

GELCAST FORMING OF NON-OXIDE CERAMICS WITH REACTIVE SURFACES

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ABSTRACT

Boron carbide (B_4C) and sintered reaction-bonded silicon nitride (SRBSN) are important non-oxide ceramic materials with a large variety of applications. The production of parts from both materials typically starts with the fabrication of green preforms by conventional methods such as die pressing or slip casting operations, both of which are limited to relatively simple shapes. Gelcasting is a forming process in which a slurry of ceramic or metal powder in a solution of organic monomers is cast in a mold and gelled to form strong, machineable green preforms of both simple and complex shapes. The present study describes the development of gelcast techniques to fabricate Si (for SRBSN material) and B_4C green preforms. Since both Si and B_4C react with water, new methods were developed to allow stable gelcast forming.

INTRODUCTION

Boron carbide (B_4C) is an important non-oxide, ceramic material with a large variety of applications. Important properties of B_4C include high hardness, second only to diamond; low density, only 2.5 g/cm³; and high temperature use capability. These properties have made it valuable for such diverse applications such as an abrasive for polishing and machining; wear-resistant parts; heat resistant applications, such as high temperature nozzles; and as protective material for personnel and helicopter armor. In addition, B_4C is a good neutron absorber and is used in shielding applications[1].

Silicon nitride-based materials are the leading candidates for use as high-temperature structural ceramics due to their low density, high strength, high toughness, and high temperature creep resistant properties. These materials find numerous applications in such diverse items as cutting tools, rotors turbine engines, and valves and cam followers for gasoline and diesel engines[2].

B_4C parts are typically fabricated from dry pressed B_4C powder, which is densified by hot pressing methods, or from B_4C -carbon mixtures, which can be pressureless sintered at high temperatures[1]. Si_3N_4 materials can be prepared from expensive Si_3N_4 powder with sintering additives, which is sintered by various methods[2]. A much cheaper grade of Si_3N_4 -based material utilizes silicon (Si) as the primary starting material. The Si is mixed with sintering additives and is then nitrated and sintered to form

sintered reaction-bonded silicon nitride (SRBSN)[3-6]. To achieve more uniform green parts than those produced by traditional pressing methods, B₄C and Si green preforms can be fabricated by slip cast methods using aqueous slurries[3,7]. However, since both B₄C and Si react with water and produce boric acid or silica plus hydrogen, respectively, the formation of green preforms is more complicated[7,8]. The need for highly uniform, defect-free green preforms stimulates research on new forming methods. Also, the use of water as a suspension medium in processing ceramics is also desired for a cost-effective and environmentally sound process[9].

Gelcasting is a simple, inexpensive forming process, which has been developed as a method for forming ceramic greenware. Gelcasting involves the preparation of a ceramic slip in a mixed monomer solution. After preparation of the slip, an initiator and a catalyst are added to polymerize and cross-link the monomers upon heating. Prior to polymerization, the slip is poured into molds, whose shape, the final gel will assume. Numerous combinations of monomers, catalysts, and initiators have been developed for use with both aqueous and organic solvent systems as dictated by the ceramic powder being gelcast[10-12]. It has been shown that gelcast preforms of alumina have up to five times the mechanical strength of die pressed green bodies of comparable volumes loading [13].

The present work was undertaken to develop a method for the fabrication of gelcast silicon and boron carbide preforms using an aqueous medium. It is felt that the excellent uniformity and dispersion that is achievable in liquid suspension can be frozen into the gelcast compacts.

EXPERIMENTAL

Determination of the Char Yields of Gelcast Additives

The amount of carbon residue formed, when gelcast chemical additives are heated, was measured by heating the individual chemicals in closed alumina crucibles at 10 °C per minute in a graphite furnace in flowing argon to 1000° C, followed by a cooldown to room temperature. Carbon conversion was calculated from the final weight divided by the initial weight of the chemical prior to heat treatment.

Preparation of B₄C Preforms

The gelcast monomer solution consisted of 20 wt % polyvinylpyrrolidone^a (PVP K-15), 11.2 wt. % methacrylamide^a (MAM), 3.8 wt. % methylenebisacrylamide^a (MBAM), 2.4 wt. % Emphos 1361^b, and 0.2 wt. % Foamaster VF^c in water. B₄C slurries were prepared by mixing 28.5 g of monomer solution with 0.9 g of tetramethyl ammonium hydroxide^a (TMOH), 0.3 g of Foamaster VF, 0.6 g of Surfynol 104E^d, and 60 g of ESK 1500 B₄C powder^e (~45 vol. %). Each slurry was either oblique blended for 1 h or ball milled for 24 h with 1.25 cm diameter partially stabilized zirconia media. After milling, 15 g portions of the slurry were weighed and 1 wt % stock ammonium persulfate^a (APS), adjusted to 8.2 pH with TMOH, was mixed with the slurry to give a final concentration of 3.7 x 10⁻³ wt. % APS (based on the slurry weight). Each slurry was then degassed in a bell jar for 3 min and the slurry poured into a 2.5 cm by 1.25 cm glass tube mold which was previously coated with AZN mold release.^f The slurry was incubated at 55 °C for 30 minutes to allow the gel to form. The gelled B₄C preforms were cooled for 10 minutes, removed from the molds, and dried in a dessicator overnight. Some gelcast pellets were isopressed at 206 MPa pressure.

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Two types of B₄C green preforms were made for comparison as control samples. For control group 1, dried gelcast samples were crushed and ball milled. These milled powders were then pressed in a 2.85 cm diameter steel die at 42 MPa. Some of the die pressed samples were isopressed at 206 MPa. A second set of control samples was prepared as follows: B₄C 1500 powder was ball milled 4 h with 1.78 wt. % Durez Resin^g in 99 wt. % isopropyl alcohol^h (IPA) using 1.25 cm diameter zirconia media, and then pan dried overnight at 55 °C. The dried powder was ball milled with zirconia media to break up the agglomerates. Both die pressed and die pressed-isopressed pellets were made using the same pressing parameters discussed for B₄C control group 1.

Processing of B₄C Preforms

B₄C preforms were placed on a bed of +10 mesh B₄C grit inside a graphite crucible, and heated in flowing argon in an Astro graphite furnace according to the following schedule: 1 °C per minute to 600°C, 10 °C per minute to 800°C, 20 °C per minute to 1000°C, 40 °C per minute to 2250°C, with a 30 minute dwell at 2250 °C, followed by a rapid cool down to room temperature. The final sintering temperature was measured with an Ircon two-color pyrometer. Sintered densities were measured by the Archimedes method with absolute ethyl alcoholⁱ.

Si Gelation Tests

The following test was used to measure the time for initiation of gelation of Si slurries prepared from Si powders manufactured by Globe^j, Eaton^k, and Ceradyne^l. Six water-based monomer solutions were prepared which consisted of 15 wt. % of the following monomer(s): (1) MAM- polyethyleneglycol dimethacrylate^m (PEGDMA) at a 3:1 mixture by weight, (2) MAM-PEGDMA at a 6:1 mixture by weight, (3) PEGDMA alone, (4) hydroxymethacrylamide^a (HMAM), or (6) MAM-MBAM at a 6:1 ratio by weight. In addition, each monomer solution consisted of 0.5 wt % Darvan 821Aⁿ, and 0.5 wt. % PVP K-15, based on the weight of the final Si powder. Approximately 20 g of Globe, Eaton or Ceradyne Si powder was added to 12 ml of each of the monomer solutions, and the solutions were vortexed in 50 cc test tubes for 1 minute. The ceramic slurries were then incubated at 40 °C, and at designated time points, the slurries were checked for gel formation, as judged by the thickening and then gelation of the slurries.

Si Gelation with Inhibitor

A second test was used to measure the effect of 4-methoxyphenol^a, a gelation inhibitor, on the time for initiation of gelation of Ceradyne Si powder. PEGDMA and MAM-PEGDMA 6:1 gelcast solutions were prepared in a similar method to the previous experiments. Either water (control) or 4-methoxyphenol (at 50, 100, 250, or 500 ppm final concentration) was added to tubes containing monomer solutions and Ceradyne Si powder. The ceramic slurries were then heated at 40°C, the slurries were checked at time intervals for the initiation of the gel formation.

Si Gelcast Parts

The 6 monomer solution types (described in a previous section) were mixed with Ceradyne Si powders to 47 vol. % loading and with 3 wt. % glycerol, 0.5 wt. % Darvan 821A, and 0.5 wt. % PVP K-15 (based on the Si weight). A duplicate set of slurries was prepared from Si and the same 6 solutions with the addition of 4-methoxyphenol at a concentration of 100 ppm. All slurries were milled for 4 hours with 1.25 cm diameter dense alumina ball media on a roll mill. After milling, each slurry was separated from the media and combined with 10⁻³ parts by wt. of tetramethylammonium hydroxide^a (TEMED) catalyst

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and 10⁻² parts by wt. of APS (pH 8.2). The slurries were degassed under vacuum in a bell jar with vibration, poured into 10 x 10 x 1.25 cm aluminum molds coated with Polyester Parafilm^o mold release, covered with parafilm tape, and incubated at 45 °C for 1 h. The molds were cooled, disassembled, and the Si parts soaked for 2 h in Polyethyleneglycol 400^p (PEG 400). The parts were then rinsed with distilled water and dried at the room temperature.

Post Gelcast Processing of Si parts

The gelcast parts were then cut in two to form two, 5 by 10 by 1.25 cm thick rectangular parts. One of the parts from each batch was shipped to Ceradyne Inc. for the binder burnout, nitridation, and sintering treatments using proprietary procedures. Strength measurements of some sintered parts was conducted using standard 4-point bending procedures with 3 by 4 by 40 mm sintered bars. The remaining 5 by 10 by 1.25 cm green parts were ground on two sides with a diamond grinding wheel on a Harig grinder-slicer, and the parts sliced into 5 by 0.475 by 0.350 cm bars. Green strengths were measure by breaking the bars in a three-point fixture on a Model 4465 Instron Test Machine.

RESULTS AND DISCUSSION

B₄C Gelcasting

This study had several goals: 1) to eliminate the methanol wash steps usually used for cleaning the B₄C powder[7], 2) to find a more effective dispersing agent for the ESK 1500 grade B₄C powder, 3) to incorporate carbon into the water-based slurries in the form of a binder or polymer, in order to aid in sintering, and 4) to gelcast the fluid B₄C slurries to form sinterable B₄C preforms.

Numerous commercial products were tested as dispersants by both sedimentation tests and viscosity observations on B₄C slurries with high (>45 vol. %) solids loading. The experimental results (not shown here) indicated that the best dispersant for ESK 1500 B₄C powder was Emphos 1361. TMOH base was also added to slurries, since it appeared to stabilize the slurry viscosity.

Since a literature search did not yield any good alternatives for water-soluble carbon additives for the B₄C gelcast preforms, tests were performed to determine the carbon recovery from common gelcasting binders and monomers. Table 1 shows the chemicals tested and the carbon recovery after heating the materials in argon to 1000°C. Durez Resin yielded the highest carbon recovery; however since it is only sparingly soluble in water, it was not used for gelcasting. Sucrose had the next highest carbon yield, but resulted in an unacceptably high viscosity in the monomer solution. Although PVP-K15 had a relatively low carbon char yield (7.4 %), it was chosen as the primary carbon source generator, since it was compatible with B₄C slurries (as tested by sedimentation tests); and it could be used at high concentrations with negligible effect on the viscosity of the slurry. MBAM was also a fair carbon source. The amounts of carbon generated by the chosen gelcast system was estimated to result in a ~ 1 % carbon addition to the B₄C after heating to 1000°C. This amount of carbon has been shown by others to be sufficient for pressureless-sintering of B₄C[14].

The final important components of the gelcast slurries were two surfactants, Foamaster VF and Surfynol 104E. If these agents were omitted from the gelcast slurries, large numbers of spherical pores (flaws) were found in the green, gelcast prefoms due to foaming of the slurry.

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Figure 1 shows the fracture surfaces of green B₄C preforms gelcast after 1 and 24 h milling. These two time points were chosen to gauge changes in the slurry that is milled for a very brief period of time, versus a slurry that is allowed to age and mill to break up agglomerates. Figure 1 shows that the sample milled for 24 h has a much finer and smoother fracture surface than the 1 h sample. The finer green structure suggests a more uniform slurry, with less powder agglomerates for the 24 h slurry.

Figure 2 shows the sintered densities for two gelcast parts; gelcast (GC), and gelcast and isopressed (GC-IP); die pressed parts made from ground gelcast materials, DP (GC additives); die pressed and isopressed parts from ground gelcast materials, DP-IP (GC additives); die pressed parts made from B₄C powders with Durez Resin additive, DP (Durez Resin); and die pressed and isopressed parts from powders with Durez Resin additive, DP-IP (Durez Resin). These data show that it was necessary to isopress the gelcast B₄C in order to achieve sintered densities above 95 % T. D. The data obtained for the GC-IP material was comparable to the DP (GC additives) material. Only a slightly higher density was obtained for the DP-IP (GC additives) sample, which was the highest density obtained of all materials. The samples with Durez Resin, the DP (Durez Resin) and DP-IP (Durez Resin) had lower densities, although the carbon content was calculated to be the same as with the PVP-K15 additive. Overall the results indicate that for mere densification, the gelcast and die press method were equivalent. The scope of the project did not allow examination of the sintered microstructures to determine if the gelcast material was more uniform than the die pressed material.

Si Gelcasting

The scope of this research was to evaluate water-based gelcasting of several types of Si powders, as part of collaborative research efforts with Ceredyne Inc. and Eaton Co. Initial gelcast trials on Si powders from Eaton showed that these Si powders reacted with the MAM-PEGDMA water-based monomer solution to cause an unexpected gelation of the slurries during the milling operation. Because of Si-induced gelation, tests were performed to determine the reactivity of the Eaton, Ceredyne, and a commercial metallurgical grade Globe Si powders with several gelcast monomer systems. Figure 3 shows the initiation time for slurry gelation for the three Si powders at 40° C, in the absence of initiator (APS) and catalyst (TEMED). These data show that all three Si powders initiate gelation of all of the monomer systems tested. It also shows that the powders have different gel initiation activities with reaction rates dependent on the gelcast monomer system.

Since this catalytic activity of the Si powders was a barrier to milling the slurries, tests were performed to determine if a chemical inhibitor could be included in the milling step, which would delay the gelation of the slurries. 4-methoxyphenol is commonly added to monomers, such as PEGDMA, to increase the storage life of this material. Figure 4 shows a repeat of the previously described gelation tests, using Ceredyne Si powder with different quantities of 4-methoxyphenol additions. When at least 100 ppm of 4-methoxyphenol was added, there was an increase in the gel initiation time for the MAM-PEGDMA gel system, and even larger delays in gel formation were observed for additions of 250 ppm of 4-methoxyphenol. Additional work was designed to test whether the inhibitor additions affected the strength of the green gelcast Si parts, and the ultimate properties of the final sintered SRBSN materials.

Figure 5 shows the green strengths for the Ceredyne Si gelcast bars made with different monomers. The data show that the MAM-PEGDMA 6:1 had the best green properties of all the monomer systems tested. The differences in the green strengths are probably relate to how the monomers cross-link. The data also indicate that the 4-methoxyphenol inhibitor addition did not affect the green strengths of the gelcast Si parts. Figure 6 shows that the 4-methoxyphenol additions did not have a significant effect on the final strengths of the SRBSN materials formed from the gelcast Ceredyne Si preforms.

CONCLUSIONS

Methods have been developed to gelcast both B₄C and Si materials using an aqueous monomer systems. Both materials present unique challenges. A new dispersant was used to achieve more fluid B₄C gelcast slurries. PVP-K15 and MBAM were found to be effective additives to provide carbon for sintering of B₄C. Acceptable densities were acquired for isopressed, gelcast B₄C parts; however these densities did not exceed those of die pressed parts.

Several gelcast monomer systems were tested for use with Si powders, and an effective gelation inhibitor was found that allowed milling of the Si powders in water. The mechanical properties of the nitrated and sintered gelcast Ceradyne materials were comparable to those derived from pressed parts. Gelcasting offers the advantage of good uniformity and high green strengths, and the capability for forming complicated shapes.

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Table 1. Weight % carbon conversion for chemical additives.

Chemical	% Wt. Conversion to Carbon
MAM	2.75
MBAM	11.61
PVP K-15	7.40
Sucrose	12.3
Durez Resin	56.28

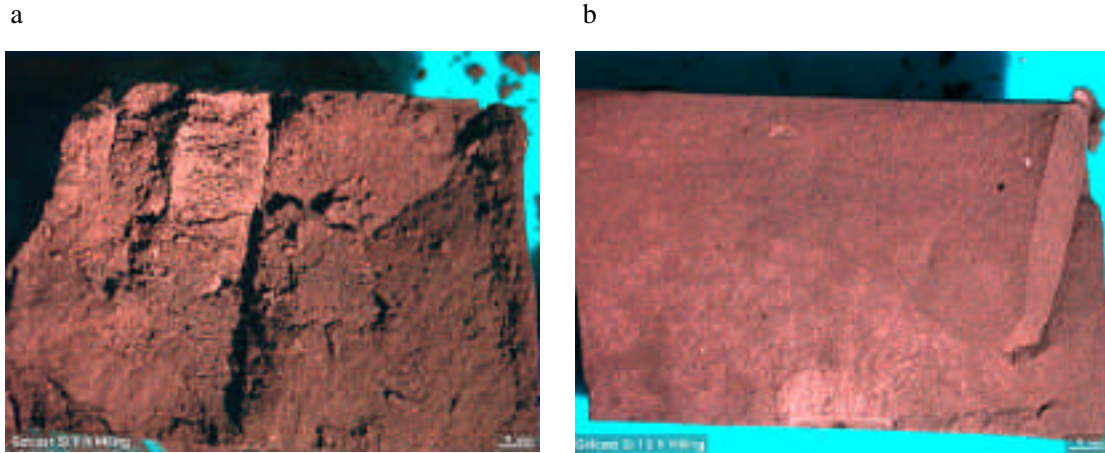


Figure 1. Photographs of fracture surfaces of green, B_4C gelcast parts which were fabricated from slurries milled for a) 1 h or b) 24 h.

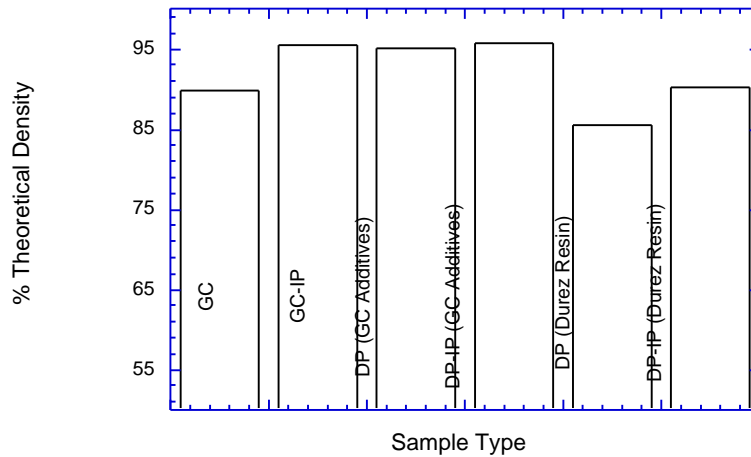


Figure 2. Sintered densities of B_4C discs prepared by different methods.

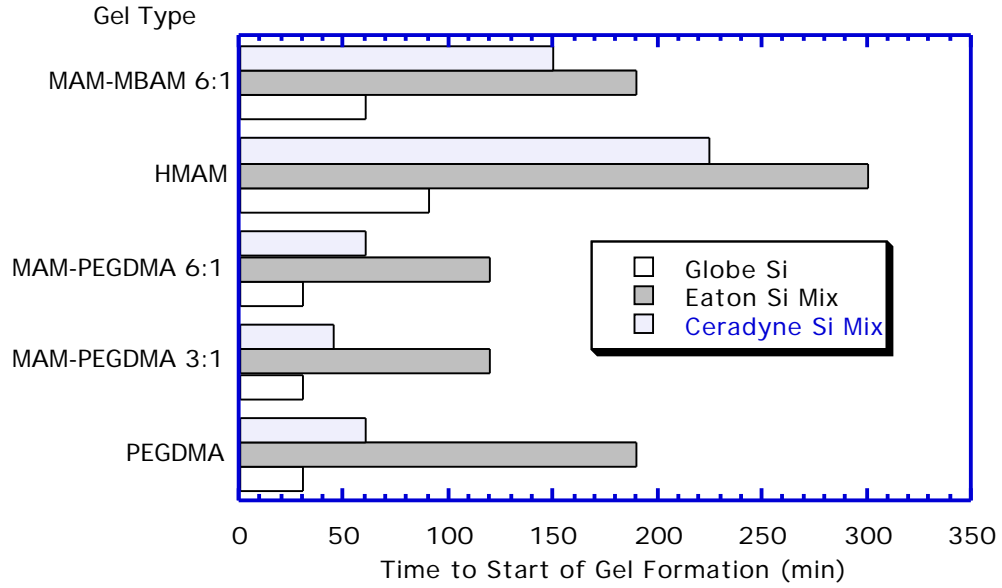


Figure 3. Gel initiation times at 40 °C for Globe, Eaton, and Ceradyne Si materials with different gelcast monomer solutions.

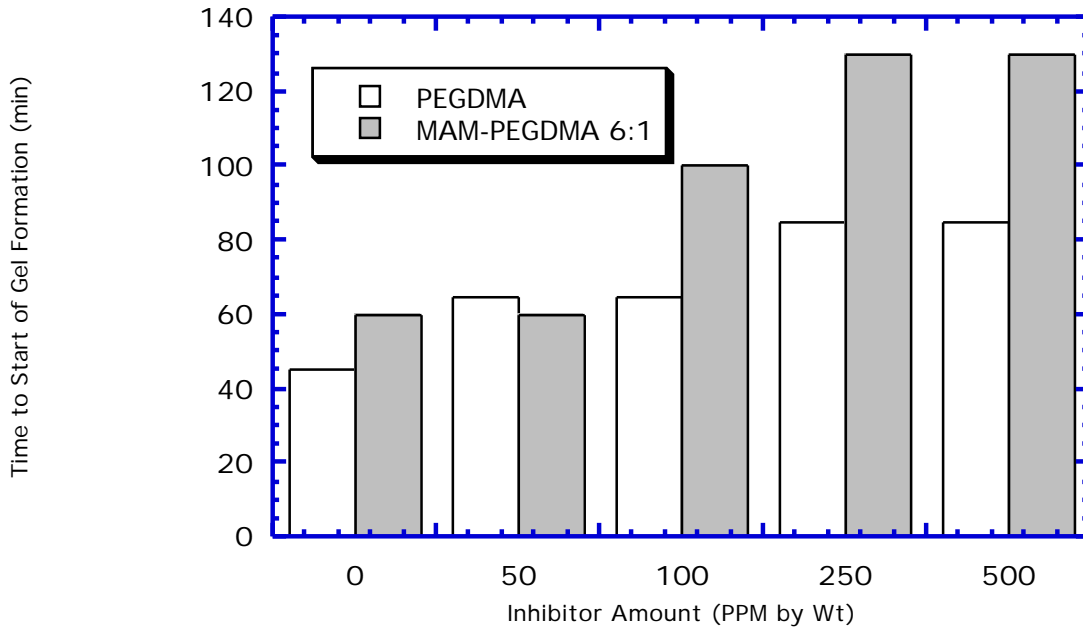


Figure 4. Effect of 4-methoxyphenol inhibitor concentration on gel initiation times at 40°C for the PEGDMA and MAM-PEGDMA monomer solutions and Ceradyne Si mix.

Figure 5. Green strength values of gelcast Ceradyne Si parts.

Figure 6. Strength values for sintered gelcast Ceradyne SRBSN materials.

