ACS Sustainable Chemistry & Engineering

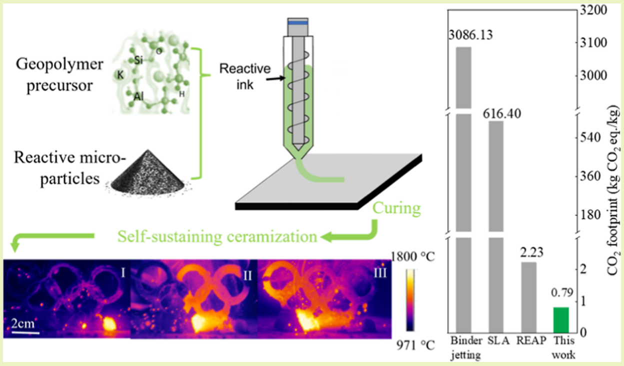
pubs.acs.org/journal/ascecg

Research Article

Low-Carbon Manufacturing of Ti−Si−C Ceramics Using Geopolymer-Binder-Integrated Reactive Feedstocks

Ruochen Liu, Aolin Hou, Jingjing Qiu,* and Shiren Wang*

Cite This: *ACS Sustainable Chem. Eng.* 2024, 12, 4858−4866



ABSTRACT: The ceramic manufacturing sector, recognized as a highly energy-consuming industry, is set to boost energy efficiency and reduce carbon footprint. Here, we present a new self-sustaining ceramization-assisted additive manufacturing (AM) of ceramic composite structures. The eco-friendly process features extrusion-based printing of geopolymer-bonded reactive microparticles, ambient environment curing, and self-sustaining ceramization. Our approach exhibits an extraordinarily low manufacturing carbon footprint with a greenhouse gas (GHG) emission of 0.79 kg of CO_2 equivalent/kg, a 1000-fold decrease compared to standard binder jetting ceramic AM. The resultant structure comprises a Ti−Si−C-based ceramic composite, simultaneously showcasing the lowest open porosity (22%) compared to other reactively 3D-printed inorganic structures. The proposed technology has the potential to pave the way for low-carbon manufacturing of geometrically intricate ceramic composite structures.

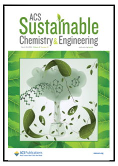
KEYWORDS: *sustainable manufacturing, self-sustaining reaction, additive manufacturing, geopolymer, Ti−Si−C composites*

1. INTRODUCTION

Ceramics' critical role has extended from ancient artistic and domestic use to modern applications in automotive,[1] aviation, aerospace,[2] IT,[3] and healthcare industries[4] due to their chemical inertness and high-temperature resistance.[5] However, ceramics are inherently difficult to process. The ceramic industries have been considered energy-intensive with their over 400 Mt CO_2 emission per year.[6] To reach the net-zero 2050 emissions goal, it is crucial to reduce carbon emissions from high-temperature ceramic production. Additive manufacturing (AM) provides an effective way to manufacture complex geometry while significantly promoting material efficiency and reducing transportation through on-demand and on-site production, resulting in increased sustainability.[7] As AM technology shifts from prototyping to mass production, its environmental impacts cannot be ignored. Although current efforts have been spent on developing sustainable feedstocks, low-carbon AM processes remain underexplored.

The utilization of low- or no-heat processes holds significant promise for advancing environmentally sustainable and energy-efficient ceramic AM.[8] Self-propagating high-temperature synthesis optimizes the use of inherent chemical energy within reactants to facilitate rapid phase transitions via a self-sustaining reaction wave, ultimately forming the product.[9] This process requires only a brief initial energy input to trigger the reaction, which then proceeds autonomously throughout the entire material without the need for energy supply. Historically, the energy released through this method has been employed for various purposes, ranging from explosives in ancient times to modern applications such as sealants, bonding materials, and the creation of specialized structures.[10] Recently, this self-sustaining reaction mechanism has been integrated with diverse manufacturing technologies to produce functional components featuring intricate geometries. The fusion of self-sustaining reactions with AM has the potential to pave the way for efficient, low-carbon, manufacturing solutions. At present, two primary strategies exist for incorporating self-sustaining reactions into AM: direct writing and two-step printing. Efforts have been made to apply self-sustaining reactions in the direct writing of thermosets,[11,12] continuous fiber composites,[13] short fiber composites,[14] multiscale composites,[15,16] and metals.[17] The two-step printing approach has been employed to fabricate cermet structures, initially, volatile gel integrated ink was used to print the preform, and subsequently, a self-sustaining reaction was initiated to convert the preform into cermet structure.[18,19] However, the resulting inorganic structures are highly porous (66.4% void) and lack mechanical

Received: November 3, 2023
Revised: March 2, 2024
Accepted: March 4, 2024
Published: March 13, 2024



https://doi.org/10.1021/acssuschemeng.3c07159

robustness, limiting their broader range of applications. Rapid energy-efficient additive-manufacturing process (REAP) was introduced by Liu et al.[20] where geometrically complex ceramic structure can be produced by self-sustaining ceramization of in situ cured preceramic polymer-binding ceramic preform. However, the preceramic polymer binder is expensive and curing of preceramic polymer requires either high temperature (>200 °C) or consistent high-power UV illumination, which are the main contributor to carbon greenhouse gas (GHG) emissions.

In recent years, geopolymers have emerged as a green and low-carbon cementitious material, gaining widespread attention and research interest globally. Its environmental friendly nature is underscored by two key aspects: eco-friendly raw material sourcing and low-carbon processing. The raw materials for aluminosilicate gel binders, such as fly ash, slag, and natural minerals, are typically derived from abundant industrial byproducts or naturally occurring sources.[21] Utilizing these materials for inorganic binder production not only contributes to waste reduction and resource recycling but also aligns with sustainable development principles. Furthermore, the production of geopolymer is notably low-carbon, emitting only 0.18 kg of CO_2 per kg of geopolymer produced, approximately one-fifth that of ordinary Portland cement.[22] Compared to traditional concrete, geopolymer concrete production reduces CO_2 emissions by about 26–45%.[23] The curing of aluminosilicate gel binders under ambient conditions requires a lower energy consumption and low carbon emissions. These characteristics render geopolymers as a promising sustainable inorganic binder. Recently, geopolymers have been tailored to accommodate various processing technologies such as molding[24] and 3D printing.[25] Reports suggest that geopolymer can facilitate the fabrication of SiC ceramics by altering rheological properties, followed by a sintering process spanning several hours.[26] Nevertheless, the eco-friendly geopolymer could be a promising binder candidate to decarbonize ceramic manufacturing.

To foster a sustainable ceramic industry and cater to the evolving demands of ceramic manufacturing decarbonization. Here, we introduce a novel low-carbon AM of ceramics that features green geopolymer binding reactive feedstock printing and ambient environment curing. Following curing, the reactive feedstock was subjected to high-temperature initiation, triggering the inorganic chemical reaction among reactive microparticles to form a self-sustaining reaction, transforming the preform into ceramic structures. The process exhibits >3000 times lower carbon footprint as compared to standard binder jetting ceramic AM, meanwhile only produces 35% GHG emissions compared to the state-of-the-art REAP approach. The geopolymer structure and concentration were tuned and their influence on the self-sustaining reaction characteristics and the open porosity of the ceramic structure were studied. Compared to other 3D printed and self-sustaining reactions formed inorganic structures, the open porosity of our manufactured ceramic structure exhibits 3.3 times reduction. This approach could open a new path for low-carbon AM of dense ceramic structures.

2. MATERIALS AND METHODS

2.1. Preparation of Geopolymer Binder. First, an alkaline activator was prepared. 55 wt % potassium hydroxide (KOH) (Sigma-Aldrich) water solution was mixed with silica fume (Sigma-Aldrich) with a 2.8:1 weight ratio. The mixed alkaline activator was magnetically stirred for 48 h in an ambient environment before use. Subsequently, various amounts of metakaolin (MK) microparticle (MetaStar 501) were mixed with the alkaline activator in a mixing container while stirring continuously until a homogeneous paste was formed.

2.2. Preparation of Reactive Microparticle/Geopolymer Feedstock. First, a reactive microparticle mixture was prepared. Commercially available microparticles of silicon carbide (SiC, <20 μm), and graphite (C, <20 μm) were purchased from Sigma-Aldrich. Titanium (Ti, <20 μm) microparticle was purchased from Atlantic Equipment Engineers. The microparticle reactants were then mixed in a molar ratio of Ti/SiC/C = 3:0.5:1. To obtain the mixture, the microparticles were first suspended in ethanol and subjected to ultrasonication for 1 h, followed by mechanical stirring for another hour. Afterward, the ethanol was eliminated from the suspension by drying at 85 °C under mild mechanical stirring overnight until the ethanol content was undetectable by differential scanning calorimetry. Subsequently, various amounts of reactive microparticle mixture were mixed with geopolymer binder with a beater blade for 5 min to obtain reactive feedstock. To cure the reactive feedstock upon extrusion-based printing, the printed structure was placed in an open-air environment for 21 days. The weight change was monitored weekly and utilized to determine the remaining water content in the samples.

2.3. Self-Sustaining Ceramization. After fabrication, the ceramic performs were moved to a glovebox filled with argon gas to conduct the self-sustaining reaction. The setup is shown in Figure S1. A tungsten basket, sourced from Kurt J. Lesker Company (model: EVB133030W), and heated by a DC power supply was used to trigger the self-sustaining reaction. We monitored the reaction's temperature evolution using an Optris PI 05 M infrared thermal camera. Roughly 10 s into the heating process, a bright glow emanating from the preform signaled the onset of the self-sustaining reaction, at which point the tungsten heater was promptly turned off. Additionally, a digital camera (DJI Osmo Action equipped with a light filter) was set up to capture the reaction in real time. Test specimens with a size of 50 × 5 × 5 mm were used to analyze the reaction characteristics. Time-resolved thermal maps were captured by using an infrared camera operating at a frame rate of 27 Hz. This allowed for detailed observation of the temporal evolution of the temperature profile associated with the propagating reaction wave. The temperature observed at the reaction front is referred to as the "'reaction front temperature." To determine the frontal reaction velocity (ν_r), the time derivative of the displacement of this reaction front temperature was calculated.

2.4. Characterizations. The rheological properties of the reactive microparticle/GP feedstock were characterized by an Anton Paar Physica MCR-301 rheometer under parallel plate mode. The parallel plate had a diameter of 8 mm, and a gap of 1 mm was used for the testing. The apparent viscosity of the reactive microparticle/GP feedstock was carried out under the shear rate from 10^{-2} to 10 s^{-1}. The viscoelastic behavior of the reactive microparticle/GP feedstock was analyzed with shear stress ranging from 1 to 10^4 under a constant frequency of 1 Hz. The microstructure and elemental analysis of the sample were conducted using a JEOL JSM-7500F scanning electron microscope, which was equipped with energy-dispersive spectroscopy and operated at an accelerating voltage of 20 kV. Additionally, X-ray diffraction patterns of the samples were obtained using a Bruker D8 Discover diffractometer with Cu Kα (λ: 1.5418 Å) radiation, operating at a voltage of 40 kV and a current of 40 mA.

The test of open porosity followed the international standard ISO 18754. The method of test followed Archimedes' principle, and the relative bulk density π_b was calculated as, $\pi_b = (m_1 - m_2)/(m_3 - m_2) \times \rho_1$, where m_1 is the mass of the dry sample, m_2 is the apparent mass of the immersed sample, m_3 is the mass of the soaked sample, ρ_1 is the density of the immersed liquid.[27]

2.5. Calculation of Manufacturing Carbon Footprint. In this work, geopolymer-binding reactive feedstock was printed by an extrusion-based machine and cured in ambient environment. Thus, the printing machine energy consumption is assumed to be the same as the REAP process. However, no external energy source was used

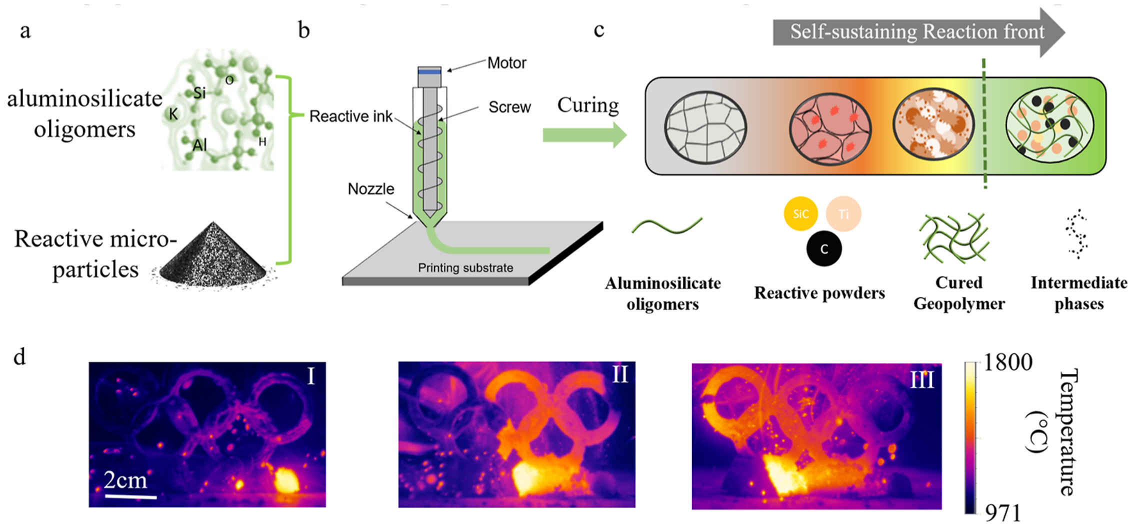


Figure 1. Schematic illustration of the implementation of geopolymer binder integrated reactive feedstock printing and ceramization. (a) Reactive microparticles and aluminosilicate oligomers were used as the printing feedstock. (b) Extrusion-based layer-by-layer deposition. (c) After curing, the ceramic preform was converted to the ceramic structure by self-sustaining ceramization. (d) Thermal images of living self-sustaining ceramization of the ceramic preform.

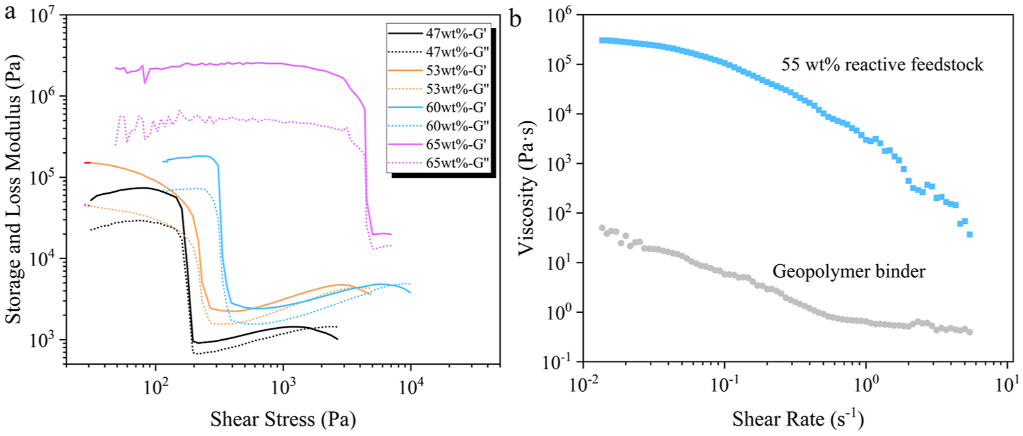


Figure 2. Rheological properties of inorganic reactive feedstock. (a) Viscoelastic behaviors for the feedstock consisting of various concentrations of reactive microparticles. (b) Apparent viscosity as a function of shear rate for geopolymer-binder-integrated feedstock.

for curing. Also, the thermal decomposition of preceramic polymer is not applicable in this case, reducing the carbon footprint for direct emission. Thus, the processing energy consumption only consists of a printing machine and initiation steps of the self-sustaining reaction. Specifically, to start the reaction, a 192 W tungsten heater was turned on for ∼12 s, which consumed 2.3 kJ of energy. Conversion of the energy consumption to CO_2 emission was based on the GHG emissions factor of 0.00012 kg CO_2 eq/kJ, which was suggested by the U.S. Environmental Protection Agency.[28] Calculation of two typical ceramic AM processes (binder jetting and vat polymerization), and REAP process were detailed in our paper.[20]

3. RESULTS AND DISCUSSION

3.1. Geopolymer Binder Integrated Reactive Additive Manufacturing. An eco-friendly reactive feedstock composition was ingeniously designed by mixing inorganic reactive microparticles with aluminosilicate gel, serving as a binder. The production of this aluminosilicate gel binder is recognized for its low-carbon emission characteristic.[21] This innovative formulation not only serves as a foundation for adopting eco-friendly ceramization processes but also showcases the pivotal role of utilizing low-carbon binders in mitigating the environmental impact. Titanium−silicon−carbide (Ti−Si−C) composites are ternary materials chosen for their excellent combination of mechanical stability, chemical resistance, and high-temperature durability,[29] making them the preferred choice for various applications. Specifically, commercially available reactive elemental microparticles including titanium (Ti), silicon carbide (SiC), graphite (C), and aluminosilicate gel were mixed homogeneously to produce the printing feedstock (Figure 1a). The printability of the feedstock is tuned by the aluminosilicate gel (Figure 1b). Upon completion of the preform printing, the resultant green structure underwent a simple room temperature setting for curing, before transitioning to the desired ceramic structures through a self-sustaining reaction process. This curing process requires no heat treatment or additional energy supply, thereby contributing to a lower carbon footprint. The aluminosilicate gel undergoes geopolymerization, which is the primary mechanism that cures the feedstock in an ambient environment as detailed in the previous literature.[21,30] A schematic illustration of the geopolymerization process is shown in Figure S2. Briefly, geopolymerization occurs in three phases:

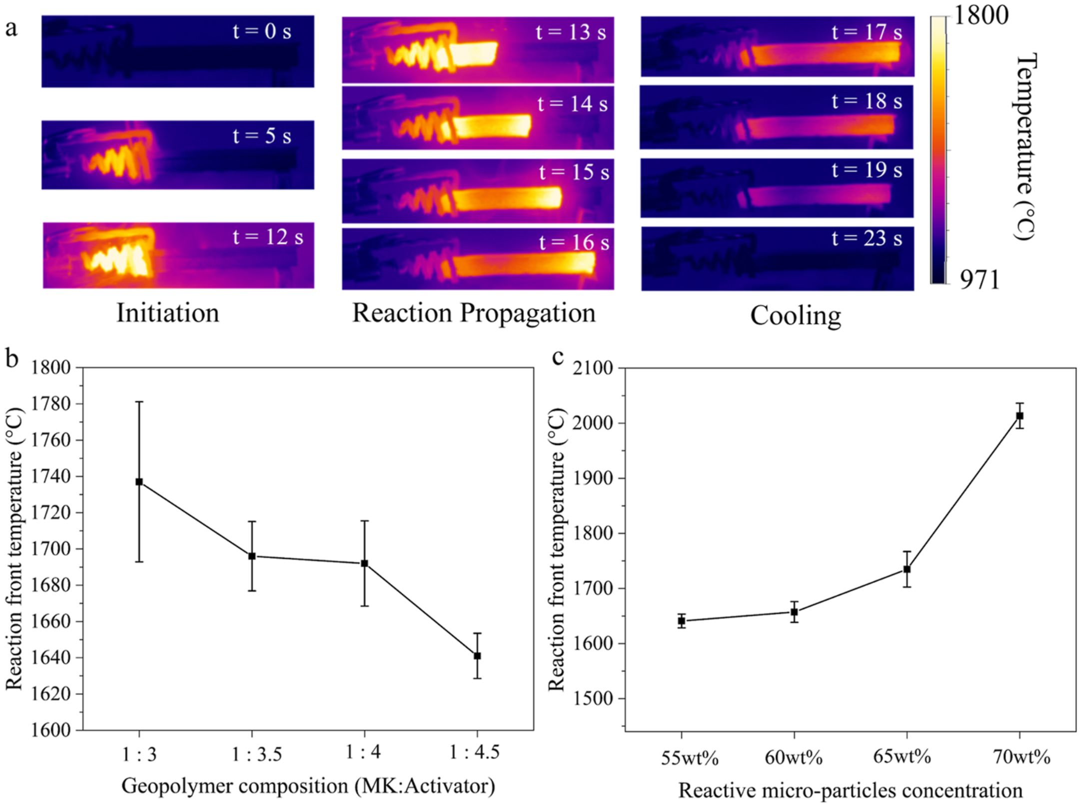


Figure 3. Characteristics of self-sustaining ceramization of geopolymer-binding ceramic preform. (a) Time-resolved thermal image of the self-sustaining reaction process, including initiation, reaction propagation, and cooling. (b) Reaction front temperature with different geopolymer compositions. (c) Reaction front temperature with different geopolymer content.

dissolution and reorganization, condensation, and polymerization. Initially, MK was used as an aluminosilicate source that undergoes dissolution and reorganization, forming various oligomers. These oligomers then link to form gels. This linkage happens as the OH groups at the ends of the oligomers meet, sharing an oxygen atom and releasing water. In this process, KOH serves as the primary source of OH groups. As the condensation continuously proceeds and water volatilizes, the geopolymer-bonded reactive rehardened and was ready to be converted to ceramic.

After curing, with a single-point thermal trigger, exothermic reactions among the Ti, C, and SiC ingredients form compounds including TiC, Ti_5Si_3, and Ti_3SiC_2.[31] Typical reaction includes Ti + C → TiC and 3Ti + SiC + C→ Ti_3SiC_2.[32] The rapid reaction is highly exothermic, which consolidates the ceramic composites produced with the desired structure (Figure 1c). To demonstrate the ability of the proposed approach to manufacture geometrically complex structure, an "Olympic Ring" structure was first printed and converted to ceramic structure with the self-sustaining reaction. Figure 1d captures the self-sustaining ceramization of the 3D printed ceramic preform. Noticeably, the self-sustaining ceramization reaction proceeded from the triggering point and spread throughout the entire structure, rapidly and steadily transforming the printed preform into ceramic. The whole ceramization process does not require an excessive external energy supply but a negligible and transient high-temperature initiation, making it a low-carbon emission process.

3.2. Rheological Behavior of Reactive Feedstock. Construction of complex structures with robust mechanical properties requires proper rheological properties. Thus, the effect of the geopolymer binder on the rheological behavior of the inorganic reactive feedstock was investigated. The viscoelastic behavior of the reactive microparticle-incorporated feedstock was studied. The results in Figure 2a revealed that the reactive microparticle incorporated feedstock exhibits elastic behavior at low shear rates where $G' > G''$. The yield stress, determined from the intersection of G'' and G' ($G' = G''$), is found to be strongly dependent on the reactive microparticle content. It was observed that reactive microparticle content greater than 47 wt % behaves in such proper viscoelastic behavior until 65 wt % of microparticle is incorporated as the viscosity increases drastically. The feedstock having 65 wt % of reactive microparticle and beyond showed high viscosity and overly high yield stress which leads to a plug flow regime, making it difficult to be processed by extrusion-based printing. A typical shear thinning behavior of reactive feedstock containing 55 wt % reactive feedstock can be observed as shown in Figure 2b. The viscosity of the reactive feedstock decreases from more than 10^5 to $\sim 10^2$ Pa·s as the shear rate increases, which is favorable for the extrusion-based printing process (Figure 2b).

3.3. Reaction Characteristics. Following the printing and curing of the reaction feedstock, the obtained ceramic preform is subjected to the initiation of a self-sustaining reaction. As shown in Figure 3a, the tungsten coil heats the ceramic preform from one end for ~12 s until a bright reaction front is visible on the preform, which marks the start of a self-sustaining reaction. As soon as the reaction front is visible, the tungsten heater is turned off, and the reaction propagates throughout the preform structure without additional energy

Table 1. Geopolymer Binder Molar Composition and Water Content of the Reactive Feedstock During the Curing Process

MK/activator mass ratio	Si/Al molar ratio	Water wt % after different days of curing					
		before cure	4 days	7 days	14 days	21 days	28 days
1:3	6.4	21.4	13.2	9.31	4.67	3.49	3.4
1:3.5	7.1	22.2	14.2	9.38	5.36	4.28	4.22
1:4	7.7	22.8	14.6	9.65	5.38	4.29	4.27
1:4.5	8.3	23.3	15.4	9.72	6.6	5.55	5.4

supply, showing a frontal propagation speed of ∼130 cm/min. The ceramic structure is formed after the reacting specimen is cooled to room temperature naturally. The reaction front temperature is usually considered an important characteristic of the self-sustaining reaction as it results from dynamic heat production, transportation, and phase transformation.[9] Thus, the structural and compositional influence of reactive feedstock on the self-sustaining reaction front temperature was studied. The geopolymer binder structure is tuned by the MK to activator ratio, which results in different Si/Al ratios, as noted in Table 1. The results in Figure 3b show that increasing the Si/Al ratio of the geopolymer binder results in a decrease of the reaction front temperature from 1737 °C corresponding to a 6.4 Si/Al ratio to 1641 °C corresponding to an 8.3 Si/Al ratio. A higher Si/Al ratio resulted in a higher water presence in the ceramic preform after the curing process, as shown in Table 1. The results show that the most water loss happens within the first 7 days of curing, which is typical for geopolymers. After 14 days the change of weight slows down, which is consistent with previous literature discovery.[33] After 21 days of curing, the weight change of the specimen becomes negligible (<3%). Thus, we selected 21 days as the time to cure the specimen. These findings are consistent with previous findings that the Si/Al ratio of geopolymer precursor can greatly affect water presence in the geopolymer structure, including the form of water (free, bound, and structural) and the content of water.[30] The volatilization of the water content at high temperatures could act as a heat sink, ultimately leading to a lower reaction temperature. Besides, it has been noted that a higher Si/Al ratio can enhance thermal conductivity[34] while diminishing high-temperature stability,[35] factors which together may influence the reaction front temperature. Furthermore, the effect of reactive feedstock composition on the reaction characteristics was investigated. Figure 3c illustrates the impact of reactive microparticle concentration on the temperature of the reaction propagation front. The results show that higher reactive microparticle loading led to an increase in the reaction front temperature, which can be simply ascribed to the enhanced exothermicity of the reactive system.

3.4. Composition and Microstructural Evolution during the Manufacturing Process. Geopolymer plays an important role in our energy-efficient manufacturing process. Apart from the rheology modifier, it also involves the self-sustaining ceramization of the reactive microparticles. Thus, the composition and microstructure evolution during the manufacturing process was analyzed. The XRD patterns of the geopolymer binder and reactive feedstock during the manufacturing process are shown in Figure 4. The XRD pattern of MetaStar 501 displays a broad dome centered at 2θ = 22°, indicative of its amorphous portion, along with distinct peaks associated with crystalline kaolinite (∼25°) and quartz (∼26.6°). Upon geopolymerization of the MK/activator mixture, a new geopolymer phase emerged. This development resulted in the shift of the hump toward a higher 2θ = 28°, which is a typical feature of geopolymerization.[36] Upon mixing the microparticles with aluminosilicate gel and subjecting them to curing, a ceramic preform is produced. The XRD patterns primarily exhibit the characteristics of the incorporated inorganic microparticles (Ti, SiC, and C), overshadowing the geopolymer phase owing to the significantly stronger peak intensities of these inorganic microparticle phases. Moreover, the data indicate that following the self-sustaining reaction, there is a significant alteration in the phase composition of the material obtained when compared to the unreacted preform. This suggests that the reaction among micropowders encompasses multiple phase transformations during the high-temperature self-sustaining reaction. The ceramic composites' XRD pattern is compared to JCPDS standards. The resulting ceramic structure consists of multiple Ti−Si−C composites, possibly including TiC, $TiSi_2$, $Ti_5Si_3C_x$, and Ti_3SiC_2. Also, SiC could be present as they are partially reacted.

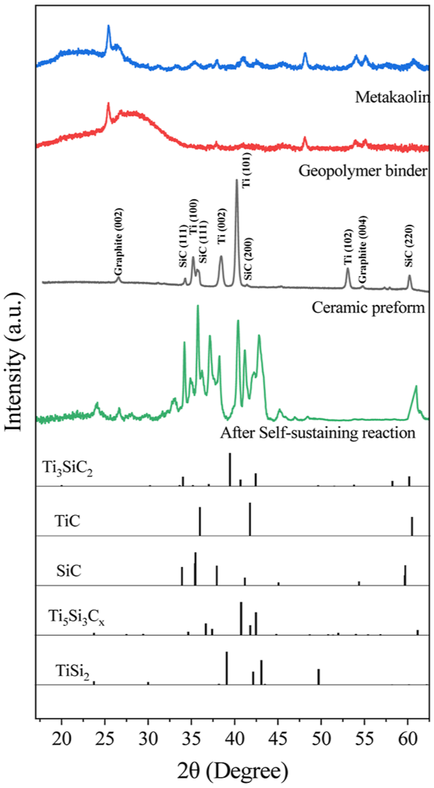


Figure 4. XRD patterns obtained from MK, neat geopolymer binder, reactive feedstock, and ceramic composite after a self-sustaining reaction.

The microstructure change of the reactive feedstock during the manufacturing process is characterized by SEM, with the findings illustrated in Figure 5. As depicted in Figure 5a, MK initially existed as loose powders before being mixed with the alkaline activator. After alkaline activation and curing in the ambient environment for 21 days, geopolymerization occurs,

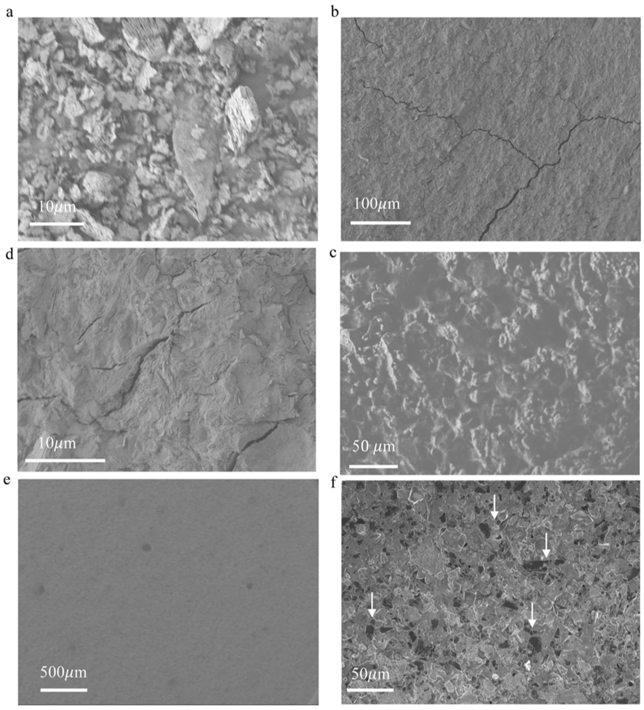


Figure 5. SEM images of (a) MK powder; (b,c) cured geopolymer binder; (d) reactive ceramic preform; (e,f) Ti−Si−C composite after self-sustaining reaction.

rendering the geopolymer binder a continuous phase, as shown in Figure 5a,c. This geopolymer structure can be employed to bind the reactive microparticles, thereby fabricating reactive ceramic preform as portrayed in Figure 5d. Following a self-sustaining reaction, the resultant Ti−Si−C ceramic composite exhibits low porosity (Figure 5e), although some pores are discernible. The pore formation can be mainly ascribed to the volatilization of structurally bound water within the geopolymer during the high-temperature ceramization process. The magnified image (Figure 5f) reveals that the ceramic composite comprises various ceramic phases, as denoted in the XRD results. These phases encompass some incompletely reacted microparticles, as indicated by white arrows, which could be partially reacted large SiC particles. Some microcracks are observable after the self-sustaining reaction. It is plausible that these microcracks result from both the high-temperature cracking typical of geopolymer binders and the rapid heating and cooling temperature changes inherent in the process.

3.5. Porosity and Mechanical Properties of the Ti−Si−C Composite.

Furthermore, the effect of the geopolymer on the porosity of the ceramic was also studied. The porosity and pore characteristics of the ceramic preform are shown in Figure S3. It was found that decreasing the Si/Al ratio of the geopolymer leads to reduced porosity of the final ceramic structure. When MK to activator ratio is 1:4.5, the corresponding Si/Al ratio is calculated to be 8.3. After self-sustaining ceramization, this geopolymer binder composition led to a ceramic porosity of 31.5%, corresponding to 21 days of curing in the ambient environment. As discussed in the previous section, the Si/Al ratio significantly influences the structure and water presence of the geopolymer binder. Increasing the MK to activator ratio results in decreasing final porosity, as shown in Figure 6a. The lowest porosity achievable is 22% when the MK to activator ratio is 1:3, indicating ∼3 times decrease compared to self-sustaining reaction-assisted 3D-printed cermet structure[19] as illustrated in Table 1, an increase in the MK to activator ratio results in a higher Si/Al ratio, which in turn leaves more water within the geopolymer structure after the curing process. This observation aligns with findings from prior research.[33] Thus, evaporation of water during high-temperature ceramization leaves pores in the ceramic structure, resulting in increased porosity. The composition of the reactive feedstocks was also varied by tuning the reactive microparticle content. The results are shown in Figure 6b, as the reactive microparticle increases from 55 to 60 wt %, the final porosity decreases due to reduced volatile water content for lower geopolymer binder loading. However, a further increase in the reactive microparticle content then causes the porosity to increase, and extrusion printing became impossible beyond reactive microparticle loading of 70 wt %. This may be ascribed to the increasing number of voids introduced during the curing stage due to the volatilization of water content in the geopolymer binder, ultimately resulting in a reduced preform density. These results show that the geopolymer binder structure and reactive feedstock composition could be used to control the ceramic part porosity. Nevertheless, energy-efficient AM through a self-sustaining reaction process assisted by an environmental-friendly geopolymer binder can be used to fabricate ceramic structures with low porosity.

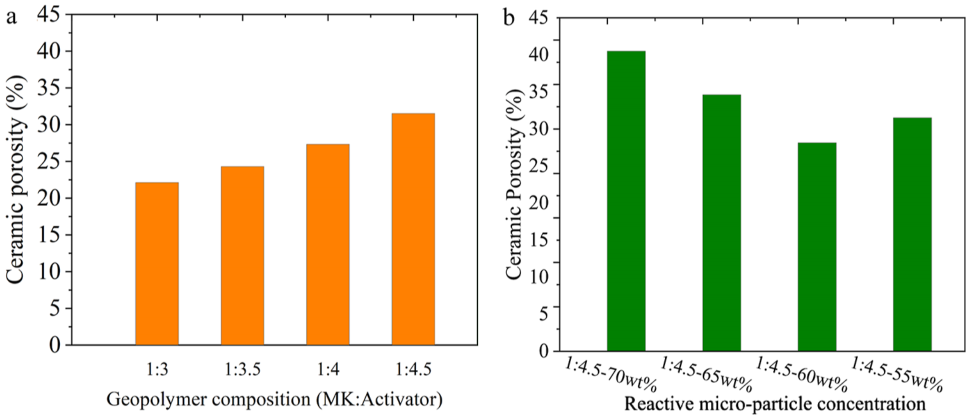


Figure 6. Open porosity of the preform and final structure (a) with various MK to Activator ratios and (b) with different reactive microparticle content.

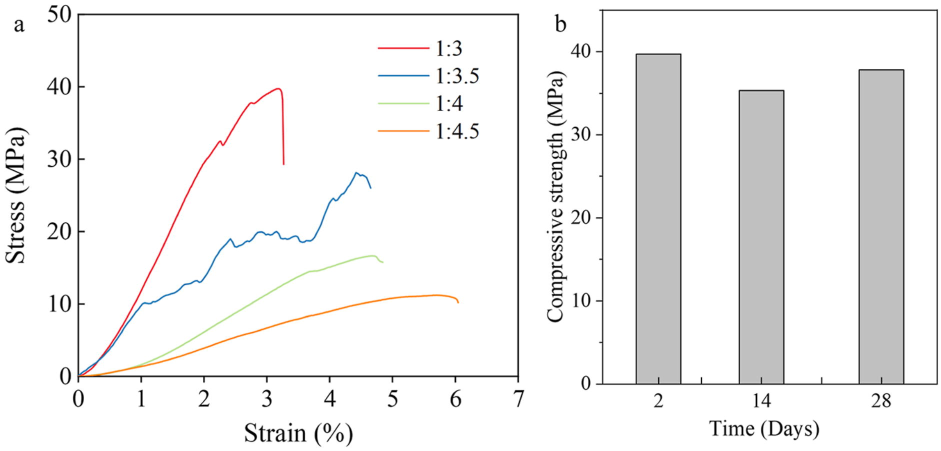


Figure 7. (a) Effect of geopolymer binder composition (MK/Activator ratio) on the compressive strength of the ceramic composite. (b) Change of compressive strength of the ceramic composite over time.

We acknowledge that despite achieving a significant reduction in porosity from 66.4 to 22% in our 3D printed reactively formed inorganic structures, the current level of porosity remains high compared to conventional ceramic AM techniques, such as binder jetting AM, which can achieve near full density. Exploring alternative binders in reactive feedstocks to reduce volatile substances is one viable avenue for future research. Additionally, controlling the self-sustaining environment, particularly temperature and pressure, during the ceramization process is another critical area for future investigation. By optimizing these parameters, we may be able to influence the rate of volatilization and the kinetics of the sintering process, thereby improving the density of the structures. Lastly, postprocessing techniques like liquid phase and chemical vapor infiltration utilize a second phase material to fill the pores in the part thereby improving the density. These post treatment processes could offer immediate industrial applicability and effectiveness in further reducing porosity.

Moreover, the mechanical properties of the ceramic composites were investigated. Compressive strength is a critical parameter in assessing the structural integrity of the structural components. It was discovered that the composition of the geopolymer binder significantly affects the compressive strength of the final ceramic composite. As shown in Figure 7a, when the MK to Activator ratio is 1:4.5, corresponding to a Si/Al ratio of 8.3, the compressive strength is measured at 11.1 MPa. However, adjusting the MK/Activator ratio to 1:3 leads to a reduction in the Si/Al ratio to 6.4, which in turn results in a compressive strength of approximately 40 MPa. This trend could be ascribed to the Si/Al ratio-induced alterations in the geopolymer structure, where a lower Si content tends to diminish the extent of hydration of the geopolymer structure, thereby leaving less structural water within the structure. This water content would be eliminated during the high-temperature self-sustaining reaction. The process of water removal is endothermic, which diminishes the exothermicity of the Ti−SiC−C system. Besides, the reaction enthalpy of the current system is already lower compared to the previous Ti−Si−C system.[31] Therefore, these factors collectively lead to a lower reaction temperature, resulting in a higher number of unreacted particles and the presence of heterogeneous intermediate silicide and carbide phases. Consequently, these effects could collectively be responsible for the observed deterioration in mechanical properties compared to systems based on preceramic polymers. Nevertheless, the reported low-carbon ceramic composite manufacturing has the potential to offer enhanced mechanical performance when compared to 3D printing and self-sustaining reactively formed cermets, which currently have a yield strength of 13 MPa.[19] Furthermore, to explore the variation in mechanical strength over time, we performed a compressive test of the same batch of ceramic composite. These samples underwent self-sustaining ceramization on the same day and were tested over an extended period, up to 28 days. The results shown in Figure 7b indicate that the ceramic composites maintain comparable compressive strength, showing no significant change (<10%) over a 1-month period. These results suggests that it holds promise as an eco-friendly method for producing load-bearing complex structures.

The surface morphology of the fractured compressive test samples is shown in Figure 8. Two samples with MK/Activator ratios of 1:3 and 1:4.5 represent the extremes in our study, having the lowest and highest strength, respectively. The observed fracture behavior in the sample with a MK/Activator ratio of 1:3 suggests the involvement of multiple fracture modes.[37] This is attributed to the enhanced interconnectivity and compactness of the different Ti−Si−C phases in this composition, as opposed to the 1:4.5 ratio samples. In the latter, increased porosity correlates with a reduction in compressive strength, indicating a less cohesive microstructural network.

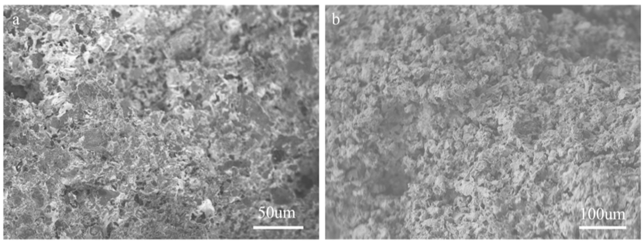


Figure 8. SEM images of the fracture surface of compressive test for sample of MK to Activator ratio is (a) 1:3; (b) 1:4.5.

3.6. Manufacturing Carbon Footprint.

The environmental impact of the proposed manufacturing process was analyzed in comparison with stereolithography (SLA), binder jetting ceramic AM, and REAP technologies in terms of equivalent CO_2 emission. The findings are depicted in Figure 9, with a thorough breakdown of the calculations presented in Table S1. Our prior research revealed that SLA resulted in 616.40 kg of equivalent CO_2 emissions per kg of ceramic produced, while the binder jetting process accounted for 3086.13 kg of CO_2 per kg. On the other hand, we have reported that REAP shows a significantly lower carbon footprint, with merely 2.23 kg of equivalent CO_2 per kg ceramic structure produced, owing to the absence of carbon-intensive pyrolysis or sintering phases. Remarkably, the current approach has further minimized the manufacturing carbon footprint to a mere 0.79 kg of CO_2 per kg, marking a more substantial reduction in GHG emissions by a factor of 2.8, compared to REAP. This notable improvement is ascribed to the milder curing conditions that lowered the curing carbon footprint coupled with a pyrolysis-free inorganic binder system that curtailed direct emissions.

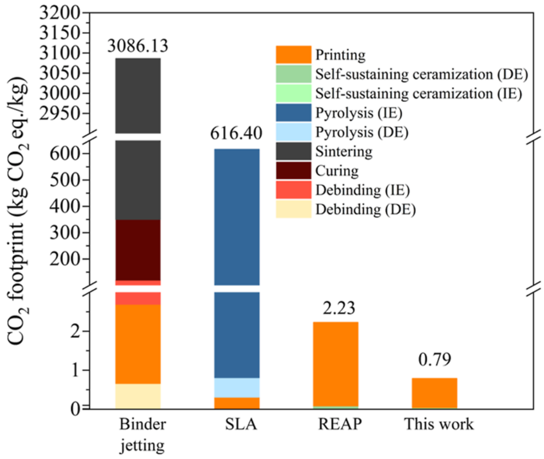


Figure 9. Manufacturing carbon footprint of this work compared to representative ceramic AM technologies and REAP.

4. CONCLUSIONS AND FUTURE WORK

This research introduces a novel methodology for the environmental-friendly AM of ceramic composites with a low carbon footprint. This approach encompasses an eco-friendly geopolymer binder-assisted ambient-environment print-and-cure process, succeeded by a low carbon footprint self-sustaining ceramization process. Our strategy demonstrates an exceptionally low manufacturing carbon footprint, with GHG emissions of 0.79 kg CO_2 equivalent/kg, indicating a reduction in manufacturing GHG emissions by over 3000 times when compared to conventional binder jetting ceramic AM. It was found that the geopolymer binder structure which is controlled by the Si/Al ratio, and geopolymer concentration can be tuned to regulate the self-sustaining reaction characteristics and the ceramic composite's open porosity. The ultimate open porosity can reach 22%, marking the lowest among self-sustaining reactions formed by inorganic materials derived from 3D-printed preforms. It was also found that a lower Si/Al ratio of the geopolymer binder led to an improved compressive strength of the ceramic composite.

Building upon the outcomes of this research, this section examines potential opportunities for future research. One of the critical aspect of the research will be focused on improving the mechanical performance of ceramic composites for load-bearing applications. This could be done by further promoting the degree of ceramization and densification. An encouraging approach to achieving this is the adoption of energy-efficient postmanufacturing treatments, such as joule heating. It is worth noting that exposing as-synthesized Ti−Si−C composites to additional joule heating treatment not only promotes further sintering but also facilitates additional reactions that lead to the formation of the desirable Ti_3SiC_2 MAX phase.[38] Future work could also be focused on the fundamental understanding of the evolution of geopolymer binders during self-sustaining reactions. Future work will explore other geopolymer binder compositions to reduce the porosity in ceramic composites. Optimizing ceramization conditions, particularly temperature and pressure, shows promise for improving the density. Additionally, postprocessing methods like liquid phase and chemical vapor infiltration could be investigated for further density enhancement.

This work unveils a new avenue toward environmentally friendly AM of ceramic composite structures.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.3c07159.

> Setup for self-sustaining reaction, illustration of the geopolymerization mechanism, additional analysis of pore characteristics, and data for energy-consumption and GHG emissions calculation PDF

■ AUTHOR INFORMATION

Corresponding Authors

Jingjing Qiu − *Department of Mechanical Engineering, Texas A&M University, College Station, Texas 77843, United States*; Email: Jennyqiu@tamu.edu

Shiren Wang − *Department of Materials Science and Engineering and Department of Industrial and Systems Engineering, Texas A&M University, College Station, Texas 77843, United States*; orcid.org/0000-0003-4516-3025; Email: s.wang@tamu.edu

Authors

Ruochen Liu − *College of Materials Science and Engineering, Beijing University of Technology, Beijing 100124, China; Department of Materials Science and Engineering, Texas A&M University, College Station, Texas 77843, United States*

Aolin Hou − *Department of Materials Science and Engineering, Texas A&M University, College Station, Texas 77843, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acssuschemeng.3c07159

Author Contributions

The paper was written through the contributions of all authors. All authors have approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge using the Texas A&M University Materials Characterization Facility.

■ REFERENCES

(1) Heimann, R. B.; John Wiley & Sons, 2010.Classic and advanced ceramics: from fundamentals to applications

(2) Padture, N. P. Advanced structural ceramics in aerospace propulsion. *Nat. Mater.* **2016**, *15* (8), 804−809.

(3) Yu, X.; Marks, T. J.; Facchetti, A. Metal oxides for optoelectronic applications. *Nat. Mater.* **2016**, *15* (4), 383−396.

(4) Punj, S.; Singh, J.; Singh, K. Ceramic biomaterials: Properties, state of the art and future prospectives. *Ceram. Int.* **2021**, *47* (20), 28059−28074.

(5) Barsoum, M.; CRC Press, 2019.Fundamentals of ceramics

(6) Furszyfer Del Rio, D. D.; Sovacool, B. K.; Foley, A. M.; Griffiths, S.; Bazilian, M.; Kim, J.; Rooney, D. Decarbonizing the ceramics industry: A systematic and critical review of policy options, developments and sociotechnical systems. *Renewable Sustainable Energy Rev.* **2022**, *157*, 112081.

(7) Gopal, M.; Lemu, H. G.; Gutema, E. M. Sustainable Additive Manufacturing and Environmental Implications: Literature Review. *Sustainability* **2022**, *15* (1), 504.

(8) Cresko, J.; Rightor, E.; Carpenter, A.; Peretti, K.; Elliott, N.; Nimbalkar, S.; Morrow, III, W. R.; Hasanbeigi, A.; Hedman, B.; Supekar, S. DOE Industrial Decarbonization Roadmap; USDOE Office of Energy Efficiency and Renewable Energy (EERE), 2022. .

(9) Borovinskaya, I. P.; Gromov, A. A.; Levashov, E. A.; Maksimov, Y. M.; Mukasyan, A. S.; Rogachev, A. S.; Elsevier, 2017.Concise encyclopedia of self-propagating high-temperature synthesis: History, theory, technology, and products

(10) Arlington, S. Q.; Fritz, G. M.; Weihs, T. P. Exothermic Formation Reactions as Local Heat Sources. *Annu. Rev. Mater. Res.* **2022**, *52*, 219−248.

(11) Robertson, I. D.; Yourdkhani, M.; Centellas, P. J.; Aw, J. E.; Ivanoff, D. G.; Goli, E.; Lloyd, E. M.; Dean, L. M.; Sottos, N. R.; Geubelle, P. H.; et al. Rapid energy-efficient manufacturing of polymers and composites via frontal polymerization. *Nature* **2018**, *557* (7704), 223−227.

(12) Gao, C.; Liu, R.; Li, W.; Qiu, J.; Wang, S. Collaborative printing and in-situ frontal curing of highly-viscous thermosetting composites. *J. Manuf. Processes* **2023**, *89*, 1−9.

(13) Zhang, Z.; Liu, R.; Li, W.; Liu, Y.; Luo, H.; Zeng, L.; Qiu, J.; Wang, S. Direct writing of continuous carbon fibers/epoxy thermoset composites with high-strength and low energy-consumption. *Addit. Manuf.* **2021**, *47*, 102348.

(14) Zhang, Z.; Liu, R.; Li, W.; Liu, Y.; Pei, Z.; Qiu, J.; Wang, S. Frontal polymerization-assisted 3D printing of short carbon fibers/dicyclopentadiene composites. *J. Manuf. Processes* **2021**, *71*, 753−762.

(15) Zhang, Z.; Gao, C.; Liu, R.; Li, W.; Qiu, J.; Wang, S. Catalyzed frontal polymerization-aided 3D printing of epoxy thermosets. *Addit. Manuf. Lett.* **2022**, *2*, 100030.

(16) Zhang, Z.; Gao, C.; Liu, R.; Qiu, J.; Pei, Z.; Wang, S. 3D Printing of Frontal-polymerized Multiscale Epoxy Thermoset and Composites. *Manuf. Lett.* **2022**, *33*, 640−643.

(17) Liu, R.; Gao, C.; Hou, A.; Wang, S. Ni/Al foil-based reactive additive manufacturing with fast rate and high energy-efficiency. *J. Mater. Process. Technol.* **2023**, *321*, 118167.

(18) Arlington, S. Q.; Vummidi Lakshman, S.; Barron, S. C.; DeLisio, J. B.; Rodriguez, J. C.; Narayanan, S.; Fritz, G. M.; Weihs, T. P. Exploring material chemistry for direct ink writing of reactively formed conductors. *Mater. Adv.* **2020**, *1* (5), 1151−1160.

(19) Arlington, S. Q.; Barron, S. C.; DeLisio, J. B.; Rodriguez, J. C.; Vummidi Lakshman, S.; Weihs, T. P.; Fritz, G. M. Multifunctional Reactive Nanocomposites via Direct Ink Writing. *Adv. Mater. Technol.* **2021**, *6* (5), 2001115.

(20) Wang, S.; Ruochen, L.; Hou, A.; Li, W.; Qiu, J. Additive manufacturing apparatus with powder-integrated preceramic mixture and related methods. *Prog. Mater. Sci.* **2023**, *116*, 100736.

(21) Davidovits, J. Geopolymers: Ceramic-like inorganic polymers. *J. Ceram. Sci. Technol.* **2017**, *8* (3), 335−350.

(22) Davidovits, J. Environmentally driven geopolymer cement applications. In *Proceedings of 2002 Geopolymer Conference*. Melbourne, Australia, 2002.

(23) Zhao, J.; Tong, L.; Li, B.; Chen, T.; Wang, C.; Yang, G.; Zheng, Y. Eco-friendly geopolymer materials: A review of performance improvement, potential application and sustainability assessment. *J. Cleaner Prod.* **2021**, *307*, 127085.

(24) Ahmad, M.; Rashid, K. Novel approach to synthesize clay-based geopolymer brick: Optimizing molding pressure and precursors' proportioning. *Constr. Build. Mater.* **2022**, *322*, 126472.

(25) Sun, Q.; Peng, Y.; Georgolamprou, X.; Li, D.; Kiebach, R. Synthesis and characterization of a geopolymer/hexagonal-boron nitride composite for free forming 3D extrusion-based printing. *Appl. Clay Sci.* **2020**, *199*, 105870.

(26) Ma, S.; Liu, X.; Fu, S.; Zhao, S.; He, P.; Duan, X.; Yang, Z.; Jia, D.; Colombo, P.; Zhou, Y. Direct ink writing of porous SiC ceramics with geopolymer as binder. *J. Eur. Ceram. Soc.* **2022**, *42* (15), 6815−6826.

(27) *Standard ISO 18754, Fine ceramics (advanced ceramics, advanced technical ceramics)-Determination of density and apparent porosity*. International Organization for Standardization 2013, *2018* (8), 15955.

(28) EPA; U.S. Environmental Protection Agency: Washington, DC, 2021.eGRID. U.S. annual national emission factor, year 2019 data

(29) Tkachenko, S.; Brodnikovskyi, D.; Čizek, J.; Komarov, P.; Brodnikovskyi, Y.; Tymoshenko, Y.; Csáki, Š.; Pinchuk, M.; Vasylyev, O.; Čelko, L.; et al. Novel Ti-Si-C composites for SOFC interconnect materials: Production optimization. *Ceram. Int.* **2022**, *48* (19), 27785−27798.

(30) Park, S.; Pour-Ghaz, M. What is the role of water in the geopolymerization of metakaolin? *Constr. Build. Mater.* **2018**, *182*, 360−370.

(31) Yeh, C. L.; Shen, Y. G. Effects of SiC addition on formation of Ti3SiC2 by self-propagating high-temperature synthesis. *J. Alloys Compd.* **2008**, *461* (1−2), 654−660.

(32) Riley, D. P.; Kisi, E. H.; Hansen, T. C. Self-Propagating High-Temperature Synthesis of Ti3SiC2: II. Kinetics of Ultra-High-Speed Reactions from In Situ Neutron Diffraction. *J. Am. Ceram. Soc.* **2008**, *91* (10), 3207−3210.

(33) Lizcano, M.; Gonzalez, A.; Basu, S.; Lozano, K.; Radovic, M. Effects of Water Content and Chemical Composition on Structural Properties of Alkaline Activated Metakaolin-Based Geopolymers. *J. Am. Ceram. Soc.* **2012**, *95* (7), 2169−2177.

(34) He, R.; Dai, N.; Wang, Z. Thermal and mechanical properties of geopolymers exposed to high temperature: A literature review. *Adv. Civil Eng.* **2020**, *2020*, 1−17.

(35) da Silva Godinho, D. d. S.; Pelisser, F.; Bernardin, A. M. High temperature performance of geopolymers as a function of the Si/Al ratio and alkaline media. *Mater. Lett.* **2022**, *311*, 131625.

(36) Lizcano, M.; Kim, H. S.; Basu, S.; Radovic, M. Mechanical properties of sodium and potassium activated metakaolin-based geopolymers. *J. Mater. Sci.* **2012**, *47*, 2607−2616.

(37) Li, N.; Liu, W.; Xiong, H.; Qin, R.; Huang, S.; Zhang, G.; Gao, C. In-situ reaction of Ti-Si-C composite powder and formation mechanism of laser deposited Ti6Al4V/(TiC+Ti3SiC2) system functionally graded material. *Mater. Des.* **2019**, *183*, 108155.

(38) Zou, Y.; Sun, Z.; Hashimoto, H.; Cheng, L. Reaction mechanism in Ti-SiC-C powder mixture during pulse discharge sintering. *Ceram. Int.* **2010**, *36* (3), 1027−1031.