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**IMPROVING THE MATERIAL PROPERTIES OF
BORON CARBIDE THROUGH ELEMENTAL
INCLUSION**

by

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**IMPROVING THE MATERIAL PROPERTIES OF BORON CARBIDE
THROUGH ELEMENTAL INCLUSION**

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ABSTRACT

Boron carbide (B_4C) is a modern ceramic designed as a lightweight, high-hardness material capable of defeating ballistic threats. B_4C is the third hardest ceramic known to man and has a density of 2.52 g/cm³. This ceramic is ideal for applications where the areal density is critical. A current issue exists where overmatched projectiles cause catastrophic failure during the impact with B_4C . Beyond the elastic limit of the B_4C , no additional strength hardening is observed. Recent publications relate this failure to an amorphous shear band. The shear band is formed when the B_4C is under compression and carbon atoms are released from the icosahedron, forming free carbon within a shear plane. This layer allows for trans-layer shearing of the icosahedra and collapse of the unit structure.

Prior research demonstrates that silicon (Si) is a preferred semimetal for elemental inclusion that can greatly increase the ductility and re-bonding of B_4C . The goal of this research is to both determine where the Si inclusion goes within the B_4C structure using X-ray diffraction, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, scanning electron microscope/energy-dispersive X-ray spectroscopy (SEM/EDS), and other techniques, and to perform equation of state studies on the materials to determine the variations in physical properties correlated to the inclusion of varied percentages of Si within the B_4C .

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LIST OF ACRONYMS AND ABBREVIATIONS

Al ₂ O ₃	Alumina
B ₄ C	Boron carbide
DFT	Density functional theory
DoD	Department of Defense
EDS	Energy-dispersive X-ray spectroscopy
ESAPI	Enhanced small arms protective insert
Fb	Beat frequency
HEBM	High-energy ball milling
HEL	Hugoniot elastic limit
HEOS	Hugoniot equations of state
NBR	None back reflecting
NIJ	National Institute of Justice
PDV	Photon doppler velocimetry
PYH	Post yield hardening
RHA	Rolled homogeneous armor
RTO	Real time oscilloscope
ROI	Region of interest
SAPI	Small arms protective insert
SEM	Scanning electron microscope
Si	Silicon
SiC	Silicon carbide
SIRHEN	Sandia InfraRed Heterodyne aNalysis
SS	Stainless steel
WC	Tungsten carbide
UHMWPE	Ultra-high-molecular-weight polyethylene
VOA	Variable optical attenuator
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

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I. INTRODUCTION

The development of personal armor systems typically addresses two main issues: the defined threat and the areal density of the protective system. In recent years performance of these armor systems has been at NIJ level IV protection. This level of protection requires the ability to defeat hardened steel armor piercing rounds. For this level of protection, a hard-front face surface must be integrated in order to blunt the incident hard sharp ogive of the incident threat. The most mass efficient approach to enable a hard-front face to the armor system is to integrate ceramics. Currently there are three primary ceramics used within personal body armor systems. These materials include alumina (Al_2O_3), silicon carbide (SiC) and boron carbide (B_4C). The densities of these three different ceramics vary greatly with Al_2O_3 having the highest density at 3.9 g/cm^3 whereas the lightest density is B_4C with a density of 2.52 g/cm^3 .

The application of B_4C offers a 35% reduction in the areal density of the hard-front face system. Two issues currently exist with the application of B_4C as a front face armor system. The first is the cost involved with hot pressing the ceramic powder to form these ceramic plates. The high manufacturing cost is related to the low transportability of the B_4C when being sintered into solid monolithic ceramic plates. To enable the forming of B_4C into ceramic plates having densities near theoretical maximum density (TMD) both high temperature and high pressure must be applied. This manufacturing process causes an increase in cost typically by a factor of 10. If an additive could be placed within the B_4C powder that would increase the mobility during sintering the cost could be greatly reduced.

The second and much more critical issue is the catastrophic failure of B_4C above the Hugoniot elastic limit (HEL). B_4C when impacted at pressures greater than the elastic limit ($\sim 20 \text{ GPa}$) forms graphite shear bands along a certain plane. The graphite shear bands are formed from the ejection of carbon atoms within B_4C 's carbon atoms located at a polar site within the icosahedron.

This catastrophic failure of the B_4C prevents applications to threats above NIJ level IV. This thesis will present a new approach to preventing the amorphous shear band

from forming through the elemental inclusion of silicon atoms. The silicon atoms have been shown to prohibit the formation of the amorphous shear band, and increase the toughness of the B_4C . Goddard et al. [1] theoretically demonstrated that replacement of the three-atom C-B-C chain, within the B_4C unit cell, with a new two atom silicon chain would enable a re-bonding of the altered B_4C unit cell.

Within this thesis a technique using high-energy ball milling (HEBM) will be incorporated to reduce the grain size of the B_4C , physically alter the molecular structure of B_4C through breaking bonds within the B_4C unit cell, and provide energy to enable Si atoms to be placed within the B_4C unit cell. Calculations have shown that the energy induced through HEBM can provide the energy to place Si within the B_4C unit cell. Through a study using density functional theory (DFT) [2] it was shown that, for the highest probability poly type of B_4C , the Si atom would be preferred the atom within the icosahedron polar site.

Within this thesis B_4C hot pressed discs of five different elemental inclusion variations will be formed. The variations will include: (1) as received B_4C powder, (2) high-energy ball milled B_4C , (3) the elemental inclusions using stoichiometric ratios equivalent to one atom inclusion, (4) two atom inclusion, and (5) a one atom inclusion of Si using a lower energy HEBM system.

All of the five different samples will be hot pressed at $2100^{\circ}C$ with an external pressure of 3000 psi. Analysis of each of the different samples will include: X-ray diffraction (XRD), scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, hardness, and density calculations. Once all of the samples have been characterized, each sample will be studied under high pressure impact using a single stage 40 mm powder gun using an impact velocity of approximately 2.0 km/s. Techniques to assess the physical changes of impact include pressure gauges and Photon Doppler velocimetry (PDV). Both techniques in combination with shorting pins will identify the impact velocity, the planarity of impact, and the physical response to the high-pressure impact. As the pressure within the different B_4C samples increases above the Hugoniot-elastic limit (HEL) the shear band failure can be observed through a drop at the cusp where the elastic/plastic transition

occurs. Based on the initial conditions of the material and the impact response of the different samples, the performance of the ceramics can be determined related to the amorphous shear band failure, and enable a new approach to developing B₄C as a viable front face material for threats above NIJ level IV.

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II. INTRODUCTION TO PERSONAL BODY ARMOR SYSTEMS

Current personal body armor protection systems used within the DOD are designed to defeat rifled projectiles with the highest mass efficiency. Armor systems are typically constructed of a front face monolithic ceramic plate backed by a high performance textile system [3]. Many of these systems can achieve mass efficiencies near to or greater than a factor of four compared to rolled homogeneous armor (RHA) [4]. Based on the threat design, alterations to the ceramic plate typically maintain the same chemistry but increase or decrease the thickness of the ceramics to defeat a specific threat level [5]–[9]. In a similar fashion to the ceramics, the textile backing system performance can be altered by the number of textile layers as well as the manufacturing process and fabric orientation applied to the armor system [10].

The basic concept of this type of personal protection armor is to enable the front face system (ceramics) to both slow down as well as blunt/breakup the incident projectile. The impact pressure is equal to the projectile force (during deceleration) divided by the incident projectile area. If the ceramic plate can either blunt or break up the incident projectile, the surface area of the projectile will be increased reducing the impact pressure incident on the textile armor [11], [12].

A armor textile fabrics have a very high mass efficiency but when a sharp ogive projectile is encountered the impact pressure typically exceeds the textile tensile strength and premature failure occurs [13]. The primary objective of the front face ceramic system is to reduce the incident pressure on the armor textile fabrics to enable the textile backing system to fully arrest the incident projectile.

Current textile armor systems include aramid fibers commonly known as Kevlar and ultra-high-molecular-weight polyethylene (UHMWPE). UHMWPE physical properties and performance exceed Kevlar. The two current trade names for UHMWPE are Dyneema and Spectrashield. UHMWPE fabric layers incorporate a two-dimensional weave where each layer of textile filaments form a repeating structure of 0° and 90° (repeated twice per layer). To obtain the highest performance of this type of textile armor

the material must be heated to a temperature of approximately 250°C and pressed to a pressure above 3000 psi [10]. A drawback to the use of UHMWPE is that the textile system, after being heated and pressed, is a non-compliant system (very rigid) unlike Kevlar which can be very compliant, Figure 1.



Figure 1. Image of a pressed UHMWPE textile armor backing system.

When a properly designed hard front face system is able to alter the incident front face surface impact area, the textile armor system can be very mass efficient. The specific conditions are related to the pressures encountered by the textile armor system when the projectile first impacts the filaments [13]. Both the type and amount of material required within the textile armor system is dependent on the performance of the front face armor system.

The optimized mass efficiency of the composite personal armor system must incorporate a study optimizing the variation in the front ceramic system and the textile backing to increase mass efficiency.

There are two common protective plates currently in use within the Department of Defense to support warfighters in combat environments. The first plate introduced was the small arms protective insert (SAPI) and the more recent enhanced small arms protective insert (ESAPI). The SAPI plate was introduced to defeat NIJ level III threats. NIJ level III threats consist of a M80 projectile (7.62x51 ball round) incident at muzzle velocity [14]. The ESAPI plate was later introduced as an upgrade to the SAPI plate where the penetration

resistance performance was upgraded to defeat NIJ level IV threats (0.30 caliber M2AP projectiles), Figure 2.

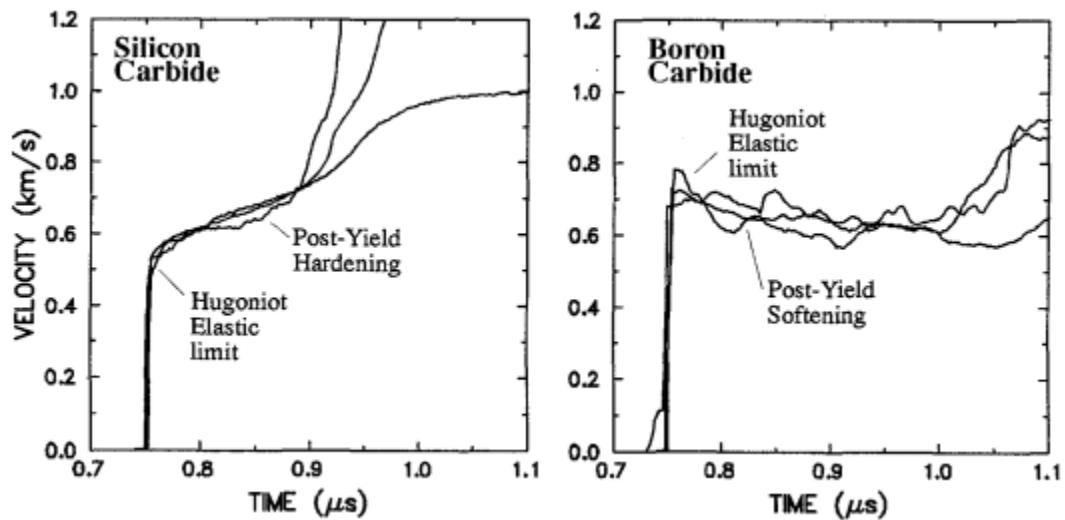


Figure 2. ESAPI personal armor plate.

Both ESAPI and SAPI plates can be constructed using either SiC or B₄C ceramics for the front face of this protection system. Both systems will defeat the threat projectiles that it was designed to defeat but the B₄C will have a lower areal density. Currently the Department of Defense (DoD) is interested in developing a higher performance protective plate to defeat threats above NIJ IV [15]. To defeat threats above NIJ IV only SiC ceramics

can be used. When B_4C is impacted above the HEL catastrophic failure occurs, Figure 3 [16]–[18].

The failure within the B_4C occurs due to the formation of amorphous graphite layers. The ejection of carbon atoms from the polar sites of the icosahedron accumulate within certain planes [19]. This causes amorphous shear band failure; armor engineers are unable to incorporate B_4C into these higher performing protective plates and are forced to use the heavier SiC .



For SiC beyond the elastic limit a hardening behavior can be observed whereas in B_4C beyond the elastic limit a strain softening occurs. Comparison of HEL of SiC and B_4C .

Figure 3. A visual comparison of the impact response of SiC (left) and B_4C (right). Source: [20].

III. INTRODUCTION TO BORON CARBIDE

B_4C is the third hardest material known to man [21] with properties softer than only diamond and cubic boron nitride. B_4C has a rhombohedral crystallographic structure with a unit cell comprising an icosahedron connected through a three-atom linear chain, Figure 4 [21]. While the nominal structure has twelve B atoms in the icosahedron and three C atoms in the chain, density functional theory (DFT) calculations of B_4C have shown that at least six polytypes exist, the polytype compositions differ in the placement of B and C within both the icosahedra and chain structures [21]. The difference in energies between the three most probable polytype structures are within 0.2 eV/atom [21]. The three highest populated polytypes include $B_{11}C^p$ -CBC (p indicates polar site), B_{12} -CCC, and B_{12} -CBC, and constitute up to 95% of B_4C , Figure 5 [21].

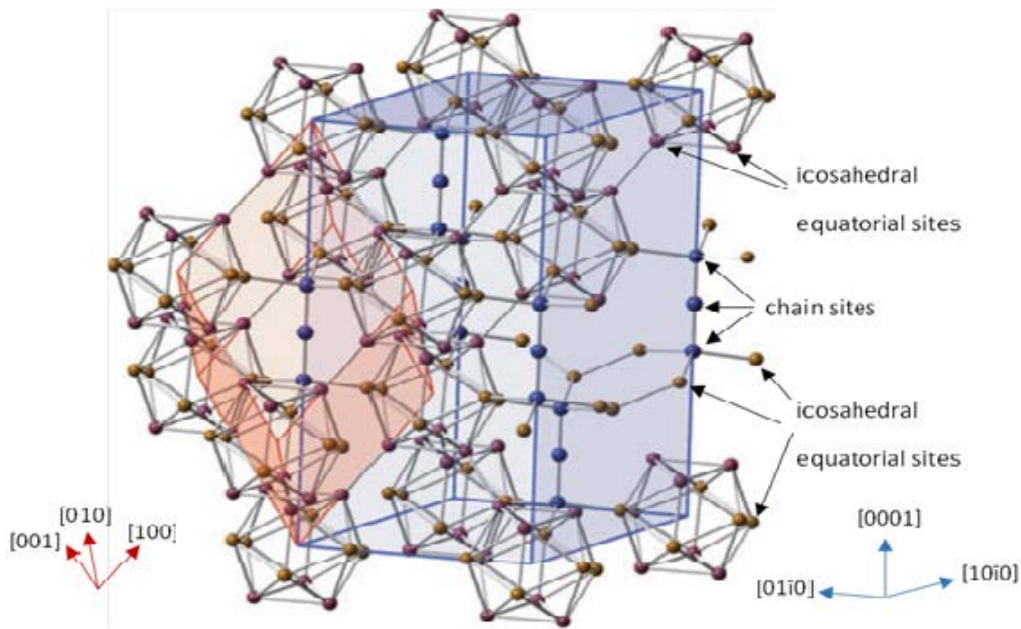
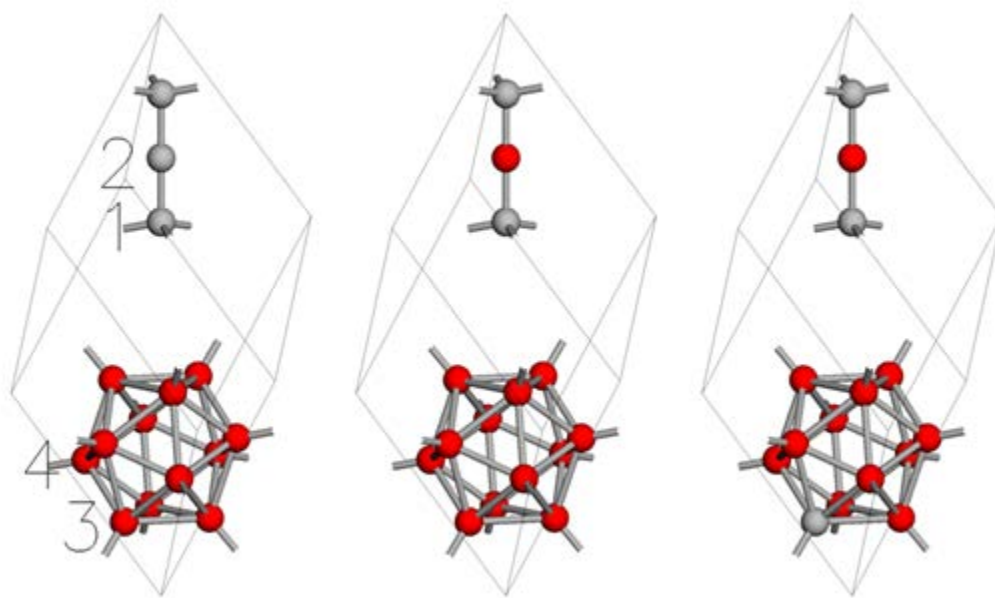


Figure 4. B_4C structure incorporating rhombohedral unit cell (red) and the larger hexagonal structure (blue). Source: [21].



The labels on the B_{12} -CCC structure show (1) the chain end, (2) chain center, (3) icosahedral polar, (4) and icosahedral equatorial substitutional sites.

Figure 5. The three polytypes B_{12} -CCC, B_{12} -CBC, and $B_{11}C^p$ -CBC, with primitive cells boron (B) represented by red spheres and carbon (C) represented by grey spheres. Source: [21].

B_4C has a high compression strength of 3900 MPa [22], a HEL of 18–20 GPa [23], and a density of 2.52 g/cm³ [2]. As mentioned previously when impacted at pressures above the HEL B_4C softens unlike SiC that demonstrates a compressive hardening beyond the HEL, Figure 3. This softening behavior within B_4C prevents many applications where increased strength above the HEL is required [17], [20], [24], [25], [26]. The softening behavior of B_4C above the elastic limit is currently explained by the formation of amorphous shear bands leading to catastrophic failure [15], [27], [28]. Multiple explanations of the amorphous shear band exist including the bending of the three-atom chains and crosslinking or breakup of the icosahedra [27], [28]. The specific details of the failure mechanisms are still uncertain but the ability to change the chemical bonding structure of B_4C may change the current amorphous shear band formation preventing the currently observed catastrophic failure. The possible insertion of various elements into the lattice could therefore have an effect on the molecular response to high impact pressures.

Elemental alterations of the three-atom chain are likely to affect chain bending, bonding of the chain to the icosahedra and conversion of the C-C-C chain variety to amorphous carbon [28]. In addition, possible replacements of the current carbon polar site within the icosahedron could reduce/prevent the release of carbon forming the amorphous shear band.

DFT

Density functional theory (DFT) incorporates a quantum mechanical approach to investigating the electronic structure of many atom systems within the solid phase to determine physical properties through lowest energy positioning. In particular, DFT can investigate both material physical performance as well as the investigation of elemental inclusion.

A previous study was performed by using libAtoms/QUIP and VASP DFT program to investigate the ability to introduce seven different elemental inclusions within B_4C [2]. One of the seven elements was Si. For the three most probable polytypes, within B_4C , the energies to incorporate Si at the four possible locations (Figure 5) are presented. For Si, DFT predicts elemental inclusion locations at the chain center only for B_{12} -CCC and the polar location for both $B_{11}C^p$ -CBC and B_{12} -CBC polytypes. As the $B_{11}C^p$ -CBC represents ~90% of the B_4C polytypes the majority of Si is expected to reside in polar locations within the icosahedron.

Table 1. Energies for substitution in B₄C lattice. Source: [2].

Structure	Element	Chain center	Chain end	Equatorial	Polar
B ₁₂ -CCC	Be	0.0	6.2	3.0	3.7
	N	0.44	0.0	1.7	1.8
	Mg	0.0	3.6	3.5	3.7
	Al	0.0	4.1	2.9	2.9
	Si	0.0	2.4	2.9	2.0
	P	0.0	0.06	1.9	0.6
	S	1.5	0.0	3.7	2.8
B ₁₂ -CBC	Be	0.0	1.6	2.7	2.8
	N	4.1	0.0	4.4	3.7
	Mg	0.0	1.4	2.7	2.6
	Al	0.0	0.9	2.3	1.8
	Si	0.3	3.3	0.6	0.0
	P	1.4	0.0	1.6	0.7
	S	1.2	0.0	2.3	1.7
B ₁₁ C ^P -CBC	Be	0.0	0.9	1.5	1.5
	N	2.1	0.0	1.9	1.4
	Mg	0.0	0.6	2.1	1.0
	Al	0.0	1.9	1.1	0.3
	Si	2.3	3.6	2.9	0.0
	P	2.2	1.3	1.6	0.0
	S	0.9	0.0	1.4	0.3

Relative energy (eV) for substituting seven presented elements within B₄C lattice sites for the three most probable polytypes of B₄C performed using DFT. All energies are relative to lowest energy site for a given structure and element.

Goddard et.al [1] performed a theoretical study related to the elemental inclusion of two silicon atoms to replace the existing CBC/CCC chain. Within this study through the replacement of the existing CBC/CCC chain with a two atom Si chain a re-bonding mechanism exists. Through molecular dynamics (MD) simulations of shear dissociation of the B₄C with the elemental inclusion of two Si atoms replacing the interconnecting linear chain within the B₄C. The re-bonding occurs as the initial Si – Si linear chain is broken and re- bonding of the Si chain to new sites within the icosahedron occur. This re-bonding supports an increase in toughness as an increase in elongation occurs within this two-stage re-bonding process.

As observed within Table 1, a total of seven different elements were investigated as elemental inclusions within B₄C using DFT. The lowest energy state of the seven

elemental inclusions varies in location between the chain center, chain end and polar and equatorial positions within the icosahedron. As $B_{11}C^P$ -CBC represents 90% of the polytypes within B_4C , the elemental inclusion locations of each of the seven locations for this polytype supports the most probable location.

The motivation within this thesis is to introduce an elemental inclusion of Si to prevent the currently observed amorphous shear band failure. Multiple mechanisms support the ejection of carbon atoms enabling the formation of carbon layers within a shear plane. The most probable mechanism is the multistage breakdown of the B_4C enabling the ejection of the carbon atom located within the polar location within the icosahedron [18]. As the Si atom has the same preferred location as the polar C within the icosahedron the ability to replace the C atom with the Si may greatly reduce the amorphous shear band failure.

There are limited approaches to enable the elemental inclusion to B_4C . Heating B_4C under atmospheric pressures to temperatures $> 1100^\circ\text{C}$ will result in the dissociation of the boron and carbon. Current wet chemistry efforts have not demonstrated a method to enable elemental inclusion of Si within the B_4C unit cell.

One technique that can support the elemental inclusion of Si is through HEBM [29]. HEBM enables otherwise unachievable chemical reactions through the mechanical transfer of energy via kinetically energized spheres of assorted sizes through collisions with the powder. Energies can support placement of Si atoms within the interstitial positions of the B_4C unit cell. In addition, HEBM enables lower temperatures preventing any dissociation of C from B_4C .

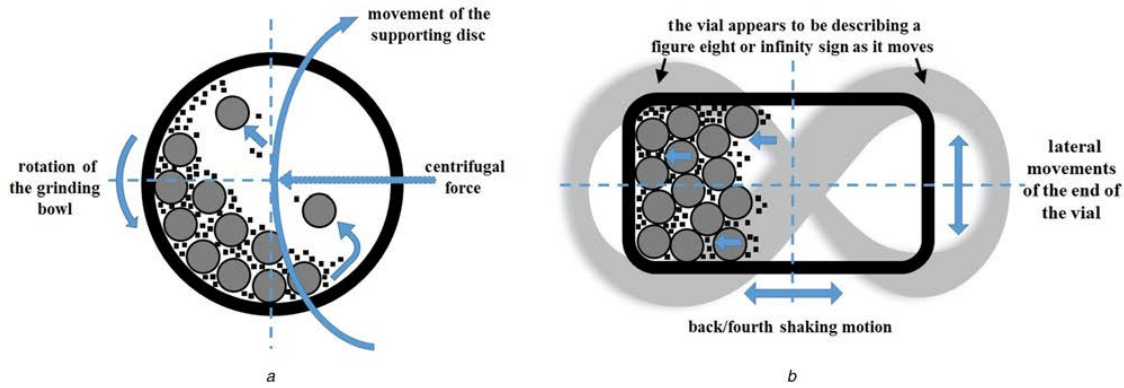
Elemental inclusion of Si within B_4C will be investigated for inclusions representing 1 atom, 2 atom, 3 atom, and 5 atom elemental inclusions as well as comparison of HEBM B_4C where smaller grain sizes may also support prevention of the amorphous shear band failure through reduced grain sizes.

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IV. EXPERIMENTAL DATA

A. HIGH-ENERGY BALL MILLING Si INTO B₄C

HEBM is a process that imparts kinetic energy into a powder of interest through kinetic collisions of the grinding media (spheres) colliding with the powders both with the ball mill chamber walls and the grinding media. HEBM can be effective both at reducing the powder grain size and enabling chemical reactions including cold alloying [30]. Figure 6 shows two of the prevalent types of HEBM, tumbler(a) and vibratory mills (b). The Retsch and SPEX are both vibratory mills [29].



The Retsch and SPEX are both vibratory mills.

Figure 6. Two of the prevalent types of HEBM: Tumbler (a) and vibratory mills (b). Source: [29].

Reduction of grain size supports three key points of interest within this thesis including: material strength (Hall Petch), reduction in the propagation dimensions of shear band formation and the reduction in particle size to support elemental inclusion within the B₄C unit cell.

Mechanically, small grains are stronger and more ductile than large grains [31]. As purchased B₄C powders from Electro-Abrasives, Buffalo NY were ball milled both with and without elemental inclusions of Si to study the variation in performance of both

reduced grain size alone and with the inclusion of Si atoms. It should be noted that the post ball milled grain size will increase during the hot pressing of the B₄C powders to the discs.

HEBM provides a mechanism to enable energies to place Si atoms within interstitial locations identified using DFT [2]. Under normal thermal heating to enable temperatures providing energies to enable Si atoms to reach calculated locations within the unit cell would cause the dissociation of B₄C. Temperatures above 1100°C have been shown to leach carbon from the B₄C lattice creating a phase separated structure of B₄C and SiC [2].

The goal within this thesis is to enable the formation of a single-phase ceramic structure B₄C:Si. HEBM keeps the macro temperature of the sample around 200°C to 400°C while the individual collisions have temperatures around 1500°C [32]. This allows for a micro alloying of the B₄C with the Si that maintains the overall integrity of the B₄C lattice while creating defects within the B₄C supporting elemental inclusion of the Si within B₄C [2].

The alloying process forming the B₄C:Si alloy incorporated the as bought B₄C powder with pure Si using chemically pure (undoped) Si wafers. The stoichiometry of B₄C:Si was defined by the atomic inclusion of Si within the B₄C unit cell where ratios from 0 to 5 were studied. The mass ratio of the elemental inclusion of one Si atom is presented below.

$B_4C + Si \rightarrow B_{12} + 2C + Si + C$, with atomic masses of B: 10.811, C :12.01, Si: 28.08.

Choosing to ratio based on B₁₂C₃;

$$12 * 10.811 + 3 * 12.01 + = 165.7g.$$

This dictates our alloy ratio, $28.08g/165.7g = 0.169$, one Si atom for every B₄C atom.

This simple alloy ratio sets the frame work for all of our alloyed samples, samples were produced in atomic concentrations of Si; 0, 1, 2, 3, and 5. Previously conducted work by other parties utilized an atomic concentration of 0.33. Their analysis showed ~15% substitution of available B₄C cells [2].

In order to produce the alloys needed for ceramic production two HEBM were utilized. Initially a Retsch Cryo Mill with a 50ml internal volume stainless steel reaction vessel was used. It was loaded with Tungsten Carbide spheres (WC) of varying sizes ranging from 9mm to 3mm, Tables 2, 3, and 4 have the total spheres utilized per run to ensure completeness of alloying [33]. It was found that sample mass to grinding media mass ratio of 1:8 worked best. Previous work utilized the same mill and reaction vessel but relied on stainless steel (SS) media with a ratio of 1:10. Duty cycles for the mill was 30Hz for 90 minutes, three times per sample as utilized in previous work [2].

The first powder prepared was the 5 atom ratio of Si to B₄C per unit cell. To produce the 135g of powder required for this one sample took twenty one individual batches for a total sample production time of 94.5 hours. Table 2 shows a typical load and the masses associated with one batch for the 5 atom sample.

Table 2. Typical 5 atom batch for the load cell.

5 Atom													
Date	Sample #	B4C (g)	Si (g)	9mm	6mm	5mm	3mm	Hz	T (min)	Cycle1	Cycle 2	Cycle 3	Note
7/18/2019	1m	3.75	3.01	4	14	12	12	30	90	1128	1305	1520	Broken Bolt
Total (g):	135												

Issues occurred during the initial runs using the Retsch HEBM. During the initial nine batches of the 5 atom sample, the mill began to break down. The system design of the Retsch was poor in that it utilized a tapered bolt to hold the counter weight to its secondary oscillator arm. The bolt continuously sheared requiring replacement and the loss of the batch as grinding consistency was lost. It was decided to pre-emptively replace the failing bolt every sixth run. From batch 10 to 21 this method worked to keep the mill operating properly. The only issue suffered was the loss of the power supply and it was replaced with an external Hewlet Packard 6286A DC Power Supply.

The second sample produced in the Retsch was a 1 atom sample this sample would only require seventeen batches to produce. Table 3 shows a typical load for one batch of 1

atom. The batch shown in Table 3 shows approximately a two-month gap. This is when the Retsch began to suffer multiple catastrophic failures.

Table 3. Typical load for 1 atom sample.

1 Atom													
Date	Sample #	B4C (g)	Si (g)	9mm	6mm	5mm	3mm	Hz	T (min)	Cycle1	Cycle 2	Cycle 3	Note
8/9/2020	2p	6.01	1.01	4	14	12	12	30	90	1335			Broken Bolt
10/4/2019	2p										1050	1625	
Total (g):	126												

Note the two month gap, this is indicative of a machine wearing out from use. The mill required extensive repair to finish this sample.

Due to the existing design issues for the Retsch HEBM, a second HEBM was purchased (dual arm SPEX 8000). The SPEX was able to run at a higher frequency (60Hz), and was able to ball mill with two vessels concurrently. The two stainless steel vessels were each 65ml in volume and both utilized WC spheres as the grinding medium.

Using the SPEX HEBM, the production output was increased by a factor of four. One batch now contained twice the total mass and could be done in half the time. With twice the speed at 60Hz and doubling of the forces sample grind time could be reduced to three 45 minute cycles. This allowed the new samples to be produced in eight batches in 18 hours.

With the SPEX mill, the 0 atom, 1 atom, 2atom and 3 atom powders were produced. It should be noted that a duplicate one atom was produced so the Retch and SPEX 1 atom powders could be compared for variation.

Table 4 shows typical loads for each of the samples produced. The C in the third column for time is for continuous milling with 90m delineating 90 minutes of run time. The SPEX can only be set to run for a maximum of 90 minutes. Needing three 45 minute cycles made it easy to break up. It was hoped that the increased duration of the interval would produce a more complete alloying and finer overall grain structure.

Table 4. Typical loads for the SPEX mill across all three samples.

0 Atom														
Date	Sample #	L: B4C (g)	L: Si (g)	R: B4C (g)	R: Si (g)	9mm	7mm	5mm	3mm	Freq (Hz)	Time (min)	1	2	3
8/12/2019	1	8.06	0	8.08	0	6	11	10	9	60	45	845	850	955
Total (g):	132													
1 Atom														
Date	Sample #	L: B4C (g)	L: Si (g)	R: B4C (g)	R: Si (g)	9mm	7mm	5mm	3mm	Freq (Hz)	Time (min)	1	2	C
8/27/2019	1	6	1.03	6.01	1.02	6	11	10	9	60	45	805	850	90m
Total (g):	112													
3 Atom														
Date	Sample #	L: B4C (g)	L: Si (g)	R: B4C (g)	R: Si (g)	9mm	7mm	5mm	3mm	Freq (Hz)	Time (min)	1	2	C
9/17/2019	1	4.51	2.29	4.49	2.3	6	11	10	9	60	45	845	850	90m
Total (g):	126													

Of note is the continuous 'C' for the second interval of 90 minutes delineated with 90m.

During the SPEX HEBM process, the 6mm and 5mm WC spheres were found to be fractured into two clean semi-spheres during a run. This fracture was rare in the Retsch but was typical for the SPEX, generally requiring the replacement of one sphere per batch per vessel.

When the switch to the SPEX HEBM was made there became a question of equivalency and comparison. Previous work done with this method utilized the Retsch mill with SS media [2]. Our HEBM efforts made two pivots to WC media and then to a mill with twice the speed. To compare the effect of the mills and media on the B₄C a Matlab code was written to compare the impact velocities of the mills and media to determine the pressures and forces being generated and the amount of work being done.

We began by taking the Hugoniot Equations of State (HEOS) for B₄C, WC, and SS. Using the Hugoniot Equation of State (HEOS) we have the relation of the shock velocity U_s to the particle velocity u_p as:

$$U_s = a + (b \cdot u_p); \quad \text{Eq 1}$$

U_s = shock velocity (m/s), a = Sound speed (m/s), b = index multiplier on the particle velocity, u_p = particle velocity (m/s)

$$\text{B4C: } U_s = 5170 + 2.78 \cdot u_p, \quad \text{Eq 2}$$

$$\text{WC: } U_s = 4930 + 3.09 \cdot u_p, \quad \text{Eq 3}$$

$$\text{SS: } U_s = 4722 + 1.441 \cdot u_p. \quad \text{Eq 4}$$

We then insert these HEOS into the Hugoniot momentum conservation equation that relates shock impedance and particle velocity to the pressure at impact.

$$P = \rho_o \cdot U_s \cdot u_p, \quad \text{Eq 5}$$

where ρ_o is the initial density of the material prior to being shocked. We substitute in our HEOS and develop:

$$P = \rho_o \cdot (a + b \cdot u_p) u_p. \quad \text{Eq 6}$$

This equation develops the right hand Hugoniot curve representing the incident material, a second back facing curve from the left representing the target material is used to enable location of the value of matching impedance satisfying the impact of the two materials at the impacting velocity. As the point of impact shares the same pressure, having the impedance enables calculation of the impact pressure.

$$P = \rho_o \cdot a + (b \cdot (u_r - u_p)) \cdot (u_r - u_p) \quad \text{Eq 7}$$

$$u_r = u_p \text{ and } \rho_o = \text{density (kg/m}^3\text{)}$$

It is important to point out here that the densities used in Eq 6 and Eq 7 are not necessarily the same. We are interested in the pressure the powder sees from the media.

The function was then plotted in Matlab and the resulting pressures annotated. To find the forces we calculated the contact area between the hard spheres [34]. The radius of that contact circle can simply be determined with the following equation.

$$1/R = 1/R_1 + 1/R_2, \quad \text{Eq 8}$$

where R_1 = radius 1st sphere, R_2 = radius 2nd sphere, R = radius of circular contact. Usefully rearranged provides,

$$R = (R_1 * R_2) / (R_1 + R_2). \quad \text{Eq 9}$$

This allows for us to find the forces through the pressure.

$$F = P * A = P * (\pi * R^2) \quad \text{Eq 10}$$

The next step is to determine the force across an individual B₄C unit cell. This will allow us to determine how much work is performed on the powder at the particle level. Our powder as delivered had a 720 nm radius. We then determine how many as delivered particles fit in the contact circle and determine the force per particle.

$$N_p = A / A_{B_4C} = A / (\pi * R_{B_4C}^2), \quad \text{Eq 11}$$

where N_p = number of particles in the contact patch, then the force per particle becomes,

$$F_p = F / N_p. \quad \text{Eq 12}$$

With the force per particle determined, we can determine the work done per particle.

$$W_p = P_p * 2R_{B_4C}, \quad \text{Eq 13}$$

where W_p has units (J/m²).

$$P_p = F_p / A_M, \quad \text{Eq 14}$$

P_p is pressure per particle, and A_M = contact area between medium and particle assumed to be spheres.

The goal is to determine the work per unit cell of sample and compare the energy relative to both the impacting material and milling speed. Table 5 shows that the forces involved when going from SS to WC are not trivial and as expected provide a large gain to the work being done on the sample.

Table 5. Work done on powders by the HEBMs.

		Retsch, up = 3m/s			Spex, up = 5.5m/s		
	Units	B4C:B4C	B4C:SS	B4C:WC	B4C:B4C	B4C:SS	B4C:WC
Pressure	Mpa	20	29	33	40	50	59.8
Force	μN	0.0814	0.472	0.537	0.162	0.8143	0.974
Work	J/m^2	2.88	4.176	4.752	5.7	7.2	8.612

*The forces and pressure markedly increased with a change in media and milling speed.

These numbers represent the first strike of the hammer and are sufficient to overcome the known fracture surface energy of B₄C, 3.27 J/m² [35] and the work separation energy required to break bonds [35]. While our calculations are a first order approximation of the mechanics involved, they provide a good first look at what process is taking place as the sample is milled. Additional results will be discussed related to the observed effects of the alloying and the prolonged milling on the samples.

B. X-RAY DIFFRACTION (XRD)

For our work the value that XRD provides is the ability to evaluate the lattice parameters of the powders and crystallite size. XRD works by taking an X-ray source and shining a monochromatic beam onto the crystalline material at a known angle. Because the lattice spacing in the crystals is similar to the wavelength of X-rays the lattice acts as a three-dimensional diffraction grating. As the relative source, sample or both is moved, the angle changes. The reflected X-rays are formed into a diffraction pattern and collected within an X-ray detector at a known angle. Some angles produce peaks while others produce nulls within the diffraction pattern. The collected patterns are unique to each element and material allowing for the determination of lattice parameters, crystallite sizes, peak shift, and other scientific insights of value.

The X-ray analysis of the alloyed powders was performed using a Rigaku MiniFlex 600 X-ray Diffractometer, with data processing using Rigaku's PDXL software, and ICDD PDF-4+ 2019 data base. All samples were subjected to the same run profile and Rietveld analysis. Table 6 shows prior work done by [2] demonstrating the expansion of unit cell

volume to include the marked length increase in the c axis, and the reduction of crystallite size due to HEBM with steel media

Table 6. XRD lattice parameters from prior work. Adapted from [2].

Sample	a(A)	b(A)	c(A)	V(A ³)	% ΔV	Crystallite Size (A)
B4C	5.59737	5.59737	12.07149	378.2	0.445	314
0.33 Atom R	5.60561	5.60561	12.08961	379.89		242

Gamache, DB card # 01-075-0424

*Prior work demonstrating the expansion of unit cell volume to include the marked length increase in the c axis, and the reduction of crystallite size due to HEBM with steel media [2].

It should be noted that there are three main differences between the current work and the work performed at the NRL which we are currently comparing. The differences include application of a denser grinding media (WC), a higher milling frequency, and the inclusion of higher percentages of Si.

As presented in the HEBM section this equates to a larger amount of work performed on the powders. Table 7 shows the initial processing of our data utilizing the same database card as previously performed by NRL [2]. This was done to provide a more direct comparison to the previous work. It is worth noting that the Retsch milled sample shows a volume increase of approximately 20% greater than the NRL studies but the crystallite size is approximately ten percent smaller.

Table 7. XRD-determined lattice parameters of samples.

Sample	a(A)	b(A)	c(A)	V(A ³)	% ΔV	Crystallite Size (A)
B4C	5.601	5.601	12.049	327.3	0.52	232
B4C Milled S	5.605329	5.605329	12.09152	329.01346		161
1 Atom R	5.607668	5.607668	12.08909	329.22212	0.58	217
1 Atom S	5.606313	5.606313	12.08865	329.05094	0.53	168
2 Atom S	5.551	5.551	12.14	324	-1.008	198

DB card # 01-075-0424

*Initial processing of sample data utilizing database card referenced in previous work [2].

Table 8 shows a card chosen by fit, this was to ensure that the fit was optimized for its own evaluation independent of previous studies and not just a direct comparison to previous work. It is worth noting that the best fit card has an initial sample unit cell volume within 0.4 percent of the previous card within the NRL paper [2]. The crystallite sizes are extremely close as well. The one point of divergence is the change in unit cell volume that is reduced (except the 1 atom R).

Table 8. XRD-determined lattice parameters of samples using best fit.

Sample	a(A)	b(A)	c(A)	V(A ³)	% ΔV	Crystallite Size (A)
B4C	5.603261	5.603261	12.08222	328.5178		232
B4C Milled S	5.604193	5.604193	12.09314	328.92425	0.124	161
1 Atom R	5.609344	5.609344	12.1073	329.91487	0.423	217
1 Atom S	5.60573	5.60573	12.09519	329.16035	0.195	172
2 Atom S	5.553	5.553	12.13	324	-1.375	200

DB card # 04-004-5365

*Card chosen by best fit to optimize data for its own evaluation. Chosen card has an initial sample unit cell volume within 0.4 percent of the previous card. Crystallite sizes are extremely close. One point of divergence is the much-reduced level of change in unit cell volumes. Exception being the 1 atom R within five percent of previous work.

The last data point of interest on Tables 7 and 8 are the negative volumes of the 2 atom samples when compared to the original un-milled B₄C powder. The decrease in volume will be discussed the analysis section.

C. XPS

X-ray Photoelectron Spectroscopy (XPS) enables chemical identification including both elemental and molecular information (bonding). Within XPS the sample of interest is illuminated with monochromatic X-rays, typically Al K α or Mg K α . When the X-rays interact with the surface of the sample of interest, photoelectrons are emitted from the surface in response to the incident X-rays. The kinetic energy of the emitted electrons is characteristic of the element as well as the bonding of the element with other elements (molecular bonding).

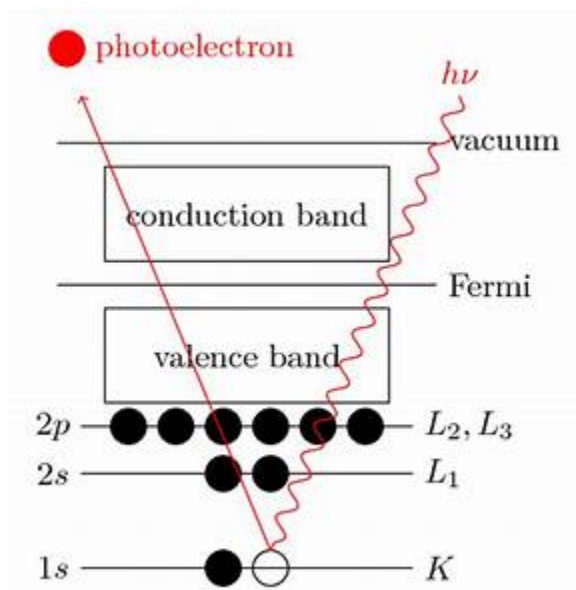


Figure 7. Photoelectron ejection due to incident characteristic X-ray.

Figure 7 presents an example of a photoelectron emitted from the K shell of an element with a studied sample. In XPS an incident characteristic X-ray causes the ejection of an electron from the K shell plus a photon. The kinetic energy of the ejected electron is characteristic of both the element and binding energy of the surrounding environment.

XPS has a limited sampling depth of 10 nm where beyond this depth, the electrons tend to be scattered as they exit the sample surface. Due to the sensitivity of the emitted electrons to scattering the XPS procedure must be performed in an ultra-high vacuum (UHV) having pressure below 10^{-9} Torr. In addition, XPS can only identify elements with atomic numbers > 2 .

The position and intensity of the peaks in an energy spectrum provide both the chemical state and quantitative information related to atomic percentages. XPS enables elemental identification as well as both the type of bonding and atomic percentages.

Using XPS, studies of delivered B₄C powder, ball milled B₄C, and elemental inclusion of Si including stoichiometric equivalents to 1 atom and 2 atom stoichiometries were studied.

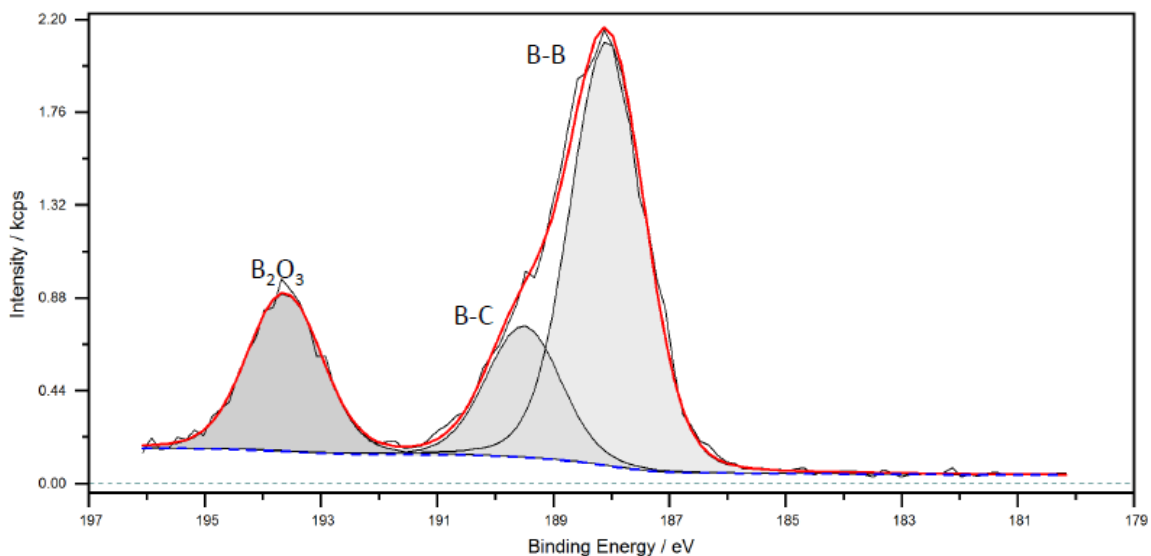
1. Un-milled B₄C Powder

The un-milled B₄C powder consists of the as bought powder from Electro-Abrasives in Buffalo, NY. The average particle size is near 700nm. It should be noted that using XPS, the only region observable is the outer 10nm surface. Due to this we expect a larger abundance of oxygen within the analysis.

From Table 9 and Figures 8 through 10, the primary elements observed of the as bought B₄C were: boron (B), carbon (C) and oxygen (O). From the analysis over 30% of the observed elements were oxygen. The oxygen was found to be bonded to both B (B₂O₃) and C (CO). With the analysis of the carbon bonding 5.91% is associated with bonding to B and 5.63% to C representing both free carbon (graphite) and the lower probability polytype where all three C atoms represent the 3-atom chain. For B 33.23% of all of the material represents B-B bonds and 10.26% of the material represents B-C bonding for both the polar and equatorial B positions.

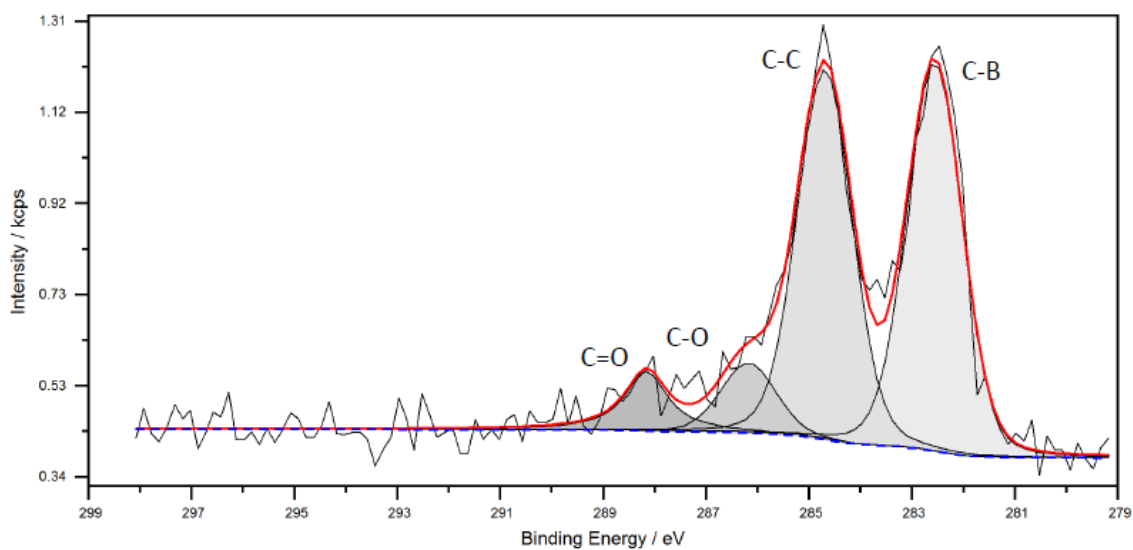
Table 9. Atomic quantification of elements including relative bonding for un-milled B₄C powder.

	Peak name	E _B /eV	Area/cps·eV	Sens. Fact.	Norm. Area	Quant./at.%	
B-B B-C B ₂ O ₃	B1s Scan Peak 1	188.07	3401.3669	10.449	325.52080	33.23	55.74
	B1s Scan Peak 2	189.52	1049.7569	10.439	100.56106	10.26	
	B1s Scan Peak 3	193.63	1252.5441	10.439	119.98698	12.25	
C-B	C1s Scan Peak 1	282.56	1177.5289	20.32	57.949257	5.91	13.59
C-C	C1s Scan Peak 2	284.69	1119.5253	20.29	55.176212	5.63	
C-O	C1s Scan Peak 3	286.18	212.95952	20.27	10.506143	1.07	
C=O	C1s Scan Peak 4	288.17	193.67695	20.27	9.5548570	0.98	
	O1s Scan Peak 1	533.23	15027.567	50.015	300.46120	30.67	30.67



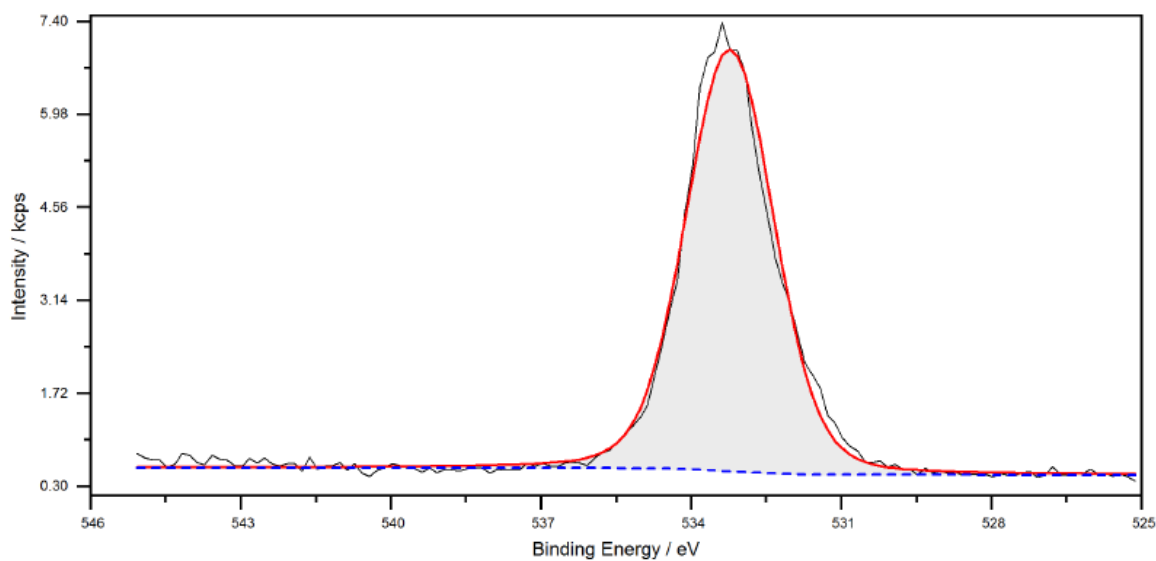
The primary bonding was the B-B bonding representing 33.23% of the observed elements followed by the B-O peak representing 12.25% and the remaining B-C bonds represent 10.26%.

Figure 8. Plot of the energy peaks of the B-O, B-C, and B-B bonding.



The primary bonding was the C-B bonding representing 5.91% of the observed elements followed by the C-C peak representing 5.63% and the remaining C-O bonds represent 2.05%.

Figure 9. Plot of the energy peaks of the C-O, C-C, and C-B bonding.



It should be noted that a higher average of O is observed due to the inability of XPS to probe deeper than 10nm.

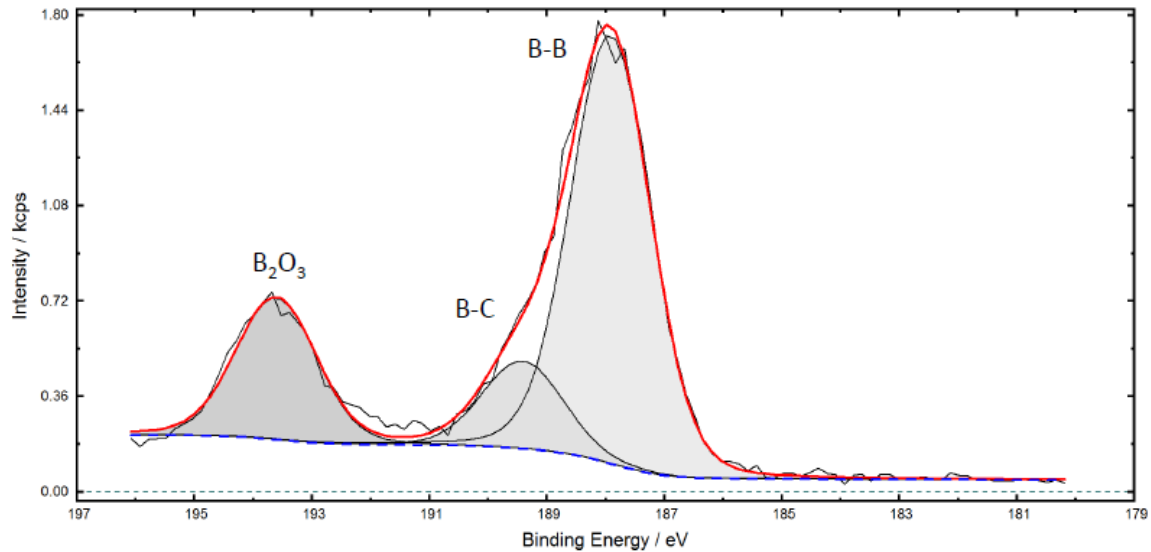
Figure 10. Plot of the O peak representing 30.67% of the overall elemental percentage.

2. Milled B₄C Powder

The milled B₄C powder consists of as bought powder from Electro-Abrasives in Buffalo, NY. The ball milling was performed using WC solid spheres of various sizes to reduce the grain size. The average particle size is near 18nm.

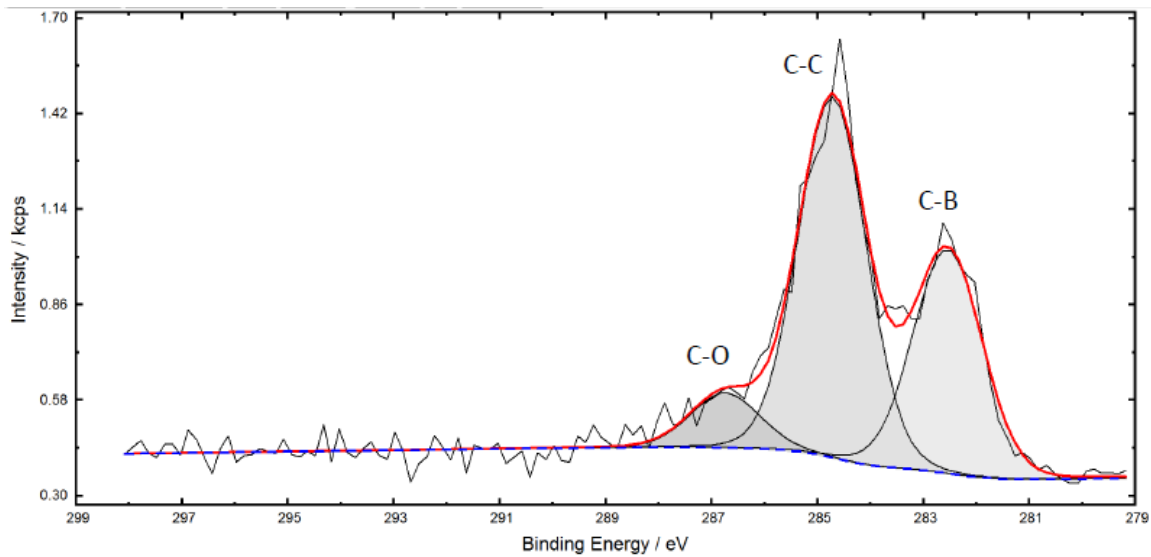
From Table 10 and Figures 11 thru 13, the primary elements observed were: B, C and O. From the analysis 29.45% of the observed elements was oxygen. The oxygen was found to be bonded to both B (B₂O₃) and C (CO). With the analysis 6.04% is associated with C bonding to B and 9.66% to C-C representing (graphite) and the lower probability polytype where all three C atoms represent the 3-atom chain. Through the HEBM a larger percentage of C-C bonds were observed (5.63[un-milled] to 9.66%[milled]). This could be explained by the separation of C from the B₄C carbon during the ball milling. For B 27.47% of all of the material represents B-B bonds and 12.15% of the material represents B-C bonding for both the polar and equatorial B positions. An additional portion of the B is associated with oxides where 13.85% of the overall observed elements is B₂O₃. As

mentioned previously this is artificially high due to the nature of sampling only up to 10nm from the surface where the oxides typically reside.



The primary bonding was the B-B bonding representing 27.47% of the observed elements followed by the B-O peak representing 13.85% and the remaining B-C bonds represent 12.15%.

Figure 11. Plot of the energy peaks of the B-O, B-C, and B-B bonding.



The primary bonding was the C-B bonding representing 6.04% of the observed elements followed by the C-C peak representing 9.66% and the remaining C-O bonds represent 1.39%.

Figure 12. Plot of the energy peaks of the C-O, C-C, and C-B bonding.

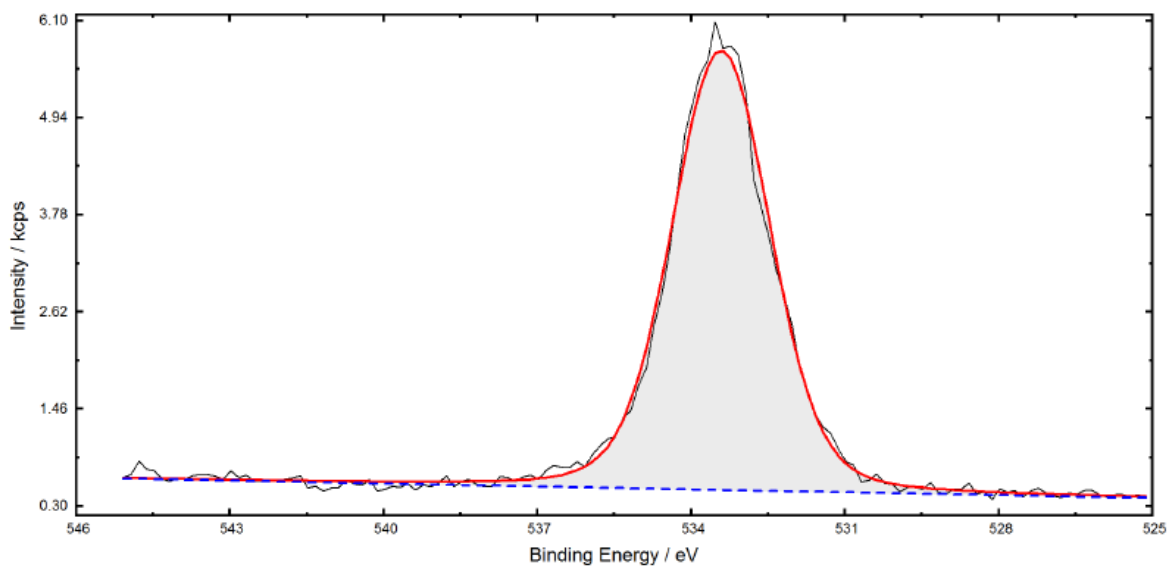


Figure 13. Plot of the O peak representing 29.45% of the overall elemental percentage.

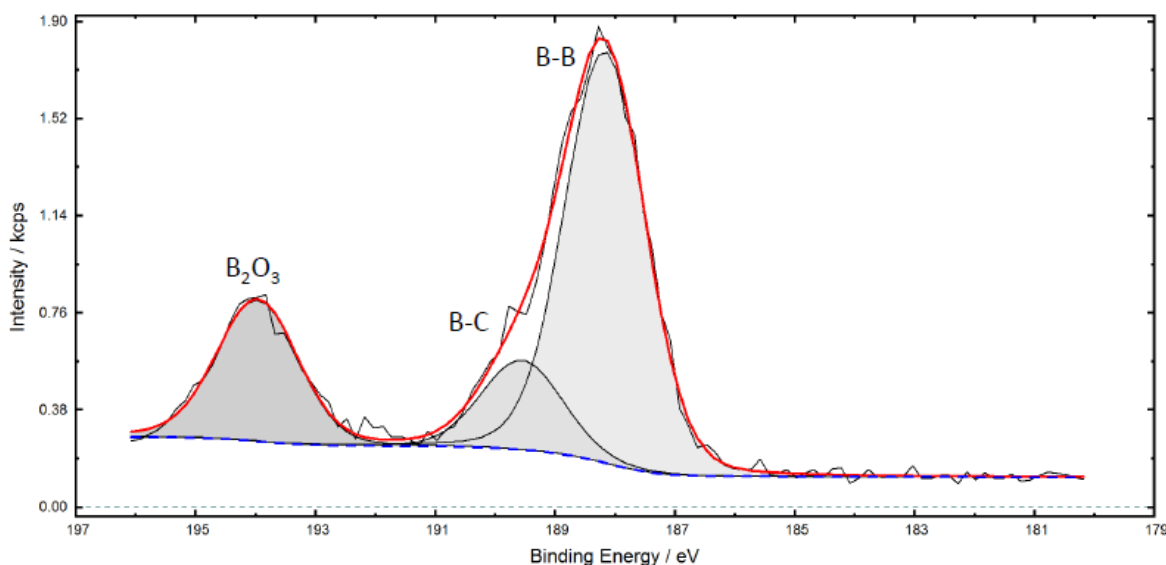
Table 10. Atomic quantification of elements including relative bonding for SPEX-milled B₄C powder.

	Peak name	E _B /eV	Area/cps·eV	Sens. Fact.	Norm. Area	Quant./at. %	
B-B	B1s Peak 1	187.88	2617.5511	10.449	250.50733	27.47	53.47
	B1s Peak 2	189.12	1156.2390	10.439	110.76147	12.15	
B ₂ O ₃	B1s Peak 3	193.63	1315.3545	10.415	126.29423	13.85	
C-B	C1s Peak 1	282.54	1118.4509	20.32	55.041877	6.04	17.09
C-C	C1s Peak 2	284.72	1786.9663	20.29	88.071283	9.66	
C-O	C1s Peak 3	286.75	256.45338	20.27	12.651869	1.39	
	O1s Peak 1	533.42	13428.367	50.015	268.48681	29.45	29.45

3. Milled B₄C:Si Retsch 1 Atom

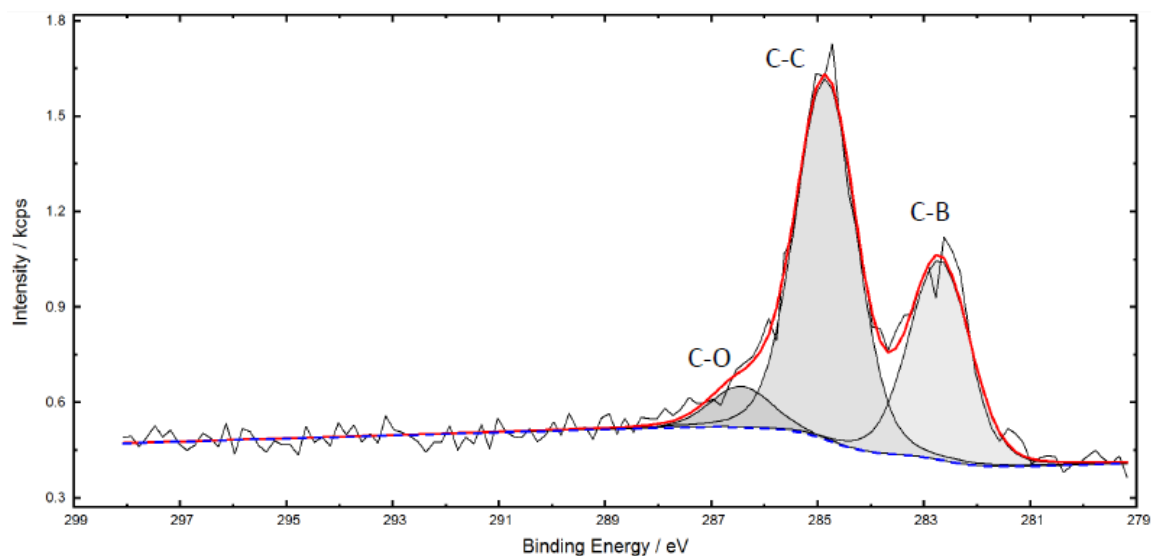
The milled B₄C Retsch 1 atom powder consists of as bought powder from Electro-Abrasives in Buffalo, NY with the addition of an elementary pure Si wafer using a mass to enable a stoichiometry of 1 Si atom per unit cell of B₄C. The average particle size is near 22nm. The material was ball milled using a Retsch ball mill with a frequency of 30 Hz.

From Table 11 and Figures 14 thru 17, the primary elements observed were: B, C, Si, and O. From the analysis 32.73% of the observed elements was oxygen. The oxygen was found to be bonded to both B (B₂O₃), C (CO) and Si (SiO₂). With the analysis 5.22% is associated with C bonding to B and 9.41% to C-C representing (graphite) and the lower probability polytype where all three C atoms represent the 3-atom chain and 1.08% C bonding to O. For B 30.33% of all of the material represents B-B bonds and 6.61% of the material represents B-C bonding for both the polar and equatorial B positions. An additional portion of the B is associated with oxides where 10.41% of the overall observed elements is B₂O₃. For the Si 6.7% is either bonded to C or B, 1.64% is Si-Si and 1.82% is SiO₂.



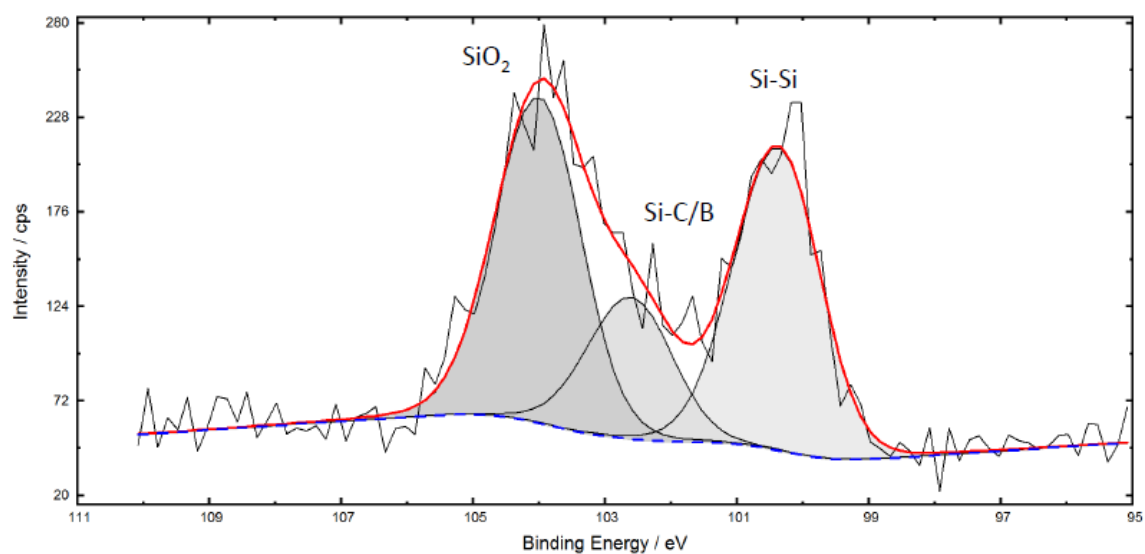
The primary bonding was the B-B bonding representing 30.33% of the observed elements followed by the B-O peak representing 10.41% and the remaining B-C bonds represent 6.61%.

Figure 14. Plot of the energy peaks of the B-O, B-C, and B-B bonding.



The primary bonding was the C-B bonding representing 5.22% of the observed elements followed by the C-C peak representing 9.41% and the remaining C-O bonds represent 1.08%.

Figure 15. Plot of the energy peaks of the C-O, C-C, and C-B bonding.



The primary bonding was the Si-C/B bonding representing 0.75% of the observed elements followed by the Si-O peak representing 1.82% and the remaining Si-Si bonds represent 1.64%.

Figure 16. Plot of the energy peaks of the Si-O, Si-C/B, and Si-Si bonding.

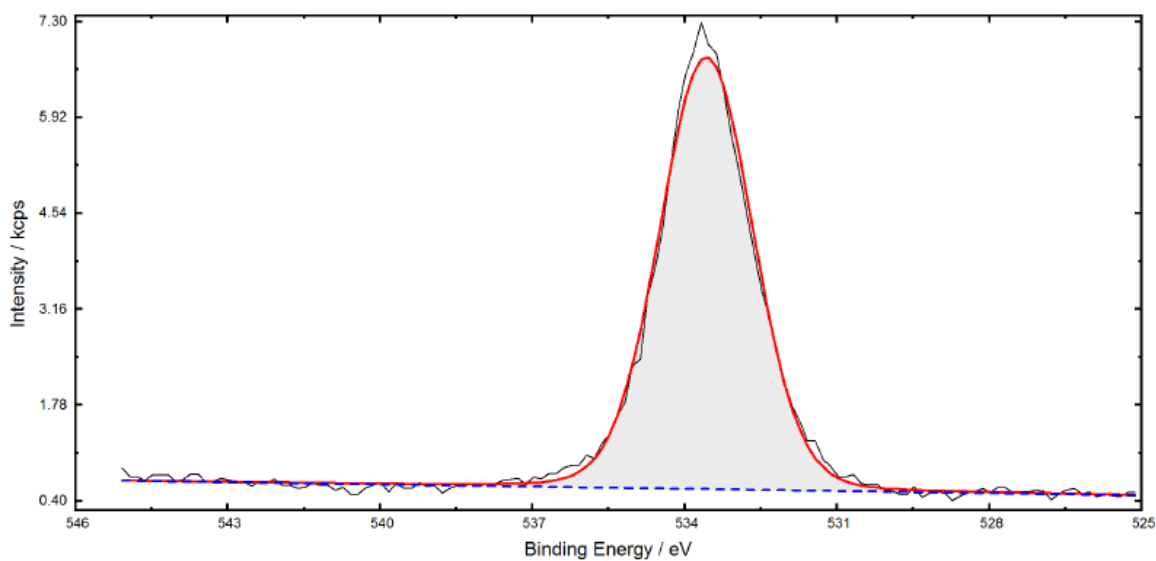


Figure 17. Plot of the O peak representing 32.73% of the overall elemental percentage.

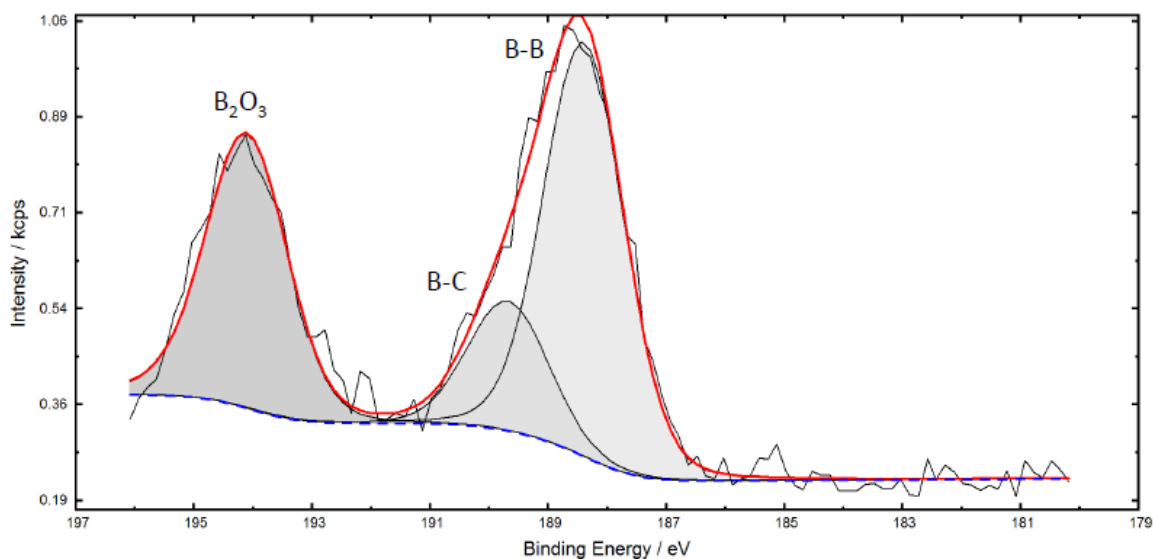
Table 11. Atomic quantification of elements including relative bonding for milled B₄C Retsch with 1 atom Si powder.

	Peak name	E _B /eV	Area/cps·eV	Sens. Fact.	Norm. Area	Quant./at.%
B-B	B1s Peak 1	188.17	2848.4084	10.449	272.60106	30.33 47.35
B-C	B1s Peak 2	189.56	620.30556	10.439	59.421934	6.61
B ₂ O ₃	B1s Peak 3	193.97	973.83582	10.41	93.548109	10.41
C-B	C1s Peak 1	282.71	952.96343	20.32	46.897806	5.22 15.71
C-C	C1s Peak 2	284.85	1716.0856	20.29	84.577902	9.41
C-O	C1s Peak 3	286.45	197.46050	20.27	9.7415145	1.08
	O1s Peak 1	533.58	14713.836	50.015	294.18846	32.73 32.73
Si-Si	Si2p Doublet 1	100.22	272.50009	18.44	14.777662	1.64 4.21
Si-C/B	Si2p Doublet 2	102.33	123.65543	18.423	6.7120143	0.75
SiO ₂	Si2p Doublet 3	103.83	300.73615	18.407	16.338140	1.82

4. Milled B₄C:Si SPEX 1 Atom

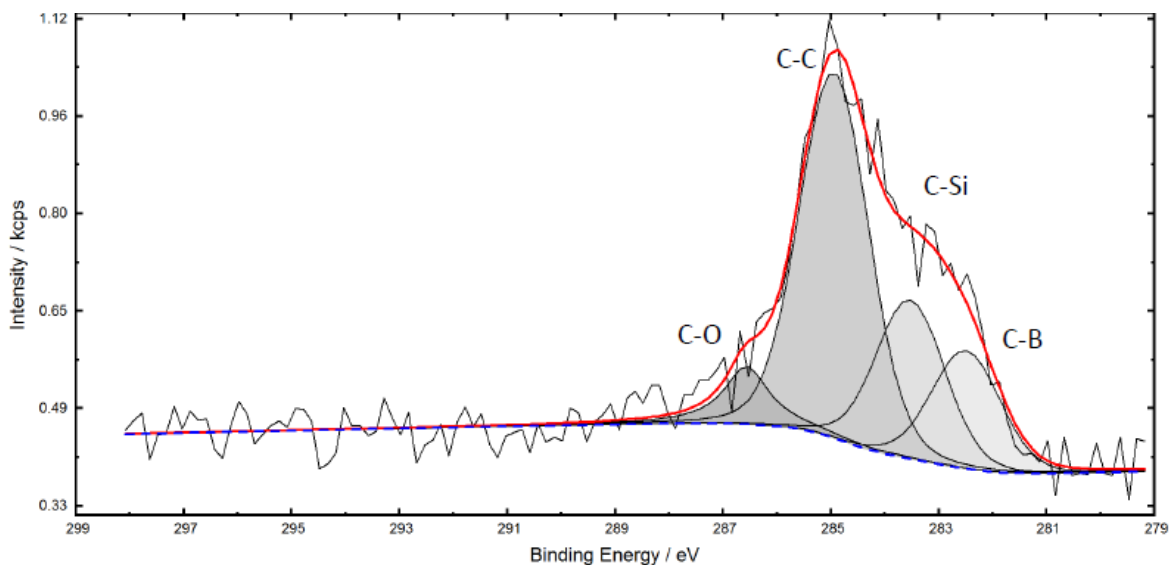
The milled B₄C SPEX 1 atom powder consists of as bought powder from Electro-Abrasives in Buffalo, NY with the addition of an elementary pure Si wafer using a mass to enable a stoichiometry of 1 Si atom per unit cell of B₄C. The average particle size is near 17nm. The material was ball milled using a SPEX ball mill with a frequency of 60 Hz.

From Table 12 and Figures 18 thru 21, the primary elements observed were: B, C, Si and O. From the analysis 46.24% of the observed elements was oxygen. The O was found to be bonded to B (B₂O₃), C (CO) and Si (SiO₂). With the analysis 1.87% is associated with C bonding to B and 5.87% to C-C representing (graphite) and the lower probability polytype where all three C atoms represent the 3-atom chain and 0.83% C bonding to O. For B 15.31% of all of the material represents B-B bonds and 4.8% of the material represents B-C bonding for both the polar and equatorial B positions. An additional portion of the B is associated with oxides where 10.18% of the overall observed elements is B₂O₃. For the Si 3.3% is either bonded to C or B, 2.74% is Si-Si and 6.29% is SiO₂.



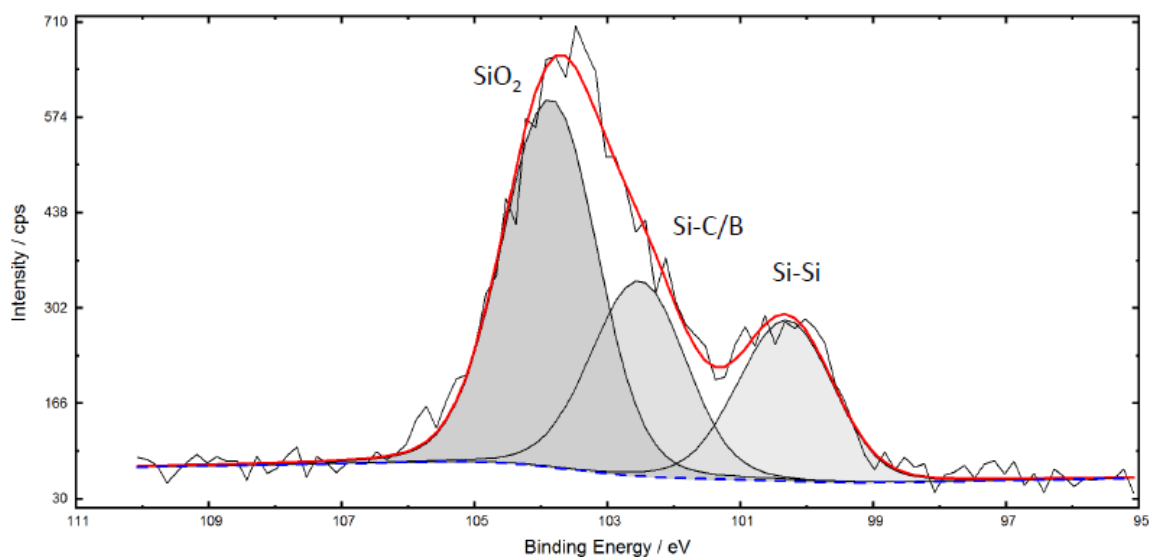
The primary bonding was the B-B bonding representing 15.31% of the observed elements followed by the B-O peak representing 10.18% and the remaining B-C bonds represent 4.8%.

Figure 18. Plot of the energy peaks of the B-O, B-C, and B-B bonding.



The primary bonding was the C-C bonding representing 5.87% of the observed elements followed C-Si at 2.53% the C-B peak representing 1.87% and the remaining C-O bonds represent 0.83%.

Figure 19. Plot of the energy peaks of the C-O, C-C, and C-B bonding.



The primary bonding was the Si-O bonding representing 6.29% of the observed elements followed by the Si-C/B peak representing 3.33% and the remaining Si-Si bonds represent 2.74%.

Figure 20. Plot of the energy peaks of the Si-O, Si-C/B, and Si-Si bonding.

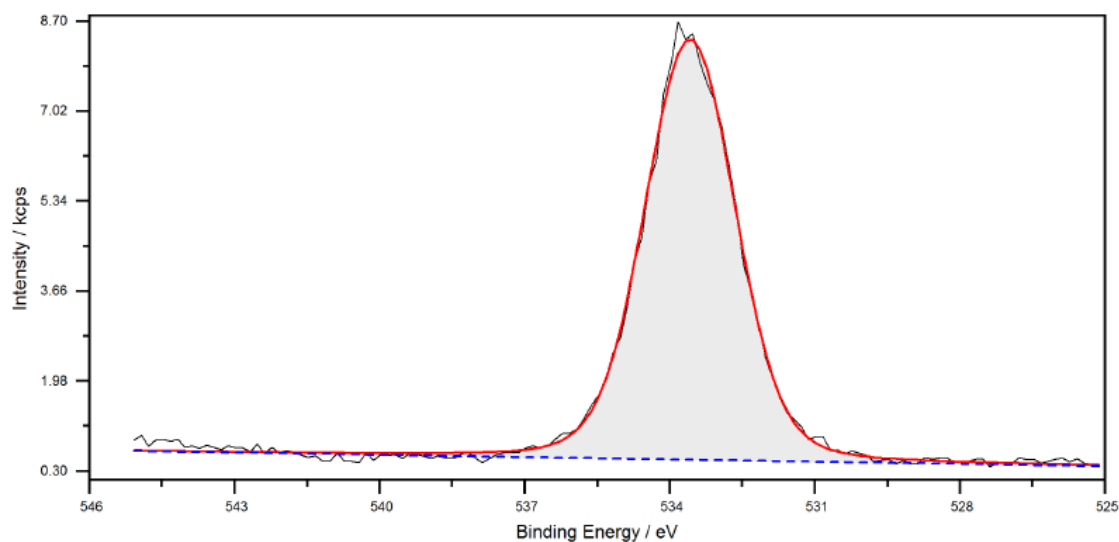


Figure 21. Plot of the O peak representing 46.24% of the overall elemental percentage.

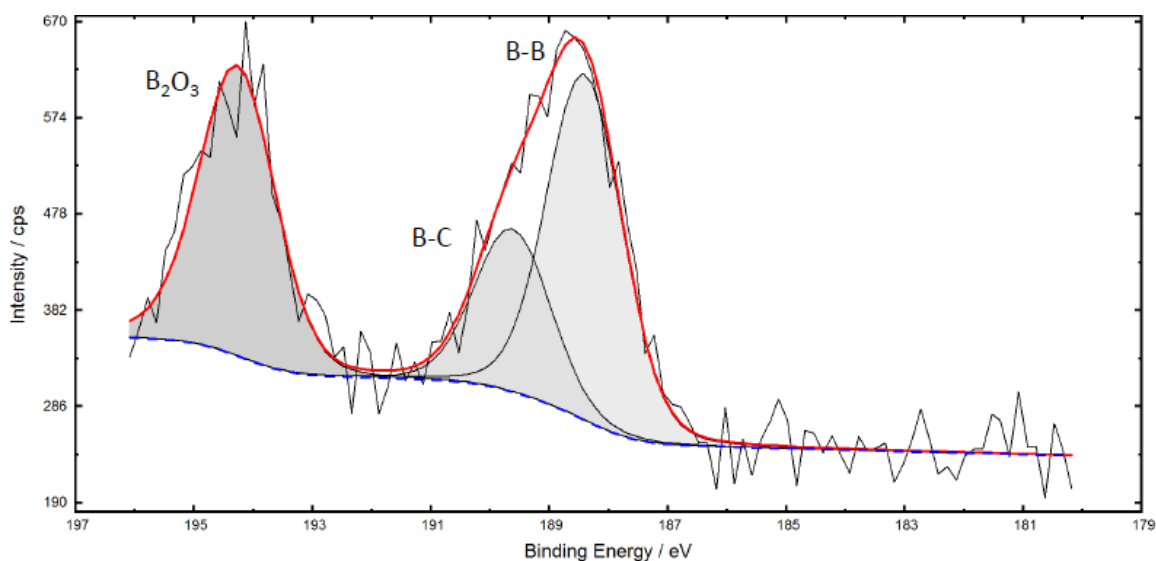
Table 12. Atomic quantification of elements including relative bonding for milled B₄C SPEX with 1 atom Si powder.

	Peak name	E _B /eV	Area/cps·eV	Sens. Fact.	Norm. Area	Quant./at.%	
B-B	B1s Peak 1	188.39	1345.1217	10.444	128.79373	15.31	30.29
B-C	B1s Peak 2	189.69	421.85006	10.439	40.410964	4.8	
B ₂ O ₃	B1s Peak 3	194.1	891.81008	10.41	85.668596	10.18	
C-B	C1s Peak 1	282.5	320.26392	20.32	15.761019	1.87	11.1
C-Si	C1s Peak 2	283.53	431.70198	20.31	21.255637	2.53	
C-C	C1s Peak 3	284.94	1002.9199	20.29	49.429271	5.87	
C-O	C1s Peak 4	286.56	141.83923	20.27	6.9974956	0.83	
	O1s Peak 1	533.58	19456.555	50.015	389.01440	46.24	46.24
Si-Si	Si2p Doublet 1	100.13	425.40221	18.44	23.069534	2.74	12.36
Si-C/B	Si2p Doublet 2	102.35	516.86158	18.423	28.055234	3.33	
SiO ₂	Si2p Doublet 3	103.69	974.19979	18.407	52.925506	6.29	

5. Milled B₄C:Si SPEX 2 Atom

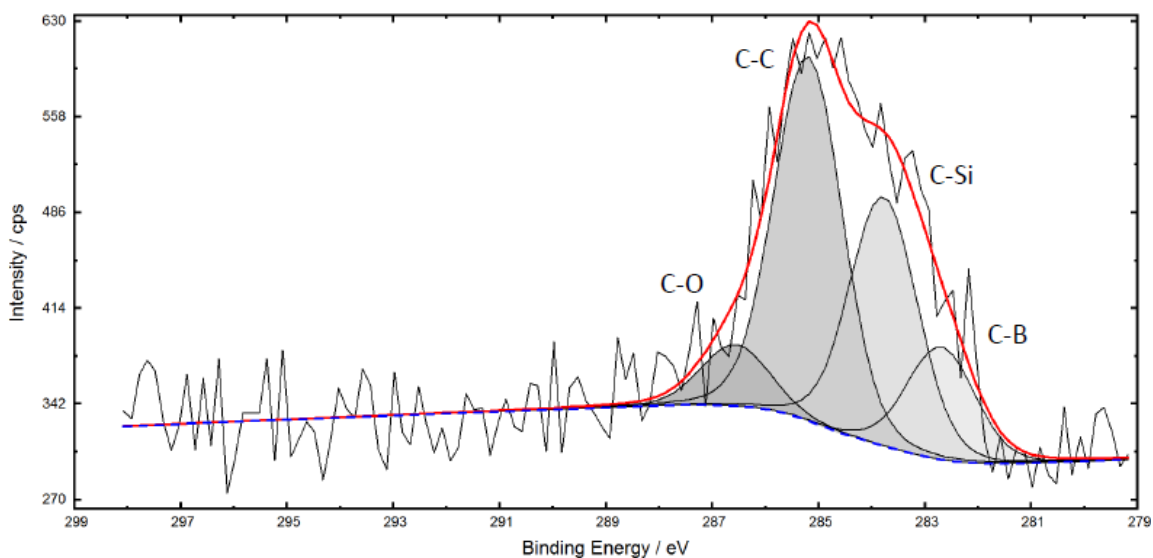
The milled B₄C SPEX 2 atom powder consists of as bought powder from Electro-Abrasives in Buffalo, NY with the addition of an elementary pure Si wafer using a mass to enable a stoichiometry of 2 Si atom per unit cell of B₄C. The average particle size is near 20nm. The material was ball milled using a SPEX ball mill with a frequency of 60 Hz.

From Table 13 and Figures 22 thru 25, the primary elements observed were: B, C, Si, and O. From the analysis 47.97% of the observed elements was oxygen. The O was found to be bonded to B (B₂O₃), C (CO) and Si (SiO₂). With the analysis 1.34% is associated with C bonding to B and 4.18% to C-C representing (graphite) 2.93% to Si-C and the lower probability polytype where all three C atoms represent the 3-atom chain and 0.75% C bonding to O. For B 9.03% of all of the material represents B-B bonds and 4.55% of the material represents B-C bonding for both the polar and equatorial B positions. An additional portion of the B is associated with oxides where 8.78% of the overall observed elements is B₂O₃. For the Si 4.57% is either bonded to C or B, 6.23% is Si-Si and 7.54% is SiO₂.



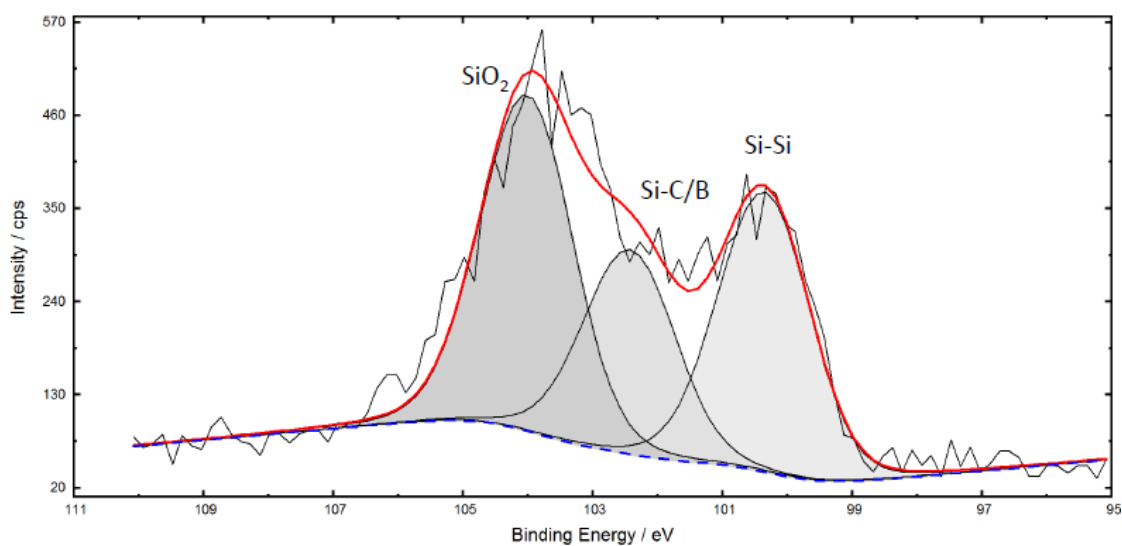
The primary bonding was the B-B bonding representing 9.03% of the observed elements followed by the B-O peak representing 8.78% and the remaining B-C bonds represent 4.55%.

Figure 22. Plot of the energy peaks of the B-O, B-C, and B-B bonding.



The primary bonding was the C-C bonding representing 4.18% of the observed elements followed C-Si at 2.93% the C-B peak representing 1.34% and the remaining C-O bonds represent 0.75%.

Figure 23. Plot of the energy peaks of the C-O, C-C, and C-B bonding.



The primary bonding was the Si-O bonding representing 7.54% of the observed elements followed by the Si-Si peak representing 6.23% and the remaining Si-C/B bonds represent 4.57%.

Figure 24. Plot of the energy peaks of the Si-O, Si-C/B, and Si-Si bonding.

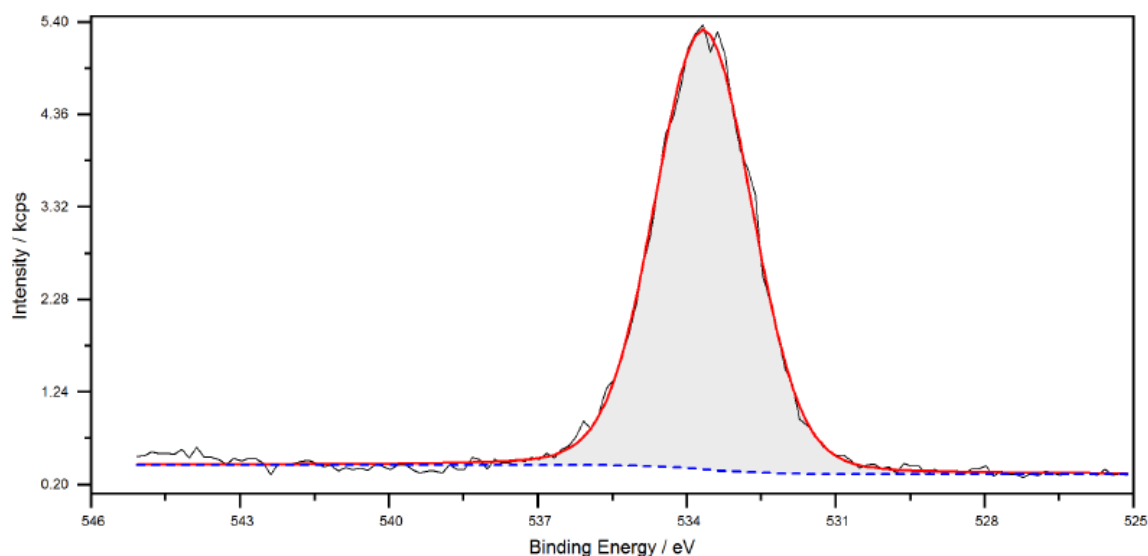


Figure 25. Plot of the O peak representing 47.97% of the overall elemental percentage.

Table 13. Atomic quantification of elements including relative bonding for milled B₄C SPEX with 2 atom Si powder.

	Peak name	E _B /eV	Area/cps·eV	Sens. Fact.	Norm. Area	Quant./at. %
B-B B-C B ₂ O ₃	B1s Peak 1	187.85	117.85977	10.449	11.279526	2.12 24.48
	B1s Peak 2	188.51	500.86051	10.444	47.956770	9.03
	B1s Peak 3	189.63	252.51889	10.439	24.189951	4.55
	B1s Peak 4	194.26	485.24987	10.41	46.613821	8.78
C-B C-Si C-C C-O	C1s Peak 1	282.7	145.11240	20.32	7.1413583	1.34 9.2
	C1s Peak 2	283.79	316.18367	20.31	15.567881	2.93
	C1s Peak 3	285.2	450.90302	20.29	22.222919	4.18
	C1s Peak 4	286.45	80.218024	20.27	3.9574752	0.75
	O1s Peak 1	533.68	12742.075	50.015	254.76507	47.97 47.97
Si-Si	Si2p Doublet 1	100.18	610.12534	18.44	33.087057	6.23 18.34
Si-C/B	Si2p Doublet 2	102.25	446.78611	18.423	24.251539	4.57
SiO ₂	Si2p Doublet 3	103.84	737.12907	18.407	40.046127	7.54

D. RAMAN SPECTROSCOPY

Raman spectroscopy is a spectroscopic technique used to determine vibrational modes of molecules. Raman can be used to identify a unit cell structure of a specific molecule as well as identify if the symmetry of the molecules has been changed.

Raman spectroscopy uses the inelastic scattering of photons from a monochromatic light to excite a lattice structure. Excitations and de-excitations of the photons interacting with the molecular structure occur through phonon coupling with the incident laser light causing the laser light energy to be shifted either up or down (Stokes/Anti-Stokes). The shift in the laser light energy gives information about the vibrational modes of the molecule.

The change in energy of the laser light is passed into a monochromator. Here all Rayleigh scattering (elastically scattered light [higher energy]) is filtered out and primarily the remaining light is the weak Raman spectra which is channeled to a detector.

Raman is applied to investigate the initial powders as well as directly after HEBM to determine if the initial B_4C unit cell has been altered either through the milling process and/or the elemental inclusions of Si. Each Raman spectra will be compared to the original space group symmetry of B_4C (R3M) to see if changes have occurred, Figure 26.

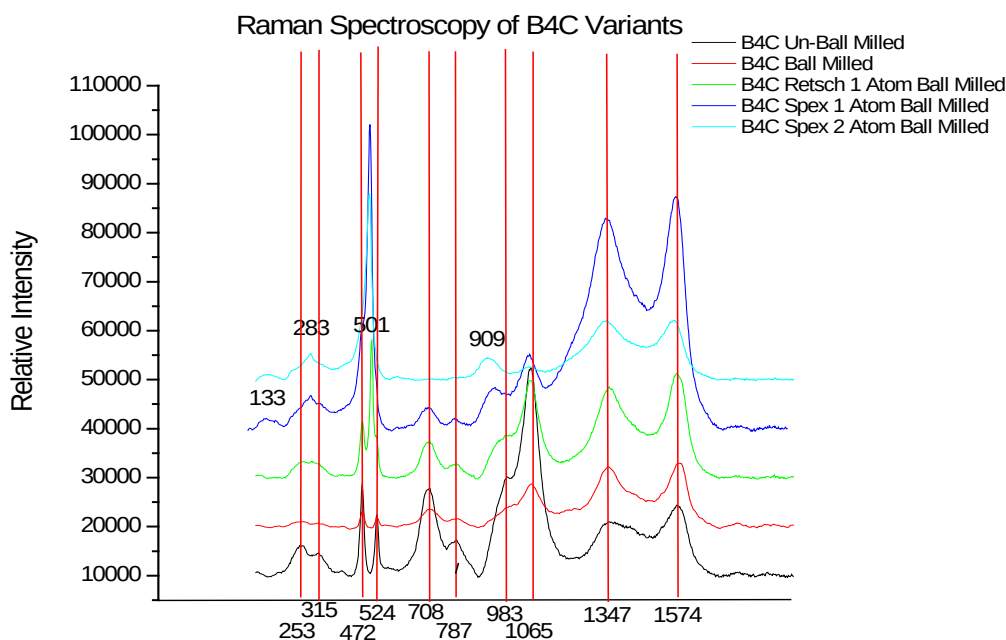


Figure 26. Raman spectrum of the five different B_4C and B_4C variant powders including HEBM B_4C and HEBM B_4C with Si inclusion of 1 atom and 2 atom.

B₄C by group theory is predicted to have 12 modes, of A_{1g} (5) and E_g (7) symmetry, that are Raman active [2]. The Raman spectrums for the five different samples were obtained using an incident wavelength of 515 nm of the as-received B₄C as well as ball milled powders including elemental inclusions of Si up to 2 atoms equivalent per unit cell. The as received B₄C powder agrees well with previous Raman spectrum of B₄C. For the five B₄C and B₄C:Si powders studied all of the spectrums exhibited some resemblance to the spectrum identified as the unaltered as received boron carbide powder.

Both the as received and HEBM B₄C presented the same spectrum for the 10 uniquely identified spectrum peaks. As we look at the Retsch 1 atom HEBM sample, this ball milling initiated a lower force on the powders due to the lower oscillating speed of the ball mill (30 Hz). Nine of the peaks remained the same but the 524 cm⁻¹. Decreased in wave number down to 501 cm⁻¹.

A more significant change is observed in the spectrum of the SPEX HEBM of the 1 and 2 atom powders. In both powders significant changes to the spectrum occur. The first is a new peak at 133 cm⁻¹ followed by the migration of the 253 cm⁻¹ and 315 cm⁻¹ peaks to a single peak at 283 cm⁻¹.

Both of the 524 cm⁻¹ peaks showed a similar migration as the Retsch 1 atom spectrum down to 501 cm⁻¹. Lastly a shift in the 983 cm⁻¹ peak was also shifted to the left down to 909 cm⁻¹.

E. PURIFICATION OF ALLOYED POWDERS

The final preparation of the powders was a cleaning process prior to hot pressing. Though great care to prevent contamination of the samples was taken, some oxides will form and metal contamination from the HEBM process will occur. In order to eliminate this contamination, it was decided to utilize a solution of 90% Methanol (CH₃OH) and 10% HCl, the methanol would react with the oxides, and the HCl would consume the metal contamination and the powders would then be washed with distilled water to remove the byproducts of the reaction [36].

The first sample washed was the ball milled B₄C powder; using filter paper in a funnel, powder was then added with just enough CH₃OH/HCL to make a light slurry (~10ml). After a period of one hour the powder was rinsed with ~100ml of distilled water. The sample was left under a fume hood to finish draining and drying. After a 12-hour period the powder, under inspection, was found to have whitish crystals and the filter paper became discolored (green). The crystals are indicative of metals coming out of solution, this means the acid wash solution had evaporated off and the contaminants remained with the powder (did not work through the filter) [37].

It appeared that the light slurry/heavy solution had possibly clogged the filter paper. As a second attempt the powder was broken down into smaller batches, and washed again. The solution, additionally, was much lighter with the anticipation that the acid solution with contaminants would properly flow through the filter. initial observations showed that the sample was draining, but 12 hours later the crystalline surface and the paper discoloration again occurred.

From the two attempts to clean the powder, it appears the particle size of the powder was clogging the filter, the filter was small enough to allow the acid solution to pass through in very light solution, but it resisted the removed contaminants from passing.

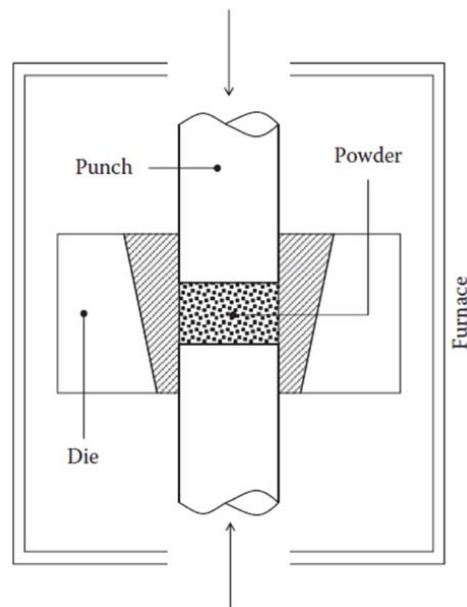
A final attempt was performed using a plain paper coffee filter having a much looser weave than the previously used filter paper. The coffee filter paper did not clog but the loose weave allowed large portions of the sample be rinsed away with the reactants from the purification process.

The excessive loss of the sample powders added additional time to re-make loss powders, in addition to research filtration techniques for nanometer size particles would additionally take more time. The decision was made to forgo the purification process and send the powders to the hot-pressing facility as is. While not entirely satisfying it was necessary for the completion of this work.

F. HOT PRESSING B₄C POWDERS

The B₄C:Si powders require hot pressing to enable densities close to theoretical maximum density (TMD). As mentioned the B₄C powders at high temperatures enable diffusion of the carbon. Through the combination of high pressures with the high temperatures, the diffusion of carbon atoms is prevented. Correct values of both temperature and pressure can achieve densities near TMD and prevent phase separation forming B₄C and SiC.

Our sample alloys were sent to a foundry where they were put into cylindrical graphite molds each sample produced was pressed to 3000 psi and heated to 2200°C which are characteristic of B₄C construction (it should be noted that the optimized pressure and temperature are specifically for B₄C and the parameters may not be optimized for the powders with Si inclusion). Figure 27 shows a simple representation of what the pressing process looks like [38].



They were pressed at 3000 psi and heated to 2200°C.

Figure 27. Representation of the process our alloyed powders took to become ceramic armor. Source: [38].

Figure 28 shows a post load view of the die with the samples still sandwiched between the graphite punches. Both the punches, and the die had release powder on their contacting surfaces. This is to ensure the foundry can separate the ceramic from the punches and the die.



The ceramic armor samples are still between the punches.

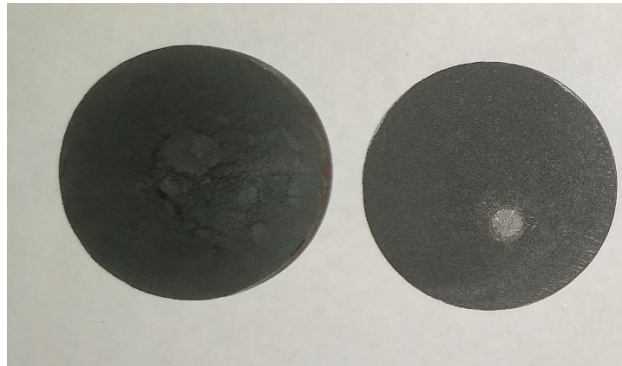
Figure 28. A bench view of the die, punches, and powders post-heating and pressing.

Figure 29 shows that despite best efforts, not all the samples could be separated from the punches. This 5 atom sample has large cracks on the surface are indicative of cracks throughout the interior of this sample indicating porosity. Figure 30 shows that this cracking was not just isolated to the 5 atom samples, it was also prevalent in the 2 and 3 atom samples as well. The overabundance of Si in the sample enables interaction with the graphite molds possibly enabling an exothermic reaction in the formation of SiC.



The large cracks on the surface are indicative of cracks throughout the interior of this sample indicating porosity.

Figure 29. Sample could not be separated from the punch.



Notice the moon of Si alloy on the face of the 2 atom disk.

Figure 30. Cracking was not just isolated to the 5 atom samples but was also prevalent in the 2 and 3 atom samples.

The overabundance of Si in the powders lead to an exothermic reaction with the graphite molds. During the pressing process the free Si and graphite enabled an exothermic reaction causing ejection of the 5 atom discs prematurely. The reaction between Si and C that produces SiC is exothermic and produces ~ 127.6 KJ/Mol [39]. Creating a violent increase in the heat and pressure in the system, causing the failure. Figure 31 shows the split top plate and the damaged samples from the exothermic reaction within the production run.



It split the top plate of the furnace and critically damaged the ceramic disk required for testing.

Figure 31. Damage caused by the 5 atom alloyed powder.

As mentioned hot pressed B_4C must be 98% or greater of its TMD. Knowing the density of B_4C we will utilize molar mass and determine a unit cell volume within our density calculations.

Knowing the density of B_4C we will utilize the molar mass and determine a unit cell volume to work from in our density calculations. This approach is reasonable because we know that HEBM leaves the bulk of the lattice intact and creating superficial defects for the Si to react [2].

Beginning with $B_{12}C_3$, we know the atomic masses of; B: 10.811 g/mol, C: 12.01 g/mol, ρ : 2.52 g/cc, and $N_0 = 6.022e23 \text{ mol}^{-1}$

$$\rho_0 = \frac{N_{\text{Boron}} * A_{\text{Boron}} + N_{\text{Carbon}} * A_{\text{Carbon}}}{N_0 * V_C}, \quad \text{Eq 15}$$

can be suitably rearranged to

$$V_C = \frac{N_{\text{Boron}} * A_{\text{Boron}} + N_{\text{Carbon}} * A_{\text{Carbon}}}{N_0 * \rho_0}. \quad \text{Eq 16}$$

We find $V_C = \frac{12 * 10.811 + 3 * 12.011}{6.022e23 * 2.52} = 1.09235e-22 \text{ cc}$. Taking this unit cell volume, we now work to determine the maximum theoretical density of our alloyed ceramics. Starting with the 1atom samples we have two possibilities of atomic replacement.

$$\rho_{B_4C+Si} = N_{Boron} * A_{Boron} + N_{Carbon} * A_{Carbon} + N_{CSilicon} * A_{Silicon} / N_0 * V_C \quad \text{Eq 17}$$

$$P_{B_4C+Si} = 11*10.811+3*12.011+1*28.08/6.022e23*1.09235e-22 = 2.78 \text{ g/cc; 1 less Boron}$$

$$P_{B_4C+Si} = 12*10.811+2*12.011+1*28.08/6.022e23*1.09235e-22 = 2.76 \text{ g/cc; 1 less Carbon}$$

We now know the replacement of a B or C atom with Si results in 0.7 percent difference in maximum density between the two. This provides the range of acceptable densities for 1 atom samples. For the 2 atom sample we simply removed one of each from the mix.

$$\rho_{B_4C+2Si} = 11*10.811+2*12.011+2*28.08/6.022e23*1.09235e-22 = 3.02 \text{ g/cc;}$$

Using both 1 less Carbon and 1 less Boron.

We did not do calculations for 3 atom or 5 atom because the replacement of C and B would be the same as the 2 atom.

Of particular interest is the work of Goddard [1] on the possibility of a double bounded Si pair replacing the CBC chain between icosahedron when the polar sites become available as those carbon atoms under stress liberate from the lattice. If that indeed happens then the density could be measurably altered too.

$$\rho_{B_{11}Si_2} = 11*10.811+2*28.08/6.022e23*1.09235e-22 = 2.66 \text{ g/cc; 1 less Boron \& 2 less Carbon}$$

G. DISC SURFACE PREPARATION

Struers Metallog provides information regarding the polishing and grinding of different types of materials. B₄C is polished by method G. Method G represents the polishing of alloyed ceramics. Figure 32 shows the initial starting point for out polishing work [40].

Grinding

Step	PG	FG
Surface	MD-Piano 220	MD-Plan
Abrasive	Diamond	DiaPro Plan 9
Grit/ Grain size		9 µm
Lubricant	Water	
Rotational speed [rpm]	300	150
Force[N]/ specimen	30	35
Time [min]	Until plane	10

Polishing

Step	OP
Surface	MD-Chem
Abrasive	OP-S NonDry
Grain size	0.25 µm
Lubricant	
Rotational speed [rpm]	150
Force[N]/ specimen	20
Time [min]	1

Figure 32. Struers guidance for polishing alloyed ceramics. Source: [40].

Using an Allied TECHPRESS 3 phenolic press two B₄C test samples were pressed into and encapsulated within phenolic molds. The prepared B₄C samples were mounted onto an Allied METPREP3 Grinding/Polishing System (GP). In order to balance the grinding wheel phenolic spacers were used to fill the remaining three holes. In order to ensure that the ceramic test pieces would be ground planar, both of the test pieces and the spacers were set to 0.25in below the deck of the grinding wheel using a Vernier caliper.

The initial polishing step utilized a 120 Grit Allied Diamond grinding wheel on the GP. Specifications on the initial step of polishing used 30lbs (~26N) pressure on the samples with the sample wheel set to rotate counter to the abrasive wheel at 150 rpm for

both the wheel and abrasive disc. Within this process water was used as the lubricant. Both samples were polished for 50 minutes with 30 minutes being spent at 33lbs (~30N).

The second phase of polishing incorporated a 9 μ m Diamond Solution specific to this process Allied 9 μ m DiaLube matched with a Plan B grinding pad. The force per sample was set at 39 lbs (~35N), the platform (pad) was set to 100rpm and the wheel to 50rpm, both wheels are counter rotating to each other. The guide calls for 10 minutes but a total of 20 minutes provided better results.

The final phase required switching to the 1 μ m Diamond Solutions, Allied 1 μ m DiaLube with a “White Label” polishing pad (by Allied) was used to prepare this process. The platform and sample wheel rotation speeds were kept the same as the 9 μ m polish phase (pad 100rpm and the wheel to 50rpm counter rotating). The force was reduced to 22lbs (~20N). The guide calls for one minute but an additional cycle improved the polish properties.

After rinsing the wheel and samples with water to remove the diamond solution the surface was visually inspected where a highly polished surface was observed.

H. POLISHING TARGET SAMPLE

To test the variation in performance of the varied alterations to B₄C, the samples will be tested both for hardness and dynamic material strength (ballistic impact). For ballistic impact experiments the target samples require both a high degree of planarity as well as smooth polishing down to a minimum of 1 μ m on both faces to ensure a high planarity impact photonic doppler velocimetry (PDV)

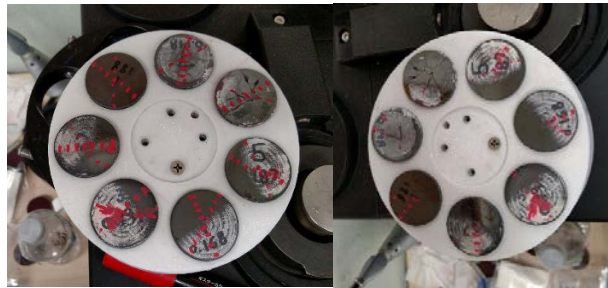
Initial efforts were to set the alloyed ceramic samples in phenolic and utilize the factory wheel to grind and polish the samples. To verify that after polishing that the ceramics could be easily separated, a test sample of B₄C was encapsulated within the phenolic and then attempted to be removed. The force to remove the ceramic was quite large and caused damage to the ceramic, Figure 33.



Figure 33. Damaged test sample with high polish.

A new approach was performed using a 3D printed seven sample head using ABS plastic. A problem arose in that the target sample thicknesses were supposed to be either 5mm and 6mm. But upon inspection the pucks went from 4.4mm to 6.5mm. This created an issue related to uneven contact of the samples when multiple samples were loaded at the same time.

Multiple heads customizing to sample thicknesses were printed but uneven polishing still occurred, Figure 34. Due to the high hardness of B₄C a new technique is required that enables precise height positioning of each individual B₄C sample.



Then an hour later a check to see if the paint was trending in a direction that indicated improvement.

Figure 34. The samples after several hours of work with new paint marks to check wear.

A two-sample head with the ability to set the deck height was developed to enable the ability to properly set the deck height of each sample individually. The first prototype was developed by first milling the entire bottom to remove the seven sample mounts. Then

1.5” holes were cut to hold the PC sample holders from the previous attempt. Holes were drilled and tapped to allow for 8-32 set screw to hold the samples in place for grinding.

The system was set to the needed grinding speed with a light to load to verify design integrity. GP head stability was not good, the assembly had a bad wobble indicating the sample holders were not secure with one set screw. A second set screw was added and a second trial run completed. While the samples showed no noticeable signs of grinding, the general head stability was good.

Using the two-sample head multiple loads using 80 grit diamond included: 4 lbs of load for 10min, the runs at 5 lbs for 10 minutes, 6 lbs for two runs of 10min, and lastly 7 lbs for two runs of 10 minutes. Each load increase was precipitated by a noticeable stop in the progression of the grinding across the face of the samples. The issue was set screws digging into the holders under load as the grinding took place. This shifting of the set screws caused the samples to not sit planar to the grinding surface.

The second prototype was a modification to the of the two-sample design. In order to set the deck height and keep the samples secure the sample holders were threaded into the GP head, Figure 35.



Figure 35. Threaded two sample GP head.

The new sample holder with threaded inserts performed well during cutting for 10 minutes using 80 grit, then switching to the next finer level of 120 grit for 10 minutes. This time the fixtures were secure, except for the edge that held the sample in the holder. It flexed, enough to see the sample rotate back and forth as it was being ground causing streaks. To correct this, a one sample holder was prototyped from one of the PC sample holders, backed by a circular sheet of metal backing to take the GP load arms. This design holds a single sample securely if you put a trimmed piece of weighing behind it and wet it first, Figure 36.



Figure 36. Single sample GP head.

This design worked well enough for thin samples. For any sample close to 6mm or greater thickness, care must be taken to not overload the sample. Overloading a sample thick or thin will damage the face and it cannot be fixed.

Grinding and polishing with the single sample head required a new approach. It was found for grinding wheel work that the platform speed needed to be set to the rpm required in the guide and the sample needed to turn at a much-reduced rate. Platform speeds of 300 to 330 rpm, and sample speeds of 30 rpm, set to rotate counter clockwise to each other performed best. The load applied was under the single setting which deployed four legs to spread the load evenly across the sample.

Polishing individual samples is more challenging. The settings on the guide work well for samples that are moving through large arcs across the cutting and polishing pads. It was found that an extra pound of load with the 9 μ m diamond solution still worked well, but the speeds had to be flipped. If the speed on the platform is too high, the polishing solution moves away from the sample.

To avoid loss of the polishing solution a higher sample rpm and reduced (half) platform speed reduces the loss of polishing fluid within the area of the sample. Using counter rotation helps keep the solution towards the inside edge of the sample and requires less polishing solution to be added.

A final prototype GP head was built. This head is a two-sample design that takes the lessons learned from previous work. The main body is made from heat treated aluminum, the sample holders are from the first failed threaded insert printing, the axels are thick walled brass tubing, Figure 37.

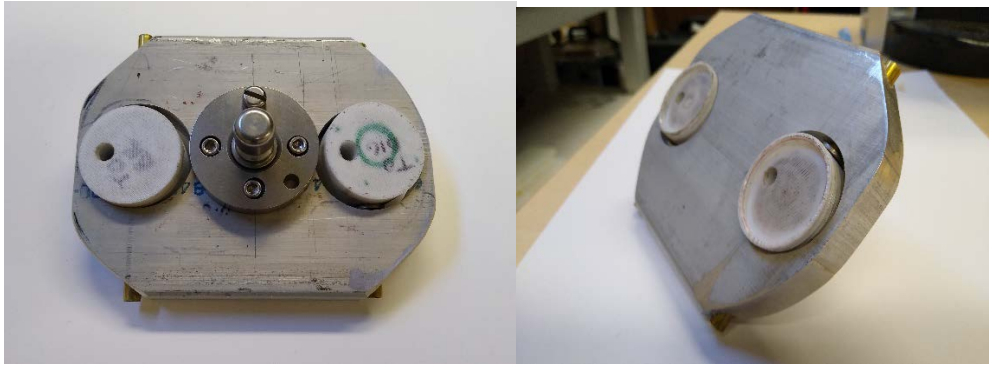


Figure 37. Aluminum two sample GP head.

The axles ensure the samples remain planar to the GP surface, the aluminum body provides mass and rigidity. In our application the added mass was a bonus allowing utilization the lowest load setting and keeping the head stable. The rigidity allows the machine pressure to be properly applied to the samples. Some of the earlier designs lacked mass, rigidity, or both, causing the poor polishing finish.

Some closing points of interest for grinding and polishing are:

1. Samples must be Blanchard ground.
2. The sample can be overloaded, so the increased load must be performed gradually.
3. Polishing B₄C:Si requires patience these samples are a hard and require hours to properly polish.

Table 14 shows the process for developing one side of a pair of samples. These samples had faces that had been Blanchard ground well enough that they made good test pieces for the new head. The DS 1µm is a courser polishing fluid, provides a good feedback for how the samples are taking increased polishing speeds as well as load in the process.

Table 14. Shows the process for developing one side of a pair of samples.

Sample 1	Sample 2	Process	Medium	Platform (rpm)	Sample (rpm)	Rotation	Fluid	Load (c or s)	Time (min)	Cycles
B4C Ground	B4C Ground	Polish	DS 1µm	50	100	Counter	NA	2 lb, s	30	1
		Polish	DS 1µm	50	100	Counter	NA	3 lb, s	30	1
		Polish	DS 1µm	50	100	Counter	NA	4 lb, s	30	1
		Polish	DS 1µm	40	150	Comp	NA	5 lb, s	30	1
		Polish	DS 1µm	40	150	Comp	NA	6 lb, s	30	1
		Polish	DS 1µm	40	150	Comp	NA	7 lb, s	30	1
		Polish	DS 1µm	50	100	Counter	NA	7 lb, s	30	1
		Polish	DS 1µm	70	80	Counter	NA	8 lb, s	30	1

These samples had faces that had been Blanchard ground well enough that they made good test pieces for the new head. The DS 1µm is a courser polishing fluid, provides a good feedback for how the samples are taking speed and load in the process.

1. Vickers Hardness

The high hardness of ceramics is part of the reason why they make good armor. The Vickers hardness of B₄C is generally accepted to be greater than 30GPa. Testing the hardness of our samples is important because we want to know if the hardness is maintained, and or affected by the amount of Si in the ceramic. The Vickers hardness test method consists of indenting the test material with a diamond indenter, in the form of a right pyramid with a square base and an angle of 136 degrees between opposite faces subjected to a load that is applied for 10 to 15 seconds [41]. The two diagonals of the indentation left in the surface of the material are measured using a microscope and their average calculated [41]. That average is used to calculate the area of the indentation. The Vickers hardness is the quotient obtained by dividing the load by the area of indentation [41], Figure 38.

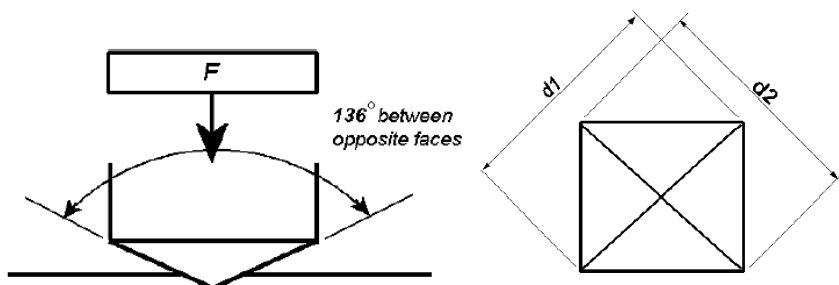


Figure 38. Diagram of Vickers hardness test. Source: [41].

A Stuers Dura Scan with Ecos workflow software was used for all hardness measurements. It should be noted that figures with red lines were manually adjusted. Microscopic surface voids and granular nonuniformity presented some challenges. Table 15 presents the best gathering of the sample data. Of importance here is that hardness while reduced are still above 30GPa which is an acceptable hardness for B_4C . It should be noted that both 1 atom samples are very close in hardness. Ground B_4C is slightly less hard than standard B_4C .

Table 15. Measured Vickers hardness.

Sample	HV	#	GPa
B ₄ C	1	3526	34.57948
B ₄ C Grd	1	3375	33.09863
1 Atom R	1	3249	31.86294
1 Atom S	1	3230	31.67661

Note hardness is still above the 30GPa for the milled and alloyed disk.

Figures 39 thru 42 are the actual images of the samples from the DuraScan/Ecos system. Please take the time to note the surface granularity on the samples. Of note there was no good comparable data for the 2 Atom and 3 Atom samples. The surface porosity of their surfaces made developing a good surface to evaluate not possible.

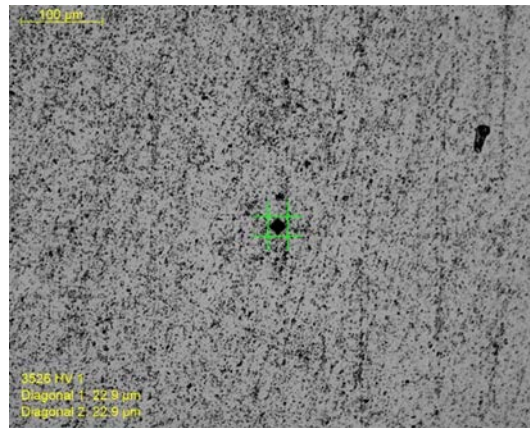


Figure 39. B_4C .

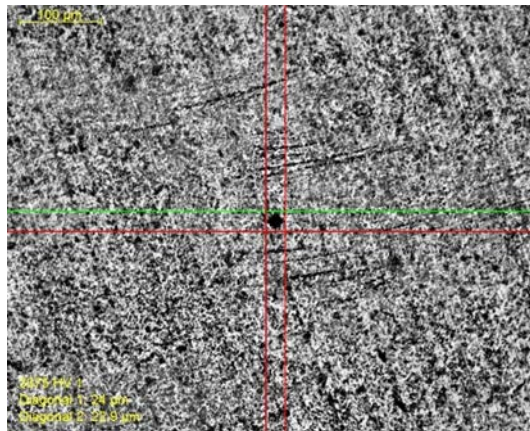


Figure 40. B_4C ground.

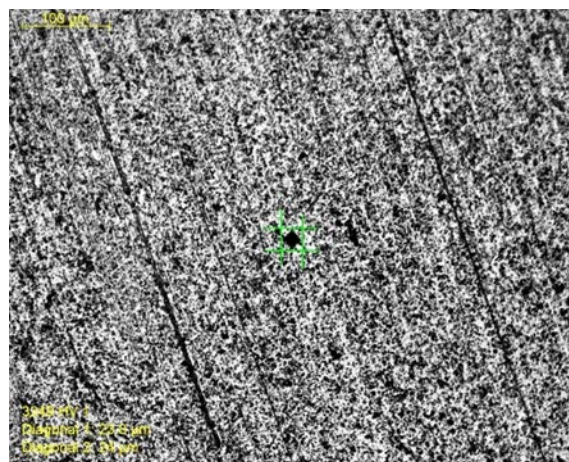


Figure 41. 1 atom Retsch.

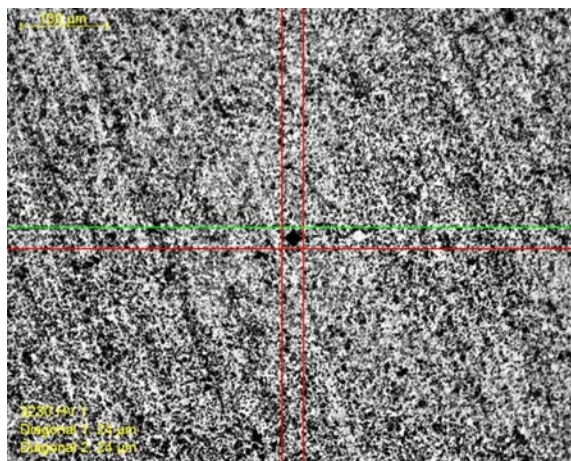


Figure 42. 1 atom SPEX.

2. SEM/EDS

Like the utilization of XRD to validate the more macroscopic changes to our B_4C through milling and inclusion. The scanning electron microscope (SEM) in conjunction with energy-dispersive X-ray spectroscopy (EDS) allows us to evaluate the sample on the atomic level. The system utilized was a Zeiss Gemini SEM with a METEK EDAX attachment, we used the EDS TEAM software to develop the samples.

The SEM uses an electron beam to interact with a sample of interest. As electrons have much shorter wavelengths as compared to light the ability to resolve smaller particles is enabled.

The EDS is utilized to identify chemical species with in a surface. Here EDS uses X-rays to identify chemical elements down to an atomic number of 5. The EDS X-rays excite some electrons out of the inner shells of an element. When a hole is created in a lower shell, a higher energy electron can come down to fill the vacancy. When this happens an x-ray is produced, dispersing the excess energy. Because every element has different energy levels in its electron shell structure the dispersed x-rays are characteristic to a given element. This allows us to separate out the elemental constituents of a sample and their concentration.

Tables 16 through 19 provide insight into the effects of alloying on the constituent ratios of elements in the ceramic. We see a ten percent shift in B and C ratios between the as delivered and milled samples. When we look at the 1 atom S sample we see relevant amounts of Si as we expect. The chart shows that in terms of mass, Si makes up roughly three percent, as compared to the 19 percent included in the alloying process. 2 atom S provides a very perplexing ratio B to C; C predominates the sample, at levels much higher than are found in B₄C. This increase in C is also marked by a factor of three increase in Si incorporation. This will be discussed further in the analysis section.

Table 16. B₄C as delivered.

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
B K	69.62	71.95	592.99	3.74	0.5298	0.9856	0.7718	1.0000
C K	29.90	27.82	91.22	12.50	0.0224	1.0343	0.0723	1.0000
O K	0.13	0.09	1.47	99.99	0.0002	0.9870	0.1284	1.0000
SiK	0.35	0.14	42.25	6.52	0.0032	0.8937	1.0176	1.0094

Table 17. B₄C milled.

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
B K	59.87	62.54	483.50	3.73	0.4239	0.9811	0.7213	1.0000
C K	39.60	37.23	142.20	10.16	0.0342	1.0295	0.0837	1.0000
O K	0.06	0.04	0.60	25.11	0.0001	0.9826	0.1215	1.0000
SiK	0.47	0.19	56.60	1.21	0.0042	0.8897	1.0060	1.0089

Table 18. 1 atom SPEX.

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
B K	44.91	50.42	116.40	6.41	0.2024	0.9901	0.4551	1.0000
C K	45.96	46.45	102.80	9.95	0.0490	1.0399	0.1026	1.0000
O K	1.61	1.22	9.00	10.46	0.0019	0.9938	0.1215	1.0000
SiK	3.22	1.39	185.90	1.54	0.0278	0.9018	0.9524	1.0042
CrK	0.30	0.07	6.70	3.13	0.0028	0.7632	1.0315	1.1691
FeK	1.04	0.22	18.60	2.90	0.0096	0.7585	1.0270	1.1966
NiK	0.15	0.03	2.30	5.93	0.0015	0.7652	1.0215	1.3033
W L	2.82	0.19	10.10	3.51	0.0165	0.5368	1.0716	1.0154

Table 19. 2 atom SPEX.

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
B K	9.58	11.43	80.90	8.22	0.0257	0.9752	0.2749	1.0000
C K	77.22	82.96	2214.70	8.51	0.1925	1.0244	0.2433	1.0000
O K	1.07	0.86	28.10	10.28	0.0011	0.9791	0.1054	1.0000
Si K	9.84	4.52	3037.30	1.66	0.0819	0.8886	0.9362	0.9997
W M	1.90	0.13	237.10	7.98	0.0191	0.5920	1.6911	1.0045
Fe K	0.38	0.09	32.90	2.06	0.0031	0.7470	1.0254	1.0462

I. 40MM POWDER GUN SYSTEM

A 40mm single-stage powder gun built by Physics Applications Inc (PAI) was used to enable impact velocities from 0.3 to 2.7 Km/sec [42]. The 40mm gun system consists of a two-piece, 40mm launch tube 5.5 meters in length backed by a catch tank system supporting both Hugoniot based ballistic impact studies and projectile arresting, Figure 43. The gun system is typically fired within a vacuum environment both to reduce pressure within the catch tank region but also to prevent thermal heating during impact from rapidly compressed gases just prior to target impact. A Leybold D65B vacuum pump capable of pumping a vacuum at 53 CFM was used to pull a vacuum of ~100 millitorr.



Figure 43. 40mm single-stage powder gun.

The 40mm gun system incorporates electro-pneumatic valving to remotely control all vacuum and venting of the gun system. As vacuum is required to be pulled up to the time of the gun firing remote operation is a requirement, Figure 44.

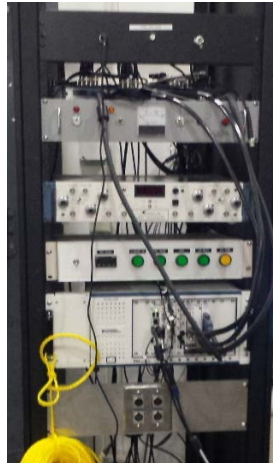


Figure 44. Gun system computer.

The gun system incorporates a sting tube to serve as the propellant system containment and ignition. The sting tube consists of a short and long version. The short version contains a lower volume (up to 400 grams) whereas the long sting can accommodate loads up to the maximum of 700 grams, Figure 45. For the primary charge two types of powder were utilized, they have equal performance characteristic from an industry stand point, Vihtavouri HE and Hodgdon H50BMG. Both are 0.50 caliber propellants.



Figure 45. Sting tube.

The firing chain for the 40mm consists of 1.5 grams of Hodgdon 777 propellant within a primed 300 Winchester Magnum followed by 11 strands of Benite that are contained within the sting tube (used to enable even burning of the propellant). As the Benite burns much faster than the propellant a uniform radial burn of the propellant occurs (avoid any travelling waves).

To initiate the Winchester Magnum an electro-mechanical firing system is incorporated. This firing system is activated by a 300 volt capacitive discharge to a solenoid with an iron plunger rod. When the iron plunger rod solenoid is activated the plunger is pulled towards the center of the solenoid striking the firing pin and initiating the firing chain through the primed Winchester Magnum cartridge, Figure 46



Figure 46. The breach plug securely constrains the main charge, holds the secondary charge, and attaches the firing solenoid.

After launch the projectile will travel down the launch tube towards the target system. Just prior to target impact both a means to trigger instrumentation as well as measure the incident velocity must be performed.

J. TARGET AND PROJECTILE ASSEMBLY

All of the ballistic impacts used to probe the dynamic strength of a target material require a very high planarity impact between the projectile and target. The target holder must both enable a high precision alignment to the projectile as well as the ability to exactly measure the alignment and incident velocity during impact.

The target base is 3-D printed from ABS plastic. It provides the structure on which the target assembly is built and is the interface that secures the assembly to the gun system. The mounting ring is 12.9mm tall with an outer diameter of 88.6mm an inner diameter of 63.2mm, the floor is 1.5mm thick with a 36mm hole in the center for the target to mount. Around the circumference of the central hole, four hollow cylinders, 19mm tall, with an ID of 0.9mm are used to hold the four shorting pins, Figure 47



Figure 47. Target base.

Within the 36mm center hole of the target base, the ceramic target is placed. The ABS plastic base provides a snug, hand pressed fit to the ceramic target disc. The target and ceramic disc are placed on an optical flat to ensure planarity between the two, Figure 48.

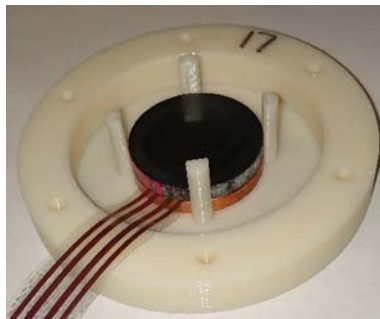
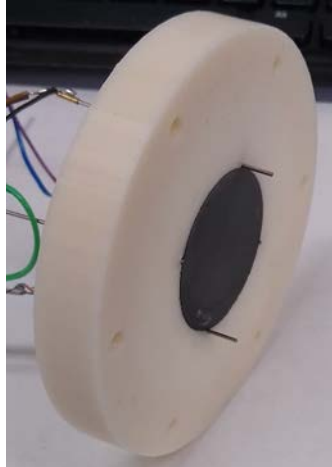


Figure 48. Ceramic press fit to developing target assembly.

Once the ceramic is properly aligned and adhered to the target holder, the shorting pins are installed. A total of four pins are used for each shot placed directly around the perimeter of the ceramic target 90 degrees apart. Two of the pins 180 degrees apart protrude past the face typically at a set distance of .25" while the second pair remain flush with the target. The incident velocity prior to impact can be measured through the time separation

between impacting the two pin sets and the known separation distance (0.25"). In addition to the incident velocity, the impact planarity can be determined, Figure 49.



Note that this target does not have a secondary impactor.

Figure 49. Shorting pins installed: Two set flush with target surface, two set 0.25" depth.

A cross bar is placed on the back side of the target holder to align a fiber optic collimator used to perform PDV. The cross bar is printed out of ABS plastic (just like the base), the none back reflecting (NBR) probes utilized are commercially available. Two were utilized, a Thor Labs part# 50-1550A-APC, and an OZ Optics serial# 240349-19. The Thor collimator was placed near the center of the focal point referencing the distance from the back side of the target with the front side of the collimator, Figure 50.



Figure 50. Cross bar and NBR probe.

The crossbar height needs to be set to $\sim 17\text{mm}$ from the back of the ceramic to put the collimator near its focal point of 15mm . The variation in target thickness requires adjustment in the collimator separation distance through shimming washers to set the collimator close to the focal point separation between the probe and back face of the target, Figure 51.

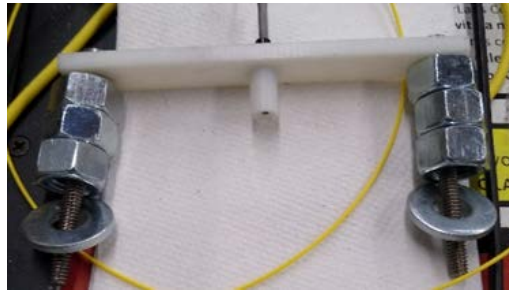


Figure 51. Cross bar with hardware and NBR probe.

At this point our target assembly is built and ready to be mounted to the base plate within the catch tank of the 40mm gun system. The base plate is made of steel, with an outer diameter of $11''$, an inner bore of $3''$ and a plate thickness of $0.777''$. The target system mounts with six small 8-32 screws and the base plate mounts to the catch tank, Figure 52.



Figure 52. Base plate.

It is critical that the base plate is aligned perpendicular to the projectile. To ensure proper alignment a proximity sensor is mounted within a 40mm OD bar that can be rotated within the gun bore. A stop is placed on the cylinder insert to maintain a fixed location of the proximity sensor for the end of the gun muzzle. As the proximity sensor is rotated 360 degrees the separation distance variation can be observed. The mounting of the target base plate enables both course and fine adjustment of the angular position of the base plate. After final alignment of the base plate, the proximity sensor should be able to be rotated with no variation in the separation distance from 0 to 359 degrees.

K. PROJECTILE

The projectile consists of a polycarbonate cylinder with a front machined cavity to insert a 38mm impactor as well as a skirted back with o-ring grooves to enable a vacuum seal during pump down of the gun system. The projectile is 40mm in diameter 85.5 mm in length, and weighs approximately 120 grams, Figure 53



Figure 53. Sabot.

The impactor used within these studies is a copper disk 38mm in diameter and 6mm thick, its faces are planar to within 0.00127 cm and a smooth machine finished, with a mass of ~ 60 grams, Figure 54.



Figure 54. 38mm diameter Cu impactor.

The sabot and the impactor together complete the projectile, total mass of the projectile is 180 grams, Figure 55.

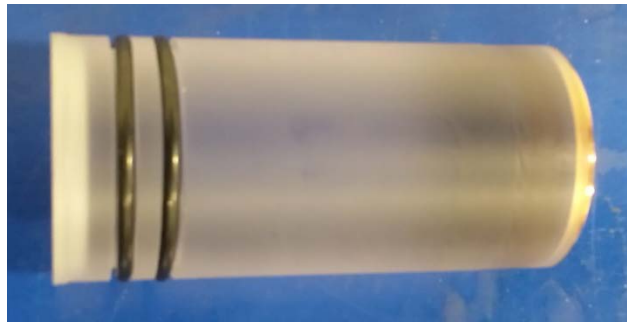


Figure 55. Assembled 40mm projectile.

1. Determining Impact Pressure

A key determination is the quantity of powder needed to accelerate projectiles to the target with sufficient impact velocity to exceed the HEL of B4C. It is well known that the HEL of B4C is ~20GPa and that its final Hugoniot state (HL) is ~40GPa [20]. From equations 18–21 below, we can determine the required impact velocity.

$$P = \rho_o U_s u_p \quad \text{Eq 18}$$

$$U_s = A + B u_p \quad \text{Eq 19}$$

$$P = \rho_o (A + B u_p) u_p \quad \text{Eq 20}$$

We can rearrange the formula and complete the square to find

$$u_p = \sqrt{P/(B \rho_o)} - (A/2B). \quad \text{Eq 21}$$

To exceed B₄C's HEL and HL will require a projectile impact speed of ~2000m/s. The 40mm did not come with a charge to projectile mass ratio (CPR) velocity curve. Using our own collected data from Table 20 a CPR velocity curve was developed, Figure 56. This curve provides a good estimate of how much powder the main charge will require based on the projectiles CPR and the desired impact velocity.

Table 20. Charge and impactor velocity.

labtest #	velo type	ave velo, m/s	charge mass, g
11	shear	1876	350
12	shear	1727	350
13	shear	1990	500
15B	Cu BW	2048	300
17	Cu BW	1737	300
18	Graph BW	1264	300
20	Graph BW	1476	400
23	Short	2387	700
26	Short	2737	700
27	Short	2086	540
28	Short	2186	545

*Shows the relations ship of charge mass to impactor velocity. It is worth noting that the Cu BW provided inconsistent results. The other three methodologies were consistent.

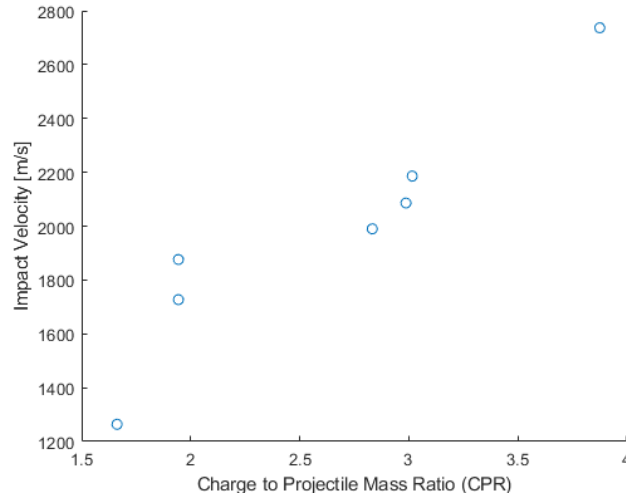


Figure 56. Charge projectile to mass ratio vs. impact velocity.

L. INSTRUMENTATION

Key measurements within the ballistic tests include:

- Impact velocity
- Planarity
- Photon Doppler Velocimetry (PDV)

1. Impact Velocity

Measurement of impact velocity uses knowledge of the change of a moving objects position divided by the time it took to change its position.

$$velocity = \frac{\Delta x}{\Delta t} \quad \text{Eq 22}$$

The key principle is to have a capability to register the projectile as it passes different known locations. At each known position an ability to record the time at each location with enough temporal resolution (less than 1% error).

Within this test series multiple velocimeters were investigated including: lasers, shear pins, graphite rods thin Cu break wires and shorting pins. Each system had its advantages and disadvantages.

Lasers were provided with the initial gun system but issues with the design caused difficulties in maintaining laser light on the fiber optics. It was determined that lasers may be the best option but a robust system designed from scratch was needed.

A second technique was shear pins. Shear pins reliably triggered but, an error in the tip position where the shear pin triggered created errors greater than 5% due to bending prior to a shorting pulse being sent. This option was additionally very costly as the shear pins were repurposed shorting pins which cost > \$25.00 per pin.

Thin Cu wires were incorporated to allow the incident projectile to cut the wires at specific locations. Here the wires were connected to a break screen circuit, when conduction is broken a pulse is sent. The key issue is the instantaneous breaks did not occur and some flexing resulted in errors in the measured velocity. In addition, this system was dependent on the tension of the Cu wire where wires under higher tension triggered earlier than wires under less tension. This issue caused the Cu wire to be dropped from velocity measurements, but was permanently incorporated into initial triggering of all instrumentation.

Graphite rods 0.5mm in diameter currently used for mechanical pencils were incorporated in the next velocimeter study, Figure 57. For lower velocities this technique was very consistent and provided repeatable results but at higher velocities the vibrations that propagated through the gun barrel leading the projectile would cause the lead rods to break prior to the projectiles arrival. It is believed that with proper mounting this issue could be resolved.

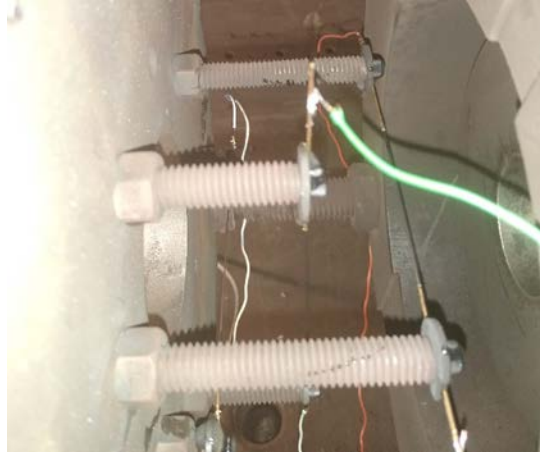


Figure 57. Graphite break wires set on the front of the base plate.

The final velocity technique incorporated shorting pins commonly used for planar impact measurements with two of the four pins separated by 180 degrees are set to protrude exactly $\frac{1}{4}$." This technique requires extremely high measurement accuracy and a very high temporal resolution. The benefit is simplicity and reliability for the velocity measurement directly before impact. All final shots incorporated in this test series used the shorting pin technique to obtain impact velocities.

Shorting pins provide a switch where the detection of an event occurs when an object comes in contact with the end surface of the cylindrical probe, Figure 58. The most common application is for planar impact studies to understand the impact orientation of the projectile relative to the target. A Dynasen pin mixer model CS2-50-300, box is used to provide a 15 volt signal when the pin is shorted.

Using the four pins we can take each pair of pins (180 degrees apart) and using the incident velocity we can use the cross product of the two vectors to determine the orientation of the projectile from normal. This measurement will enable the ability to quantify the exact orientation of the projectile Figure 58.

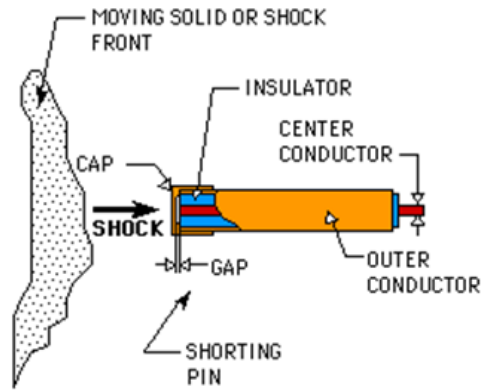


Figure 58. A shorting pin creates a short when impacted, providing an exact time stamp of when and where the projectile impacted.

2. Photon Doppler Velocimetry

A Thor Labs 50–1550-APC fiber optic collimator is connected via single mode compatible crash cable to the Non-Back-Reflecting (NBR) probe port on a Third Millennium Engineering F239B photonic doppler velocimeter (PDV) transceiver. This analog receiver has an internal 50 mW laser. From the initial 50mW laser 99% of its output is routed through a circulator thru the NBR probe to the target. The remaining 1% is routed through a variable optical attenuator (VOA) that can be tuned via voltage adjustments to match the intensity of the reflected light from the back face of the target. Properly adjusted, the amplitude of the probe signal and the VOA signal are equal allowing for the effective development of the beat signal as the two waves are added in real time when the target is moving. The beat signal is the constructive interference of the target beam with the tapped off reference. The beat frequency is related to the doppler shift in frequency of the source light. That shift is directly related the velocity of the target, Figure 59 [43]. We will take this time to develop the doppler equation, beats, and our anticipated target velocity output, because of its direct relevance to follow on instrumentation.

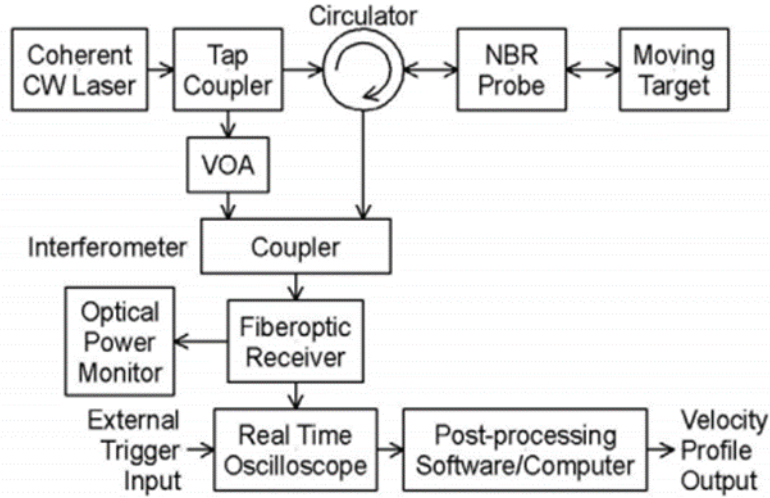


Figure 59. Homodyne PDV with NBR probe. Source: [43].

Doppler is the up or down shift in frequency or wavelength of a received signal in reference to a source. Up shifts are caused by relative signal compression (motion towards the sensor), down shifts are caused by relative signal stretching (motion away from the sensor). Eq 23 presents the wavelength dependence on an object within the field of view of the of the collimating probe.

$$\lambda' = \lambda (1 - v/c) \quad \text{Eq 23}$$

λ' is the resultant wavelength, λ is the source wavelength, v = speed of target, and c = speed of light. Note we can change c to match the speed of propagation for any medium in which we are looking to measure the speed of an object relative to a source signal.

Consider a case were a target is moving at 2.5km/s. Using the above we determine

$$\lambda' = 1550\text{nm} (1 - (2.5 \times 10^3 / 3.0 \times 10^8)) = 1549.987083\text{nm}.$$

The beat frequency can be determined.

$$f_b = c [(\lambda - \lambda') / (\lambda \times \lambda')] \quad \text{Eq 24}$$

$$f_b = 3.0 \times 10^8 (0.012917\text{nm} / 2402479.979\text{nm}^2) = 1.613 \times 10^9 \text{Hz}$$

To resolve this beat frequency requires the use of a real time oscilloscope (RTO) that can sample at least twice the beat frequency to keep us above the Nyquist limit. For a target traveling towards a probe at a velocity of 2.5km/s requires a scope bandwidth of 3.23GHz. We utilized an Agilent Technologies DSO81004A 10GHz (bandwidth), 40GS/s (sampling rate) oscilloscope to meet this requirement.

As mentioned previously, there were a few underlying challenges with developing an accurate beat test for our samples prior to the shot experiment. First, the only way to generate a beat is to have relative motion at the sensor. Some PDV setups utilize a second laser that is offset specifically to generate a beat within the system when at rest. This is called a heterodyne system and when the VOA is properly adjusted the rest beat will be present at double the input amplitude. Our system is a homodyne system, meaning our signal laser is the only source we have. In order to generate a test beat, a test structure capable of providing oscillations at frequencies up to 200Hz was required. The best performing solution observed incorporated a Pasco Scientific Mechanical Vibrator model SF-9324 enabled a reliable oscillation of the PDV probe.

Using the collimator probe attached to the Pasco vibrating shaft each target can be mounted above the oscillating probe near the focal point distance, Figure 60. The oscillating probe facing the back face of the target enables the ability to determine the correct attenuation of the tapped 1% of the incident light to optimize the amplitude of the beat frequency.

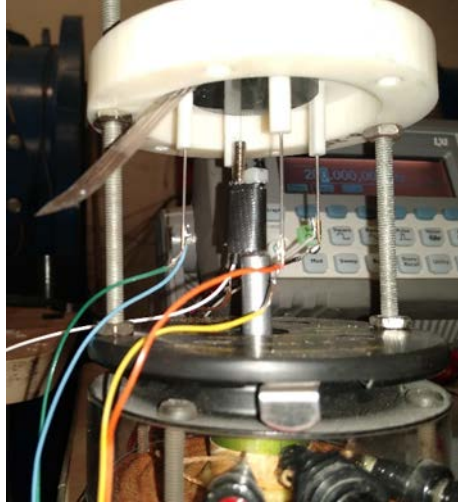


Figure 60. Target mounted to vibratory optical device.

The Pasco oscillator enabled driving the PDV probe at 200Hz enabling a clean beat pattern once the attenuation voltage was adjusted to match the amplitude of the reflected light, Figure 61. All targets prior to testing would be mounted to the vibrator and be checked for beats. The attenuation was adjusted for each target to maximize the beat amplitude.

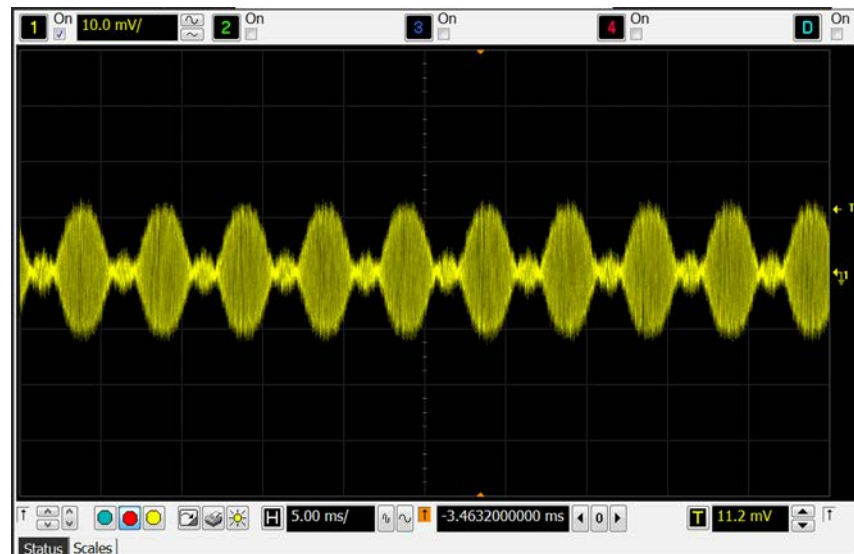


Figure 61. PDV beats at 200Hz from vibratory optical device.

M. SHOCK EXPERIMENTS

Incorporating the proper charge weight to propel the projectile impact velocities up to velocities of 2.74 km/s can enable a large range of impact pressures from less than 1 GPa to values close to 100 GPa. Impact pressures are dependent on: incident velocity, densities of the impactor and target, and their shock velocities. With the knowledge of the physical properties of both the impactor and target the impact pressure can be customized based in the impact velocity.

Each test consisted of a Cu impactor impacting a B₄C target. At impact we know the impact velocity, and the pressure at the interface based on the 1D Hugoniot jump equations. The pressure at the interface between the impactor and sample is the same. This allows us to work through the materials HEOS and determine the target particle velocity (u_p) directly after impact. The generalized process is developed below.

$$P_i = P_t, \text{ Pressure at the interface is equal between impactor and sample.} \quad \text{Eq.25}$$

$$Z_i * u_{pi} = Z_t * u_{pt}, \text{ Pressure is the product of impedance, } Z \text{ and particle speed, } u_p. \quad \text{Eq.26}$$

$$\rho_i U_{si} u_{pi} = \rho_s U_{st} u_{pt}, \text{ Impedance is the product of density, } \rho \text{ and sound speed, } U_s. \quad \text{Eq.27}$$

$$\rho_i (A_i + (B_i u_{pi})) u_{pi} = \rho_s (A_s + (B_s u_{pt})) u_{pt}, \text{ Sound speed can be determined.} \quad \text{Eq.28}$$

$$0 = B_s u_{ps}^2 + A_s u_{ps} - [(\rho_i / \rho_t) (A_i + (B_i u_{pi})) u_{pi}], \text{ Arranged into a quadratic.} \quad \text{Eq.29}$$

$$u_{ps} = \text{sqrt} [\rho_i (A_i + (B_i u_{pi})) u_{pi} / (B_t \rho_t)] - (A_t / (2 B_t)), \text{ Solved by completing the square.} \quad \text{Eq.30}$$

Table 21 provides a combined list of shock experiments. This table presents the sample type, target system, primary charge, impact velocity, and expected particle velocity. Actual particle velocity can be developed from the PDV data. It is worth noting that having the impactor particle velocity supports determining the timing of the PDV data during processing.

Table 21. Completed shock experiments.

Test		Sample			Impactor			2nd Imp		Charge	Ui	Up est
#	type	mass, g	ρ , g/cc	type	mass, g	thick, mm	type	mass, g	thick, mm	mass,g	m/s	m/s
12	Cu	51.3	8.96	Cu	60.06	5.92	NA	NA	NA	350	1727	863.5
13	B4C Grd	UNK	2.52	Cu	56.53	5.6	NA	NA	NA	500	1990	3266
14	1 atom S	9.47	2.608	Cu	60.34	5.94	NA	NA	NA		UNK	NA
15	2 atom S	11.21	2.77	Cu	60.33	5.94	NA	NA	NA		UNK	NA
15B	Cu	51.33	8.96	Cu	60.06	5.92	NA	NA	NA	300	2048*	1024
15C	Cu	51.22	8.96	Cu	60.48	5.97	Cu	51.27	6.35	300	UNK	NA
16	1 atom S	10.48	2.62	Cu	60.42	5.97	Cu	51.28	6.35	300	UNK	NA
17	2 atom S	7.647	2.77	Cu	60.22	5.94	Cu	51.28	6.35	300	1737*	1371
18	3 atom S	9.34	2.065	Cu	60.45	5.97	NA	NA	NA	300	1264	2461
19	1 atom S	10.75	2.67	Cu	60.25	5.97	Cu	5.56	0.78	400	NG	NA
20	3 atom S	9.19	2.125	Cu	60.55	5.97	Cu	6.24	0.79	400	1476*	2272
21	B4C Grd	9.64	2.53	Cu	60.23	5.97	NA	NA	NA	700	NG	NA
22	B4C Grd	11.76	2.53	Cu	60.08	5.94	Cu	6.22	0.79	700	NG	NA
23	B4C	11.76	2.53	Cu	60.55	5.97	Cu	6.22	0.79	700	2387*	3159
24	1 atom S	9.27	2.38	Cu	59.65	5.88	Cu	6.17	0.79	700	NG	NA
25	2 atom S	8.56	1.92	Cu	60.95	6.02	Cu	6.24	0.79	700	NG	NA
26	B4C	10.685	2.498	Cu	60.63	6.77	NA	NA	NA	700	2737	4398
27	B4C Grd	11.13	2.53	Cu	60.79	5.97	NA	NA	NA	540	2086	3568
28	1 atom R	7.61	2.35	Cu	60.73	5.99	NA	NA	NA	545	2186	3725

*Test 15B & 17 abnormally high U_i due to Cu break wire; 20 thru 25 low U_i due to faulty vacuum.

The PDV data generated during the experiment is post processed using Sandia InfraRed Heterodyne aNalysis (SIRHEN). From SIRHEN we can identify the velocity vs time of the target disc directly after impact. The velocity can be directly correlated to the impact pressures imparted on the target by the incident impactor.

Labtest 28 presents the shock experiment of the 1 atom Restch B₄C:Si. ceramic target. Table 22 shows the relevant data that was calculated from the derived impact velocity. This provides a guide to what should be observed in the PDV data.

Table 22. Ballistic impact data Labtest 28.

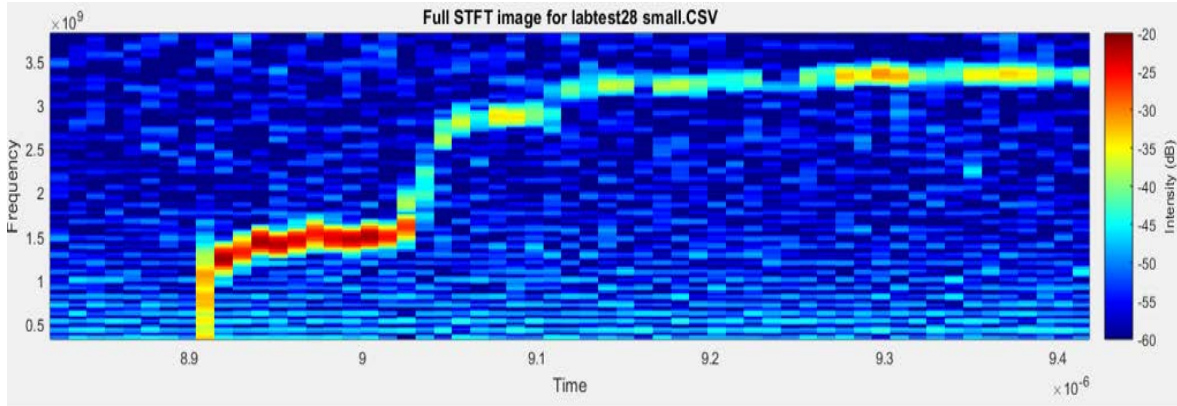
Empirical		Derived				
TOF(s)	Dist(mm)	U_i (m/s)	U_p (m/s)	P_i (Gpa)	Fb (Hz)	Tb(s)
3.02E-06	6.604	2186	3752	63.4	2.40E+09	4.16E-10

The RTO is triggered 0.777” prior to the target. The trigger enables both the PDV and shorting pin initiation. Collected data with the PDV enables determination of the shock velocity (using ion pin and initial reverberation of the target back face). The collected PDV data is presented in Figure 62.



Figure 62. RTO of Labtest 28.

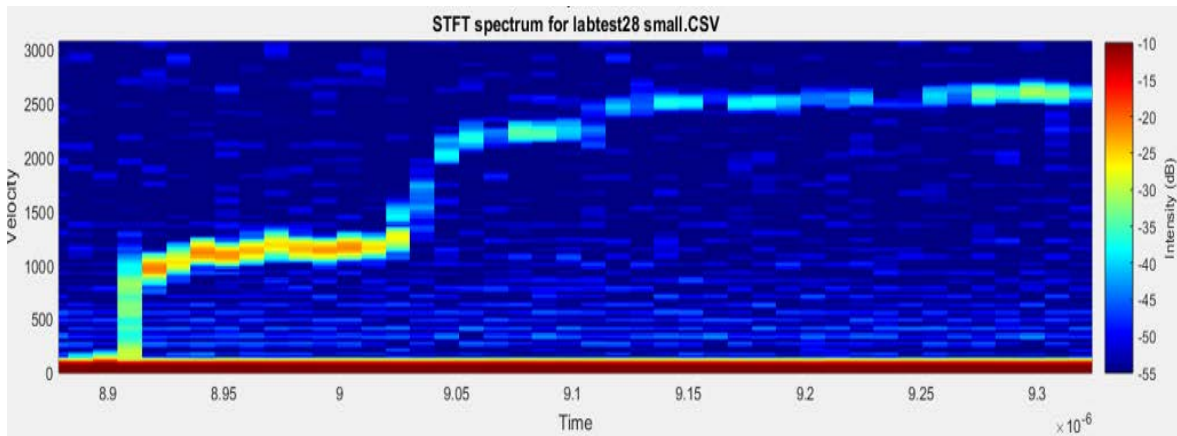
The RTO data is taken and run through SIRHEN. SIRHEN allows for a quick reduction of the RTO data through a Fourier conversion. The region of interest for this hypothesis is the elastic precursor region from 8.85μs to 9.03μs. In this section a particle velocity is developed, it is clearly represented as beats in the RTO signal that SIRHEN converts to a beat frequency (F_b) vs time plot, Figure 63.



Generated from SIRHEN

Figure 63. F_b profile.

It should be noted that the F_b 's are in the proper range of GHz and that the derived maximal value is near the peak of the curve. There are larger F_b present in the trailing section of the signal and this represents the break up of the sample. Utilizing SIRHEN the F_b vs time plot is converted into a velocity (u_p) vs time plot. We can utilize the u_p vs time plot to determine if the HEL is different than standard B₄C, Figure 64.



Generated from SIRHEN

Figure 64. u_p plot generated from F_b profile.

Taking the u_p plot from SIRHEN and processing the data through Matlab we can isolate and analyze the region of interest (ROI) where the HEL is. In Labtest 28 we see that the HEL is clearly defined and the post yield region appears to maintain a positive slope, Figure 65.

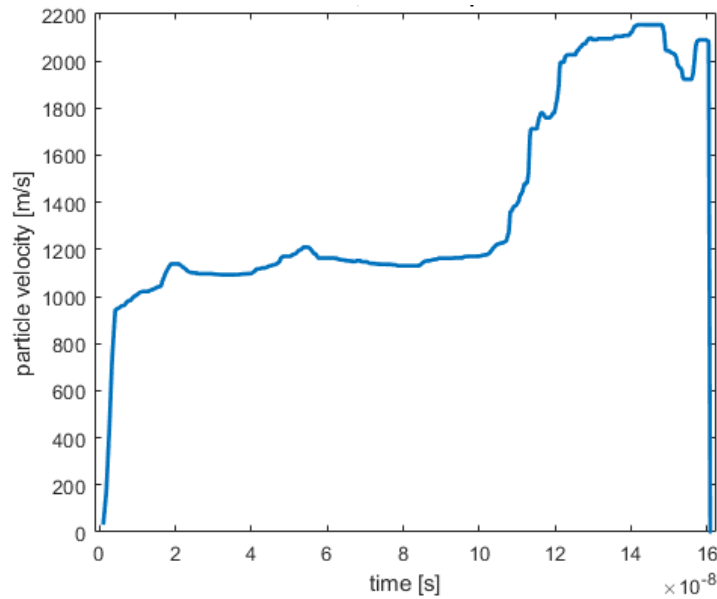


Figure 65. Labtest 28: 1 atom Retsch u_p vs. Time.

Using the equations developed earlier in the data section a pressure vs time plot is developed, this plot displays a positive slope in the elastic region, Figure 66. Simple inspection shows the HEL at ~ 900 m/s at ~ 18 GPa. After the HEL the sample post yield hardens to ~ 1200 m/s at ~ 25 GPa. In the analysis section time will be taken to compare HEL of the 1 atom Retsch to Grady's previous work.

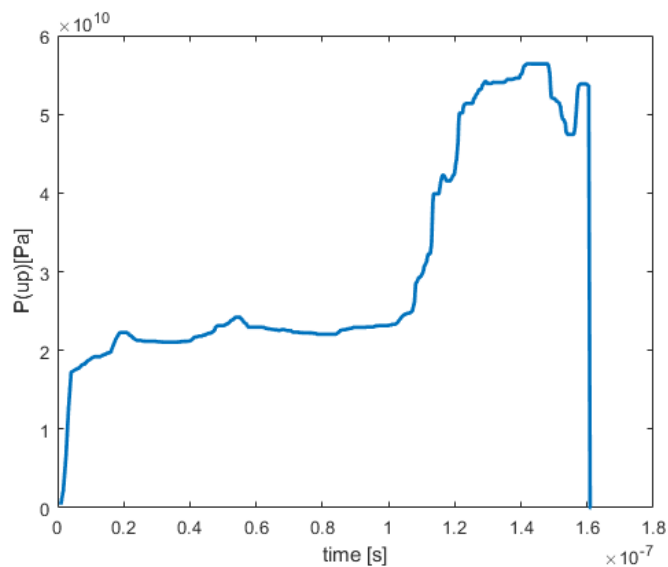


Figure 66. Labtest 28: 1 atom Retsch Pressure vs. Time.

A direct comparison of the 1 atom Retsch and standard B₄C on a pressure vs up plot provides some insight into how different our sample is to standard B₄C, Figure 67. Apparent in the plot is the shallower curvature of the 1atom sample. Less curvature indicates a lower pressure for an equivalent particle speed. This would indicate some material property change from B₄C; in the analysis section we will discuss prior work that may account for this finding.

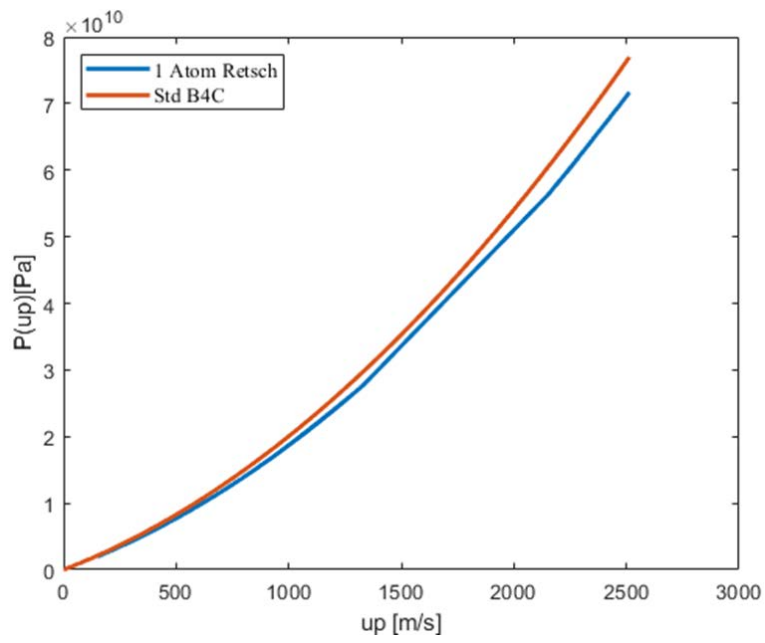


Figure 67. P vs u_p comparison of 1atom Retsch and standard B₄C.

V. ANALYSIS

A. EFFECTIVENESS OF HEBM

1. XRD

In analyzing the data it is readily apparent that HEBM is an effective technique for alloying Si into B₄C. Table 23 provides insight in to what changed in the powders physical parameters The XRD data clearly shows a reduction in crystallite size from the delivered powder to the alloyed powders.

Table 23. Alloyed powders and milled B₄C.

Sample	a(A)	b(A)	c(A)	V(A ³)	Crystallite Size (A)
0.33 Atom R	5.60561	5.60561	12.08961	379.89	242
B4C Milled S	5.605329	5.605329	12.09152	329.01346	161
1 Atom R	5.607668	5.607668	12.08909	329.22212	217
1 Atom S	5.606313	5.606313	12.08865	329.05094	168
2 Atom S	5.551	5.551	12.14	324	198

The comparison of 1 atom samples produced through ball milling of both the SPEX and Retsch show the biggest disparity in crystallite size. The SPEX ground sample is ~20% smaller than the Retsch ground sample. It is also worth noting of the two Retsch ground samples, the 0.33 atom sample [2] is ~10% larger than the 1 atom, the difference being a switch from SS grinding media to WC. Comparison of the SPEX milled alloys and powder provides insight into how much the lattice was affected by the inclusion of Si. It is not intuitive that the volume of the two 2 atom volume is reduced, yet the crystallite size was still the largest out of the three SPEX prepared samples.

2. XPS

While only being able to observe the first 10nm of depth into the sample powders, there is some useful data. Of importance is that beyond all of the oxides present at the surface, the visibility of Si being bonded to either B or C is significant. We know from

prior work done using DFT [2] that Si should be drawn to bonds broken during the milling process throughout the lattice [1], [36]. Comparison of the 1 atom samples reveals a higher inclusion of Si though out the sample, increasing from 4 (Retsch) to 12 (SPEX) percent. A point of interest in comparing the 2 atom SPEX to the 1 atom SPEX sample is the factor of 2 increase in the amount of Si-Si bounding. More important to our work is the x4 increase of Si to B/C bonding apparent in the SPEX samples. This would indicate that the SPEX derived samples have significantly more lattice defects for the Si to react with and bond

3. Raman

From the data, significant alterations to the B₄C unit cell are observed for the SPEX HEBM of the 1 and 2 atoms powders as the pressures are much higher when compared to the Retsch spectrum of the HEBM 1 atom. The change in spectrum clearly presents an alteration of the B₄C unit cell. The alterations will not be investigated in this thesis but will be incorporated in a future effort to study the alteration of the B₄C unit cell under higher energy ball milling. For now, we will simply state that the B₄C unit cell has been altered. For the HEBM with Si inclusions and larger variations in the unit cell when incorporating the larger pressures imparted with the SPEX HEBM.

B. CERAMIC DISC

1. SEM/EDS

Knowing that the milled powders show distinct lattice expansion as a result of Si inclusion it is important to understand how much of the Si for each sample was possibly retained when the alloys became ceramic discs. Using percent mass ratios, it was determined that the 1 atom SPEX retained approximately 20% of the Si included in the alloying process, roughly 7% greater than that observed by NRL [2]. The 2 atom SPEX saw a much larger increase in the amount of Si retained, approximately 37%. Coinciding with this large retention of Si was a 30% increase in the samples amount of C and a 30% reduction in B. This again raises the suspicion that an overabundance of Si is leading to a secondary formation of Si alloy.

2. Vickers Hardness

The hardness of the samples displayed in table 10 show that the hardness drops off with the inclusion of Si. This result is in conflict with the result of prior work of NRL [2]. This abundance may lead to the creation of SiC or secondary Si alloys within the sample during the manufacture of the ceramic. Even so our alloyed ceramics show hardness values higher than that of SiC (HV~ 25.50GPa). Both of the 1 atom samples are within~8% of the as delivered B₄C for hardness and~25% harder than the listed hardness of SiC. The milled B₄C is within ~4% of the as delivered B₄C.

3. Density

It is well understood that ceramic armor when produced need to be within 98% of their TMD. The samples produced for this thesis were hot pressed in line with industry standards for B₄C. Table 24 provides a break out of the sample densities compared to the TMD value that were previously determined.

Table 24. TMD compared to sample density (g/cc).

	TMD	test#	B4C Grd	test #	1 atom	test #	2 atom	test #	3 atom
Std	2.52	13	2.52	14	2.608	15	2.77	18	2.065
1 less B	2.78	21	2.53	16	2.62	17	2.77	20	2.125
1 less C	2.76	22	2.53	19	2.67	25	1.92		
Less BC	3.02	27	2.53	24	2.38				
Less CBC	2.66			28	2.347 *				

* Indicates sampel produced via Retsch HEBM. All others produced via SPEX HEBM.

Of the 14 samples that were tested, 5 failed to reach 98 % TMD. The drastic variation in density for test 18, 20, and 25 (<80% TMD) raise questions about the hot-pressing process. Test 24 and 28 are ~90% TMD and trend closely with the other 1 Atom samples that are aligned with Less CBC TMD. Coinciding with this observation test 15 and 17 align with 1 less C or B TMD. None of the samples tested showed alignment with Less BC TMD and B₄C milled maintains standard TMD.

C. EXCESSES Si

In the data section and in the analysis above there have been data points of divergence for samples over 1 atom of the elementally included Si. When evaluating the XRD data the 2 atom SPEX sample, a markedly reduced unit cell volume compared to the other SPEX milled samples was observed. The 2 atom SPEX EDS data shows a 37% increase in the amount of Si retained when compared to the 1 atom SPEX. This large increase in Si also coincided with a 30% increase in C and equivalent decrease in B. XPS likewise shows the 2 atom SPEX having a markedly higher concentration of Si than the 1 atom SPEX, and Retsch ball milled samples. In the XPS data, the increase in Si bonding from the 1 atom to 2 atom is 20% with the Si-Si and C-Si contributing equally. This large parallel increase in the Si-Si bonding points to a mechanism outside of SiC for the dramatic increase in Si retention between the 1 atom and 2 atom SPEX samples.

When taken as a whole, the data does support the conclusion that excess Si plays an active role in how the samples develop during milling and foundry operations. The coequal development of the Si-Si bonding in step with C-Si bonding raises questions regarding Si bonding to the reduced B₄C unit cell. What is not clear is whether the formation of SiC is taking place; further analysis is required.

D. SHOCK EXPERIMENT

The PDV data and the initial impact data allowed a good break down of how the 1 atom Retsch sample performed. The velocity time plot derived from the SIRHEN processed signal displays that the HEL increased to ~940 m/s (from 800m/s), this is a 140m/s increase over standard B₄C when compared to previous work [25], Figure 68.

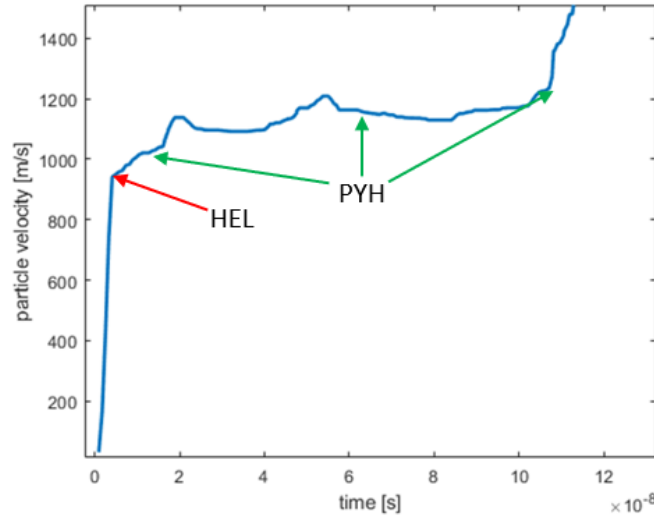


Figure 68. Elastic precursor wave profile 1atom Retsch.

Moving beyond the HEL in Figure 68 it is also apparent that the post yield softening present in B₄C is also missing. The 1 atom Retsch sample shows a distinctive positive slope from the HEL at 940m/s to 1230m/s demonstrating post yield hardening (PYH).

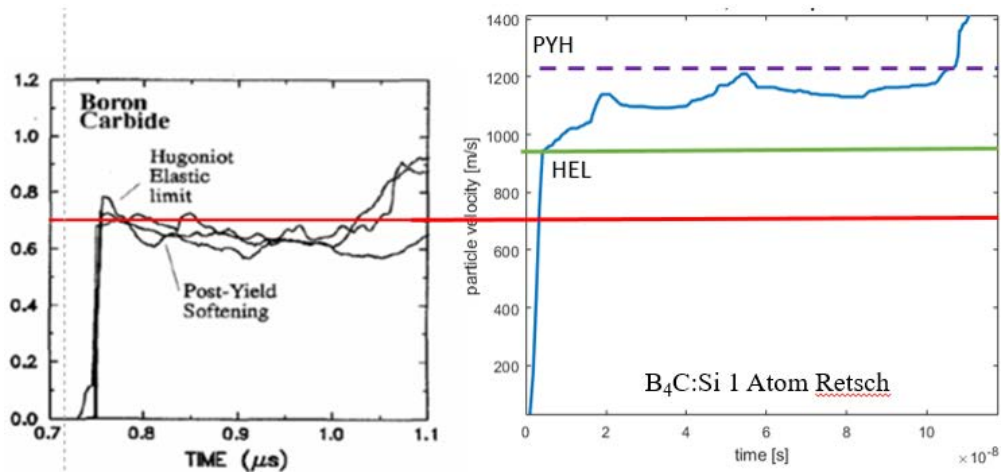


Figure 69. Direct comparison of B₄C and the 1 atom Retsch.
Adapted from [20].

Figure 69 provides a direct comparison of Grady's previous work [20] with the 1 atom Retsch plot. Using particle velocity, HEL for the standard B₄C is ~0.8 km/s whereas

the 1atom Retsch is around 0.94 km/s. Unlike standard B₄C, our sample experiences a post yield hardening that continues up to a particle velocity of 1.2 km/s which was not observed in the original B₄C study.

Transitioning from particle velocity to pressure the HEL for the standard B₄C is ~18 to 20Gpa, our samples observed HEL is ~18Gpa. Unlike standard B₄C our sample PYH to ~25Gpa. Of interest to our analysis is Grady's modified EOS for less than 30GPa [44]. Plotted against our standard EOS analysis we see Grady's EOS raises our samples HEL to ~21GPa and PYH to ~30Gpa, Figure 70.

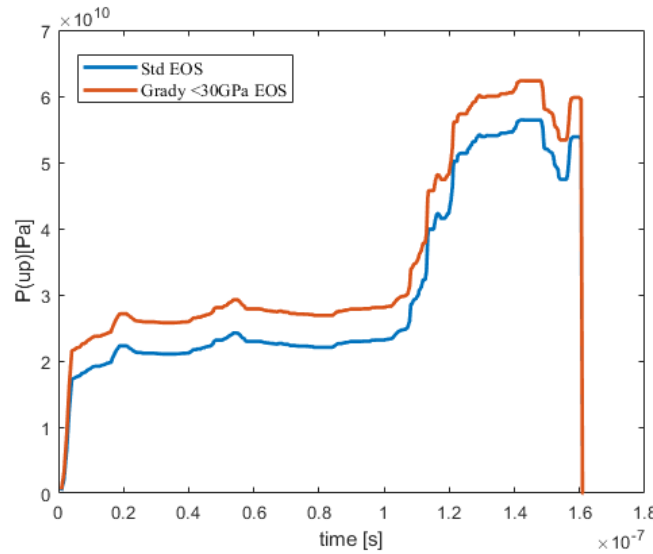


Figure 70. Comparison of HEL and PYH using Std EOS and Grady's EOS.

The Grady EOS for impact pressures below 30GPa was developed using data that was generated in previous experiments that also had targets with lower densities. The data utilized had targets ranging from 1.9g/cc to 2.4g/cc, our target was in the higher end of the range at 2.347g/cc [44]. Table 24 is from Grady's paper; our ROI is in Phase II.

Table 25. Shock EOS and phase transformation properties of boron carbide inferred from shock hugoniot data. Source: [44].

Phase	C_o (km/s)	S	p_t (GPa)	Δv_t (cm ³ /g)
B ₄ C-I	9660	1.32	Ambient phase	Ambient phase
B ₄ C-II	7700	2.15	<30	≈0.006
B ₄ C-III	9800	0.80	45–50	<0.002

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VI. CONCLUSIONS

The goal of this thesis was to determine if the elemental inclusion of Si could improve the material properties of B_4C . The main thrust of this effort aimed at preventing the graphite shear layer that develops under high shock ($>20\text{GPa}$). It is roughly accepted that under high shock the unit cell deformation enables the ejection of C enabling the formation of graphite along certain planes creating shear bands, and leading to a structural collapse of the B_4C .

Prior DFT work indicated that B_4C would readily accept an inclusion of Si into each of the three primary polytypes. Within the most probable polytype the Si would reside at the polar location within the icosahedron. This site is suggested as the most probable site for the ejection of C where if replaced by Si could prevent the graphite formation.

Prior work on B_4C indicated that traditional wet chemistry would not prove effective at incorporating Si into the B_4C lattice due to the required high temperatures necessary to enable Si within the unit structure. NRL had shown previously that HEBM was effective at alloying Si into the B_4C lattice (the results are not conclusive regarding the exact placement of Si but a uniform distribution throughout the sample is observed). The HEBM does allow effective particle size reduction, lattice defect creation, creating greater reactivity for both alloy constituents.

Our milling process was unique to the previous work performed at NRL where higher milling pressures were achieved through both higher impedance media (WC) and faster milling speeds (SPEX). WC is both denser (2x) and has a higher wave speed compared to SS, providing greater force and higher energies during the milling process. Utilization of the SPEX mill doubled the milling speed also increasing the work done on the powders.

Several techniques were utilized to quantify the effects of the HEBM with WC on B_4C and Si. Each technique provides a unique insight into how $B_4C:Si$ is unique to B_4C . XPS looks at bonding in the alloyed powders, it was shown that both the Retsch and SPEX milled Si samples developed Si-C/B bonding. It should be noted that the SPEX samples

had significantly more Si-C/B bonding than the Retsch. XRD Rietveld analysis demonstrated the volume expansions of the unit cell due to Si inclusion and the reduction of crystallite size due to milling. It is worth noting that the 1 atom Retsch was ~20% larger than the 1 atom SPEX sample. Knowing that the XRD presented physically changed lattice constants Raman spectroscopy was used to determine if the changes to lattice parameters went beyond mere expansion. Our results show that for the 1 atom and 2 atom samples developed using the SPEX mill there was significant alterations to the underlying B₄C lattice.

Coinciding with the changes in the alloyed powders are the measurable changes found in the alloyed ceramic samples. Density changed as Si was included and the EDS data further supports the alloyed inclusion of Si with B₄C post foundry. The hardness of the alloyed ceramics was also found to be within acceptable hardness standards for B₄C, even with apparent softening due to the inclusion of Si.

Thus far we have reiterated that B₄C was physically and chemically altered thru the HEBM inclusion of Si. The alloyed powders, when processed into solid ceramics, maintained their Si inclusions while also retaining B₄C characteristic hardness. Taking all of this into account we come to what is of prime interest to this thesis, the elimination of the post HEL material softening in the B₄C lattice. The shock data and its analysis bear out the remarkable effect that alloying Si into B₄C has had on the HEL and post yield properties. It has been effectively demonstrated that B₄C:Si (1 atom Retsch) exhibits an increased HEL and post yield hardening.

These findings lay the ground work for future studies of B₄C:Si applied to armor applications where traditional B₄C is unsuitable due to observed post yield softening. Future work is still required to determine if the Si to B₄C ratio can be optimized to produce a more improved result than already achieved. Development of foundry production temperatures and pressures for B₄C:Si alloy is also needed. This should aid in achieving TMD of the ceramic as the amount of alloyed Si changes. In addition, fundamental studies of the observed peak shifts in the Raman spectroscopy and the corresponding lattice changes effected by the SPEX mill, and WC media would need to be investigated to understand the structural changes occurring in the B₄C unit cell.

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