEM)
- Thermogravimetric Analysis (TGA)
- Tube Furnace Pyrolysis
- X-Ray Diffraction (XRD)

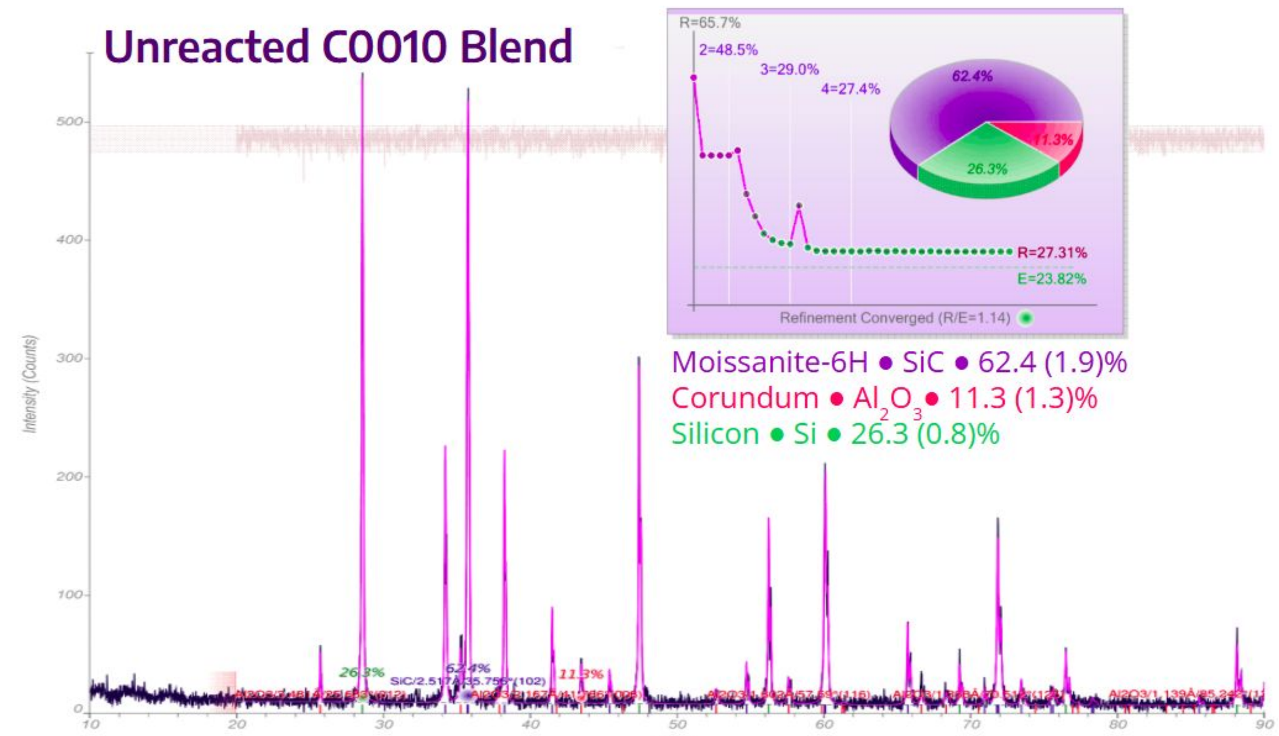
Graphite Retort




C0010-C1 and UDRI powder blends

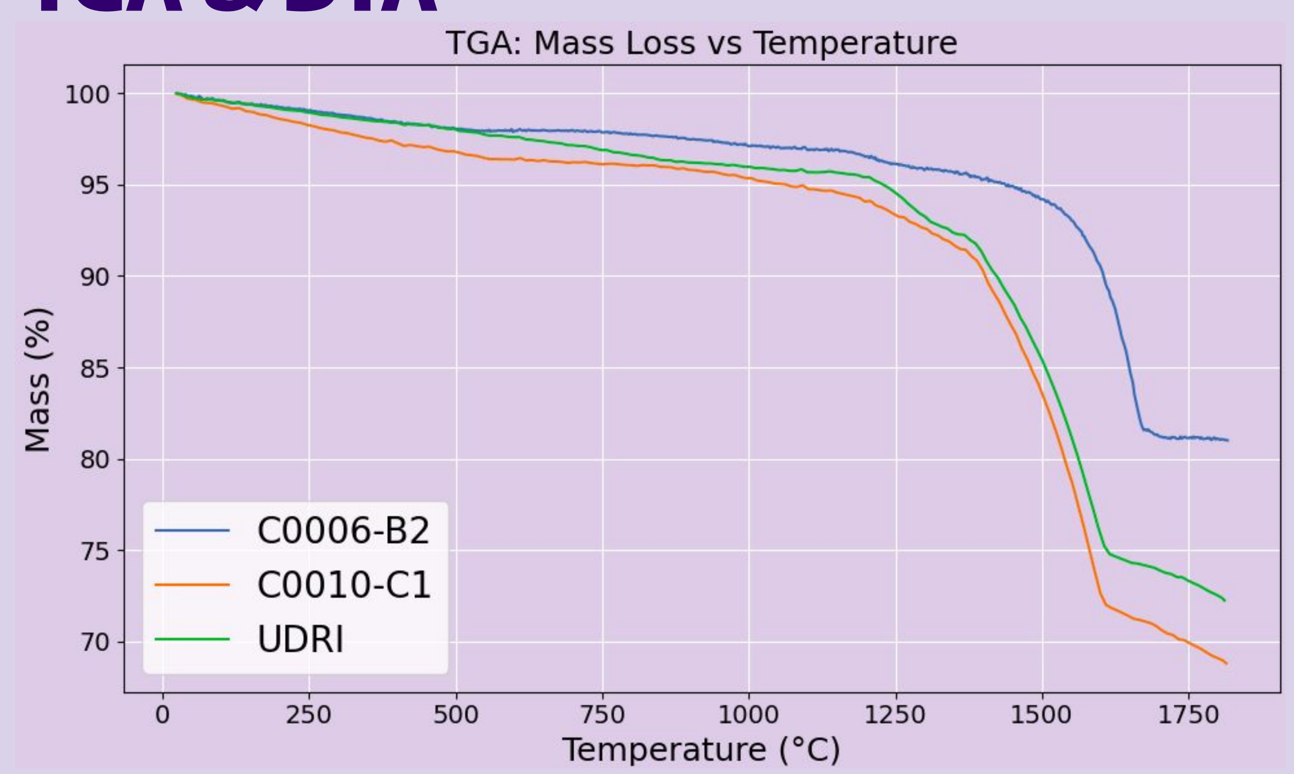
## XRD

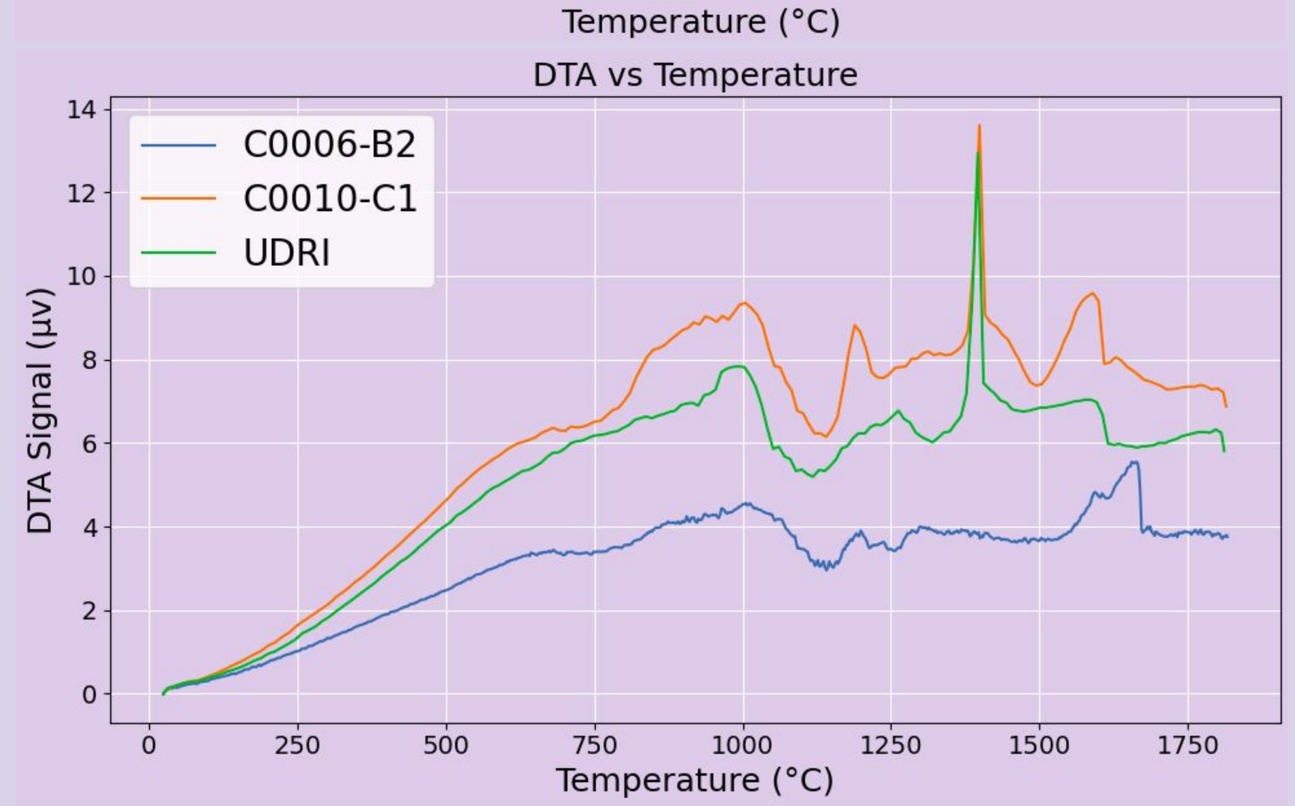



- Reacted Powder Displayed SiC (81.6%), $Al_2O_3$ (10.3%), and $Si_2NO_3$ (8.1%)
- The argon gas supply was depleted at the end of the heating ramp allowing contamination to occur.
- Resulted in the formation of $Si_2NO_3$ with nitrogen likely being an atmospheric contaminant.
- Complete reduction of all free silicon due to the excess oxygen. This will not occur in an argon environment, where the only source of free oxygen comes from reduced alumina.

## TGA & DTA




- Mass loss recorded was greater than 15% for all samples
- C0006-B2 showed the lowest total mass loss to ~ 19%
- UDRI and C0010-C1 showed mass losses in the range 28 - 31 %.
- Previous test conducted up to 1600 °C, C0010-C1 powder showing higher mass loss than UDRI powder when measured at the same conditions

## Possible Reactions

### Expected reactions and corresponding thermal events [1] [2]

Table 1: Expected Pack Material Reactions by Thermal Event

| Event | Equilibrium Temperature | Reaction |
|---|---|---|
| Event 1 | 1412°C | $Si_{(s)} \rightarrow Si_{(l)}$ |
| Event 2 | 1412°C | $Si_{(s)} \rightarrow Si_{(l)}$ |
| Event 2 / Event 3 | 2558°C | $3SiC + 4Al_{(g)} \rightarrow Al_4C_{3(s)} + 3Si_{(l)}$ |
| Event 3 | 1884°C | $Al_2O_3 + 3Si_{(l)} \rightarrow 2Al_{(g)} + 3SiO_{(g)}$ |
| Event 3 | 174°C | $Si_2O + 2Al_{(g)} \rightarrow Al_2O_{(g)} + 3SiO_{(g)} + SiO_{(g)}$ |
| Event 3 | 1732°C | $2Al_2O_3 + 3SiC \rightarrow 4Al_{(g)} + 3SiO_{(g)} + 3CO_{(g)}$ |
| Event 2 / Event 3 | 1795°C | $2SiO_2 + SiC \rightarrow 3SiO_{(g)} + CO_{(g)}$ |

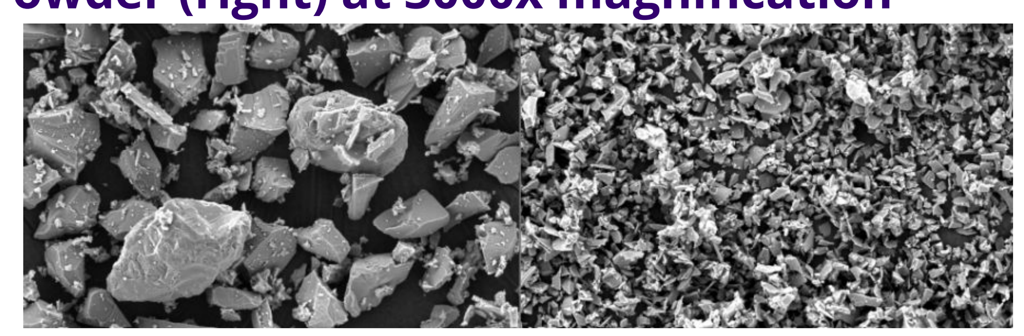
Table 2: Expected Carbon Interface Reactions by Thermal Event

| Event | Equilibrium Temperature | Reaction |
|---|---|---|
| Event 1 / Event 2 | 708°C | $2C + SiO_{(g)} \rightarrow SiC_{(s)} + CO_{(g)}$ |
| Event 2 / Event 3 | 2248°C | $C + Si_{(l)} \rightarrow SiC_{(s)}$ |
| Event 2 / Event 3 | 2331°C | $C + Si_{(g)} \rightarrow SiC_{(s)}$ |
| Event 3 | 2137°C | $2Al_2O_3 + 3C \rightarrow 2Al_{(g)} + 3CO_{(g)}$ |
| Event 3 | 2612°C | $Al_2O_3 + C \rightarrow Al_2O_{(g)} + CO_{2(g)}$ |
| Event 2 / Event 3 | 1612°C | $2Al_2O_3 + 3C \rightarrow Al_4O_4C_{(s)} + 2CO_{(g)}$ |
| Event 2 / Event 3 | 745°C | $5C + 2Al_2O \rightarrow Al_4C_{3(s)} + 2CO_{(g)}$ |

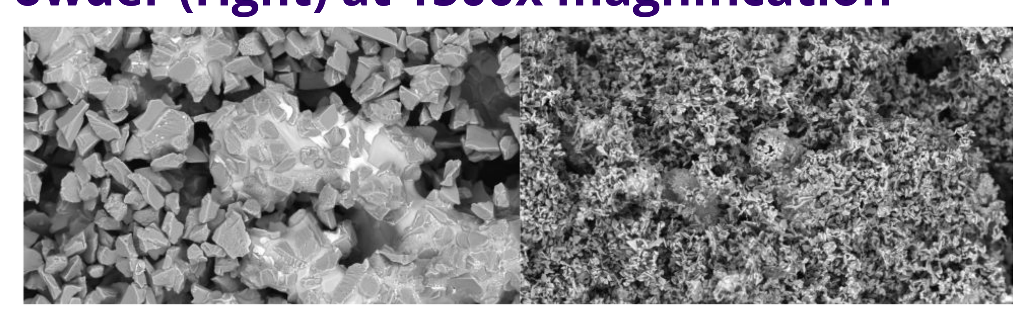
- Primary gaseous evolution of the dry pack material is reliant on the formation of SiO, and CO.
- The only source of free oxygen in an inert cementation environment occurs from the decomposition of $Al_2O_3$, which at 10% by weight in the initial dry pack is equivalent to 6.47% molar fraction of oxygen in the system.

## SEM & EDS Images

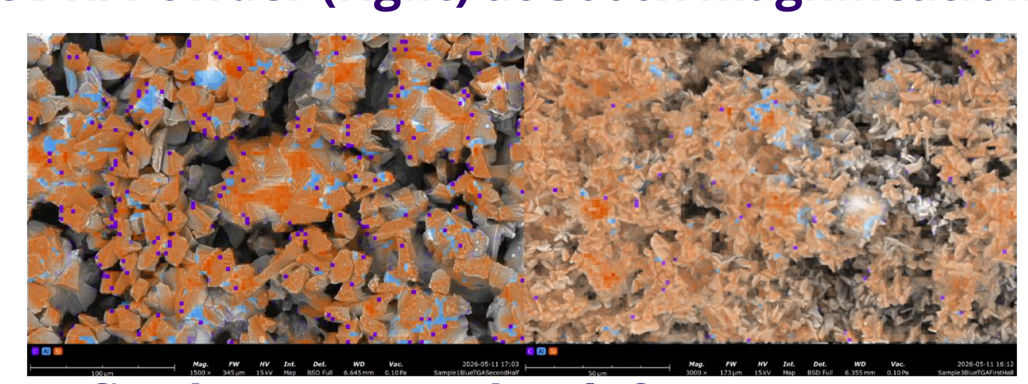
### Pre-fired C0006 Powder (left) and the UDRI Powder (right) at 3000x magnification



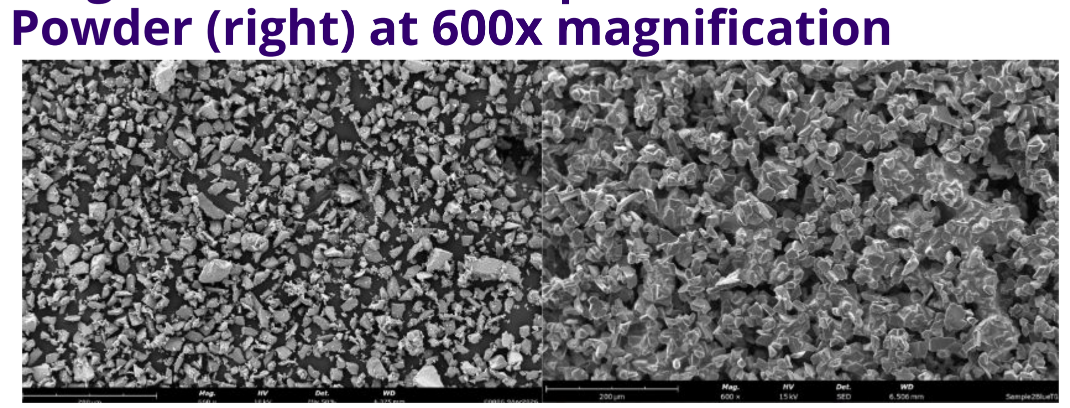
### Post-fired C0010 Powder (left) and the UDRI Powder (right) at 1500x magnification



### EDS comparison of the post-fired C0010 Powder (left) at 1500x magnification and the UDRI Powder (right) at 3000x magnification



### Pre-fired C0010 Powder (left) at 600x magnification and the post-fired C0010 Powder (right) at 600x magnification



## Findings

- Known that UDRI and Blue Origin blended powders have different particle sizing.
- XRD characterization shows both the UDRI and Blue Origin blended powders have the same phases and close to quoted atomic composition.
- SEM imaging and LSPSA quantify the particle sizing difference to be significant, with the UDRI powder being roughly four times finer than the Blue Origin blended powders. The C0006 Powder had an average particle diameter 24.41 µm whereas the UDRI powder had an average particle diameter of 6.43 µm.
- Comparison of SEM imaging of the pre- and post-firing powders has shown a different melt coat morphology between the two powders, implying that the particle sizing significantly affects the reaction kinetics and final morphology of pack cementation process.
- EDS analysis shows the local atomic compositions of the powders, reveal that the powder blended at Blue contaminated with Fe, N, Ti, V (Invar 36 and Ti6Al4V common additive materials in space propulsion), and a significant oxygen loss, implying reaction to completion of the gaseous reactions.
- The post fired melt aggregate sizing significantly differs between UDRI and Blue Origin.
- TGA and DTA analysis shows three distinct reaction regimes and specific temperature at which phase changes and different reactions begin.

## Recommendations/ Next Steps

- Blue Origin enforces stricter particle size tolerances.
- More controlled blending protocol when producing the in-house C0010 dry pack powder.
- Next steps to run samples in the tube furnace at reaction points.
- Obtain refractive index of powder at multiple different firing steps and obtain particle sizing, SEM imaging, and XRD at different firing steps.
- Run TGA/DSC at WCET using sapphire crucibles.

## Acknowledgements

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Blue Origin's Blue Moon