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Improved Processing of Armor Ceramics for Reduced Emissions of VOC's and Greenhouse Gases

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1.0 - Project Background

The use of armor ceramics by U.S. military forces is increasing. The manufacture of armor ceramics requires extensive use of energy, raw materials, capital equipment and consumables. The environmental impact of processing these materials is considerable in terms of produced green house gases, the release of volatile organic compounds (VOC's), and the consumption of natural resources. The industry needs to identify which steps in the processing route can be modified to prevent pollution without affecting the function of the materials. Common armor ceramics materials are Boron Carbide (B_4C), Silicon Carbide (SiC), Tungsten Carbide (WC), Aluminum Nitride (AlN), and Aluminum Oxide (Al_2O_3). Of these materials B_4C and SiC are of the most immediate interest in the industry due to their low densities and high hardness. B_4C is used as the hard face for SAPI (Small Arms Protective Inserts) bulletproof vests (6 lbs each) for the Marine Corps' and Army's Interceptor Body Armor Systems and in the protection system of all USA rotor wing aircraft, while SiC is being tested for armor systems in future land vehicles. It is projected that each vehicle will use 2 – 3 tons of ceramic armor.

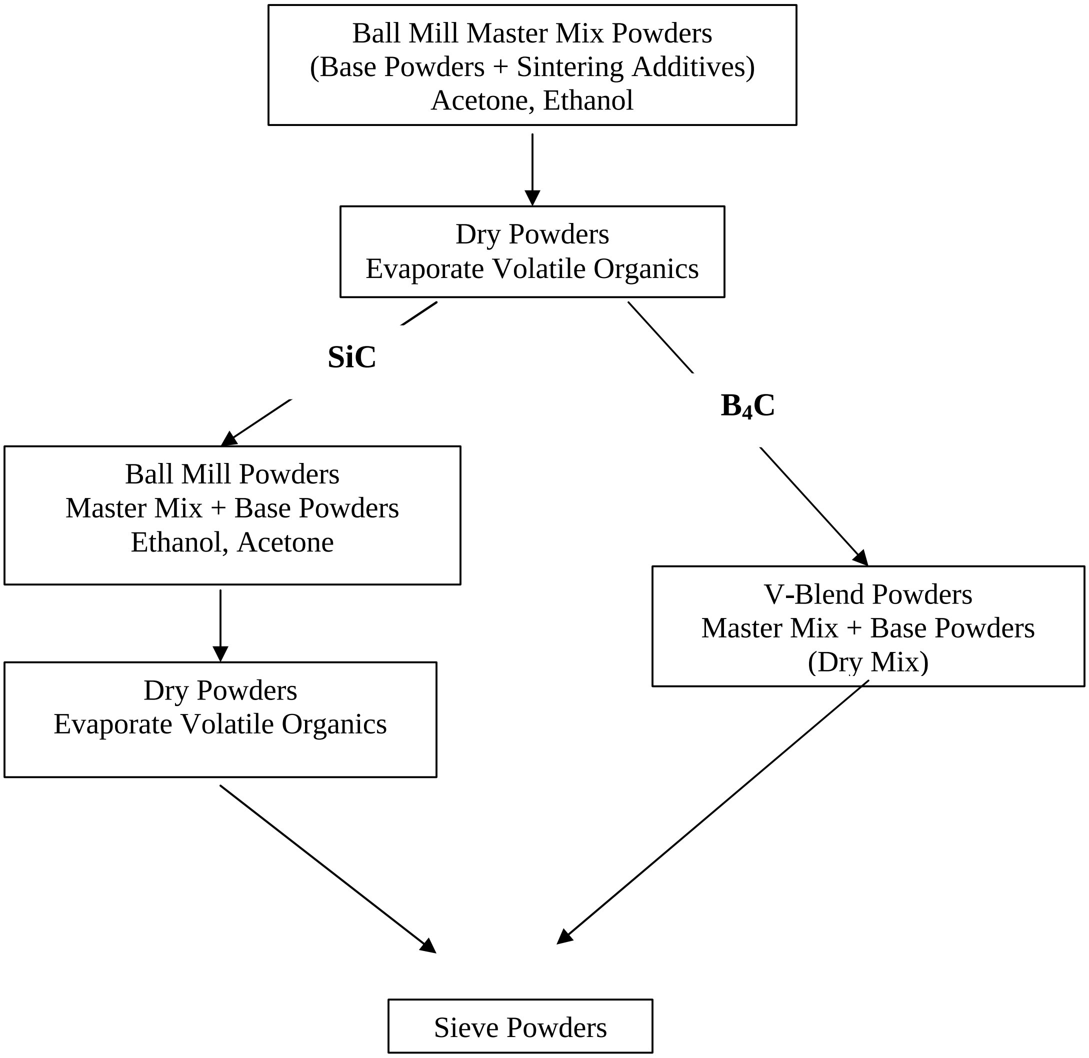
Cercom is a leading manufacturer of armor ceramics and makes a broad range of armor ceramics by hot pressing. This process produces the necessary fine grain microstructure, full density, and good mechanical properties in covalently bonded carbides and nitrides required for armor ceramics. Both net shape components such as plates and vests and machinable blanks can be manufactured by hot pressing. For production of net shape components the part is first formed into a green body using blended powder and then densified, while for machinable blanks the blended powder is pre-compacted in a graphite mold and densified.

The process for making blended powders depends on the type of powder used and the sintering aids added to it. For non-oxide ceramics, organic liquids are commonly used to prevent oxidation of the material during blending. Table I shows the amount of volatile organic compounds (VOC's) used as liquids at Cercom for blending different products. Figure 1 shows the processing procedure for blended B_4C and SiC powders.

Table I – Estimated Amount of VOC's for Year 2000

	Amount Produced	Liquid Media	Amount of VOC's
B_4C Armor	41,000 lbs	Ethanol	2,500 lbs
SiC Armor	22,500 lbs	Acetone, Ethanol	20,000 lbs

Figure 1



2.0 Objective

The goal for the SERDP SEED project is to use the principles of colloidal chemistry, ceramic processing and ballistic testing to develop, test and assess the effects on ballistics of replacing the volatile organic components (VOC's) used in milling of the B_4C and SiC powder blends with water. Successful development of water base processing for B_4C and SiC powders would substantially reduce the release of VOC's in this process. The transition plan for phase two of this project would be to increase the scale of production and assuming ballistic equivalence integrate full water processing into the present and future manufacturing lines for these materials. This would lead to substantial reduction in use of VOC's and potential reductions in pollutants and creation of green house gases.

3.0 Technical Approach

Organic solvents are often used for wet milling of ceramic powders. This is done to insure the chemical stability of the powders during processing and good dispersion and mixing of the powders. These organic solvents are either evaporated into the atmosphere during processing or burned off using an after-burner. Changing the liquid during wet milling to deionized distilled water would reduce the environmental impact of producing this material.

There are a number of technical issues that need to be overcome before using water for milling. One is the prevention of oxidation of the powders during milling. This is particularly the case for SiC and B_4C where the preferred sintering additives are typically non-oxides such as metals, carbides and nitrides. Since milling of powders involves the creation of new surfaces and fresh reaction sites these reactions can occur quickly and significantly change the chemistry of the powder. Maintaining the original chemistry of the additive in the final powder mix is important for densification and properties of the material.

The oxidation of powder during processing has been considered a major problem for processing non-oxides. A number of different approaches have been considered in the literature. One approach is the absorption of a polymer that minimizes interaction with the water by steric stabilization during processing and another is the adjustment of the solution pH to a value in which the oxidation reaction is reduced. Much work has been done to allow for spray drying of non-oxide powders but not on ball milling, the process currently used by Cercom for mixing powders. In spray drying the powder is simply mixed with water-binder solution and then spray dried. The time in water is generally low. For ball milling the time in water is longer and the mechanical energy is much higher.

The effective dispersion of the powders is another area of concern for ceramic processes. The dispersion of powders in water is complicated by it being a polar liquid, which means that most materials when brought in contact with it acquire a surface charge[1]. This charge influences the distribution of nearby ions in the liquid and leads to a double layer of charge around the particle. Understanding and controlling this double layer is critical in achieving good dispersion and mixing of fine grain powders in water. Each material and often powders of the same material manufactured by different companies/methods will have a characteristic surface chemistry.

The thickness and electrical potentials of this layer can be controlled by the solution pH and electrolyte concentration. Both silicon carbide[2] and boron carbide[3] have strongly

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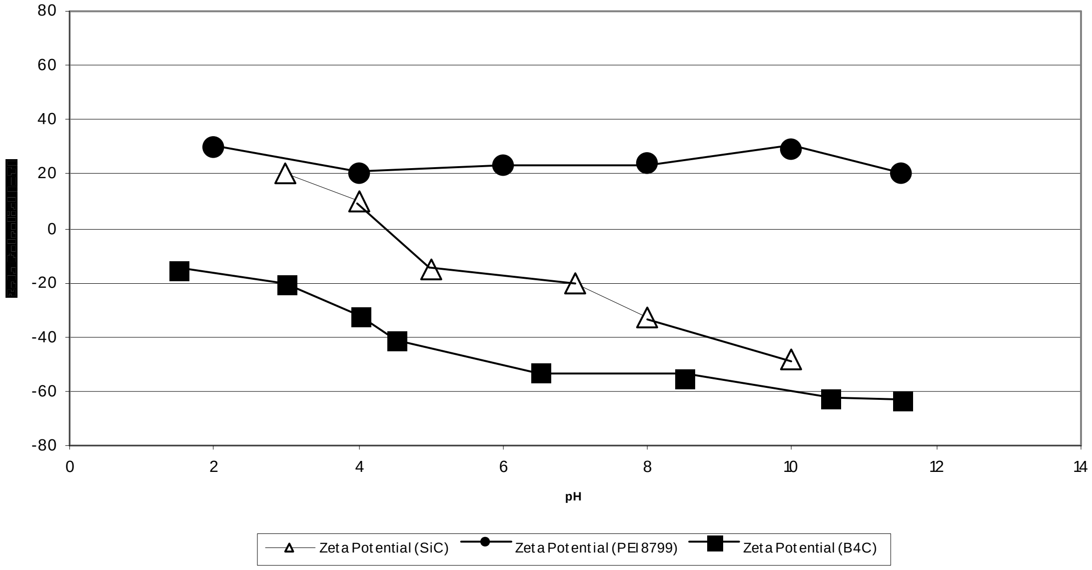
[1] D.J. Shaw, *Introduction to Colloid and Surface Chemistry*, Butterworth, Boston, 1980.
[2] M. Persson et al, "Steric Stabilization of Silicon Carbide Slips," pp. 623-632 in *High Tech Ceramics*, ed. By P. Vincenzini, Elsevier, Amsterdam, 1987.
[3] P.D. Williams and D.D. Hawn, "Aqueous Dispersion and Slip Casting of Boron Carbide Powder: Effect of pH and Oxygen Content," J. Am. Ceram. Soc., **74**, 1614-18 (1991).

acidic surfaces when immersed in water, which give these powders a negative surface charge for most pH's (see figure 2). The sintering additives used for SiC and B_4C likely have a surface charge that is different as a function of pH. Powders generally flocculate at pH's near the zero point of charge or when there are two powders of different surface charge. Avoiding flocculation in polyphase systems can be difficult.

To overcome restrictions on the pH used for mixing or other difficulties with slurries a surface active organic compound can be adsorbed on the surface of powders to provide steric stabilization. These surfactants are generally long chain organic compounds that have one end of the compound preferentially adsorbed on the surface of the powder and the other dangling free. The dangling surface prevents the powders from coming into contact and flocculating. This method of dispersion has been effectively used for slip casting SiC powders over a broad pH range. Figure 3 shows the zeta potential of SiC with surfactant PEI 8799 adsorbed on it.

Figure 2 – Zeta Potential vs pH for SiC and B_4C Powders (Literature Values)



4.0 Summary

Water processed boron carbide and silicon carbide were successfully produced and compared to conventionally processed boron carbide and silicon carbide in terms of mechanical properties, chemistry and ballistic performance by screening tests. The water processed boron carbide was compared to both boron carbide made by free loaded powders and to boron carbide billets that had been processed using manufacturing methods used for producing body armor vests. The water processed boron carbide showed slightly higher strength, similar hardness, similar Weibull modulus and lower oxygen than conventionally processed boron carbide. The ballistic results on the 6 tiles made from the three types of boron carbide showed only small differences of approximately 5%, with the water processed boron carbide having intermediate results. Full ballistic testing would be needed to determine definite differences in performance.

Water process silicon carbide was compared to conventionally made Cercom silicon carbide armor materials. The water processed materials showed slightly lower strength and Weibull modulus than conventionally processed silicon carbide and showed slightly higher oxygen content. The water processed tiles showed similar ballistic performance, within 1% of conventionally processed tiles. Silicon carbide is being used as protection against both light and heavy threats. Lightweight threats were used in testing for this project. Higher threat levels would require expensive metal encapsulation for testing.

Ballistic test results will only be reported in relative terms because the low areal density of the material makes it classified for the threat used for testing. The principle behind the ballistic testing was to overmatch the materials to see possible differences in the material. Differences between water processed and conventionally processed materials was generally less than 5%.

5.0 Project Accomplishments

5.1 Introduction

For carbides, borides and nitrides used for armor applications, low self-diffusion constants require the addition of sintering aids for densification and the control of oxygen content during processing and densification. Oxygen is often considered harmful to densification of these covalently bonded ceramics by impeding volume diffusion and allowing grain growth by surface diffusion. Special heat treatments are often used to remove oxygen during the sintering process.

The sintering aids used for densification are typically added by wet milling to insure even distribution of additives. For non-oxide ceramics this milling is generally done with volatile organic compounds (VOC's) that need to be dried using a low temperature oven and an after-burner to prevent release of VOC's into the atmosphere that causes ozone formation. The use of water processing would reduce the use of VOC's, simplify the processing, increase safety and eliminate the need for costly and energy consuming pollution control technology.

To substitute water for volatile organics requires understanding the surface chemistry of the powders, the change in the surface chemistry with pH and the use of processing aids that can protect the powders from oxidation during processing. Implementation of water processing also requires that the material properties are similar and that the material behaves equivalently for ballistics. For each ballistic application, testing is generally needed and can require the use of 200 tiles. Screening tests are generally performed using 6 tiles to determine a v_{50}[5].

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[5] The velocity in which 50% of the projectiles will penetrate through the material.

In this work several methods for water processing SiC and B_4C were considered and the most promising methods were down selected for material property measurements and ballistic screening tests. The ballistic screening tests were performed for threats envisioned for personal armor vests.

5.2 Methods and Procedures

The wet milling of SiC and B_4C was studied both in terms of chemical stability of the base powders and sintering aids and the mixing and dispersion of them. The chemical stability of the powders in distilled deionized water was studied as a function of pH, solids loading, buffering agent (organic/inorganic acids/bases), adsorbed organics, and milling time. Leco Analysis (infrared analysis of CO_2) was used to measure the oxygen content of the SiC and B_4C powders. Weight gain, gas evolution techniques and Leco Analyses were used to determine the stability of sintering additives in water. The oxygen content of the powders was determined after drying (85 °C) and after binder burnout. All test specimens were dried at 110 °C prior to testing to remove chemisorbed water.

The zeta potentials of the SiC, B_4C and sintering additives (when possible to measure) were determined as a function of pH. A Matec MBS 8000 was used for multi-point analysis (function of pH) and a Beckman Coulter Delsa 440SX was used for confirmation of results at specific pH's. The multi-point analyses gives the zero point of charge for the different powders and the pH's in which the powders have a negative and positive surface charge.

Succinic acid, an organic acid, was used for stabilizing sintering additives for boron carbide. Silane coupling agents were added to silicon carbide slurries to provide stability to the sintering additives and prevent oxidation. The viscosities of the slurries with succinic acid and silane coupling agents were measured with a Brookfield viscometer. Different silane coupling agents were used and evaluated. They will be labeled in the results section as S1-S5 and are shown in Table II.

Table II – Chemical Names for Different Silane Processing Aids

Silane Additive	Liquid Medium for Silane Additive	Chemical Name
S1	Water	aqueous amino/alkyl-functional siloxane co-oligomer
S2	Alcohol	N-(2-aminoethyl)-3-aminopropyltrimethoxysilane
S3	Alcohol	3-aminopropyltrimethoxysilane
S4	Alcohol	N-ß(aminoethyl)-?-aminopropyltrimethoxysilane
S5	Alcohol	?-aminopropyltriethoxysilane

The silicon carbide was ball milled, dried at 85 °C, sieved and processed as typical PAD SiC. The boron carbide was processed differently than production boron carbide. Upon drying of the powder milled in water, boron oxide was found to crystallize and segregate in the drying pan. This segregation was considered to be unacceptable, so a filtering step was added to remove the water. Despite the addition of a filtering step some boron oxide was found to remain as crystals in the dried filter cake. To evaluate the effect of these crystals the material was sieved and processed as is and another lot was dry milled and then sieved.

The water-processed boron carbide and silicon carbide were hot pressed in Cercom vacuum hot presses (VHP) using typical production cycles. The SiC was hot pressed into 12 x 12” billets and the B_4C was hot pressed into 12” x 16” billets. The water processed SiC and B_4C were evaluated for microstructure and material properties. From these tests one composition of SiC and one composition of B_4C were down-selected for ballistic testing. The material properties tested were hardness, density, strength, and Weibull Modulus. The microstructure was characterized by optical microscopy and SEM (Scanning Electron Microscopy).

Ballistic testing was conducted on 0.250” thick SiC tiles and 0.320” thick boron carbide tiles. The tiles were backed with 30 plies of Kevlar. As noted earlier, due to the thickness of the tiles and type of projectile used the results from these tests cannot be published. The relative results will however be presented and discussed.

5.3 Results

5.3.1 Stability of Powders without Additives

To determine the effect of the powder on pH of distilled deonized water, 3 g of powder were stirred in 100 ml of deionized water at room temperature for 1 ½ hrs. The change in pH is shown in Table III. It is seen that the sintering aid for SiC shows the greatest change and suggests this powder is most reactive with water. The drop in pH for pure water is due to a reaction with the CO_2 in air to produce carbonic acid.

Table III – Change in pH for Dilute Slurries

Powder	Starting pH	Final pH
Boron Carbide	5.6	5.8
Silicon Carbide (Grade 1)	4.1	4.3
Sintering Aid (B_4C)	5.6	5.3
Sintering Aid (SiC)	5.6	7.6
Water	5.6	5.0

Table IV shows the change in oxygen content of the different powders before and after treatment in water.

Table IV – Change in Oxygen Content for Water Treated Powders

Powder	Raw Powder – Oxygen Content	Water Treated Powder – Oxygen Content
Boron Carbide	0.47%	0.31%
Silicon Carbide (Grade 1)	0.56%	0.39%
Sintering Aid (B_4C)	0.24%	3.53%
Sintering Aid (SiC)	1.06%	24.9%

It is seen that the sintering aid for boron carbide shows only moderate oxidation while the sintering aid for SiC shows significant oxidation. Both the boron carbide and silicon carbide powders show lower oxygen contents when processed in water. This suggests that oxides on the surface of the boron carbide and silicon carbide go into solution. For boron carbide the oxide is B_2O_3 and is known to form boric acid in solution while for silicon carbide the oxide is SiO_2 and is known to form silicic acid in solution. Besides silicic acid other species such as colloidal silica or soluble silicate can be present in SiC.

Table V shows the measured oxygen content when the sintering aid for SiC is milled at solids loading of approximately 30 volume percent with different grades of SiC and dried at temperatures of 60 and 85 °C. From this data it is seen that the amount of oxidation varies with the grade of silicon carbide and that drying temperature has a significant effect on the amount of oxidation. The variation in amount of oxidation with grade of silicon carbide suggests that there is an interaction between the silicon carbide and the sintering aid. Grade 2 is a leached silicon carbide that has been cleaned of impurities and oxides.

Table V

Powders	Liquid	Drying Temperature	Oxygen Content
Silicon Carbide (Grade 1) + Sintering Aid	Organic	85 °C	0.59%
Silicon Carbide (Grade 1) + Sintering Aid	Distilled Water	60 °C	0.84%
Silicon Carbide (Grade 2) + Sintering Aid	Distilled Water	85 °C	1.77%
Silicon Carbide (Grade 1) + Sintering Aid	Distilled Water	85 °C	1.28%

5.3.2 Zeta Potentials of Powders

To understand the surface chemistry of the silicon carbide and boron carbide the zeta potential versus pH was performed. Figure 3 shows the change in surface potential as a function of pH for grade 1 silicon carbide. It is seen that the surface potential is highly positive at low pH and then becomes slightly positive at neutral and basic conditions. Figure 4 shows the change in surface potential as a function of pH for boron carbide. It is seen that the zeta potential is positive in acidic conditions and becomes negative in basic conditions. Due to the unusual zeta potential versus pH curve for silicon carbide (grade 1) the data was re-checked at a different vendor using a different piece of equipment. Table VI shows the zeta potential at a pH of 3 for the silicon carbide (grade 1), another manufacturers silicon carbide (grade 2), and the sintering aid for silicon carbide. It is seen that silicon carbide (grade 1) has a positive zeta potential from both vendors and that silicon carbide (grade 2) has a negative zeta potential. The zeta potential of the sintering additive for silicon carbide is strongly positive at these pH's. From these measurements it suggests that the sintering additive would be repelled from the surface of grade 1 silicon carbide and would be attracted to the surface of grade 2 silicon carbide. The zeta potential for the sintering additive used for boron carbide could not be measured.

Figure 3 - Zeta Potential as a Function of pH for Silicon Carbide (Grade 1)

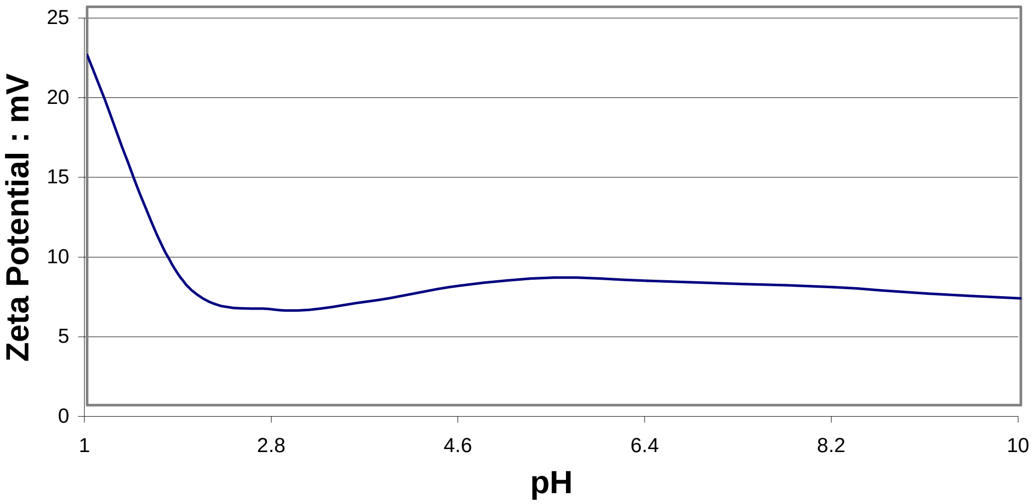


Figure 4 - Zeta Potential as a Function of pH for Boron Carbide

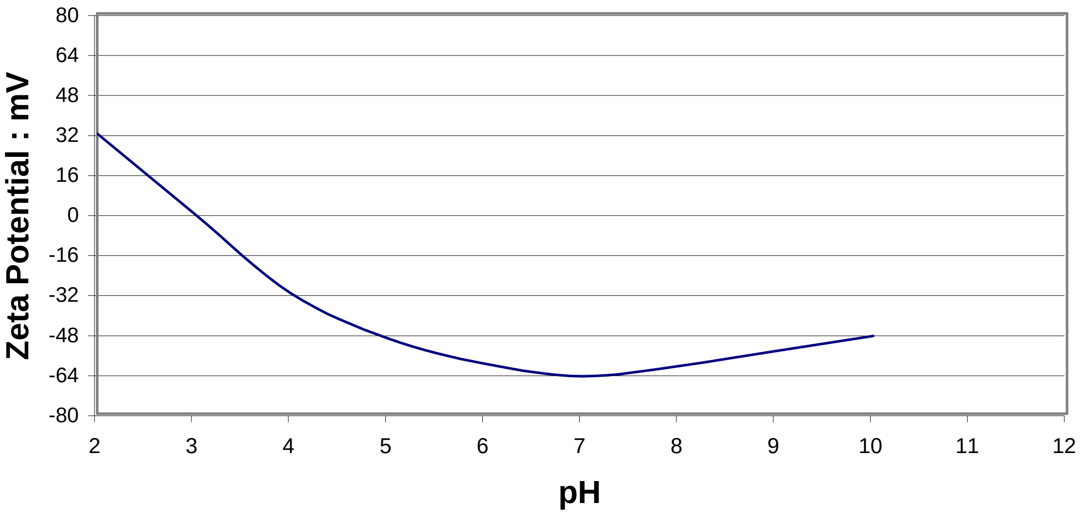


Table VI – Zeta Potential at pH 3 for Different Powders and from Different Laboratories

Powder	Zeta Potential at pH = 3	Laboratory
Silicon Carbide (Grade 1)	8 mV	Aveka
Boron Carbide	0 mV	Aveka
Silicon Carbide (Grade 1)	24.4 mV	Coulter
Silicon Carbide (Grade 2)	-12.2 mV	Coulter
Silicon Carbide Sintering Aid	50.1 mV	Coulter

5.3.3 Results from the Use of Succinic Acid as a Processing Aid

Succinic acid, $C_4H_6O_4$, an organic acid that buffers the pH of an aqueous solution and is known to be adsorped onto the surface of different sintering aids commonly used for ceramics was used as a processing aid. Table VII shows the oxygen content of slurry made with boron carbide powder and 0, 5 and 10% sintering aid. The solids loading was 35 volume percent and the succinic acid concentration was 0.05%. Due to the stability of the boron carbide sintering additive against oxidation, succinic acid was down selected as a processing additive for boron carbide. The processing methods used will be discussed in more detail in a later section.

Table VII – Oxygen Content of Milled Boron Carbide Powder using Succinic Acid as a Processing Additive

Composition of Solids in Slurry	Measured Oxygen Content
100% Boron Carbide Powder	0.58%
95% Boron Carbide Powder + 5% Sintering Aid	0.80%
90% Boron Carbide Powder + 10% Sintering Aid	0.88%

Table VIII compares the measured oxygen content of different silicon carbide slurries processed with succinic acid to those milled in organic liquids. It is seen that the succinic acid was not effective at preventing oxidation of the silicon carbide sintering aid in these tests

Table IX shows the viscosity of slurry made with different grades of silicon carbide. It is seen that viscosity is significantly higher for grade 1 silicon carbide than grade 2 silicon carbide. The pH of the slurries were between 2.5 to 3.5. The grade 2 silicon carbide is a finer grained powder than grade 1 and typically has a higher viscosity than grade 1 powder.

Table VIII - Oxygen Content of Milled Silicon Carbide Powder using Succinic Acid as a Processing Additive

Composition of Solids in Slurry	Liquid	Milling Time	Measured Oxygen Content
Silicon Carbide (Grade 1) + Sintering Aid	Organic	8 hours	0.74%
Silicon Carbide (Grade 1) + Sintering Aid	DI Water + 0.13% Succinic Acid	8 hours	2.35%
Silicon Carbide (Grade 2) + Sintering Aid	DI Water + 1.3 % Succinic Acid	8 hours	1.59%

Table IX – Viscosity of Silicon Carbide Slurries as a Function of Grade

Composition of Solids in Slurry	Liquid	Solids Loading	Viscosity
Silicon Carbide (Grade 1) + Sintering Aid	DI Water + 0.13% Succinic Acid	30 volume percent	4650 cp at 6 rpm (projects to 1050 cp at 30 rpm)need value
Silicon Carbide (Grade 2) + Sintering Aid	DI Water + 1.3 % Succinic Acid	30 volume percent	820 rpm at 30 rpmneed value

5.3.4 Results from Use of Silanes as a Processing Aid

Hydrophilic silanes, such as $C_6H_{17}NO_3Si$, have been used as processing aids for a variety of powders that are sensitive to water. These processing aids have terminal amino groups that act to protect the powder when the molecule is adsorped onto the powder. Table I shows the chemical name for the different silane additives and Table X shows the oxygen contents of silicon carbide slurries milled with different silanes after drying at 80 °C.

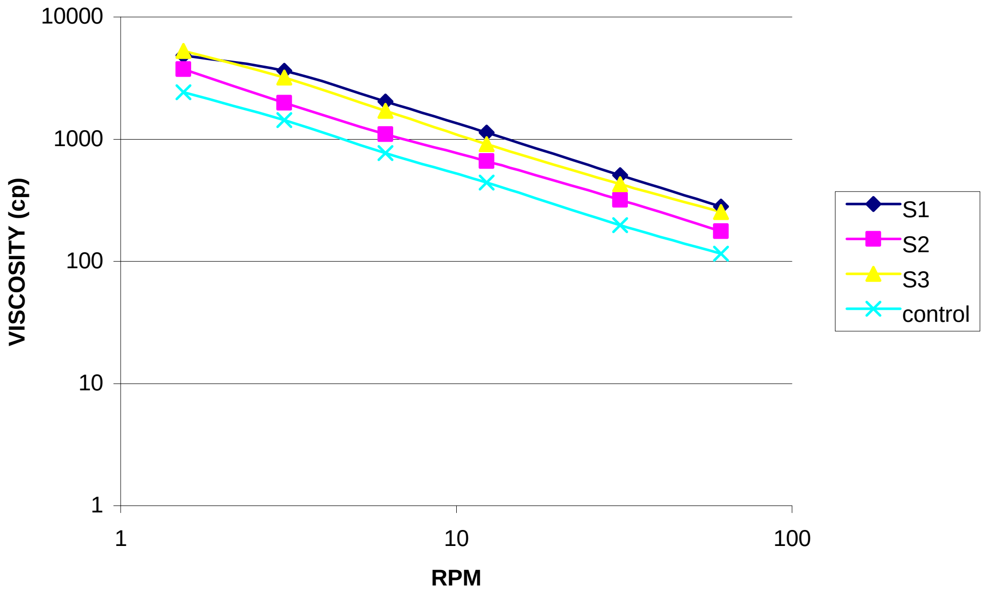
Table X - Oxygen Content of Milled Silicon Carbide Powder using Different Silanes as a Processing Additive

Silane Additive	Liquid Medium	Oxygen Content
None	Organic	0.68%
S1	Water	1.32%
S2	Water	0.78%
S3	Water	0.76%
S4	Water	0.83%
S5	Water	0.84%

The increase in oxygen content for the powder processed with silane additives was considered to be due in part to the oxygen associated with the silane molecule and part due to oxidation of the sintering additive. An increase in the nitrogen content was also noted that could be related to the presence of nitrogen from the silane. Due to the stability of the sintering aid in water, silanes S2-S5 were down-selected as possible processing aids. S1 was down-selected because of environmental and safety advantages in using a water-based silane. This was despite its higher oxygen content.

Figure 5 shows the viscosity of the silicon carbide slurries (grade 1) at 30 % solids loading and as a function of processing additive and spindle speed. The control sample is the conventionally processed material with volatile organic compounds. For the silicon carbide slurries a dispersant was added to aid in dispersion.

Figure 5 – Viscosity as a function of processing aid and spindle speed



5.3.5 Processing Methods Using Down-Selected Processing Aids

5.3.5.1 Boron Carbide

Figure 1 shows the processing route for making boron carbide powders for production at Cercom. The sintering aids are added by ball milling a master mix (sintering additive + boron carbide) followed by v-blending the master mix with raw boron carbide powder. The ball milling uses an organic liquid for a medium while v-blending is done dry. The powder lot sizes are 50 to 100 kg. Following v-blending the powder can be loaded directly into graphite dies to form flat plates. For forming curved plates the powder is blended with organic plasticizers and binders to form a green body. This material is green-formed with curvature and is hot pressed to the desired shape. For purposes of comparison, plates with binder and plasticizer were formed and pressed as flat plates for this project. No volatile organic compounds are used in mixing of the binder and plasticizer for these plates. The binder removal step, however, requires the use of an after-burner to reduce the release of pollutants to the atmosphere.

The material produced in this project was wet milled as a single batch such that the sintering additive was added at the desired percent. The material was mixed using an attrition free mixer with Hochmeyer Blade run at 1500 rpm. This method of mixing reduces batch size and makes experimentation possible. This processing method is considered possible to scale-up or adapt to larger batch sizes. After mixing, two drying processes were used. One method was to pan dry the slurries followed by dry milling. The second method was to filter press the slurries followed by drying and dry milling.

5.3.5.2 Silicon Carbide

Figure 1 shows the processing route for making silicon carbide powders for production at Cercom. Water processed silicon carbide was processed in the same way as PAD Silicon Carbide except that water was used as the liquid medium and that a dispersant and silane processing additive were added. The amount of silane additive used was approximately 0.25%. Compositions with different silane additives were made.

5.3.6 Results from Initial Vacuum Hot Press Runs

5.3.6.1 Silicon Carbide

Six compositions were hot pressed using a standard hot press cycle for Cercom PAD SiC in which the temperature and the pressure is controlled versus time and monitored by ram displacement versus time (rate of densification). Table XI shows the density for the six billets. The theoretical density for PAD SiC is 3.22 g/cm^3 and the minimum density is 3.20 g/cm^3.

Table XI – Density of Water Processed PAD SiC

Billet Number	**Silane Processing Additive**	**Density**
18-0066-7	S1	3.22 g/cm^3
18-0066-8	S2	3.21 g/cm^3
18-0066-9	S3	3.22 g/cm^3
18-0066-10	S4	3.22 g/cm^3
18-0066-11	S5	3.22 g/cm^3
18-0066-12	None (Control Processed in Organic Liquid)	3.21 g/cm^3

Table XII shows the oxygen content of the billets after hot pressing. It is seen that the oxygen content is generally higher for the water-processed powders. This is despite the use of silane processing additive.

Table XII – Oxygen Content of Water Processed PAD SiC

Billet Number	Silane Processing Additive	Oxygen Content
18-0066-7	S1	0.86%
18-0066-8	S2	0.64%
18-0066-9	S3	0.74%
18-0066-10	S4	0.83%
18-0066-11	S5	0.95%
18-0066-12	None (Control Processed in Organic Liquid)	0.56%

Table XIII shows the strength and Weibull Modulus of the billets made from water processed silicon carbide. It is seen that the billet with the highest oxygen content has the lowest strength and that compositions made with S2, S3 and S5 are fairly similar to the control sample. The Weibull Modulus, which is the measure of the uniformity of strength (higher value corresponds to greater uniformity), varies somewhat for the different compositions.

Table XIII – Strength and Weibull Modulus of Water Processed PAD SiC

Billet Number	Silane Processing Additive	Strength	Weibull Modulus
18-0066-7	S1	365 MPa	19
18-0066-8	S2	582 MPa	13
18-0066-9	S3	621 MPa	26
18-0066-10	S4	542 MPa	11
18-0066-11	S5	584 MPa	25
18-0066-12	None (Control Processed in Organic Liquid)	630 MPa	19

Table XIV shows the hardness of the water-processed and the control samples. It is seen that the hardness shows little variation with processing method or type of silane additive.

Table XIV – Hardness of Water Processed PAD SiC

Billet Number	Silane Processing Additive	Hardness
18-0066-7	S1	2373 kg/mm^2
18-0066-8	S2	2403 kg/mm^2
18-0066-9	S3	2392 kg/mm^2
18-0066-10	S4	2359 kg/mm^2
18-0066-11	S5	2401 kg/mm^2
18-0066-12	None (Control Processed in Organic Liquid)	2375 kg/mm^2

Figure 6 shows optical micrographs of the polished sections of the billets. The dark grains in the photomicrographs are oxide-rich second phase. It is seen in billet 18-0066-7 that there are large veins of oxide-rich material present. The other compositions did not show any vein regions of oxide but did show some variations in amount of second phase. Billet 18-0066-12, the control billet, appears to show the least amount of second phase. The light colored phase is metallic impurities. The composition of the veins and metallic phase were determined by elemental analysis using SEM (Scanning Electron Microscopy). The low strength found in billet 18-0066-7 was due to oxide veins acting as flaws.

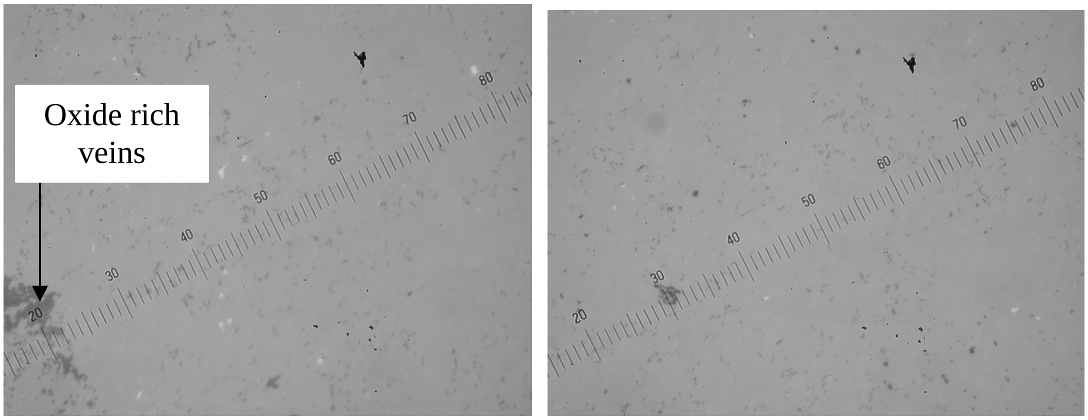
Table XV shows the average grain size as a function of processing additive. It is seen that there are only small variations in grain size.

From the material properties and microstructures compositions S2, S3 and S5 were down-selected to make billets for ballistic tiles. From these three compositions one was chosen for testing.

Table XV – Average Grain Size of Water Processed PAD SiC

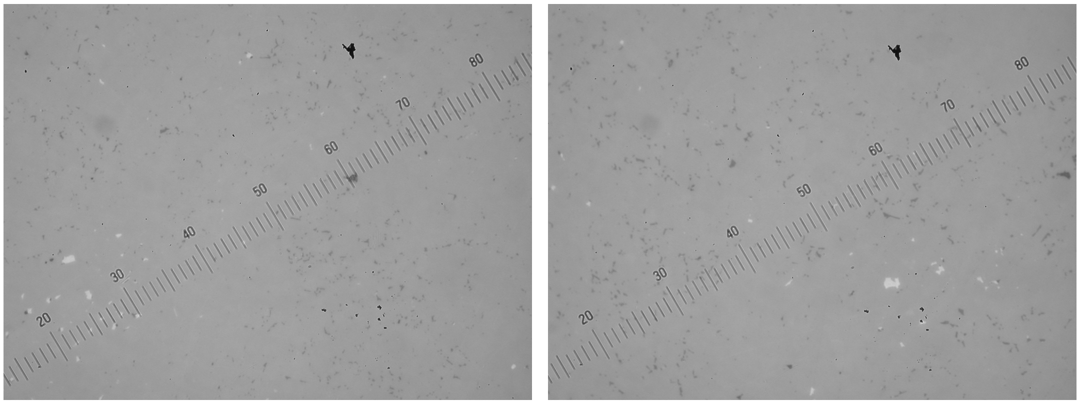
Billet Number	Silane Processing Additive	Average Grain Size (microns)
18-0066-7	S1	3.5
18-0066-8	S2	3.2
18-0066-9	S3	3.5
18-0066-10	S4	3.4
18-0066-11	S5	3.2
18-0066-12	None (Control Processed in Organic Liquid)	3.9

Figure 6 – Photomicrographs of Water Processed PAD SiC
(Reticule Unit equals 2.5 microns)



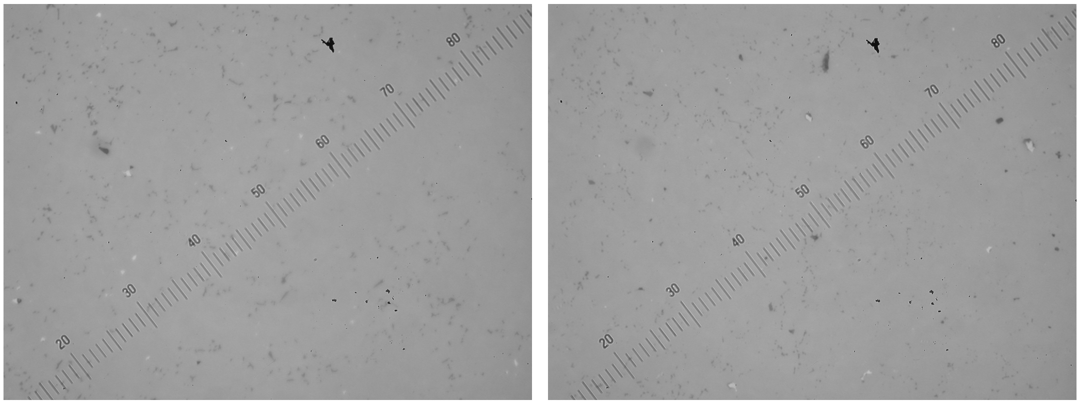
Billet 8-0066-7

Billet 8-0066-8



Billet 8-0066-9

Billet 8-0066-10



Billet 8-0066-11

Billet 8-0066-12

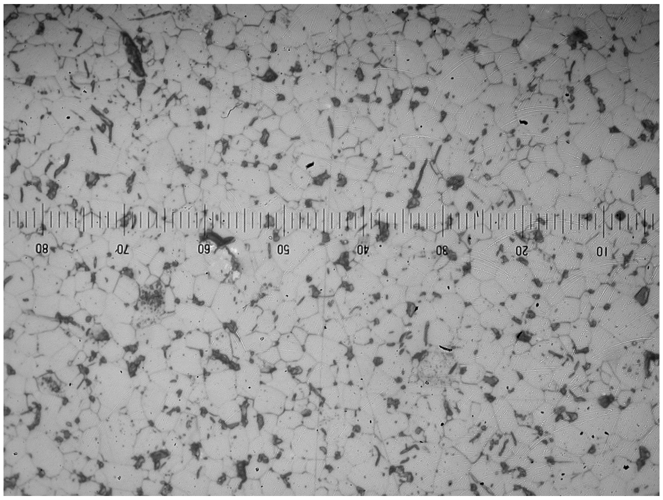
5.3.6.2 Boron Carbide

Billets of water-processed boron carbide were made and the properties were determined. Table XVI shows the oxygen content of pan dried boron carbide, the filtered boron carbide and the standard process control sample. Typical microstructures of etched samples are shown in the optical micrographs in Figure 7. The amount of pullout during polishing was less in samples made by filter pressing than those by pan drying and was a criteria for down selection. The mechanical properties of the different materials were similar.

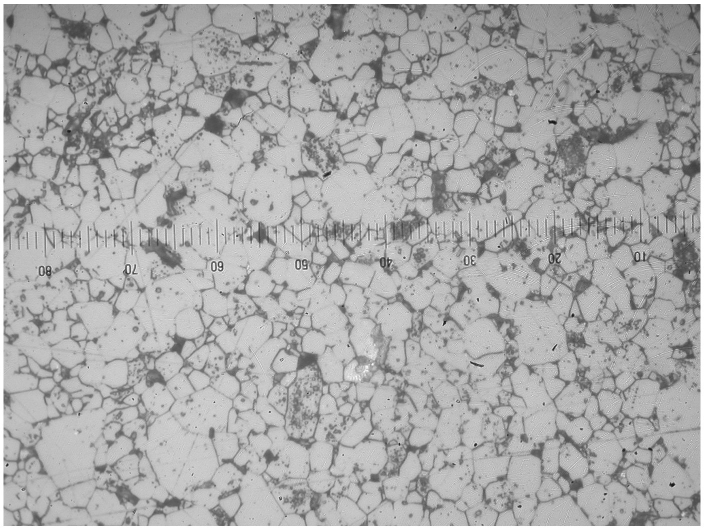
Table XVI - Oxygen Content of Water Processed PAD B_4C

Billet Number	Processing Route	Oxygen Content
7-0201-13	Water Processed (Pan Dried and Dry Milled)	0.15%
2-1935-3	Water Processed (Pan Dried and Dry Milled)	0.016%
2-1935-5	Water Processed (Filter Pressed and Dry Milled)	0.095%
2-1940-10	Control Processed in Organic Liquid and V-Blended	0.37%

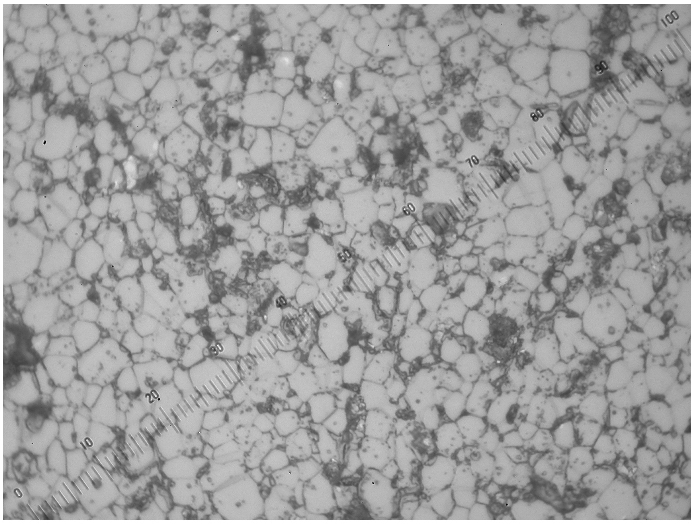
Figure 7. Optical micrographs of etched polished surfaces of water processed PAD B_4C (Reticule Unit equals 2.5 microns)



Billet 2-1935-5 (Pan Dried)



Billet 2-1935-3 (Filter Pressed)



Billet 11-0275-19 (control sample)

Table XVII shows the strength and Weibull Modulus of the billets made from water processed boron carbide and compared to conventionally processed boron carbide. The strength distributions are similar for all the process conditions studied.

Table XVII - Strength and Weibull Modulus of Water Processed PAD B_4C

Billet Number	Processing Route	Strength	Weibull Modulus
12-0216-1	Water Processed (Pan Dried and Dry Milled)	436 MPa	11
2-1935-5	Water Processed (Filter Pressed and Dry Milled)	450 MPa	10
14-0204-11	Water Processed (Vest Process as a Flat Plate)	432 MPa	9
1-2000-4	Control Processed in Organic Liquid and V-Blended	440 MPa	11

Table XVIII compares the hardness of the billets made from water processed boron carbide to conventionally processed boron carbide. It is seen that the hardness shows minimal variations.

Table XVIII - Hardness of Water Processed PAD B_4C

Billet Number	Processing Route	Hardness
7-0201-13	Water Processed (Pan Dried and Dry Milled)	2629 kg/mm^2
2-1935-3	Water Processed (Pan Dried and Dry Milled)	2616 kg/mm^2
2-1935-5	Water Processed (Filter Pressed and Dry Milled)	2660 kg/mm^2
14-0204-11	Water Processed (Vest Process as a Flat Plate)	2647 kg/mm^2
2-1940-10	Control Processed in Organic Liquid and V-Blended	2637 kg/mm^2

5.3.7 Results from Final Hot Pressing of Billets for Ballistic Testing

5.3.7.1 Boron Carbide

Boron carbide processed by filter pressing and then dry milling was down-selected for use in ballistic testing. The hardness of the down-selected material is shown in Table XIX.

Table XIX - Final Down-Selected Boron Carbide Materials

Billet Number	Processing Route	Hardness
2-1972-3	Filter Pressed and Dry Milled	2645 kg/mm^2

5.3.7.2 Silicon Carbide

From the oxygen analysis and strength measurements shown in Tables XII and XIII, three silane processing aids were down-selected. The three were S2, S3 and S5 and were used to make larger batch sizes and thicker billets. The material after hot pressing was machined and polished. Inspection of the samples showed typical microstructures for S2 and S3 and veining in S5 (as seen in billet 18-0066-7 in Figure 6). Table XX shows oxygen content for the three materials. It is seen that the oxygen was highest in the billet made with S5 as the processing aid. Table XXI shows the strength and Weibull Modulus of the material made from S2 and S3. The material with S2 processing additive was down-selected for testing due to high strength, higher Weibull Modulus and low oxygen content.

Table XX – Strength and Weibull Modulus of Water Processed PAD SiC

Billet Number	Silane Processing Additive	Oxygen Content
8-0200-6	S2	0.29 %
8-0200-2 (not ballistically tested)	S3	0.76 %
8-0200-4 (not ballistically tested)	S5	0.89 %

Table XXI – Strength and Weibull Modulus of Water Processed PAD SiC

Billet Number	Silane Processing Additive	Strength	Weibull Modulus
8-0200-2	S3	525 MPa	9.5
8-0200-6	S2	591 MPa	22

5.3.8 Results from Ballistic Testing for Silicon Carbide and Boron Carbide

Ballistic testing was conducted on 5” x 5” x 0.250” thick SiC tiles and 5” x 5” x 0.320” thick boron carbide tiles according to MIL-STD-662F. The tiles were backed with 30 plies of Aramide (Kevlar). A lightweight projectile typical of that used for testing of small arm protective vests was used. The thickness of the tiles was chosen: to normalize the weight of the boron carbide (density – 2.50 g/cc) and silicon carbide (density - 3.20 g/cc) and to slightly overmatch the ceramic to provide means to distinguish differences in the material. The v_{50} results will however be presented and discussed in a normalized manner.

Figure 7 shows the ballistic results normalized to conventionally processed PAD Silicon Carbide. It is seen PAD B_4C behaves better than the PAD SiC for these lightweight threats. It is also seen that the three PAD B_4C materials are all within 5 – 6% of each other and that two PAD SiC materials are within 1 – 2% of each other. Differences in ballistic performance generally become meaningful when greater than 5 - 10%. It therefore appears from these tests that there may be differences in the PAD B_4C materials but that there are no major differences in PAD SiC. It should however be noted that the ballistic performance depends on region impacted during a ballistic event. The ballistic performance of a material is thought to depend in part on population of flaws in the material. For flaws with a low population this may require extensive testing of multiple lots. The similarity in strength and Weibull Modulus of the tested material however suggests a similar flaw population.

Table XXII and XXIII shows the oxygen content of the water processed and conventionally processed boron carbide and silicon carbides that were ballistically tested. It is seen that water-processed silicon carbide had slightly higher oxygen content than conventionally processed silicon carbide and that the water processed boron carbide had slightly lower oxygen content than conventionally processed boron carbide.

Figure 7 - V_{50} Results for Lightweight Targets
(Normalized to VOC Process Silicon Carbide)

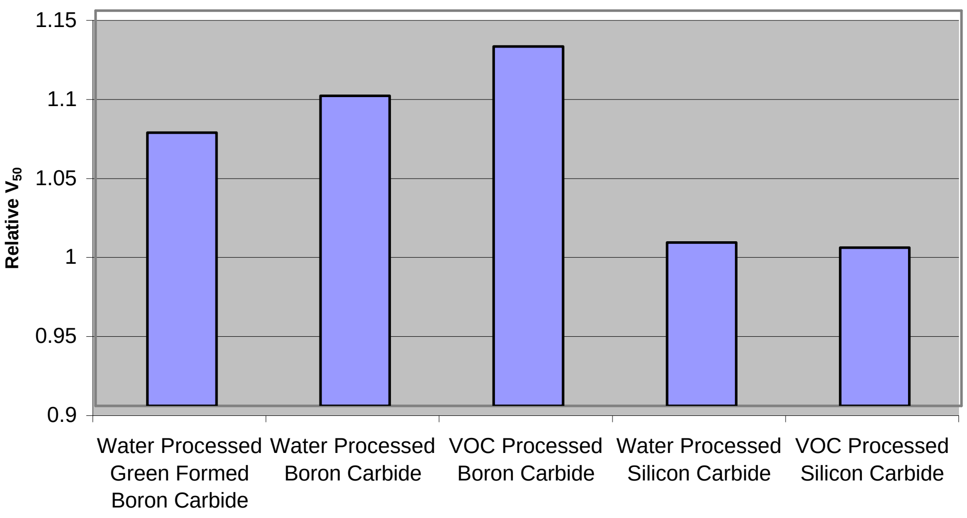


Table XX - Oxygen Content of Down-Selected Boron Carbide

Billet Number	Processing Route	Oxygen Content
2-1972-3	Filter Dried and Dry Milled	0.066 %
2-1972-3	Filter Dried and Dry Milled	0.046 %
2-1972-4	Filter Dried and Dry Milled	0.15 %
14-0148-10	Alcohol Process and V-Blended	0.34 %
9-0132-10	Alcohol Process and V-Blended	0.14 %
15-0025-9	Alcohol Process and V-Blended	0.47 %
14-0208-10	Water Processed (Vest Process as a Flat Plate)	0.34 %
14-0208-10	Water Processed (Vest Process as a Flat Plate)	0.44 %

Table XXI - Oxygen Content for Final Down-Selected Silicon Carbide

Billet Number	Silane Processing Additive	Oxygen Content
8-0200-6	S2	0.29 %
8-0200-6	S2	0.56 %
8-0200-6	S2	0.56 %
6-0018-10	None (Control, Processed in Organic Liquid)	0.45 %
6-0018-10	None (Control, Processed in Organic Liquid)	0.28 %
6-0229-4	None (Control, Processed in Organic Liquid)	0.26 %
8-0200-2 (not ballistically tested)	S3	0.76 %
8-0200-4 (not ballistically tested)	S5	0.89 %

5.4. Discussion of Results

The sintering additives used for Cercom PAD B_4C and Cercom PAD SiC are easily oxidized in water. Processing additives that reduced the oxidation were found to be necessary. For boron carbide the sintering aid could be protected by succinic acid at low concentrations of 0.05%. The succinic acid was believed to be adsorbed on the surface of the sintering aid and prevent oxidation. This mechanism was effective for preventing oxidation for slurries containing up to 10% sintering additive. This would allow the processing of master mix blends using water. The production processing procedure shown in figure 1 could therefore be used.

As discussed earlier, the water processing of boron carbide leads to the dissolution of boron oxide from the oxide surfaces of boron carbide and reprecipitation of it as larger crystals. The formation of these crystals upon drying was considered to be a source for possible flaws in the material. A filtration step was therefore added to the processing procedure to remove as much water as possible from the powder before drying. It however is unclear what the distribution of oxygen is in the material. From the limited number of oxygen analyses it appears that the addition of a filtration step significantly reduces the oxygen content of the material but that some oxygen is still present and that it varies from point to point.

Strength and Weibull Modulus measurements on water-processed boron carbide were typical of those processed with organic solvents. This suggests that boron oxide is not acting as large flaws and reducing the strength. But sample volume for strength measurements is small compared to the volume tested during a ballistic event, so it is unclear if the boron oxide is a problem for ballistic performance. It however is clear that further steps could be taken to reduce the oxide formation. A second filtration step could be added to significantly reduce the boron oxide content.

For silicon carbide slurries, silane processing aids were shown to significantly reduce oxidation of the sintering additive. It appears that some oxidation however occurs. From early experiments with succinic acid it appears that oxidation can occur both during the milling of the silicon carbide powder mixture and during drying. The processing aid must therefore have stability at temperatures in which water evaporates. This requirement for stability during drying may be the root cause for variation in the amount of oxidation with different processing aids.

It is also seen that the effectiveness of the silane processing aid can vary from run to run. The S5 processing aid was effective in the initial hot press runs but was not effective in the second run. Veining was found in this material. It was also found that the strength of the silicon carbide made from S3 decreased from 621 MPa in the first run to 525 MPa in the second run. The Weibull Modulus also decreased from 26 to 9.5. These results suggest that there are some oxide rich regions in the material that might be acting as flaws. The material made from S2 processing aid however showed good strength, high Weibull Modulus and similar ballistic performance as conventionally processed SiC. This result is promising and suggests that more work in this area is warranted.

6.0 Conclusions

It has been shown that both Cercom PAD B_4C and Cercom PAD SiC can be produced by water based processing and that the material properties are similar to that of Cercom PAD B_4C and Cercom PAD SiC processed with organic liquids (VOCS). The chemistry of the final product has been shown to vary slightly in terms of oxygen content. For PAD B_4C water processing reduces the oxygen content and for PAD SiC it increases the oxygen content slightly.

For PAD SiC, silane processing aids were necessary to prevent oxidation of the sintering aid during aqueous processing. It was found that the different silane processing aids varied in their ability to prevent oxidation during processing. The water-based silane was not effective at protecting the sintering aid during milling and oxide rich veins were found in the hot pressed material as well an increase in the oxygen content of the as-pressed billet. Alcohol-based silanes showed better performance but did show some increases in oxygen content when compared to standard material processed in organic liquids.

Succinic acid was found to be an effective processing aid for boron carbide slurries. The sintering aid was shown to be chemically stable in water when processed with this processing aid. Processing in water, however, was found to result in dissolution and reprecipitation of boron oxide in the original starting powder. The reprecipitation of the boron oxide led to regions rich in boron oxide. These boric oxide crystals were considered potential processing defects and required further processing to eliminate them.

Ballistic screening tests on water processed PAD B_4C and PAD SiC were performed using threats envisioned for future body armor. The water-processed material passed the screening test and was comparable to conventionally processed Cercom PAD B_4C and Cercom PAD SiC. More extensive ballistic testing needs to be performed to confirm these results and to determine the effects of different flaw populations. In addition, further tests using different threats needs to be done.

7.0 Transition Plan

To transition to water processed SiC would require first that it be demonstrated by screening tests to have similar ballistic properties for heavy threats as conventionally processed PAD SiC. Screening tests in the SEED program suggested similar ballistic properties for lighter threats. As noted, material used for heavier threats would likely have to be encapsulated in metal. Production of material for 6 – 8 encapsulated targets, besides providing data for screening purposes, would allow more extensive study of material properties and microstructure. This would give a measure of the robustness of the process and possible ways to improve it.

If screening tests against heavier threats are successful, methods for integrating water processed PAD SiC into new processing methods to form near net shape parts for body and vehicular armor should be funded. This would entail changing the process from free loaded powders to green formed parts. Some of the new applications envisioned for PAD SiC are extremely high volume and would benefit from water processing. The use of water processed PAD SiC would be more environmentally friendly, reduce the need for costly and energy consuming pollution control equipment and would increase safety. Improvements in water processed PAD SiC should be integrated with this near-net-shape forming. Once integrated, prototype parts should be more extensively tested for ballistic performance against light and heavy threats. Full ballistic testing is extremely expensive and would likely necessitate it to be tied into another program.

To transition to water processed B_4C would require increased testing of parts for ballistic performance, determining manufacturing methods to remove boron oxide from water processed boron carbide and integrating the technology into different programs. Effective removal of boron oxide from boron carbide could likely be achieved by double filtration. The first filtration would remove the majority of the boron oxide and the second would remove most of the remainder. Since the boron oxide becomes concentrated on the edges of the pans during evaporation even a double filtration process would need to be evaluated. If this was unsuccessful, a fluidized bed dryer could be used to prevent migration of the boron oxide during drying. The promising ballistic results achieved in the SEED program from single filtration suggest a fluidized bed dryer is probably not necessary.

Boron carbide, unlike silicon carbide, is primarily used for lightweight threats. Its application areas are body armor and helicopter armor. The material tested in the SEED program was free loaded powder. Water processed B_4C should be integrated into green formed B_4C. Presently this material doesn't use VOC's and uses V-blending to mix a master mix and raw powder. This process probably can easily be integrated. Free-load and green-formed materials made from wholly water processed PAD B_4C should be extensively tested for ballistic performance. Full ballistic testing, though relatively expensive, will be considerably less expensive than testing PAD SiC for heavy threats.

8.0 Recommendations

The expected demand for Cercom PAD SiC armor is great due to this material's superior performance for FCS vehicular applications. It is expected that each vehicle will require 3,000 – 5,000 lbs of silicon carbide and that the demand could be as great as 1,000,000 lbs per year. The first priority of the transition plan would be scale-up production techniques for the methods used in this SEED program and to test materials made from the increased batch size. In parallel, an effort should be made in testing this material using heavier threats that are envisioned for FCS applications. This material would need to be encapsulated to give a measure of true performance. In addition, other processing techniques should be considered along with forming methods. Due to the accelerated schedule for the FCS vehicle, this work should be done in the FY04 and FY05 time periods. Due to the significant cost associated with ballistic testing, this program should only fund proof of principle screening tests and full-scale tests should be funded either by ARL (Army Research Laboratory) or other institutions involved in the FCS program.

Cercom PAD B_4C is a current production material for SAPI (Small Arms Protective Insert) bulletproof vests used by the US Army. Cercom's present processing method only uses organic liquids (VOC's) for making the master mix and has eliminated VOC's from other processing steps. To fully eliminate VOC's from boron carbide production, it is likely that a double filtration process would be required to fully remove boron oxide from the master mix. Testing a double filtration process would require the purchase of some capital equipment and the ballistic testing of a sufficient number of plates to ascertain that the material is truly equivalent to organic liquid processed PAD B_4C.