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A. N. Pearson, R. Lu, W. L. Du Frane, R. L. Landingham, J. D. Kuntz

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Gelcasting low-carbon B_4C for cermets

Allison Pearson[1,2], Ryan Lu[2], Wyatt DuFrane[2], Richard Landingham[2], Joshua Kuntz[2]
1. University of California, Berkeley
2. Functional Materials Synthesis Group, Lawrence Livermore National Laboratory

ABSTRACT

A boron carbide (B_4C) gelcasting suspension involving melamine formaldehyde (MF) resin was developed to obtain green bodies with low carbon after pyrolysis. MF resin allows highly complicated B_4C parts to be produced with little to no shrinkage when gelcast into molds. A MF binder content of ~7.5 wt % consistently produced green bodies with sufficient strength to withstand demolding and handling. Variations in B_4C particle size, curing temperature, and pH were investigated in order to optimize the suspension for casting. Resin pyrolysis trials showed that 90.0 ± 0.9 wt % of resin mass was lost during pyrolysis, corresponding to < 1 wt % of binder residual in the overall green bodies. The minimal carbon content in the green bodies is favorable for the infiltration of aluminum into open pore spaces. Due to the high hardness of B_4C and the ductility of aluminum, the ceramic-metal (cermet) composite formed is ideal for applications such as light-weight armors.

1. Introduction

As the third hardest material, boron carbide has superior wear resistance with relatively low density, making it ideal for application in light-weight armors, blasting nozzles, and grinding wheels.[1-5] However, its hardness makes it difficult to machine into complex shapes, while its brittleness limits its applications.[6, 7] Gelcasting followed by aluminum infiltration to create a B_4C-Al cermet are scalable techniques to overcome these challenges.

In gelcasting, a low-viscosity, aqueous suspension of ceramic particles and a polymeric binder is prepared. After the casting suspension is poured into complex-shaped molds and the binder heat-cured, a near net-shape green body can be obtained.[8-10] Subsequently the binder is pyrolyzed, a process which can leave behind a significant portion of binder mass in the form of amorphous carbon.[4,11,12] In the production of complex shaped ceramics, this carbon is desirable as a sintering aid, allowing nearly full-density to be achieved with pressureless sintering.[12]

In some cases, it is advantageous to exchange some of the hardness of a pure ceramic for greater toughness and ductility. Aluminum infiltration into porous boron carbide can create a lightweight cermet material that retains some of the hardness of boron carbide while providing ductility to overcome the inherent brittleness of ceramics.[13,14] However, as is the case with all carbide-Al cermets, the reaction with Al and C forms a weak aluminum carbide phase which is problematic in B_4C-Al cermets.[15, 16] There is much research into ways to prevent this reaction or treat the final material to reduce the adverse effects, such as low temperature processing under magnesium vapor, post-processing heat treatment, and post-processing chemical vapor deposition.[16 -18] Since addressing the levels of free carbon inherent to all carbide ceramics is already a challenge in carbide-Al cermets, it is crucial to select a gelling agent that will pyrolyze with limited residual carbon when gelcasting boron carbide with the intent of Al-infiltration.

The presence of aromatic rings increases the rigidity of polymer networks by preventing sliding through steric hindrance and rotation through the rigidity of pi bonds.[19,20] However, phenyl groups are the typical motif in most aromatic-ring containing polymeric systems. The stability of a phenyl ring favors a high conversion to amorphous carbon when pyrolyzed—approximately 50 wt % for systems such as resorcinol-formaldehyde and many of the phenolic resins favored for use in conjunction with pressureless sintering.[4, 11, 12]

Possessing an aryl-group in the form of a triazine ring, melamine can react to form a rigid aerogel polymer network with formaldehyde, creating strong green bodies with little shrinkage or cracking (*Fig. 1*). The triazine ring is significantly less stable than a phenyl group, and can begin decomposition at temperatures as low as 400 ºC, even in an inert gas environment.[21] These properties make melamine formaldehyde a useful option when gelcasting parts for Al infiltration.

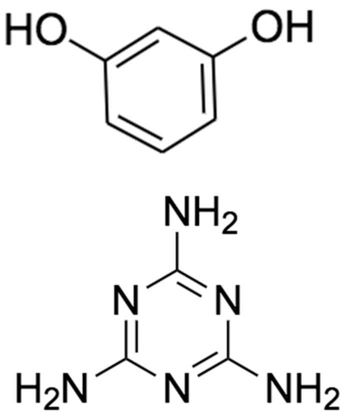


Fig. 1 Top: resorcinol, a phenyl-ring containing monomer used in high-carbon gelcasting. Botton: melamine, a triazine ring monomer which can be used for low-carbon gelcasting

2. Methodology

2.1 Precursor synthesis [a]

Melamine has a very low aqueous solubility, creating a non-uniform resin distribution when melamine (M) and formaldehyde (F) are added directly to a B_4C suspension. However, a class of reaction intermediates—methylolated melamine—is water soluble. Prior to the resin condensation reaction, a range of mono- to hexa- methylol melamines form, with the distribution and stability dependent upon the molar ratio of formaldehyde to melamine.[22] When melamine and formaldehyde are reacted in approximately a 3:1 F:M ratio, the dominant product is trimethylol melamine, the most soluble form.[22, 24] Therefore, the MF resin can be used as the binder in aqueous gelcasting if the reaction between melamine and formaldehyde is started separately, and the resultant resin precursor added to a boron carbide suspension before condensation has begun (*Fig. 2*).

The precursor was prepared from a 37 wt % formaldehyde solution (Sigma-Aldrich, ACS reagent grade) lowered to a pH of 8 using a 20 mM solution of sodium hydroxide (Emsure, ACS reagent grade). Melamine (Sigma-Aldrich, 99%) was slowly added with stirring for a final molar ratio of 3.17:1 F:M. The reaction was sealed and heated to 85 ºC over the course of 15 minutes, and subsequently allowed to react for an additional 20 minutes, or until the melamine had dissolved completely. Aggregation and premature resin formation were prevented with vigorous stirring. Due to mass loss during the condensation reactions of curing, it was estimated that 9.2 wt % melamine and formaldehyde in B_4C would be needed to achieve ~7.5 wt % binder. [b]

a) Procedure was adapted from methods of trimethylol melamine synthesis outlined in references 21, 22, 23
b) See discussion in section 3.1

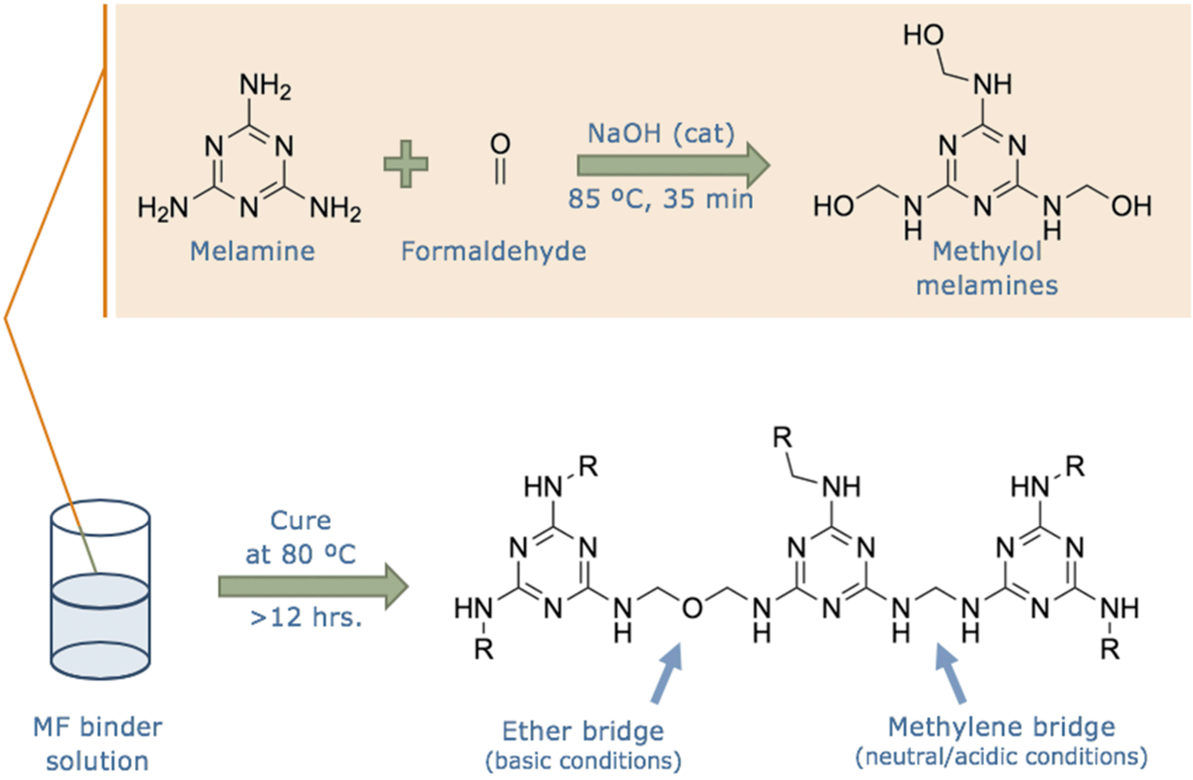


Fig. 2 Synthesis of water soluble precursor for melamine-formaldehyde gelcasting

2.2 Suspension preparation

When prepared as previously described, the precursor solution has approximately a 1:1 ratio of binder material to water, therefore, the boron carbide suspension must be prepared at a higher solids loading than desired in the final casting suspension. According to *Fig. 3*, the appropriate solids loading of B_4C was selected, and the suspension prepared by incremental loading of 1500F (1.8 µm average particle size) B_4C powder (3 M Technical Ceramics, Germany, > 96% purity) into an aqueous solution containing 1.4wt % 25,000 MW branched polyethyleneimine (PEI) (Sigma, ACS reagent grade) relative to the B_4C powder. A planetary centrifugal mixer (Thinky AR-250) at 2000 rpm was utilized between each loading increment

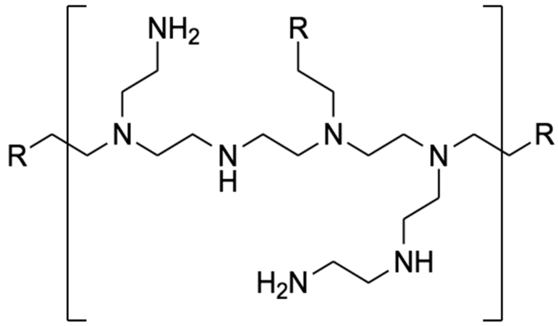


Fig. 3 PEI, a cationic dispersant

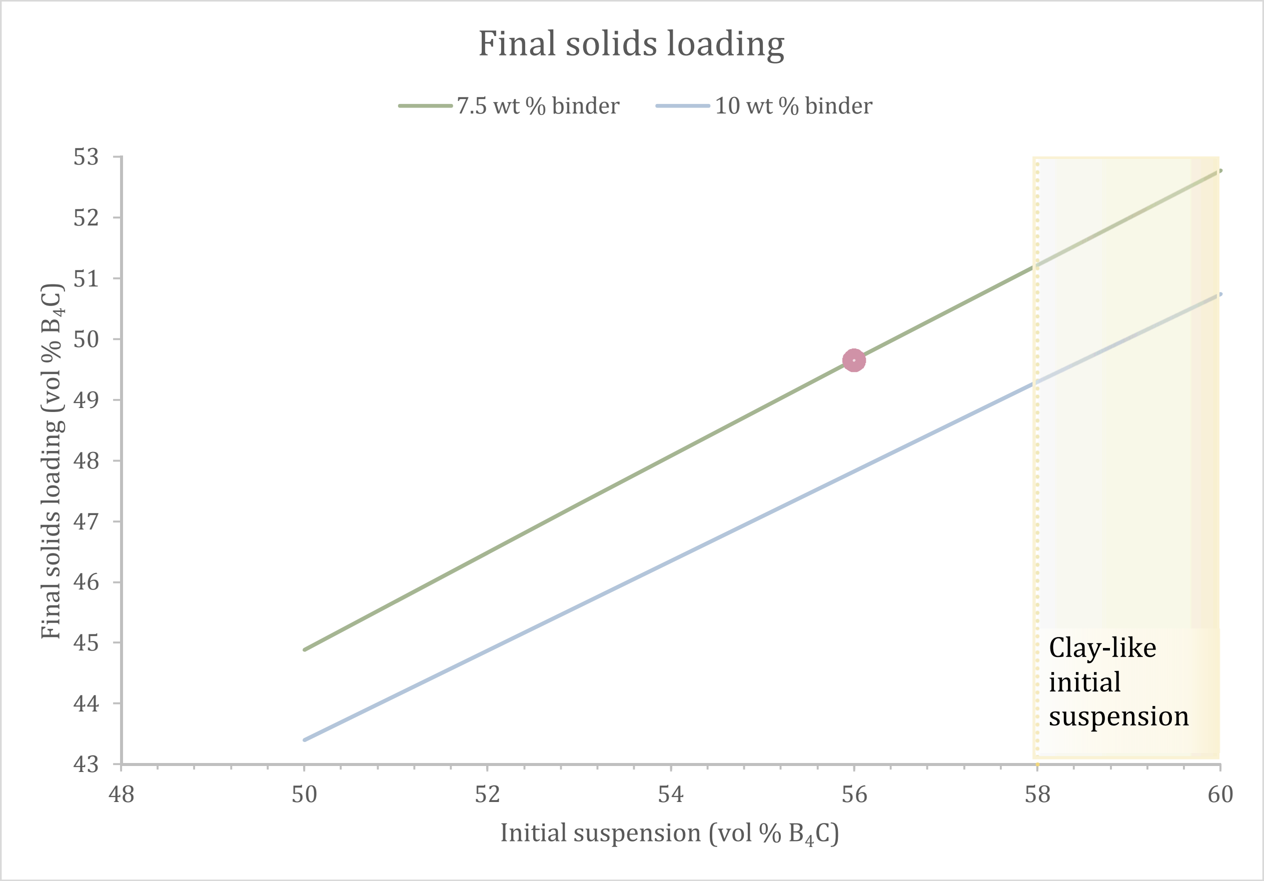


Fig. 4 Initial B_4C suspension solids loading required to achieve final desired solids loading

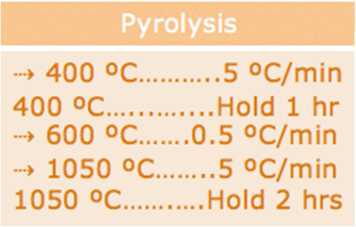
2.3 Gelcasting and curing

Precursor solution was immediately incorporated into the B_4C suspension through planetary mixing and the final casting suspension then poured into the desired mold. Maximum working time for casting ranged between approximately 5 and 30 minutes, depending on solids loading, pH, and heat exposure during the mixing process. For test disks and cylinders, the suspension was cast in mixing jars or cylindrical silicone rubber molds. Complicated mold shapes were 3-d printed with a Lulzbot Taz 6 fused filament printer. Due to its ability to dissolve in acetone for simple demolding, acrylonitrile butadiene styrene (ABS) was selected as the filament material (eSUN).[12]

Molds were placed in airtight secondary containers to prevent water loss and cured in an 80 ºC oven for a minimum of 12 hours. The green bodies were transferred to an acetone wash to remove any excess reactants and—if applicable—dissolve the mold. Furthermore, the acetone wash serves as a solvent exchange, preventing the potential for cracking due to the capillary stresses of evaporating water.[12]

2.4 Pyrolysis and infiltration

Green bodies were pyrolyzed in a glass tube furnace under 96:4 wt % argon:hydrogen forming gas flowing at 500cc/min, according to the temperature program outlined in *Fig. 5*. Due to the high volume of decomposition products, it was necessary to protect the outlet hose to the mineral oil gas bubbler from obstruction by solid condensate. A new outlet hose was used for each run, and glass fiber was used to fill the last 2-4 cm of the tube furnace before the gas outlet. These measures—along with a slow ramp rate through the temperatures where the most mass loss was qualitatively observed to occur—sufficed in preventing obstruction of gas flow and subsequent pressure buildup.


Pyrolysis

→ 400 °C...........5 °C/min
400 °C….........Hold 1 hr
→ 600 °C.......0.5 °C/min
→ 1050 °C........5 °C/min
1050 °C….......Hold 2 hrs

Fig. 5 Pyrolysis temperature program

The pyrolyzed green bodies were infiltrated with aluminum in an evacuated (<60 milliTorr) alumina tube furnace for 2 hours at 1100 C with a ramp rate of 5 °C/min.[13] Providing that there was excess aluminum, infiltration was achieved with the placement of the aluminum either underneath or on top of the B_4C part.

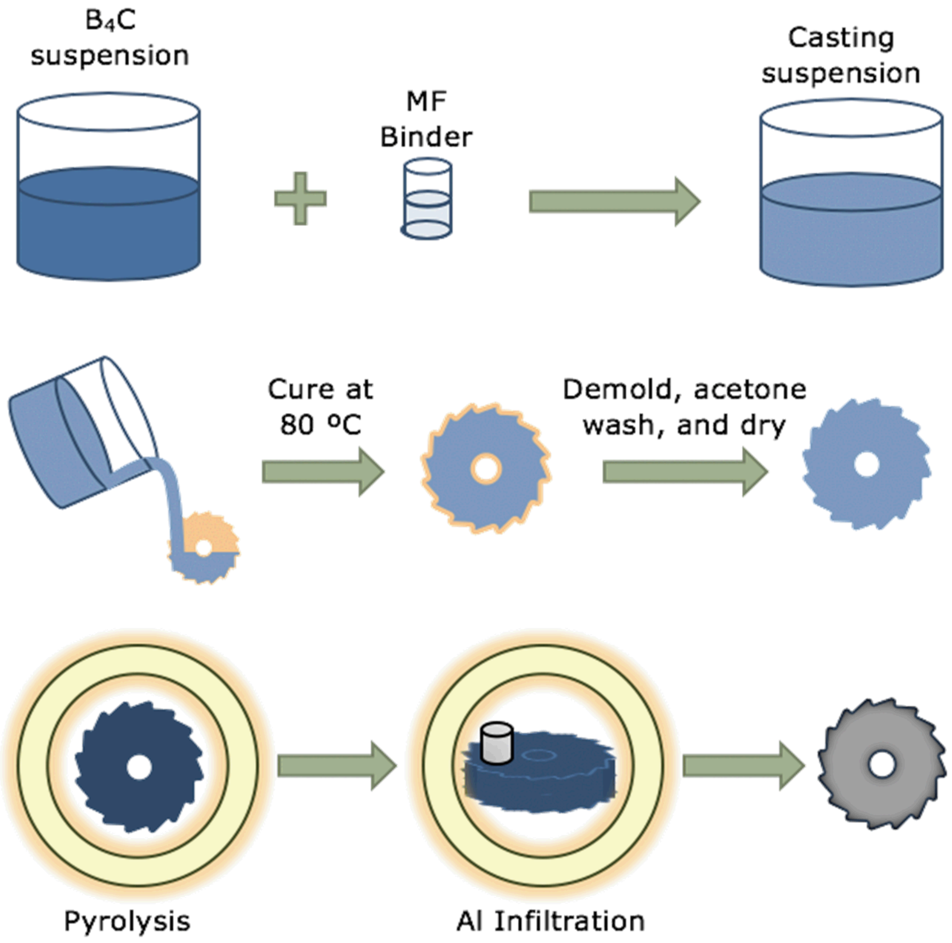


Fig. 6 Summary of MF gelcasting procedure

3. Results and discussion

3.1 Resin and suspension

For optimal results, the precursor solution was added to the boron carbide suspension within minutes of becoming clear. Solutions that were either allowed to continue reacting or to cool to room temperature demonstrated viscosity increases and visually apparent resin agglomerates, rendering them useless.

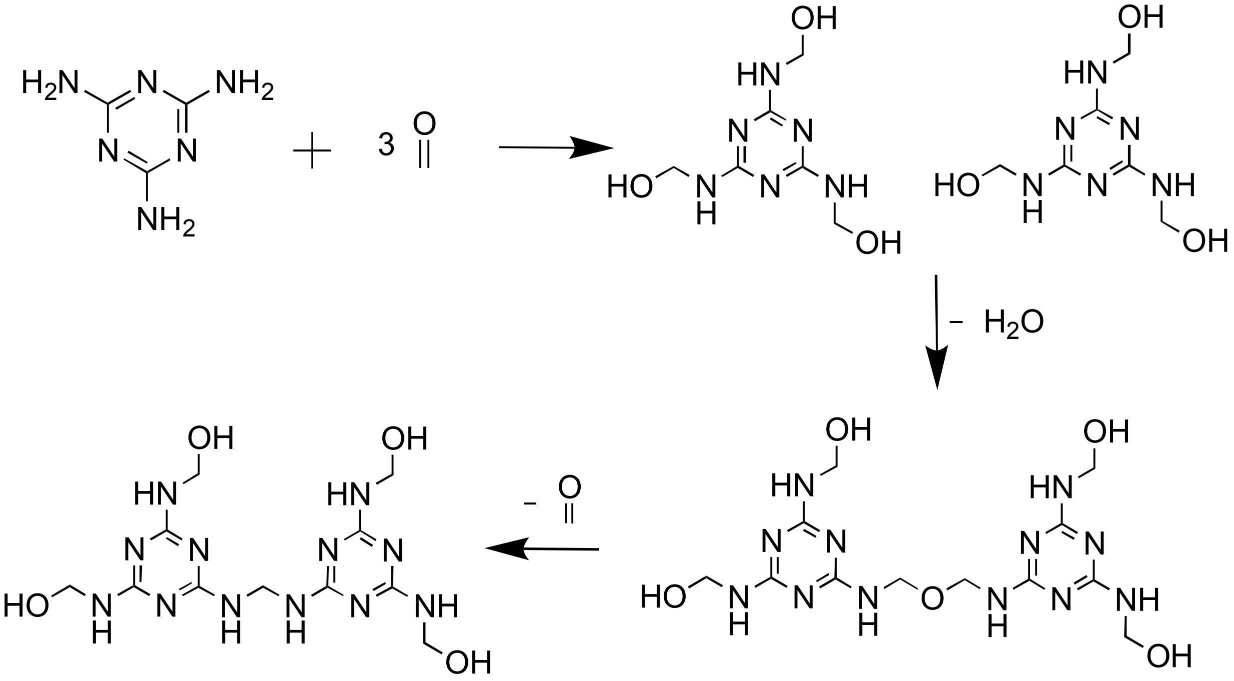


Fig. 7 Scheme of two major condensation reactions in melamine formaldehyde resin formation

The resin precursor has excess formaldehyde, and releases water and formaldehyde through the condensation reactions of curing. To obtain a desired binder content, a significantly higher amount of precursor must be added to account for this mass loss. Acidic-neutral conditions and high cure temperature favor methylene bridges, while basic conditions and low cure temperature favor ether bridges (Figure 7)[21, 23]. For boron carbide suspensions in the vicinity of 50 vol % solids loading and prepared as described, the pH was typically ~8. For this reason, a mixture of methylene and ester bridges was expected, with ester bridges dominating. However, the presence of boron carbide and PEI proved to have a dramatic effect on the reaction, further complicating the determination of binder content. When the precursor alone was placed in the curing oven at 80 °C, curing took several days, yet when the precursor is added to a solution of PEI or the boron carbide suspension, curing occurs on the order of hours. The effect of these compounds on the rate of reaction is clear, but the corresponding ratio of ester to methylene bridges is unknown. Attempts to infer the binder content from mass changes were ineffective due the hydroscopic nature of boron carbide, and the exact binder composition and content in the gelcast parts is

$$m = \frac{(a)\times(b)}{126.12+1.8\times 30.03}$$

where

m = moles melamine required

a = desired binder wt %

b = grams boron carbide

126.12 and 30.03 are the molar masses of melamine and formaldehyde, respectively.

Eq. 1

unknown. Typically, strong, rigid melamine formaldehyde resins react in ratios of 1.8-2 F:M.[25] In order to determine the amount of precursor necessary to approximately yield the desired binder content, 1.8 was selected as a reasonable number to use in the calculation shown in *Eq 1.* The value obtained for *m* was used for precursor synthesis, along with the amount of formaldehyde required for a 3.17:1 molar ratio.

Of course, it is not accurate to calculate weight percent of melamine-formaldehyde resin from the molar masses of melamine and formaldehyde, but the values obtained from this approximation make physical sense giving the pH and cure temperature, corresponding to a 4:1 ratio of ester bridges to methylene bridges in the cured resin (Table 1). For simplicity, this paper refers to binder content to according to the aforementioned calculation. It must be kept in mind that these are crude and temporary estimates, and it is essential to conduct further research to determine the exact content of cured binder in the green bodies so that more precise measurement and control of the residual carbon can be accomplished.

F/M in precursor	100 % methylene	100 % ester	25 % methylene, 75% ester
6.1%	4.0%	5.2%	5.0%
9.2%	6.0%	7.9%	7.5%
12.3%	8.0%	10.5%	10.0%

Table 1 Estimates of binder composition assuming 100% condensation and varying ratios of bridges

3.2 Optimization

Test disks were cast with binder contents of ~5, ~7.5, and ~10 wt % to determine the minimal amount required to produce green bodies that consistently had sufficient strength withstand handling and demolding. Casts with ~5 wt % binder varied dramatically in resilience, with some batches able to cast complicated gyroid shapes and others unable to cast a simple disk. Therefore, ~7.5 wt % was selected for use in most purposes.

A final solids loading of 50 vol % was selected for use with the ~7.5 wt % binder, which was achieved through an initial suspension solids loading of 56 vol %. This suspension approaches the maximum suspendibility of B_4C; the 58 vol % suspension used to make 50 vol %, ~10 wt % casting suspension was clay-like in nature (*Fig 8*). Regardless of the initial suspension solids loading and MF binder content, the final 50 vol % casting suspensions had no noticeable difference in viscosity, and were comparable in viscosity to 50 vol % casting suspensions with resorcinol formaldehyde binder.

Fig. 8 56 vol % suspension (left) vs 58 vol % suspension (right)

A thin layer of resin was observed on the surface of short test disks, and was assumed to be due to the syneresis effect. Because the PEI also participates in the resin reaction, boron carbide may be able to begin to settle from the suspension, creating a greater concentration of resin on the top surface. Further slowing the reaction by curing at a lower temperature (60 C), increased the amount of surface resin, supporting this hypothesis.

This procedure was developed using 1500F B_4C. However, previous experimentation had shown that higher solids loading can be achieved with a smaller particle size and that when gelcasting with resorcinol formaldehyde, syneresis in parts cast with 1500F B_4C was not present in casts using 3000F B_4C (0.5 µm average).[12] Therefore, 50 vol % casting suspensions with ~7.5 and ~10 wt % binder (56 and 58 vol % B_4C suspensions) were prepared using 3000F B_4C. It was hoped that this would allow for higher solids loading in the initial and casting suspensions, but this was not the case. There was no noticeable difference between the viscosities of B_4C suspensions with 3000F versus 1500F. When working time at room temperature was qualitatively assessed, 3000F casting suspensions cured at roughly twice the rate as the equivalent 1500 F suspensions, masking the benefits that a lower viscosity would have offered. In addition, parts cast from 3000 F B_4C were too brittle to survive demolding.

Some green bodies obtained from the optimized suspension possessed visible porosity, the cause of which remains undetermined. It is possible that in-situ bubble formation from the excess formaldehyde may be the cause, however, these pores have only been observed in recent samples cast from the 50 vol % B_4C, ~7.5 wt % MF casting suspension. A more probable explanation is that the high viscosity of 56 vol % suspension may have caused air bubbles to become trapped as additional powder was added, as no pore formation has been in observed in samples cast with lower solids loading. Potentially, greater care may need to be exercised in preventing water loss during suspension preparation and storing, and ultimately, solids loading of the optimized formulation may need to be decreased. Further experimentation is necessary to resolve this issue.

3.3 Pyrolysis and infiltration

Due to the inability to say with certainty the amount of cured resin in the green bodies, mass loss was estimated by pyrolyzing the resin alone. The MF resin was prepared using the same procedure as the casting suspension, but without boron carbide loading step. Trials of MF resin alone indicated that 10.0 ± 0.9 wt % of MF/PEI resin remains, corresponding to <1 wt % of carbon remaining in green bodies gelcast with ~7.5 wt % binder, even when utilizing the higher estimates shown in *Table 1*.

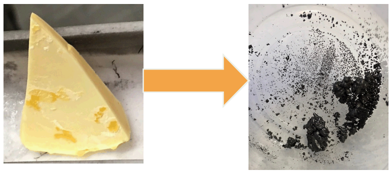


Fig. 9 Resin before and after pyrolysis

Although infiltration was successful from both the top and bottom—even in more complex, curved structures—side infiltration was not efficacious due to difficulty in ensuring that the melted aluminum flowed in the direction of the B_4C sample. Furthermore, in samples with the aforementioned porosity, some of the larger pores remained unfilled.

3.4 Rheology and working time

According to the literature, the condensation of methylol melamine can be catalyzed by both heat and acid.[21,23]

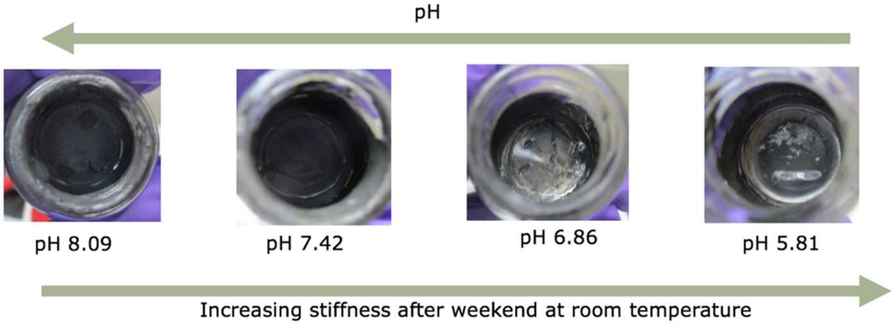


Fig. 9 Casts after 48 hours of curing at room temperature

This was qualitatively supported by the preparation of 4 casts with decreasing pH values (*Fig. 9*). After 48 hours at room temperature, the casts showed a clear gradient in degree of curing; at the extremes, the cast with pH 5.81 was completely cured, while the unadjusted cast with pH 8.09 was claylike in texture. This was confirmed with rheology testing of the unmodified suspension (pH 7.95) and an acidified suspension (pH 6.62), shown in *Fig. 10*.

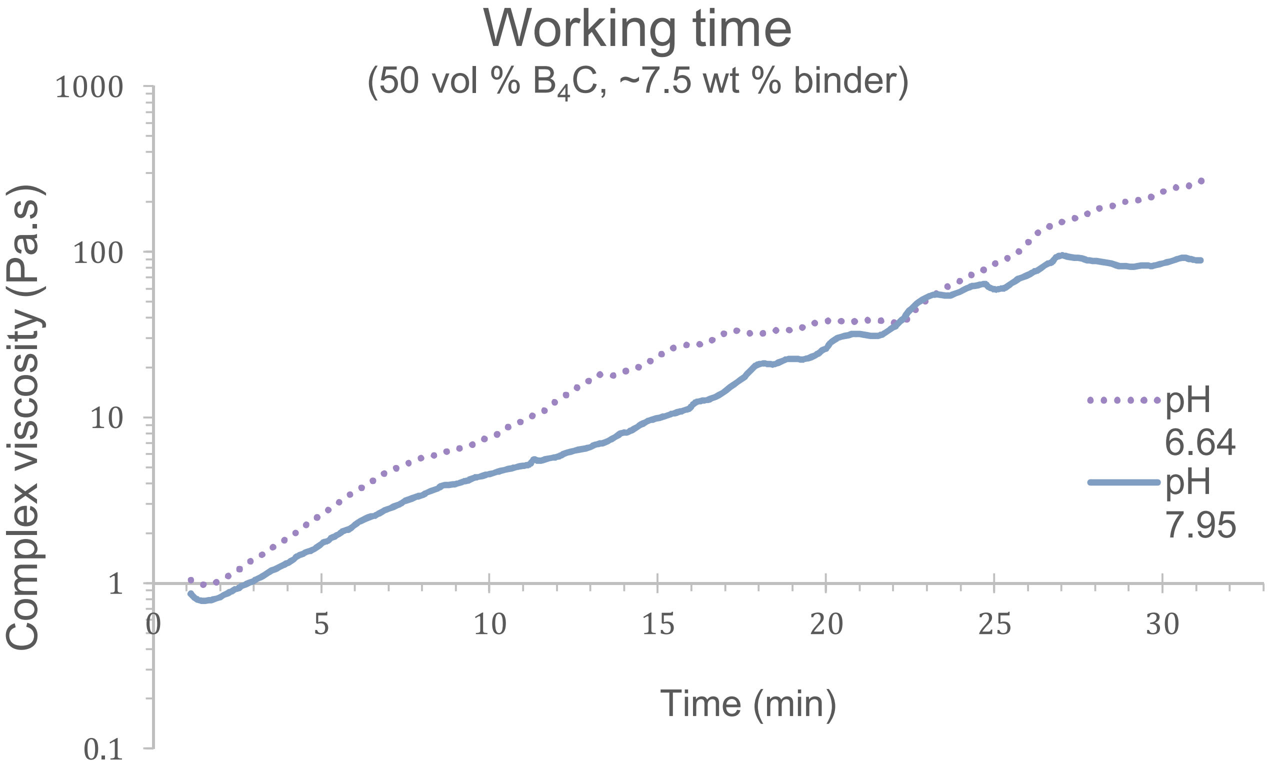


Fig. 10 Rheology tests during room temperature curing of MF casting suspensions to determine working time

Given this information, one would expect increasing the pH to increase working time. However, this was not the case. PEI is a cationic dispersant, and as such, it becomes less effective at higher pH. Between pH 2-8, the zeta potential of 25,000 MW PEI ranges between 65-75 mV, but sharply decreases from 70 at pH 8 to 40 at pH 10.[26] This corresponds to the observation that at a pH of 9, the suspension became dramatically more viscous, and when attempting to increase the pH to 10—as is often done in commercial practice to slow MF curing—the boron carbide completely settled out of solution.[27] For this reason, it was concluded that there was no benefit to modifying the pH of the suspension.

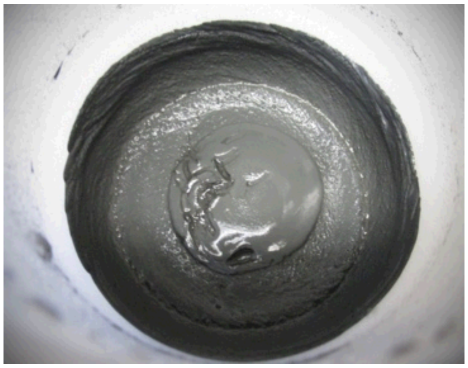


Fig. 11 ~56 vol % B_4C suspension after pH adjusted to >9

3.5 SEM

SEM images were taken of a green body, pyrolyzed part, and B_4C-Al cermet cast from the same suspension (Fig. 13)

Particle size in the parts was consistent with distribution measurements of 1500F conducted by R. Lu et al.[12] Subtle differences were evident in the surface appearances between un-pyrolyzed and pyrolyzed samples; the pyrolyzed surface appeared less dense, and perhaps even demonstrated a different size distribution of particles at the surface. These observations seem reasonable since very little binder remained in the pyrolyzed sample, which may make it favorable for more massive particles to fall and smaller particles to be blown from the part. This is consistent with the fragile, almost chalklike nature of the pyrolyzed green body.

Unfortunately, all the disks cast for SEM possessed the previously discussed pores—however, the images showed that these deformities only existed on a scale visible to the naked eye (*Fig. 13*).

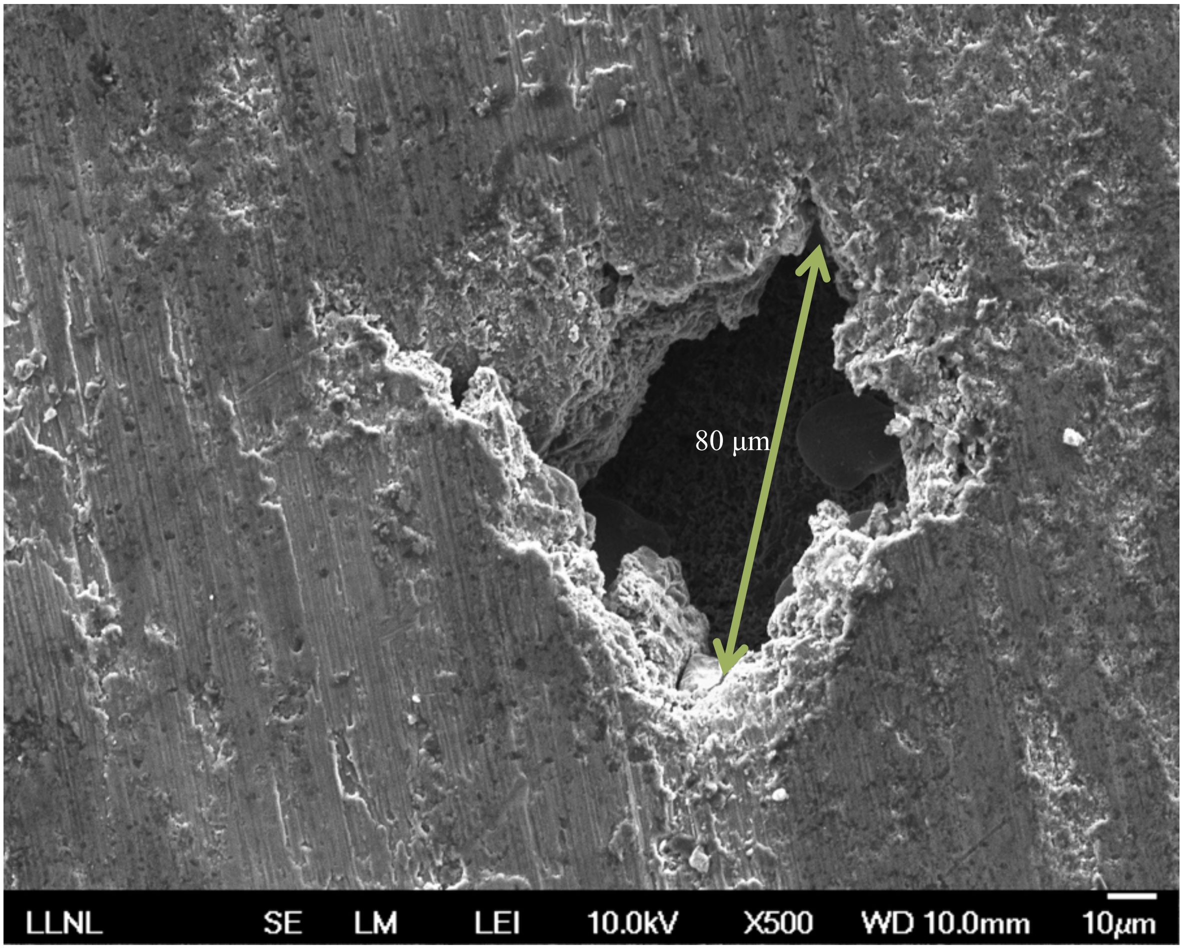


Fig. 12 A pore in the B_4C-Al cermet. At 80 µm, this pore was visible to the naked eye.

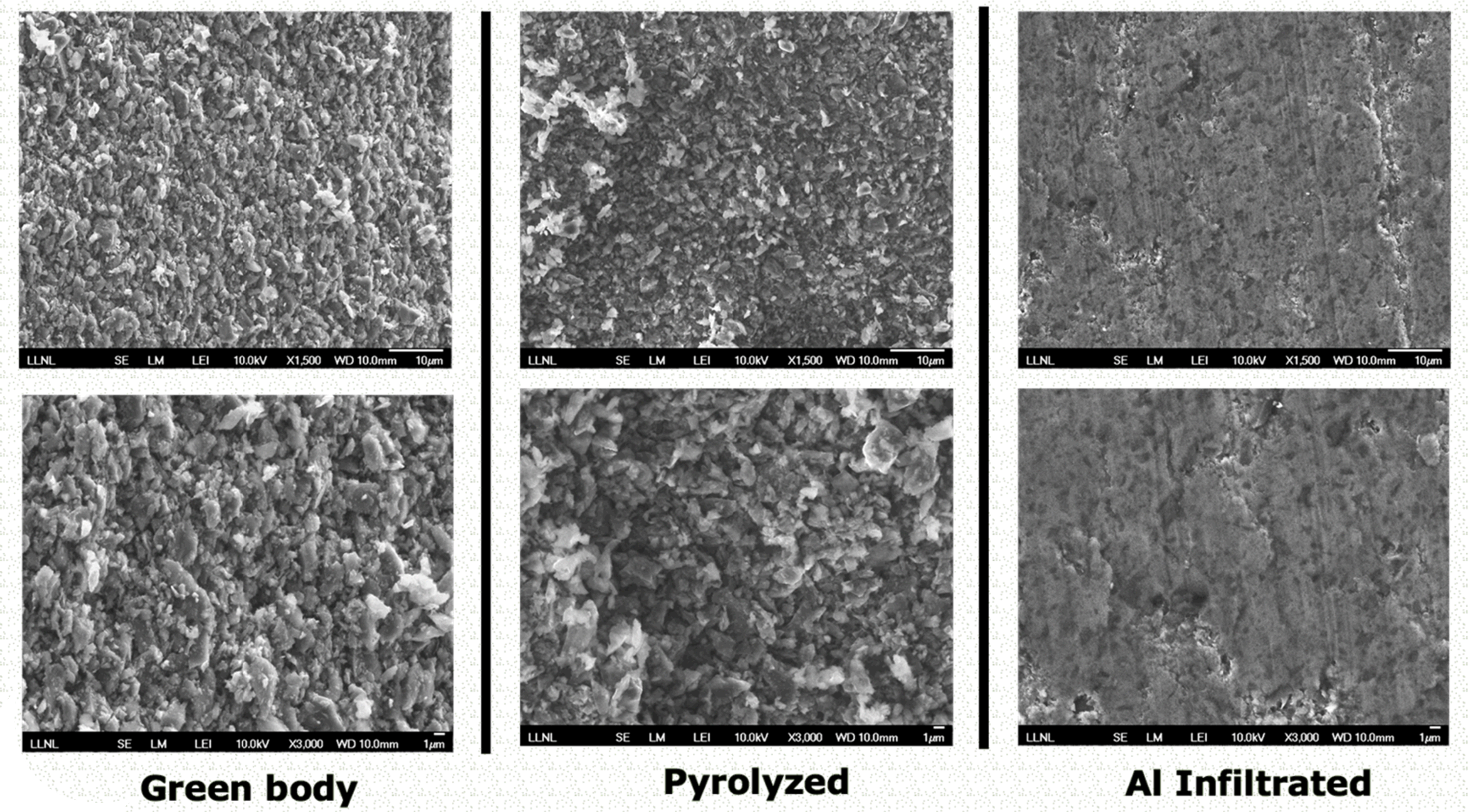
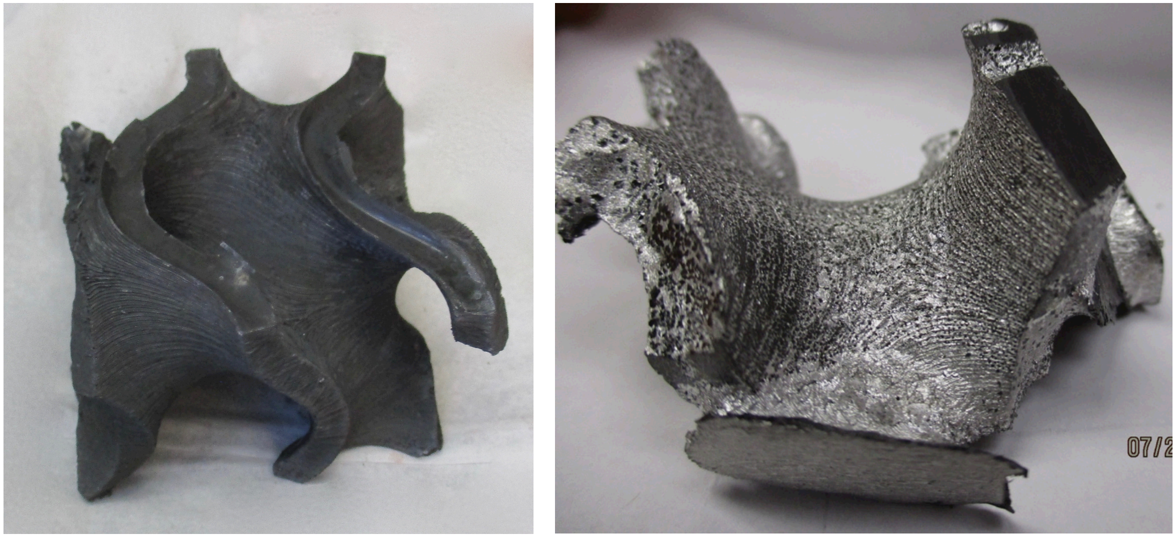


Fig. 13 SEM images of green body, pyrolyzed body, and cermet material at 1 and 10 μm scale.

3.6 Complex part

Casting and infiltration of complex shapes were achieved. Fineness of features is limited by the fragility of the piece post-pyrolysis, when very little binder remains. Pictures of some complex casts are shown below.



A semigyroid with ~5 wt % binder and 46 vol % solids loading was cast and a piece of it completely infiltrated from the bottom up.

The helmet was cast using ~7.5 wt % binder and 50 vol % solids loading and infiltrated from the sides and bottom. It demonstrated sufficient strength to withstand considerable force around the nose and cheek guards during mold support removal. The thinnest feature was ~ 2 mm.

A shield with lettering was cast using ~7.5 wt % binder and 50 vol % solids loading and infiltrated from the bottom (a thickness of 2.3 cm). The shield details were created from 1.5 mm deep and 1 mm wide negative lettering in the cast, which subsequently filled with aluminum during infiltration.

4. Summary and conclusion

Melamine-formaldehyde resins can be used as a lower-carbon alternative in boron carbide gelcasting of complex shapes. However, there are still constraints to the procedure developed, such as lack of MF binder storage stability, shorter working time, and limitations in solids loading. Furthermore, additional testing is needed to determine how these parts compare with the mechanical properties of cermets made from higher carbon containing gelcasts and cold-pressed B_4C parts. Nevertheless, the ability to have < 1 wt % carbon—while maintaining structural integrity—gives MF gelcasting a great potential for use in applications where free carbon is undesired, such as in complex shaped B_4C-Al cermets for uses including lightweight armors.

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DOE SULI Program

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