NOVEL PROCESSING OF BORON CARBIDE (B_4C): PLASMA SYNTHESIZED NANO POWDERS AND PRESSURELESS SINTERING FORMING OF COMPLEX SHAPES

James Campbell, Melissa Klusewitz, Jerry LaSalvia, and Ernest Chin
U.S. Army Research Laboratory
Aberdeen Proving Ground, MD 21005-5069

Robert Speyer and Namtae Cho
Georgia Institute of Technology
Atlanta, GA 30332

Noel Vanier, Cheng-Hung Hung, Edward Abbott and Peter Votruba-Drzal
PPG Industries
4325 Rosanna Drive
Allison Park, Pennsylvania 15101

William Coblenz and Toni Marcheaux
DARPA, Defense Sciences Office
3701 N. Fairfax Drive
Arlington, VA 22203-1714

ABSTRACT

Boron carbide, most often used in personnel armor systems, is rather difficult to form and is almost always densified from ceramic powders under heat and pressure. Recent developments by PPG and Georgia Tech are allowing for the full densification of nano-sized powders through a pressureless sintering route. PPG is manufacturing these powders in a plasma processing technique, and they are less expensive than traditionally produced powders. The powders are formed directly in the plasma, and they can be doped with densification aids. Pressureless sintering techniques developed by Georgia Tech offers a low-cost processing route for B_4C that was previously unavailable. Together both efforts will lead to boron carbide with shapes and sizes unavailable today and using a fine-grained domestically produced starting powder.

1. INTRODUCTION

Boron carbide is an important armor ceramic that is primarily used in personnel protection applications due to its very low density and its ability to defeat small arms threats. Boron carbide has a density of 2.5 g/cm^3, compared to 3.2 g/cm^3 for silicon carbide (SiC) and 3.9 g/cm^3 for aluminum oxide (Al_2O_3).

Traditionally, boron carbide (B_4C) armor is manufactured through the hot pressing of ceramic powders, which requires the application of uniaxial pressure during the sintering (densification) process. This processing route allows for only very simple shapes to be formed, such as flat plates or those with some curvature, such as a Small Arms Protective Insert (SAPI) plate. Until recently, it has been very difficult to densify this ceramic to full density via a pressureless sintering route. Sintering would give the ability to make components with much more complicated geometries, such as conformable body armor and helmet liners. Georgia Institute of Technology (GIT) has developed a sintering approach with a follow-on hot isostatic (gas) pressing (HIP) to produce pressureless sintered, additive-free, B_4C components at full density.

Currently, almost all B_4C powders used in armor applications are imported due the high amounts of electricity required to manufacture the material. It is formed in an electric arc furnace as a large billet of material, which is then ground down into the powders used to make ceramic bodies. PPG offers an alternate approach to making the powders. The starting materials are reacted in a plasma and powders are formed directly. These powders are nano-sized and the process allows for the addition of sintering aids directly into the powder.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **DEC 2008**	2. REPORT TYPE **N/A**	3. DATES COVERED **-**

4. TITLE AND SUBTITLE **Novel Processing Of Boron Carbide (B4c): Plasma Synthesized Nano Powders And Pressureless Sintering Forming Of Complex Shapes**	5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **U.S. Army Research Laboratory Aberdeen Proving Ground, MD 21005-5069**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S) 11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES

See also ADM002187. Proceedings of the Army Science Conference (26th) Held in Orlando, Florida on 1-4 December 2008, The original document contains color images.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**UU**	**7**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

2. TRADITIONAL B_4C POWDERS

Like SiC, B_4C is a man-made material; the ceramic powder is typically produced through the carbothermal reduction of boron oxide in an electric arc (Acheson) furnace, Figure 1. The end product is a large ingot of B_4C that must be pulverized and ground down into the desired grit and powder sizes. Both the high temperature furnace operation and the subsequent grinding operations make it a very energy-intensive approach to making B_4C powder; and this accounts for the high cost of the powder and the limited powder production capacity in the United States. After the B_4C powder is ground and sized, only a portion of the powder is of armor grade quality, since there is variability of the material in the ingot. The remainder must be used for other applications such as the abrasives industry. Nearly all B_4C powder is imported, with China becoming a major player in the B_4C powder business. Figure 2 shows the two main suppliers of boron carbide to the United States are China and Germany. It should be noted that these numbers are for all grades of powder, not just armor-grade material. But it is interesting to note that major military procurement programs for body armor were going on during this period of rapid increases in powder imports. Typically, armor-grade B_4C powder has a cost of approximately $50/lb, while a sintered aluminum oxide might be $5/lb for the finished tile.

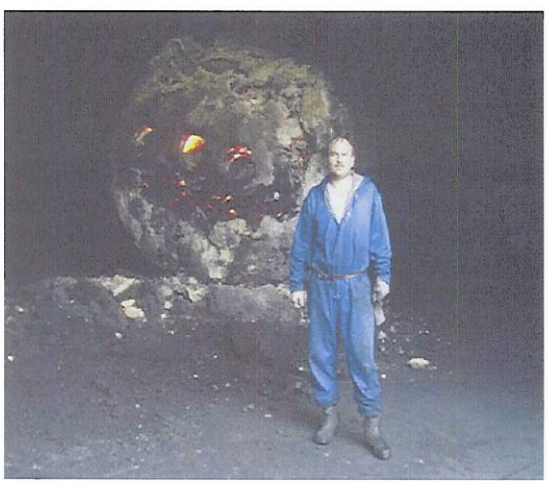

Figure 1. A large B_4C ingot is manufactured in an Acheson furnace, and is subsequently ground into powder of various grades.

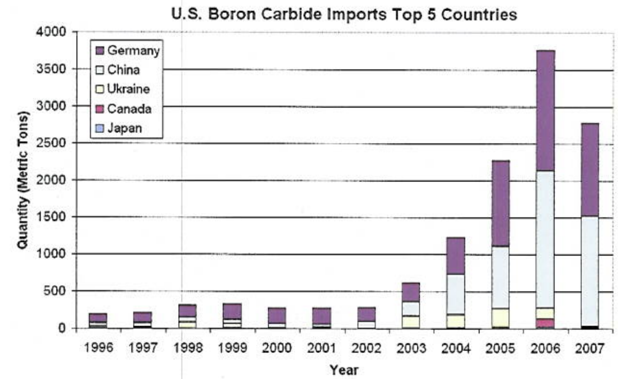

Figure2. B_4C powder imports as a function of country and year

3. PPG NANOPOWDERS

PPG is producing their B_4C powders through a very different method, in which the ceramic powder is formed by directly by reacting the precursors in a gas. The raw materials are vaporized and atomized in the thermal plasma, along with any sintering aids. The basic reaction would be a boron precursor, such as boron oxide (B_2O_3), and a carbon source (carbon or a hydrocarbon) are vaporized and atomized in a thermal plasma. As the plasma cools as it moves through the reactor, B_4C powder is formed through the following reaction:

$$2B_2O_3 + 7C \rightarrow B_4C + 6CO$$

The B_4C powders are then collected. Depending on the residence time in the reactor, powders of nano-scale particle sizes are formed. Reactor parameters must be chosen such that the reaction has time to progress to completion but the time/temperature/pressure profile must minimize reversal of the reaction. The powders are collected in a filter system and the powder is then washed to remove any residual B_2O_3 that remains.

For this process, the powder is formed directly from the starting materials, and the final powder should have a more consistent chemistry and less contamination, since there are no grinding operations. Currently, the powders were manufactured in a laboratory scale plasma system and larger systems are planned. Cost estimates show that powders produced through this method would be considerably less expensive than B_4C powders manufactured through traditional methods. Since powders are manufactured directly, the costs associated with grinding disappear. It also eliminates contamination of the powder with the materials in grinding medium and grinding vessel. The high electric costs and pollution associated of the traditional electric arc furnace have limited the amount of domestic production of B_4C powders. A process such as the gas plasma system demonstrated here will allow for the domestic production of B_4C powders. It is targeted that powders produced by this process may be less expensive when produced in large quantities, when compared to $50/lb which is a common cost for armor-grade powder produced by traditional methods.

Initial powders produced by the process were very uniform and with a very fine grain size, but they showed great difficulty in sintering to high density, even attempts to hot press were unsuccessful. Therefore, sintering aids were added directly to the plasma. These sintering aids were added as oxides and sometimes more than one were added together. A large number of sintering aids and dopants were investigated and densification studies were conducted. The studies looked at densification rates throughout the sintering schedule and to determine which combination of furnace conditions (hold times, ramp rate, atmosphere, etc) would provide the highest densities for a particular powder system. The goal would be to produce sintered densities that would be high enough so that a post-sinter hot isostatic press (HIP) could be done to close the remaining porosity and allow for full density to be achieved. Georgia Tech conducted a number of dilatometry studies on these powders Figure 3 shows a typical densification experiment for one of the PPG compositions, where the temperature profile with a ramp rate to 2300°C is shown as well as the dimensional changes that were measured by the dilatometer. In the upper temperature ramp, rapid densification is apparent, which slows at the isothermal soaking. The nano-sized grains are very unstable at these temperatures; their melting temperatures are significantly lowered, resulting in near-instantaneous grain growth at the temperatures corresponding to the momentary expansions shown in the sintering curves. The final result often is a B_4C with micron-sized grains; typical to what is observed when conventionally produced powders are used.

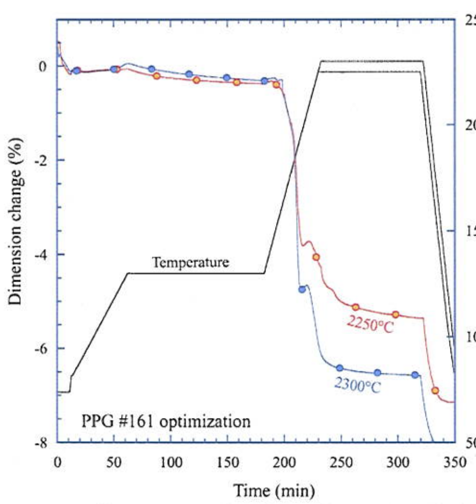

Figure 3. Dilatometry showing dimensional changes over time for the shown furnace temperature profile

4. B_4C HOT PRESSING

After B_4C powder is produced, regardless of how it was manufactured, it has to densified to form a useful armor product. Traditionally, all B_4C is manufactured through hot pressing, in which the powder is densified at a high temperature with the concurrent application of uniaxial pressure via graphite dies. In the US, there are two main commercial manufacturers of boron carbide: Ceradyne, Costa Mesa, CA and BAE-Advanced Ceramics Division, Vista, CA. Verco Materials, Atlanta, GA is a start-up company from the same Georgia Tech research group that conducted the dilatometry studies on the PPG powders. They are manufacturing complex-shaped B_4C through pressureless sintering with a subsequent HIP step. They are producing armor tiles and extremity armor using conventional powders, and supplying them to a number of armor system suppliers and laboratories. Verco has also produced armor tiles using the PPG nanopowders, which were tested at ARL.

Traditional hot pressing is a batch process, where the "green" (undensified) powder compacts are formed through some method with the ceramic powder and loaded into a hot pressing die. The die and powder are brought up to the sintering temperature and a load is applied to the die. Due to the very high temperature required for sintering, graphite tooling and specialized furnaces are required. Many of these non-oxide ceramics require sintering temperatures in excess of 2000°C. As the size of the ceramic part increases, the load required for the desired pressure becomes quite large. Since body armor inserts are the most common B_4C parts manufactured, the load frames in the hot pressing equipment needs to be quite large. To increase throughput, commercial vendors typically stack a number of plates together with machined graphite spacers and apply pressure to the entire stack. Although parts of simple geometry are most easily manufactured by hot pressing, the commercial vendors have introduced forming methods to allow for curved plates to be manufactured, such as a Small Arms Protective Insert (SAPI) plate. When armor tiles are manufactured by hot pressing, billets of the material are produced and the tiles ground and sectioned. B_4C is a very brittle material with low fracture toughness. Therefore, it is very difficult to machine and prone to edge chipping, which adds additional expensive to hot pressed B_4C tiles.

Hot pressing allows for the use of coarser ceramic powder and less reliance on sintering aids to form a fully dense part. Therefore, the powders may be more expensive for sintering; however, the expendable furnace and any post-densification machining would add more expense to a hot pressed part. Overall, it is anticipated that it would be considerably less expensive to manufacture parts, such as a SAPI plate, using a pressureless sintered technique.

Figure 4. B_4C plates formed via hot pressing with a curved shape.

Commercial B_4C shows a large number of lenticular graphitic inclusions, Figure 5. Inclusions of this type are also observed in fracture surfaces; therefore suggesting that these are not polishing artifacts. It is difficult to ascertain how these inclusions are introduced into the material - in the starting powders, during green forming or during densification. Interestingly, the ballistic properties don't seem to be particularly sensitive to these inclusions. However, these inclusions do affect the mechanical properties of the materials and they act as crack initiation points in flexure testing.

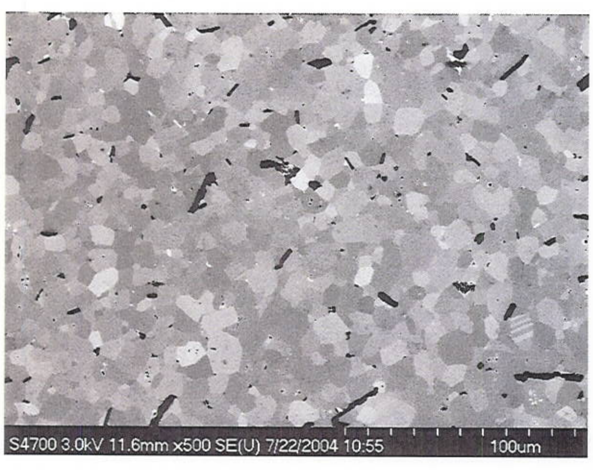

Figure 5. SEM micrograph showing large lenticular graphitic inclusions in commercial hot pressed B_4C

5. B_4C PRESSURELESS SINTERING AND HIPING

Georgia Tech and Verco Materials have developed methods to manufacture B_4C without the aid of uniaxial pressure during densification. They have been able to develop sintering profiles that allow for high densities to be achieved. By understanding when chemical reactions occur, when compounds breakdown and how materials out-gas, a sintering schedule can be developed that minimizes time at temperature ranges where unfavorable transformations occur. A differential dilatometer was used to develop these sintering schedules and understand when these reactions occur, similar to the data shown in Figure 2. They have attained closed-porosity microstructures which can then be successfully post-hot isostatically pressed to a zero-porosity state. HIPing involves heating the part in the presence of high-pressure inert gas which applies a hydrostatic pressure on the part which is shape preserving. HIPing closes the remaining porosity and theoretical density can be achieved. HIPing is done commercially in very large vessels and large number of parts can be densified at one time. Therefore, this step adds marginal cost to the overall process.

A major opportunity for pressureless sintering is parts of complex geometry, which cannot be produced by hot pressing. The undensified "green" bodies" for these parts are made by established ceramic processing methods, such as extrusion, injection molding, or slip casting. Figure 6 shows a throat and upward blast protection B_4C insert that Verco Materials produced via pressureless sintering. This processing route would allow for the manufacture of complex-shaped pieces for conformable body armor, such as shoulder inserts and neck protectors.

Figure 5. Complex shaped part of B_4C manufactured by Verco Material via pressureless sintering using conventional powders.

Summary

Boron Carbide is an important armor ceramic that is used primarily in personnel protection due to its low density. Pressureless sintering techniques developed by Verco Materials for B_4C would allow for lower costs and the ability to form conformable shapes. Traditional B_4C powders are all imported and are rather expensive. PPG is manufacturing B_4C powders through a different route. These powders are nano-sized and offer the opportunity to produce price-competive powders domestically. The PPG powders have been densified to full density by Verco Materials.

Quality Assurance and OPSEC Review

This form is an approval record for ARL generated information to be presented or disseminated external to ARL. Note: Submit all manuscripts in electronic format or camera ready copy. See attached instructions. If more space is needed, use reverse of form *(include block numbers)*.

A. General Information

1. Present Date: 09/22/2008

2. Unclassified Title: NOVEL PROCESSING OF BORON CARBIDE (B4C): PLASMA SYNTHESIZ

3. Author*(s)*: James Campbell, Melissa Klusewitz et al.

4. Office Symbol*(s)*: AMSRD-ARL-WM-MD

5. Telephone Nr*(s)*: 4-0896

6. Contractor generated ☐ No ☐ Yes
If yes, enter Contract No. and ARL COR

7. Type: ☐ Report ☐ Abstract ☒ Publication ☐ Presentation *(speech, briefing, video clip, poster, etc)* ☐ Book ☐ Book Chapter ☐ Web

8. Key Words: boron carbide, nanopowders, sintering, body armor

9. Distribution Statement *(required)* Is manuscript subject to export control? ☐ No ☐ Yes
Circle appropriate letter and number. *(see instructions for statement text)*
☒ B C D E F X ☒ 2 3 4 5 6 7 8 9 10 11

10. Security Classification: unclassified

B. Reports

11. Series	12. Type	13. No. of pages	14. Project No.	15. Period Covered	16. Sponsor

C. Publications

17. Is MS an invited paper? ☒ No ☐ Yes

18. Publication is a refereed journal? ☒ No ☐ Yes

19. Material will be submitted for publication in
Journal: Proceedings of the 2008 Army Science Con
Country: USA

D. Presentations

20. Conference Name/Location: 2008 Army Science Conf., Orlando

21. Sponsor: ASAALT

22. Conference Date

23. Due Date

24. Conference is ☐ Open to general public ☐ Unclassified/controlled access ☐ Classified

25. For nonpublic meetings: Will foreign nationals be attending?
☐ No ☐ Yes *(If yes, list countries and identify International Agreement(s))*
☐ Don't know

26. Material will be
☐ Oral presented only ☒ Oral presented and published in
Proceedings of the 2008 Army Science Conference
(If published, complete block 18 and 19, Section C.)

E. Authors Statement:

27. All authors have concurred in the technical content and the sequence of authors. All authors have made a substantial contribution to the manuscript and all authors who have made a substantial contribution are identified in Block 3.

James Campbell [signature] — ARL Lead Author or COR — Date: 09/22/2008

F. Approvals

28. First line Supervisor of Senior ARL Author or COR
Ernest Chin [signature] — Name — Date: 09/25/2008

29. Reviewer*(s)* *(Technical/Editorial/NA)*
Kevin Doherty [signature] — Name*(s)* — Date: 9/25/2008

30. Limited distribution information for release to foreign nationals

Foreign Disclosure — Date

31. Classified Information
Classified by
Declassified on

Command Security Manager — Date

ARL Form 1
October 2003

OPSEC REVIEW CHECKLIST

OPSEC POC: Complete and explain any positive responses in block 9.
Note: ARL must be the proponent of the proposed information for release.

1. Does this material contain Sensitive Information? ☐ YES ☒ NO

2. Does this information contain state-of-the-art, breakthrough technology? ☐ YES ☒ NO

3. Does the United States hold a significant lead time in this technology? ☐ YES ☒ NO

4. Does this information reveal aspects of reverse engineering? ☐ YES ☒ NO

5. Does this material reveal any security practices or procedures? ☐ YES ☒ NO

6. Does this information reveal any security practices or procedures? ☐ YES ☒ NO

7. Would release of this information be of economic benefit to a foreign entity, adversary, or allow for the development of countermeasures to the system or technology? ☐ YES ☒ NO

8. Does this material contain:

a. Any contract proposals, bids, and/or proprietary information? ☐ YES ☒ NO

b. Any information on inventions/patent application for which patent secrecy orders have been issued? ☐ YES ☒ NO

c. Any weapon systems/component test results? ☐ YES ☒ NO

d. Any ARL-originated studies or after action reports containing advice and recommendations? ☐ YES ☒ NO

e. Weakness and/or vulnerability information? ☐ YES ☒ NO

f. Any information on countermeasures? ☐ YES ☒ NO

g. Any fielding/test schedule information? ☐ YES ☒ NO

h. Any Force Protection, Homeland Defense *(security)* information? ☐ YES ☒ NO

i. Information on subjects of potential controversy among military services or other federal agencies? ☐ YES ☒ NO

j. Information on military applications in space, nuclear chemical or biological efforts: high energy laser information; particle beam technology; etc? ☐ YES ☒ NO

k. Contain information with foreign policy or foreign relations implications? ☐ YES ☒ NO

OPSEC Approval Statement

I, the undersigned, am aware of the adversary's interest in DOD publications and in the subject matter of this material and that, to the best of my knowledge, the net benefit of this release out weights the potential damage to the essential security of all ARL, AMC, Army, or other DOD programs of which I am aware.

J.W. Adams Jane Adams 09/25/2008

OPSEC Reviewer *(Printed name/signature)* Date

9. Space for explanations/continuations/OPSEC review comments

Final Release Clearances

32. Public/Limited release information

a. Material has been reviewed for OPSEC policy.

ARL OPSEC Officer Date

b. The information contained in this material is ☐ / is not ☐ approved for public release/ has received appropriate tech/editorial review.

Steven H. McKnight, Chief, Materials Division

Division Chief Date

c. This information is accepted for public release.

Public Affairs Office Date