

## Midlands Advanced Ceramics for Industry 4.0

# CASE STUDY

REF No: 2406005

## WS7 - Scale up SILICON NITRIDE BONDED SILICON CARBIDE KILN FURNITURE FOR AEROSPACE COMPONENTS

MODELLING  
& DESIGN

RAW  
MATERIALS  
PROCESSING

FORMING

DRYING &  
SINTERING

ANALYTICAL

### THE CHALLENGE

Kiln furniture is crucial to firing ceramic parts, its purpose: securely hold parts during firing and prevent deformation. It is especially useful for parts with overhanging segments that require support during firing to retain the shape and integrity of the original green body. An example of this is conventional tableware such as plates and bowls. In recent years, there's a growing demand for kiln furniture in advanced ceramics. Advanced ceramics are a group of materials which exhibit a range of unique properties including high temperature stability, abrasion resistance, low thermal conductivity, etc. Examples of advanced ceramics materials include Alumina, silicon carbide, zirconia, and barium titanate. Additionally, the growing demand for ceramic matrix composites, which tend to have large and complex forms, has further increased the need for advanced kiln furniture. The key challenges at this stage is the need for bespoke design in low numbers making it difficult to procure them through the established supply chain.

Additive manufacturing and in particular robocasting could enable a fast and efficient manufacture of kiln furniture prototype.

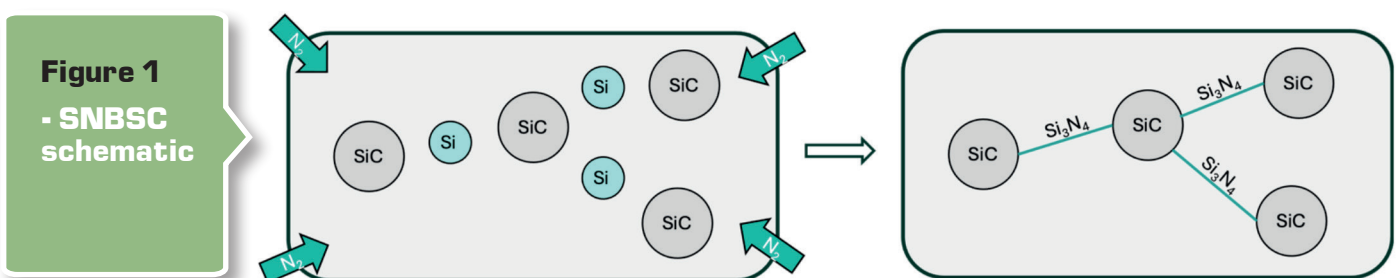
Robocasting involves depositing paste in a 3D, layer-by-layer pattern to produce a shape and it is essential for the paste to have specific rheological properties to support its weight as the layers are laid. Lucideon has previously developed several ceramic paste formulations for robocasting, including alumina formulations which produce parts with densities as high as 90%. However, densification of typical technical ceramics such as alumina is associated with a linear shrinkage of 15-20% from the green to sintered form. This shrinkage poses a significant challenge when attempting to produce complex forms, perhaps that require interlocking, and with strict dimensional tolerances.

In this work we explore the use of a low shrinkage advanced ceramic solution, silicon nitride bonded silicon carbide (SNBSCI), and assess its feasibility to be used with the robocasting technology to produce kiln furniture. Lucideon will use its expertise in the formulation of robocasting paste to develop and trial printable SNBSC material and assess its interaction with an Ox/Ox CMC when used as kiln furniture.

# WHAT WE DELIVERED

We successfully produced silicon nitride bonded silicon carbide (SNBSC) formed through the robocasting technique, achieved through nitriding of additively manufactured parts, demonstrating the capability to produce intricate parts. This accomplishment was facilitated by delivering a printable paste, informed by a literature review and established expertise in formulations for robocasting, ensuring printability and correct rheological properties for additive manufacturing and final part functionality.

Our literature review identified SNBSC as a good candidate for kiln furniture as it exhibits high strength at elevated temperatures, chemical inertness, corrosion resistance, and exceptional thermal shock resistance. The primary advantage of SNBSC is that minimal shrinkage/expansion occurs during the nitriding process. This means the dimensions of the printed part are close to identical to the final ceramic, allowing better tolerance and accuracy from the green to final part. SNBSC formation occurs at a relatively low nitridation temperature of 1350 - 1450 °C, within this temperature range, nitrogen reacts with solid, molten, and gaseous silicon within the SiC/Si matrix, as illustrated in Figure 1.



The novel paste featured a solid loading content of 46% vol, where two-thirds by weight of the solid composition comprised silicon carbide powder P1000. The remaining solids being silicon metal powder. Other components—solvents, binders, and dispersants—play distinct roles, influencing both immediate printability and the ultimate characteristics of the final part. The paste-making process utilised a high-speed planetary mixer, a resonant acoustic mixer, and ball mills, to ensure thorough dispersion. Analytical techniques such as rheology measurements aided in assessing paste printability. Sufficient rheological properties enabled the printing of paste on the Delta WASP 2040. Printed geometries were first designed in CAD software and subsequently processed through a slicer, converting the design into instructions via coordinates for the printer.

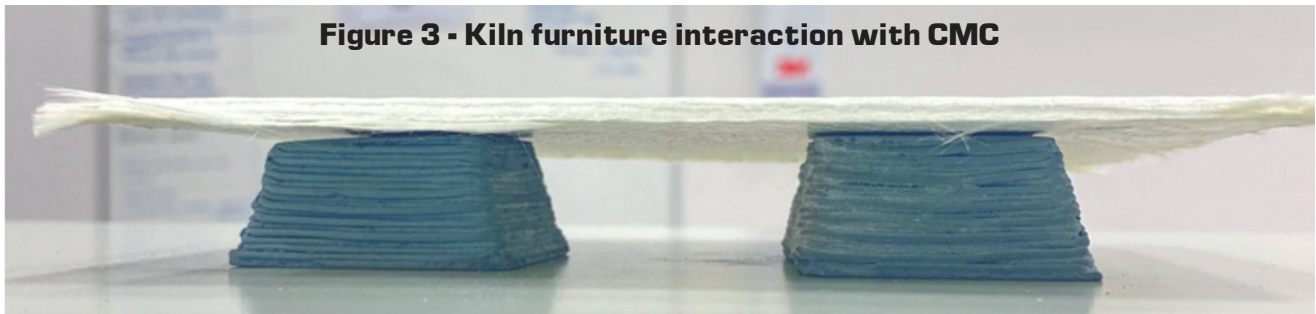


**Figure 2 - SNBSC kiln furniture**

The nitriding process started with debinding in an electrically heated box furnace in air. The temperature was ramped at 3 °C/min to 900 °C, held for 1 hour, then cooled at 3 °C/min to 20 °C. Direct nitriding of the parts was conducted in a Carbolite tube furnace, where nitrogen flowed through the tube furnace throughout the program: ramping at 5 °C/min up to 1450 °C with a 6 hour hold at 1450 °C, then naturally cooled. The nitrided parts, displayed in figure 2, underwent XRD testing to determine their composition.

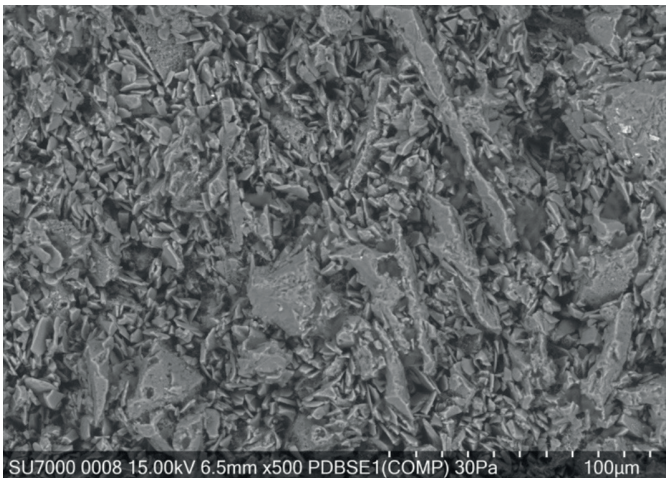
The results indicate nearly complete nitriding of silicon, with only 0.3% residual silicon remaining in the tested sample. Table 1 illustrates an almost equal distribution between  $\alpha$  and  $\beta$  forms of silicon nitride, signifying successful nitridation. Notably, the material's strength is known to improve as silicon transforms into  $\alpha / \beta - \text{Si}_3\text{N}_4$ .  $\alpha - \text{Si}_3\text{N}_4$ , considered less thermodynamically stable, transitions to  $\beta - \text{Si}_3\text{N}_4$  at elevated temperatures, whereby microstructural changes occur, the needle like  $\alpha - \text{Si}_3\text{N}_4$  transitions into a more isometrical morphology of  $\beta - \text{Si}_3\text{N}_4$ .

COMPOSITION	
Silicon Carbide 4H (SiC)	9.9 wt%
Silicon Carbide 6H (SiC)	39.1 wt%
Silicon Carbide 15R (SiC)	3.7 wt%
Alpha Silicon Nitride (Si <sub>3</sub> N <sub>4</sub> )	23.8 wt%
Beta Silicon Nitride (Si <sub>3</sub> N <sub>4</sub> )	23.3 wt%
Silicon (Si)	0.3 wt%

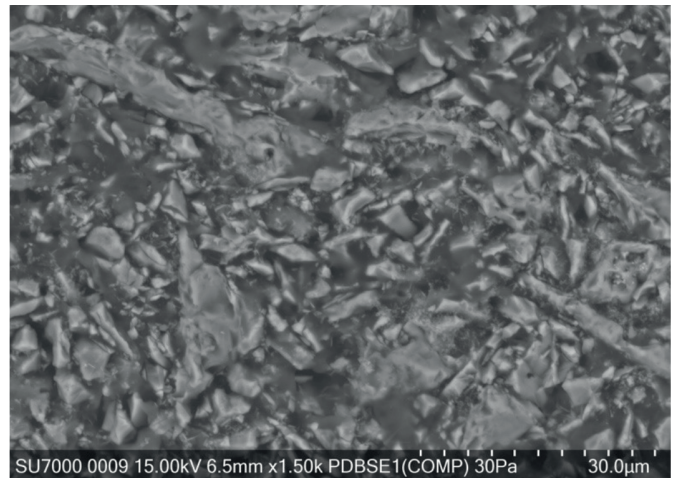


**Figure 3 - Kiln furniture interaction with CMC**

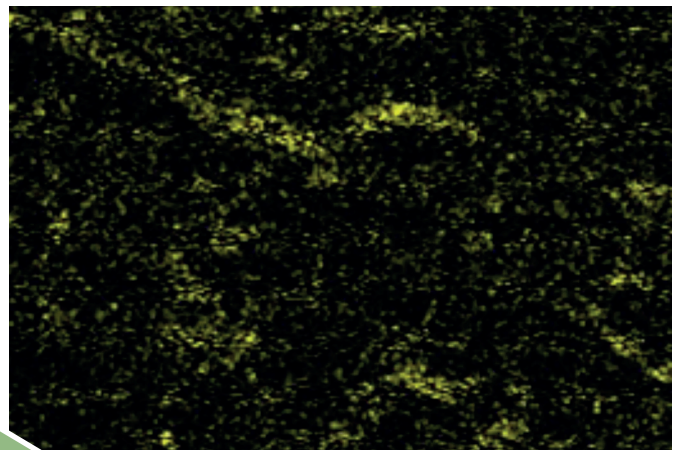
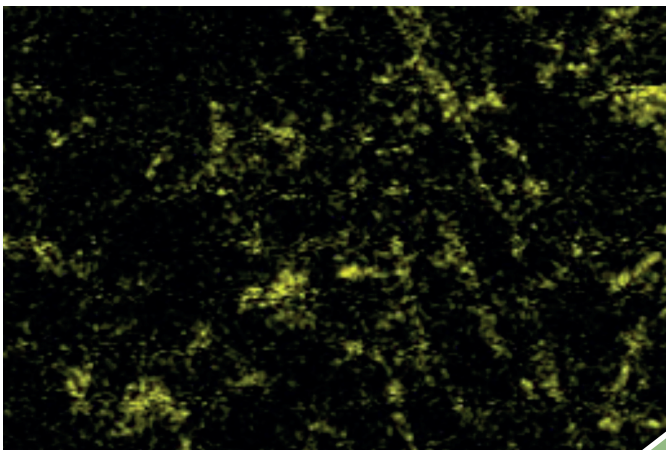
Final parts were then successfully used to support CMC laminates undergoing sintering, the set up can be seen in figure 3. Figure 4 illustrates the microstructure of our SNBSC printed parts at two magnifications 500x and 1500x, and their corresponding EDS maps for nitrogen. At both magnifications the needles and isometric grains are clearly visible in both back scatter detector images and more clearly highlighted in yellow by nitrogen suggesting successful nitridation of silicon carbide.



**NK SERIES**



**NK SERIES**



**Figure 4 - SNBSC SEM images and EDS mapping at x500 & x1500**

There were some considerable challenges associated with the SNBSC, in both printability and final properties. Firstly, the robocasting paste exhibited highly elastic behaviour and variable rheological properties over time. The elastic nature of the paste caused considerable difficulties during printing. Secondly, the strength of nitride parts was poor, some having a dusty texture and were prone to fracture due to low strength. This is most likely caused by the poor green density achieved from the robocasting paste.

## IMPACT

This project demonstrates the feasibility of modernising the production of kiln furniture through the use of robocasting as a cost-effective additive manufacturing technology. It can produce one off complex forms without the need for moulds and tooling. There are also additional opportunities to fully exploit its design potential, for example using lattice infill, produce shell structures, and incorporate internal features to reduce the thermal mass of kiln furniture and enhance air flow around parts during sintering.

The silicon nitride bonded silicon carbide trialled in this work has several advantages over the alumina material previously used. SNBSC is low density and has a low CTE meaning that it is resistant to thermal shock and is capable of rapidly heating and cooling without degradation. The nitride bonding process also means there is negligible dimensional change between the green and nitrided form, meaning that complex forms can be manufactured and machined green with confidence that the form will not alter during the nitriding process. Whilst this project has demonstrated the feasibility of this material as kiln furniture, it has highlighted several challenges with use of the SNBSC in combination with the robocasting process, namely poor print behaviour and low strength due to a lack of density. Additional development effort is required to address these challenges before the material is taken forward to scale up and implementation.

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