

Representative Title

Binder Jet Additive Manufacturing (BJAM) of Silicon Carbide Reactor Assemblies for High-Temperature and Hydrogen Leak-tight Applications

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Problem Definition

Additive Manufacturing (AM) has revolutionized the manufacturing landscape over recent decades, offering unparalleled flexibility and efficiency in producing complex components. Among the various materials utilized in AM, ceramics have emerged as a critical focus due to their exceptional properties, such as high temperature resistance, chemical stability, and mechanical strength. Ceramic AM holds significant promise for diverse industries, including refractory, aerospace, biomedical, and automotive sectors, by enabling the creation of intricate and high-performance components that are difficult to achieve with traditional manufacturing methods in terms of huge material and time wastage. Despite these rapid advancements, current ceramic AM processes are predominantly constrained to producing small-scale prototypes or coupons, resulting in a relatively low Technology Readiness Level (TRL) for larger and more complex structures. As industrial demand grows for large-scale ceramic components with sophisticated geometries, particularly those requiring gas-tight integrity for fluid containment, the existing TRL gap poses a substantial barrier. For example, chemical processing vessels such as catalytic reactors necessitate large volumes to enhance throughput and must be significantly engineered with intricate designs to optimize efficiency. The primary obstacles include the limitations of existing ceramic 3D printing techniques such as Stereolithography (SLA) and Binder Jet Additive Manufacturing (BJAM), which, while effective for smaller components, fall short in scalability for larger parts.

To address these challenges and elevate the TRL of ceramic AM for large-scale applications, innovative approaches are required. This technical brief presents a novel technique designed to obtain large, leak-tight ceramic components by assembling 3D printed smaller components, thereby overcoming the current limitations in ceramic AM. This approach involves a comprehensive method that includes testing multiple design configurations to identify optimal structures that inherently support gas-tightness, as well as exploring various post-processing techniques applied at different temperatures to enhance the bonding and sealing of ceramic segments. This innovation marks a significant leap forward in BJ-AM for ceramics, offering a scalable solution for producing complex ceramic structures. By overcoming existing TRL limitations, our method paves the way for broader industrial adoption of ceramic AM, enabling the realization of larger-scale applications across high-demand sectors such as aerospace, automotive, and chemical processing.

Background Perspective

Conventional ceramic manufacturing techniques, such as slip casting and sintering, are reliable but not optimized for large-scale, high-temperature chemical reactor applications. These methods are time-intensive and struggle to accommodate the complex geometries and large dimensions required for high-efficiency reactor designs. In contrast, ceramic 3D printing techniques like Binder Jet Additive Manufacturing (BJ-AM), Stereolithography (SLA), and Direct Ink Writing (DIW) enable the fabrication of intricate geometries more efficiently and at a manageable scale. Among these, BJAM stands out as a relatively cheaper and hassle-free powder-based 3D printing method, widely utilized in mold making, manufacturing composites, and creating complex geometries. However, BJAM is still limited by its print volume, making it unsuitable for many industrial applications that demand larger components.

Addressing the growing market needs for large-scale 3D-printed ceramic components, we have innovated a robust joining technique. As a case study, Dimensional Energy, a chemical technology and engineering company, requires chemical reactors capable of high throughput to convert carbon dioxide and hydrogen gases into Synthesis Gas (syngas) via the Reverse Water Gas Shift (RWGS) reaction. To achieve a 2kW output capacity, a large reactor was designed and optimized computationally (as shown in Figure 1(a)).

Manufacturing this reactor necessitated fluid leak-tightness of the process gasses (particularly hydrogen) and large dimensions, which were accomplished by utilizing the BJAM technique in combination with a secondary joining method. This secondary technique involved polymer infiltration and pyrolysis (PIP) and Chemical Vapor Infiltration

(CVI) as post-processing steps, resulting in leak-tight ceramic components. Several designs were evaluated on the basis of contact surface area, mechanical and thermal properties to optimize a final design that serves best on for a leak tight joint. The following section will detail the features and designs incorporated in this component manufacturing process. Additionally, the samples with joints reached 68% flexural strength in comparison to the samples without any joint, while the thermal properties remained the same. This work demonstrates a meticulously designed large ceramic component that exemplifies BJAM for ceramics, ensuring mechanical robustness, gas tightness, and thermal stability. These advancements position BJAM at the forefront of high-performance ceramic manufacturing, effectively addressing the limitations of traditional and alternative methods.

Technical Overview

The BJAM technique is a powder-based additive manufacturing process in which powder particles from a feedstock which are uniformly spread over a build box and leveled using a roller. Subsequently, binder droplets are selectively deposited onto the powder layer according to the CAD geometry (Autodesk Fusion 360), followed by drying with a UV light source. This layering procedure is repeated to build the desired structure incrementally. For this study, five distinct designs were created for Silicon Carbide (SiC) (Panadyne Inc, PA) samples printed using an ExOne Innovent+ binder jet 3D printer (Pennsylvania, USA), which utilizes an AquaFuse binder—a mixture of ethylene glycol and 2-butoxyethanol. After printing, the build box containing the samples was placed in an oven and cured at 190°C for six hours. Upon completion of the curing process, the samples were carefully removed to preserve their structural integrity and had ~49% theoretical density. The printed design (post-processed result in Figure 3(b)) of the two tubes had a specific joint design (Figure 3(b)) that allowed them to fit together for post-processing. Many joint designs were printed and post-processed with different shapes that were similar to those of woodworking. Due to the resolution and characteristics of the powders, it was empirically determined which design allowed for post-processing into the most leak-tight and mechanically-stable structure.

The post-processing steps were also screened by empirical examinations and CT analyses to understand porosity and failure modes. These included various methods to initially attach the multiple joints, then sealing and densification.

To enhance the structural properties of the green samples along with the joints, they were first joined using a SiC slurry (MS154+10 w% PB055+ 20V% SiC). The joined samples then underwent polymer infiltration (MS154+ 10w% PB055) and pyrolysis (PIP) at 900°C for one hour in an inert atmosphere to increase density. This PIP cycle was performed twice to reach a theoretical density of 74%. This was followed by a CVI process using Methyltrichlorosilane (MTS) and Hydrogen (H₂), which allowed carbon particles to fill in the pores in the 3D-printed parts over two cycles. These post-processing steps increased the density of the samples to approximately 89% of the theoretical density. Mechanical and thermal testing was conducted to evaluate the structural integrity of the processed samples. The results showed that the samples exhibited an average flexural strength of 128.23 ± 6.7 MPa and 120.1 ± 14.9 MPa after thermal cycling at 1000°C, compared to 208 ± 17 MPa and 198 ± 25 MPa for samples without any joints at 225°C. Additionally, 3D-printed SiC tubes joined via PIP and post-processed with CVI were subjected to leak tests following ASTM 2095 guidelines. Samples were tested under a pressure of 20 bar for 30 or 60 minutes using H₂ gas (Figure 3(b)). The leak testing was successfully performed on the 3D-printed and joined coupons, with joined samples demonstrating a leak rate of 7.21×10^{-6} atm cc/s, ensuring sufficient safety for reactor applications.

A computational fluid dynamics (CFD) model was simulated using ANSYS to analyze both mechanical and chemical conversions of a reactor with proprietary internal structures, flanges and internal tubes. The simulation revealed the necessity of engineering the internal baffle unit with a gradient pitch design. A prototype reactor version (1:5 scale) containing three joints (both external and internal components) was printed and joined to understand the printability and any susceptible stresses (Figure 2(b)).

A scaled-up version as shown in Figure 1 was printed with the shell in three segments, and with internal exhaust tube separately in three segments. The printed segments were subsequently joined, infiltrated with polymer, and pyrolyzed (see Figures 1(b)). The reactor structure has yet to undergo CVI for further densification and testing for syngas production. This comprehensive approach demonstrates the successful fabrication of large, mechanically robust, gas-tight ceramic components using BJ-AM, positioning BAAM as a leading method for high-performance ceramic manufacturing.

Reflections

This innovative approach to large-scale ceramic additive manufacturing has profound implications for both the team and the broader industrial landscape. By successfully integrating BJAM with advanced post-processing methods such as PIP and CVI, the team has overcome significant challenges related to density, gas-tightness, and structural integrity, which are critical for high-performance reactor applications. To the best of our knowledge, this is the first time a hydrogen leak-tight joint has been fabricated using AM methods, providing routes to scalable BJAM assemblies.

The ability to fabricate large, complex ceramic components with reliable mechanical and thermal properties not only enhances the team's capability to design and produce efficient reactors but also positions them as leaders in the field of BJAM. The relevance of this work is underscored by the increasing demand for high-throughput chemical production systems, where efficient and scalable reactor designs are paramount. Moreover, the efficiency of BJAM combined with the robust performance of the final components offer substantial economic benefits, making advanced ceramic reactors more accessible for industrial applications. This advancement significantly benefits the team's approach by providing a validated methodology that ensures the production of high-quality ceramic components, fostering innovation and enabling the development of next-generation reactors. Additionally, the successful demonstration of mechanically robust components leak-tight to the notoriously leaky hydrogen gas opens new avenues for research and collaboration, leading to further enhancements in ceramic AM technologies and their applications across various high-demand sectors. Ultimately, this work not only addresses current manufacturing limitations but also sets a foundation for future innovations in multi-component, hermetically-sealed joint assemblies, reinforcing the team's commitment to advancing manufacturing technologies and meeting the evolving needs of the industry.

