Synthesis and spark plasma sintering of nano-structured ceramic materials for armour application

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2015

Xie, S. S. (2015). Synthesis and spark plasma sintering of nano-structured ceramic materials for armour application. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/65464>

<https://doi.org/10.32657/10356/65464>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**SYNTHESIS AND SPARK PLASMA SINTERING OF
NANO-STRUCTURED CERAMIC MATERIALS
FOR ARMOUR APPLICATION**

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2015

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NANO-STRUCTURED CERAMIC MATERIALS
FOR ARMOUR APPLICATION**

School of Materials Science and Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirements for the degree of
Doctor of Philosophy

2015

ABSTRACT

The use of extremely high hardness and light weight ceramic-based materials against ballistic threat is gaining popularity over the recent years. However, ceramics materials are often susceptible to tensile cracking and fragmentation due to its inherent brittleness which affects its performance as a protective material. On the other hand, high fracture toughness is highly desirable to minimise the fragmentation on impact but hardness and toughness tend to be mutually exclusive in most materials.

Researches on complex structured bio-composites have shown that their outstanding mechanical properties could even exceed that of its constituent materials. Therefore, this leads to new field of research into biomimetic materials to produce a new class of complex hierarchical structure superhard composite with advanced toughening mechanisms. In the current research, various form of superhard nanostructured crystals of boron carbide, B_4C , (nano-particles, nano-wires, nano-ribbons and nano-flakes) and boron suboxide, B_6O , (star-shaped nano-plate) have been synthesized as potential basic building block for assembling into such complex structured material.

Spark Plasma Sintering (SPS) is a novel powder consolidation process that utilises pulse current to achieve rapid densification at a relatively lower temperature than traditional sintering techniques. These reasons make SPS suitable for the consolidation of nano-structured materials that could minimise grain growth during sintering process and also retain the initial structure of the material. SPS was used in the consolidation of synthesized B_6O nano-plates.

Result from the SPS of B_6O show high hardness of 34.8 GPa and fracture toughness of $4.0 \text{ MPa.m}^{1/2}$. These results were some of the highest reported values compared to earlier literature and were only possible through the fast consolidation of SPS sintering technique.

Using a novel reactive-SPS technique, the unique core-shell structure of boron carbide and boron nitride (B_4C -BN) structured composite material was produced. High localised hardness of 56.0 GPa was registered using Berkovich indentation technique. The result also shows that an optimum amount of BN of up to 3% is desirable to achieve an even redistribution of stress to the load-bearing material structure. The toughness of the SPS-sintered B_4C -BN shows a parabolic increasing trend when the sintering pressure increases from 30 MPa to 90 MPa. The increase in toughness was attributed to the control of porosity in the composite which was possible through the introduction of nitrogen and oxygen. The research findings show a clear relation in material toughness enhancement with SPS consolidation. This reactive-SPS technique could also be used to optimise other B_4C -based composite materials.

ACKNOWLEDGEMENT

I would like to thank Assoc. Prof. Alfred Tok Ing Yoong for giving me the opportunity to pursue my doctorate in the field of ballistic protection materials. I will also like to thank him for providing the resources, advice and supervision in the project.

Deepest appreciation to Dr. Su Liap Tat and Dr Oleg Vasylykiv for their patience, sharing of their expertise, support and guidance throughout the project. It has been a great pleasure to work alongside them and greatly motivated by their passion in research.

I will also like to express my gratitude to the colleagues and staff in the School of Materials Science & Engineering (MSE) and Temasek Laboratories, TL@NTU, for providing the technical support to enable a smooth running of the project.

Special mention to the late Professor Ma Jan who have been an inspiration to me and many others in the School of MSE and TL@NTU. His contribution in research, particularly in the defence materials, has benefited a lot of students and researchers even after his departure.

Special thanks to my wife Eva for being supportive in my doctorate studies and also taught me the meaning of life beyond academic studies. Appreciate her for bearing with all my late nights in the laboratory and irregular work hours.

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CHAPTER 1: INTRODUCTION

1.1. Background

Ceramic-based ballistic protection materials are gaining popularity in the past decade due to its extremely high hardness and light weight as compared to metallic-based armour. When an armour material is sufficiently harder than the impacting projectile, it will fracture, fragment and deform, protecting the personnel or vehicular system. However, due to the brittle nature of high hardness ceramic materials, it is often susceptible to tensile cracking and fragmentation which degrade multiple-hits performance.^[1] High fracture toughness, on the other hand, is highly desirable to minimise fragmentation, therefore enhance the ability of the material to defeat multiple impacts.^[2,3] Unfortunately, high hardness and high toughness tend to mutually exclusive in most materials.^[3] High hardness, high toughness and light-weight materials are highly desirable for defence application against high velocity ballistic threats.

In recent years, the study of bio-mimetic material system has gained significant interests among material scientist and engineers.^[4] Biological materials have undergone millions of years of evolution to evolve into complex hierarchal structured composites whose outstanding mechanical properties could even exceed that of its constituent materials. One example of such complex structure bio-composite is the nacre of mollusc shell, which layered 'brick-and-mortar' structure could achieve an remarkable work of fracture that is three thousand times greater than its constituent component^[5] with negligible lost in the elastic modulus.^[6] Among the research groups that had attempted to

mimic the nacre structure of mollusc shell using advanced ceramic materials, only some of which have achieved significant improvement in mechanical properties.^[7-12] Although a highly ordered bio-mimetic structured materials has been proven as a viable solution in the enhancement of mechanical properties, improvement of toughness without any sacrificial loss in hardness have never been reported. An important feature of toughness-enhanced biological materials that has often been overlooked in bio-mimetic materials is the complexity of hierarchical structure that ranges from nano-scale level up to macro-scale level.^[13] The multi-scale level hierarchical structure design is critical as different scale level interacts and complements one another when a load is applied, advancing the mechanical properties beyond its monolithic counterparts.

The understanding of the contribution from the nanostructured material design to the toughening mechanism is still very limited ^[2,14] and the use of bio-inspired design in armour material application is still at the early stages of research. Consider that the bio-minerals are generally weaker in nature, using high performance synthetic materials to mimic the complex structured design in toughened biological composite will definitely scale the mechanical properties of novel structured composite material to an unprecedented height.

1.2. Objectives

The objectives of the project is to emulate the toughing mechanisms in biological materials using synthetic high hardness structured nanomaterials to produce a high hardness and high toughness structured composite for ballistic protection application. Below is the list of sub-objectives for the current study:

- Synthesize and study the growth mechanism of boron carbide (B_4C) and boron suboxide (B_6O) nano-structure materials as potential candidates for bio-mimetic structured composite material.
- Use spark plasma sintering to form complex shape nano-structure B_6O for the development of full dense, high hardness and high toughness structured composite.
- Understand the effect of structured composite in the enhancement of mechanical properties by fabrication and mechanical testing of core-shell structured B_4C -BN composite material.

1.3. Scope of work

The scope of the thesis will primarily be focusing on light weight (low-Z), superhard materials namely, B_4C , B_6O and B_4C -BN composite. High pressure superhard materials such as diamond and cubic boron nitride will not be covered as it is technically and economically not viable to produce large quantity of samples for testing in a laboratory-scale setting. The medium for powder consolidation will solely focus on spark plasma sintering as the only technique possible to achieve rapid sintering of nanostructured material without destroying the initial shape and also preventing of excessive grain growth.

CHAPTER 2: LITERATURE REVIEW

2.1. Armour Materials & Properties

Several criteria must be considered in the selection of materials for ballistic protection armour system. Some of these considerations include characteristics of the threats to be defeated, limitation on the weight of material system, and overall fabrication, maintenance and system replacement cost. Due to the many design criteria required, there is no single best material for every ballistic threats and situations. For example, vehicular armour steel that provides reasonable protection against standard issued military rifle will be insufficient if the allowable weight is reduced for personnel body armour. This is the reason why different armour materials are being used depending on the material performance and situational requirement.

The key to improve armour performance is to understand the material properties in relation to good anti-ballistic capabilities. However, armour material performance could not be linked to any single material properties due to the complexity of an dynamic ballistic impact.^[15] Empirical ballistic testing of armour system are typically carried out by actual firing test before it is deemed as being capable to defeat a certain threat with respect to specific standards, such as the projectile type, projectile velocity and the number of bullets that the armour can withstand before penetration occur. However, it is a known fact that material properties play an important role for screening potential candidates before ballistic testing.^[15] Some of these materials properties and their respective role in enhancing ballistic performance are listed in Table 1.

Table 1 Mechanical properties of material and their respective role in ballistic performance enhancement ^[1]

Property	Role/Effect in ballistic performance
Microstructure Grain size Minor phases Phase transformation or Amorphization (stress induced) Porosity	Affects all properties listed in the left-hand column below
Density	Weight of the armor system
Hardness	Damage to the projectile
Elastic modulus	Stress wave propagation
Strength	Multi hit resistance
Fracture Toughness	Multi hit resistance, field durability
Fracture Mode (inter vs. trans granular)	Energy absorption

An armour system typical consists of a hard ceramic surface to deform or destroy the projectile followed by a composite backing to trap any residual fragment that may cause penetration. To improve the ballistic protection capability of armour materials, it is vital to first of all understand the sequence of events that occur during a ballistic impact. ^[15-17]

- (1) A projectile impacts and transfers kinetic energy to the armour plate;
- (2) Shock wave causes tensile, compressive and shear stresses in the material;
- (3) A three-dimensional conical-shape crack is formed in the armour;
- (4) Armour plate reflects the stresses back to the impacting projectile;
- (5) The projectile is deformed, fragmentised or eroded;
- (6) The deformed projectile and/or fragments continue to pierce through;

(7) Fragments from the projectile and shattered armour could penetrate and trap within the backing composite material;

(8) Residual transmitted force cause deformation on the back of the armour;

In the worst case scenario, excessive blunt force trauma could cause severe internal bleeding or damage to the body organs. Fragments from both projectile and ceramic armour could also continue to penetrate into the wearer's body.

For the ceramic armour to successfully defeat the impacting projectile, it has to be sufficiently robust to deform or fragmentise the bullet, reducing significant kinetic energy to prevent penetration and back-face trauma. When a projectile is adequately destroyed by the ceramic surface without any further penetration, it is known as 'interface defeat'.^[15] To engineer such armour material requires in-depth knowledge of the complex relationship between the material properties, structure and processing technique. Some of the key parameters in armour ceramic selection include the density, hardness, grain size, fracture mode, and toughness. Table 2 summaries the materials commonly used for armour application and their corresponding mechanical properties. The most widely employed design configuration for armour consists of a hard impact face and a softer backing material. The purpose of the hard face, typically made up of hardened steel or advanced ceramic material, is used to deform and/or fragmentise the projectile. The soft material on the other hand acts as a 'net' to capture the residual fragments to prevent penetration. Therefore an extremely hard frontal material is often desirable to provide the highest level of protection. However, hard materials are typically brittle and exhibits large collateral damage as shown in Figure 1.

Table 2 Materials commonly used for armour application and their corresponding mechanical properties. [\[16,18-27\]](#)

Material	Designation	Density ρ (g/cc)	Grain Size (μm)	Young's Modulus E (GPa)	Flex Strength σ (MPa)	Fracture Toughness K ($\text{MPa}\cdot\text{m}^{1/2}$)	Fracture Mode	Hardness (kg/mm^2)	HK 2 kg (kg/mm^2)	Areal Density lb/sf (PSF)*
Al_2O_3	CAP-3	3.90	--	370	379	4-5	--	1440 (HK 1 kg)	1292	20.2
B_4C	Ceralloy-546 4E	2.50	10-15	460	410	2.5	TG	3200 (HV 0.3 kg)	2066	13.0
	Norbide	2.51	10-15	440	425	3.1	TG	2800 (HK 0.1 kg)	1997	13.0
SiC	SiC-N	3.22	2-5	453	486	4.0	IG, TG	--	1905	16.7
	Ceralloy 146-3E	3.20	--	450	634	4.3	--	2300 (HV 0.3 kg)	--	16.6
	Hexoloy	3.13	3-50	410	380	4.6	TG	2800 (HK 0.1 kg)	1924	16.2
	Purebide 5000	3.10	3-50	420	455	--	TG	--	1922	16.1
	SC-DS	3.15	3-50	410	480	3-4	--	2800 (HK 1 kg)	--	16.4
	MCT SSS	3.12	3-50	424	351	4.0	TG	--	1969	16.2
	MCT LPS	3.24	1-3	425	372	5.7	IG	--	1873	16.8
	Ekasic-T	3.25	1-3	453	612	6.4	IG	--	1928	16.8
SiC (RB)	SSC-702	3.02	45	359	260	4.0	TG	1757 (HK 0.5 kg)	--	15.7
	SSC-802	3.03	45	380	260	4.0	TG	--	1332	15.7
	SSC-902	3.12	45	407	260	4.0	TG	--	1536	16.2
SiC/ B_4C (RB)	RBBC-751	2.56	45	390	271	5.0	TG +Ductile Si	--	1626	13.3
TiB_2	Ceralloy 225	4.5	--	540	265	5.5	--	--	1849	23.4

Sources: CAP-3, SC DS: CoorsTek; Ceralloy, Ekasic-T: Ceradyne; Norbide, Hexoloy: Saint Gobain; Purebide: Morgan AM&T; SiC-N: Cercom (BAE); SSC, RBBC, BSC, SSS and LPS – M Cubed Technologies (MCT). Properties for other manufacturer's materials are from their respective websites except for 2kg Knoop hardness, grain size and fracture mode. *Areal density (PSF): weight of 12 x 12 x 1 inch panel in pounds. TG – Transgranular fracture, IG – inter granular fracture

Figure 1 Shattered pattern of boron carbide (left) & relationship of hardness to penetration resistance of conventional armour material (right). [\[28\]](#)

2.2. Superhard Materials

Superhard materials typically referred to materials with a Vickers hardness of more than 40 GPa.^[29] Apart from protective materials application, they are also widely used in the industries as abrasives, in cutting tools and wear-resistant mechanical parts or coating. Figure 2 summarised the groups of elements, compounds and structures to form hard materials together with the general research direction to achieve high hardness materials. The elements typically associated with high hardness materials are listed in the first row of the table. They are mainly the light elements (low-Z) and transition metals in the periodic table. The second row lists the hard compound synthesized from the elements from the first row. Hard compounds can generally be classified as low-Z compounds, various forms of structured carbon and transition metal compounds which consist of both low-Z and transition metal element. This list basically includes all the known and proven hard and superhard materials that can either be synthesized or found in nature.

The last row in the table summarised the general research direction toward superhard material fabrication. The three general directions are ternary compounds, nanostructured materials and high pressure phase elements/compounds. To achieve superhard values exceeding that of natural diamond, it is also possible to employ multiple approaches. One such material is the B-C-N compounds^[30], which is a super hard, high pressure phase of a ternary compound. Nano-composite is another topic that has been actively researched in the recent years. This approach deals with the synthesis of nano-composite with different morphology nano-size particles and consolidation. Some

example of potential nano-composites combination that have been researched include WC/TiC ^[31], Si₃N₄/TiC ^[32], SiC/Al₂O₃ ^[33], TiC/Al₂O₃ ^[34] and TiN/TiB₂ ^[35]. However, in most cases, research in nano-composite does not seek a breakthrough in the hardness value but rather maintaining of high hardness together with improvement of other mechanical properties such as toughness of the material.^[36] The ability to control toughness together with high hardness will significantly increase its engineering application for usage in extreme environment.

Figure 2 Illustration of the relationship between the elements, hard compounds and general approach to achieve high hardness property. ^[36]

Looking backing in Table 1, on the material properties role in ballistic protection, there is no doubt that a multitude improvement of material properties hold greater technological significance than a single ultimate high hardness material. The overall

improvement in mechanical properties without sacrificial reduction in hardness is a likewise a great challenge in material research. The complexity in the preparation of nano-composite should also not be underestimated. This thesis has chosen to focus on boron-based nano-structured materials and composites. The introduction and reason for selecting this group of low-Z compounds as potential ballistic protection material will be covered in the following sub-sections.

2.2.1. Boron Carbide (B_4C)

Boron carbide (B_4C) is an extremely hard material, with a typical Vickers hardness of 40 GPa just behind of diamond and cubic boron nitride and it is also one of the lightest with a density for 2.52 g/cm³. B_4C has a rhombohedral crystal structure and lattice space group $R\bar{3}m$. Unlike diamond and cubic boron nitride, which are metastable high pressure phase cubic structure materials, B_4C crystal structure and its mechanical properties remain stable up to high temperature which make it an excellent choice for armour application.

The atomic arrangement of B_4C typically consists of 12 atoms icosahedral cluster which are covalently bonded to a 3 atoms inter-icosahedral chains. Figure 3 shows a typical illustration of B_4C ball-and-stick diagram of its atomic structure arrangement where the icosahedral is assumed to be boron atom and inter-icosahedral assumed to be carbon atoms. However, past experimental and computational research have shown that the simple atomic arrangement of boron and carbon atoms in B_4C was more complex than expected.^[37,38] For brevity, we would refer boron carbide nominally as B_4C except when the stoichiometry of the compound is discussed in details.

Figure 3 General structure of boron carbide consisting of B_{12} icosahedron (in black & white) and connecting carbon chain (in grey).

Boron-Carbon (B-C) phase diagram in Figure 4 shows that B_4C between 1000°C to 2100°C possess 8.8 to 20 atomic percent of carbon content. This variation in carbon content is possible due to the substitution of boron and carbon atoms within both icosahedra and inter-icosahedral chain.^[39] To understand the structure-property relationship in B_4C crystals, it is important to studying the atomic composition and arrangement within its crystal structure.^[38]

Figure 4 Boron-Carbon phase diagram.^[40]

There have been much debate in the exact sequence of the 3 atoms inter-icosahedral chain such as C-B-C or C-C-C.^[41] To make the understanding of B-C atomic arrangement even more complex, atomic vacancy in the crystal could also be present which make the compound under-stoichiometric. Fanchini et al.^[42] have found that the most energetically favoured under-stoichiometric poly-type is B₁₂-(CBC) and the stoichiometric poly type is B₁₂-(CCC) by calculating the Gibb's free energy for different poly. However, for the B_{12-n}C_n icosahedrons, the number *n* and the location of the carbon atoms is not known exactly.^[43] There could also be some degree of randomness, as the 6 chain-connected icosahedron and the 6 icosahedron-connected icosahedral could not be differentiated. Table 3 listed all the possible atomic arrangement of boron and carbon in boron carbide crystals.

Table 3 Possible atomic arrangements boron and carbon atoms in boron carbide crystals.^[44]

at. % C	Chain	Icosahedron
26.7	C-B-C	B ₁₀ C ₂
20	(C-B-C) ₂	B ₁₁ C ^p +B ₁₁ C ^{p'}
20	(C-B-C) ₂	B ₁₀ C ₂ ^p +B ₁₂
20	C-B-C	B ₁₁ C ^e
20	C-C-C	B ₁₂
20	C-C-B	B ₁₁ C ^p
20	C-B-B	B ₁₀ C ₂ ^p
18.8	C-B-C	B ₁₂
15.4	C-V-V	B ₁₁ C ^p
14.3	C-B-V	B ₁₁ C ^p
14.3	B-V-C	B ₁₁ C ^p
13.3	B-B-C	B ₁₁ C ^p
12.5	C-B-C	B ₁₂
12.5	C-B-B	B ₁₂
12.5	none	B ₁₁ C+B ₁₀ C ₂
11.1	C-B-C	B ₁₁ C+B ₁₂
10.	C-V-C	B ₁₂
8.3	none	B ₁₁ C ^p
7.7	B-V-V	B ₁₁ C ^p
7.7	V-B-V	B ₁₁ C ^p
7.4	C-B-C	B ₁₂ +B ₁₂
7.1	C-B-V	B ₁₂
7.1	B-V-C	B ₁₂
7.1	B-B-V	B ₁₁ C ^p
7.1	B-V-B	B ₁₁ C ^p
6.7	C-V-V	B ₁₂
6.7	B-B-C	B ₁₂
6.7	B-B-B	B ₁₁ C ^p

Many studies have been done on nanostructured B₄C synthesis process. Most of the researches revolve around the use of a catalyst to achieve a controlled directional growth of nano-structure B₄C.^[45-48] Figure 5 shows a micrograph of a synthesized B₄C nano-wire using iron catalyst. The catalysts that are commonly used in the synthesis process are metallic nano-particles and inorganic salt.^[49] Residual catalyst in most cases will remain in the final product and require additional purification stage to remove them. In addition, high reaction temperature of up to 1950 °C^[50] is sometime required to synthesized the nanostructured materials. To date, aside from nano-particles of B₄C, other forms of nano-structured B₄C are still not commercially available due to the difficulty in the synthesis process and the challenges to achieve consistent morphology. However, the potential of nanostructured B₄C as a candidate for armour application should be studied in details.

Figure 5 Growth of boron carbide nanowires using Fe as catalyst.^[49]

2.2.2. Boron Suboxide (B_6O)

In the recent years, boron suboxide (B_6O) has been recognised internationally as a novel high hardness material with values close to those of B_4C . Since it was successfully synthesized half a century ago,^[51] B_6O have been known to possess extremely high hardness and widely studied by many research group. For example, Badzian^[52] demonstrated in his research the ability of B_6O to scratch natural diamond hardest (1 1 1) crystallographic plane. Superhard value of 45 GPa was also previously reported by He et al.^[53] from B_6O single crystal. Figure 6 compares the high hardness of B_6O with other superhard materials.

Figure 6 Comparison B₆O with other superhard materials.^[54]

Apart from high hardness, B₆O is also known for its high melting point, high chemical stability and low density. Despite the many favourable properties of B₆O, it still possesses many drawbacks such as poor crystallinity and sinterability^[53,55-57] which still required much research before it could be used for any actual technical application. Like other boron-rich solid, the mechanical properties and thermodynamic^[56] of B₆O are still not well understood.

Research has also focused on the synthesis process of various structures of B₆O. Nanocrystalline ceramics are known to possess unique mechanical properties such as enhanced plasticity and high strength.^[58] Nanostructure such as nano-wires,^[59] nano-platelets,^[60] nano-films^[61,62], have already been reported in the literature. One unique structure of B₆O is the icosahedra-shaped particle as shown in Figure 7. Selected-area

electron diffraction (SAED) patterns of the synthesized icosahedra B_6O shows neatly aligned 5-fold symmetry and symmetrical icosahedral twinning.^[63]

Figure 7 SEM image of a single icosahedron B_6O .^[63]

One particular structure that has not been reported is the star-shaped nano-plate of B_6O crystal. Several literature have reported star-shaped crystals of other compounds being synthesized such as ZnO produced by CVD and solution process,^[64,65] low temperature PbS synthesize by aqueous solution^[66] and hydrothermal technique^[67] and gold nano-particles.^[68] Star-shaped B_6O crystal formation was earlier reported by Jiang et al.^[59] which involved the growth of B_6O nanowires by cyclic twinning crystal structure. Cyclic twinning is known to be common in boron-rich compounds such as B_6O . Studies have shown that α -rhombohedral boron-rich compound crystal lattices changes due to different interstitial atoms.^[59] Therefore the tuneable cyclic twinning could be used to meet the geometric requirement for a star-shaped B_6O by stoichiometry variation. In this thesis report, the potential of B_6O in the formation of novel two dimensional star-shaped nano-plates as a potential candidate to construct high hardness and high toughness composite material will be explored.

2.3. Material Structure in Biological Materials

Biological material structures have always been fascinating to both biologist and material scientists. Through millions years of evolution process, biological materials are able to form complex hierarchical structured materials with superior mechanical properties that could even exceed its constituent materials.^[4]

Complex hierarchical structured biological ceramic composite materials, usually consist of a soft bio-polymeric matrix and hard bio-minerals, is able to remain stiff while being toughen by several order of magnitudes higher than their constituent minerals. The unique properties of the hierarchical structure effect could be observed in Ashby material properties chart for natural materials as shown in Figure 8 below. It is shown that the biological ceramic composite material toughness could be enhanced by up to four orders of magnitude^[4] when compared to its monolithic constituent minerals.

Figure 8: Ashby plot of toughness vs modulus. The guidelines indicate the materials ability to resist fracture under different loading. [6]

The enhanced toughness is most notable in enamel layer found in teeth and nacreous layer of mollusc shell with their respective primary constituents of hydroxylapatite and calcium carbonate. Advancement in mechanical properties, usually examined at macro-scale, is achieved through the interaction between the core and matrix at multiple scale down to the molecular level. [13] When a load is applied, the toughening mechanisms act over different length scales with a synergy effect in stress transfer, dissipate energy and resist cracking. [13] This provides a template for bio-mimetic of

advanced ceramic material to be used for the construct of high hardness and high toughness composite materials.

2.3.1. Complex hierarchical structure in biological materials

Complex hierarchical structured biological material continuous improvement of its structures and properties are built up upon multi-functionality purposes and adaptability for its own survival.^[69] Such complex structures are possible owing to the assembling of material from the molecular level.^[4] Furthermore, it is known that biological materials could perform self-recovery and also adapt itself to its surrounding environment.^[70]

The bone is one of the most well studied biological structure material produced by nature that exhibits all these amazing properties stated in the earlier paragraph. Like other biological systems, bone is a complex hierarchical composite with up to seven level of structure as illustrated by Launey et al.^[71] in Figure 9. In addition to the bone primary role as a supportive framework and offering protection for the internal organs, it is also a smart material that changes shape and remodel when an external force is exerted on the surface.^[71] Other biological materials that are known to exhibit outstanding toughening capabilities^[6] include but not limited to mollusc shell, dentin, wood and etc.

Figure 9: Hierarchical structure of bone showing seven levels of hierarchy.^[71]

One common characteristic of the toughening mechanism in biological materials is the highly anisotropic morphology found in their structure. Natural material could correspondingly align such anisotropic structure and mechanical property to their advantage by aligning the growth of the most robust surface to the most vulnerable area to enhance its survivability. For example, in timber, fracture toughness could reach an order of magnitude higher than a fibrous composite with the same fraction of fibres and matrix due to the tree vertical directional growth pattern;^[70] Bones, as shown in Figure 10(a), have high fracture toughness in the ‘breaking’ direction as compared to the ‘splitting’ direction which allows the structure to maintain its support at moderate impact;^[72] Dentin, in Figure 10(b), shows cracking typically occurring in the plane of the collagen fibres due to a lower fracture toughness.^[73] Therefore, the anisotropy structure found in biological materials has shown us the ability to use directional growth pattern to enhance the mechanical properties of weaker constituent materials and arranged in a way where the toughest surface meets with the most possible direction of impact or controlled failure to minimise the overall damage.

Figure 10 (a) Orientation and crack length-dependent of fracture resistance in human bone;^[72] (b) Average fracture toughness values of elephant dentin for five-tubule orientations.^[73]

The nacreous layer in mollusc shell is another interesting example of complex hierarchical structure found in nature with enhanced mechanical properties. Unlike bone and tree, which grow generally in a single direction, nacre has a two dimensional growth

pattern which provide an area of protection under its shell. Nacre is platelet-reinforced composite material with a brick-and mortar-like structure consisting of up to ninety-five volumetric percent of highly ordered inorganic polygonal aragonite (a form of calcium carbonate) and a few percent of soft bio-polymer as the matrix materials. The multi-scale hierarchical structure of Nacre is shown in Figure 11.

Figure 11: Multi-scale hierarchical structure of Nacre ^[13].

The nacreous layer of mollusc shell can achieve an impressive work of fracture three thousand times greater than its constituent materials. ^[5] In addition, there is little or no loss in stiffness observed from the toughening behaviour. ^[6] Moreover, the ability to stop fast travelling crack due to the change in material orientation has been observed. ^[5,74] One approach to harness the toughening mechanism of biological material is to mimic the structure of hard and soft structure composite to create an efficient medium for mechanical stress transfer, energy dissipation and crack resistance. ^[4,75,76] High hardness and high toughness material could be utilised in a wide range of personnel and vehicular armoured systems.

2.3.1. Toughening mechanism in structured composite materials

Limited deformation in materials is critical in toughness enhancement that will enable stress dissipation and preventing material failure. Hard material usually tends to be more brittle while ductile material tends to be tougher as shown in Figure 12(a). Deformation mechanisms usually arise from a wide variety of patterns such as the sliding of mineralised collagen fibrils in dentine ^[77], friction between platelets in mollusc shells^[78], micro-cracking occurred in bone^[79]. The key to enhance toughness is to achieve a compromise between strength and ductility, although these two properties tend to be inversely proportional to each other.

The toughening behaviours are broadly classified as intrinsic and extrinsic toughening mechanisms. In intrinsic toughening processes, the toughening mechanisms compete with propagation of the crack tip to prevent further destruction. In extrinsic toughening process, the toughening mechanism acts behind the crack tip to reduce the crack energy as it propagate.

Intrinsic toughening makes the cracking process more difficult by enlarging the plastic zone in the material. Therefore, such mechanisms are effective for stopping the crack initiation and the crack propagation process. Extrinsic toughness on the other hand, does not change the inherent fracture resistance of the material. However, its mechanisms acts after the crack are formed, reducing the localised stress and strain. This ultimately reduces the crack energy which will otherwise be used to extend the cracks further.^[70,80,81]

By acting upon the crack growth process, extrinsic toughening mechanism basically needs a crack before the toughening effect can be observed. In addition, this effect is largely dependent on the crack size. During the onset of crack formation, the area of extrinsic toughening rapidly increases, thus increasing the fracture toughness. As the crack propagates further into the materials, it causes the area of extrinsic toughening to remain fairly consistent and thus the fracture toughness start to reach a plateau. The extrinsic toughening effect could be observed from the measurement of a load vs crack length relation, known as a crack resistance R-curve. Figure 13 shows the extrinsic toughening mechanisms acting on bulk metallic glass alloy (Zr-Ti-Nb-Cu-Be) which affects the crack-growth shown in the pattern of an R-curve.

Figure 12 (a) Ashby plot for strength vs toughness for engineering materials;^[82] (b) Illustration of the extrinsic and intrinsic toughening behaviour with respect to a crack extension.^[83]

Figure 13 Extrinsic toughening mechanisms acting on bulk Zr-Ti-Nb-Cu-Be metallic glass alloy which affects the crack-growth through the characteristic R-curve.^[83]

2.4. Artificial Complex Nanostructured Composites

Superhard ceramic nano-structured materials are prized for their extreme mechanical robustness and are ideal candidate for the construction of nano-composite with promising properties of high strength, high toughness and low density. Combination of a high hardness with the possibility to control other physical properties is extremely advantageous for practical technical application.^[36,84,85] As shown in the work of Veprék and Argon, nano-sized crystals with monolayers of amorphous coating could produce a superhard nano-composite material with mechanical properties that exceed its constituent materials.^[86] Another possible approach to achieve superior mechanical properties is by assembly of nano-structure materials into complex hierarchical structure as shown in the previous sub-chapter 2.3. This approach could be commonly seen in nature creation where bio-polymer and bio-ceramics self-assembled into complex structures that bestow the structured biological materials with enhanced mechanical properties.^[87] For examples, Weaver et al. research have shown that the radular teeth of chiton, which consist of closely packed rod-like highly-aligned magnetite crystallite bundle, have high hardness comparable to hard ceramic materials like alumina and zirconia.^[88]

Nacre's brick and mortar structure is one the most widely studied and mimicked biological structure by using advanced synthetic materials. Figure 14 below shows the evolving trend in perfecting of the brick and mortar structure with reference to natural nacre.

Figure 14: Evolving architecture of nanocomposites. (a) Poorly dispersed nanoplates (blue) form aggregates in polymer (red) nano-composite; (b) Bilayer nano-composite; (c) Basic ‘unit cells’ of Nacre ^[89].

To list some of the recent work in the field of bio-mimic of nacre, Tang et al. (2003) create a layered organic-inorganic composites made from montmorillonite clay platelets and polyelectrolytes by layer by layer assembly method;^[7] Deville et al. (2006) uses ice-template technique to form alumina-Al-Si composites.^[8] Bonderer et al. (2008) used alumina platelets and a chitosan polymer for the assembly of the inorganic building blocks with a colloidal-based technique;^[9] Munch et al. (2008) fabricated a ceramic/polymer hybrid material made up of alumina and polymethyl-methacrylate (PMMA) using freeze casting of the ceramics suspensions followed by polymer infiltration;^[10] Burghard et al. (2009) uses a low temperature chemical bath deposition of titanium with layer by layer assembly of polyelectrolytes^[11] and Kakisawa et al (2010) used non-alkali, flake-like shaped, glass powder coated with silver and fabricated the structured composite material using a 3-D printing machine and hot-press to consolidate the powder.^[12] Figure 15 and Figure 16 shows two examples of artificial nacre-like structured material fabricated through a colloidal assembly approach and freeze casting technique respectively.

Most researches focused on ceramic-polymeric and ceramic-metallic approach to form structured composite materials, ceramic-based matrix composites however were

seldom used. This was mainly due to inability of ceramics to flow and high melting temperature, which make it extremely difficult to control and form the desired structured materials. Therefore, it is essential to look into novel techniques to form light-weight, high hardness and high toughness ceramic-matrix composite.

Figure 15 SEM image (left) of structured composite based on alumina platelets and chitosan assembled by a colloidal-based approach and mechanical properties (right) shows enhanced toughening effect for the artificial hybrid film.^[9]

Figure 16 SEM image (left) of structured composite based on alumina platelets and PMMA fabricated by freeze-casting technique followed by polymeric infiltration. Mechanical properties (A and B) of the structured composite shows higher fracture toughness, K_{IC} , than both its constituents but with lower strength, σ , than monolithic Al_2O_3 .^[10]

Although much work have been done on nacre microstructure and its mechanical properties, most researchers agreed that properties enhancement of nacre is still unrivalled by any man-made ceramic composites^[13] and the structure-property behaviour

of nacre is still not well-understood.^[2] Katti, et al. (2001), for example, mentioned more information at the molecular level is required to study on the organic and inorganic interface to better understand the material behaviour.^[14] Similarly, Sarikaya (1994) stated that the future direction for bio-mimetic research will be on microstructure-property correlations, micro-mechanisms of toughening and strengthening.^[14] Therefore, there are still much room for improvement in the field bio-mimetic materials research.

2.5. Ceramic Consolidation Processes

Many processes were used to sinter ceramic materials commonly found in personnel armour plates. These processes advantages and disadvantages are summarised in Table 4. Conventional sintering processes often utilise high temperature or both high temperature and high pressure to achieve maximum densification. However, the drawback of conventional sintering methods is the grain coarsening effect which will adversely affect the mechanical properties of the sintered ceramic.

Table 4 Manufacturing processes for ceramic armour.^[90-97]

Process	Materials (Properties in Table I)	Advantages	Disadvantages
Hot Pressing (HP)	Ceralloy B ₄ C, Norbide B ₄ C, Ceralloy SiC, SiC-N, TiB ₂	Lower temperature, lowest porosity	Shape limitation
Solid State Sintering (SSS) or pressureless sintering	Hexoloy SiC, Purbide SiC, MCT SSS SiC	No grain boundary phase, low porosity	Higher temperature, grain coarsening
Liquid phase sintering (LPS)	Ekasic-T, MCT LPS SiC	Lower temperature, fine grains, low porosity	Oxide grain boundary phase
Reaction bonding (RB)	Si/SiC, Si/B ₄ C (MCT RBSC, RBBC)	Low temperature, excellent complex shape capability	Residual silicon

The reaction bonding sintering was introduced in the mid-1970s to fabricate ceramic materials without the use of high temperature. This was done by infiltrate silicon

in the reaction to aid in the particles bond rather than using high temperature to initiate grain contact follow by necking. However, silicon introduced during the reaction bonding process also causes the built up and segregation of residual silicon which would impair the overall mechanical robustness of the material. One alternative approach to overcome the limitation of conventional consolidation method is by using the Spark Plasma Sintering (SPS) technique.

2.5.1. Spark Plasma Sintering (SPS)

Spark plasma sintering (SPS) or Field Assisted Sintering Technology (FAST),^[98-101] have been gaining much attention in both the research and industrial community. The mechanical properties of B₄C fabricated by SPS technique have been studied extensively in the past few decades. It is well known that mechanical properties of B₄C such as elastic moduli, flexural strength, hardness and Hugoniot elastic limit (HEL) decreases with increasing porosity and grain size.^[38,102-108] However, research has shown that SPS processed B₄C allows faster and more economical fabrication of the product without any significant loss in mechanical properties.^[109] To list some of the work in SPS processed B₄C, Ghosh et al.^[110] has applied SPS to submicron B₄C powder and achieved up to 99.2% relative density. Recently, Hayun et al.^[109] similarly reported the SPS conditions that could produce fully dense B₄C specimens without using any sintering additives.

The SPS process is based on the electrical spark discharge phenomenon using a high energy, low voltage pulse current to briefly induce spark plasma with high localised temperatures. SPS sinter temperature usually ranges from room temperature up to 2000 °C. However, the sintering temperatures of SPS usually required 200 to 500 °C lower

than conventional sintering processes to control grain growth without affecting the sintered ceramic quality. The actual sintering process typically complete within 5 to 20 mins. Figure 17 shows schematic of SPS process and pulsed current path passing through the machine.

Figure 17 Schematic of spark plasma sintering process and pulsed current path passing through the machine.^[11]

During SPS processing, the impurities attached to the powder particle surfaces are more easily removed and necking are also easier to be activated as compared to conventional sintering.^[111] High quality sintered material could be obtained at lower temperature and in shorter time than with traditional methods. Figure 18 illustrates the path of the pulse current flowing through the particles during SPS processing.

Figure 18 Pulse currents flowing through the particles in a SPS process.

The excellent mechanical properties obtained by this technique have led to strong research and commercialisation in the SPS processing. SPS is currently a fundamental tool in the preparation for advanced ceramic materials, especially of nano-structured material due to the fast sintering rate. In the current research, SPS would be used extensively in the preparation of superhard nano-structured materials.

CHAPTER 3: SYNTHESIS OF NANOSTRUCTURED B₄C

3.1. Introduction

Boron carbide (B₄C) is one of the hardest materials, only behind that of cubic boron nitride (c-BN) and diamond. Due to its low density, B₄C have extremely high strength-to-weight ratio which makes it favourable for ballistic protection application.^[112] Unlike diamond and cubic boron nitride which requires intense high pressure in the synthesis process^[113], B₄C could be synthesized at atmospheric pressure in an inert environment with milder temperature and without the use of catalyst in its fabrication process.

In this current chapter, the objective is to come up with a novel approach to control the synthesis process of zero, one and two dimensional nano-structured B₄C as potential candidates to form high hardness and toughness structured composite material. The hypothesis is that the various nano-structure of B₄C produced could be controlled by varying the precursor mix and catalyst used. Novelty in this research is the ability to achieve tuneable morphology of B₄C by controlling the processing conditions. The understanding of growth mechanism will also allow the control of the growth pattern of other boron-rich materials and also enable a higher level of control in the size and morphology of the crystals to be used in nano-structured composite for ballistic protection application.

3.2. Experimental Procedures

Boric acid (99.99% purity) and sucrose (ACS reagent grade) from Sigma-Aldrich were used as precursors for the synthesis of B₄C. The precursors were weighed precisely according to specific weight ratio and homogeneously mixed in an agate mortar. Next, finely ground powders were loaded onto a graphite crucible lined with graphite foil to ease sample collection after the reaction process.

The reaction was conducted in an inert environment using a horizontal gas tube furnace (Carbolite, UK) with continuous supply of Ar gas flowing at a rate of 50 cc/min. Figure 19 illustrates the reaction process in a gas tube furnace. The maximum temperature was fixed at 1500 °C with a ramp rate of 5 °C/min and dwell time of 60 mins. Catalysts were not used in the nano-particle and nano-flake synthesis process to avoid any side reaction or contamination. Nanostructured B₄C was achieved from the carbothermal reaction process through various mass ratios of boric acid and sucrose. This ratio was tested for both 2:1 and 10:1. The presence of higher boric acid content supersaturates the gaseous boron oxide within the mixture. Through the vapour-solid growth process, the super-saturation of boron suboxide favours the formation of the superhard phase of B₄C nano-flakes.

Figure 19 Schematic of carbothermal reaction process using a gas tube furnace.

Thermo-gravimetry (TGA) and differential thermo-analysis (DTA) were done using a simultaneous TG-DTA analyser from Netzsch (STA449C, Germany). The heating profile uses a maximum of 1500 °C at a rate of 5 °C/min in Argon gas. Mixture of boric acid and sucrose in 2:1 mass ratio were ground and loaded into an alumina crucible before it was placed into the analyser. The results obtained from TGA-DTA were used to determine the onset of precursor decomposition, vaporization and reaction to form B₄C.

Transmission electron microscopy (TEM) images were collected digitally using a multiscan CCD camera equipped in the TEM (JEM-2100F, Japan) with point resolution of up to 0.19 nm and operated at 200 kV. Simulated HRTEM images were calculated using the Multislice method.^[114] Field-emission scanning electron microscopy (FESEM) micrographs were obtained by using JEOL (JSM-6340F, Japan) with 1.2 nm accelerating voltage.

The crystal characteristics of the B₄C nanostructures were investigated by using powder X-ray diffraction in a reflection mode on a Bruker AXS diffractometer (D8 Advance, Germany) fitted with Cu-tube, Cu K α ($\lambda = 0.154$ nm) radiation, recorded with a 2θ step size of 0.02° and step time of 1 second. The crystal structure of the B₄C was refined by Rietveld analysis with a fundamental parameter approach in the TOPAS program.^[115,116] The starting model for refinement was based on the crystallographic data published for B₄C.^[117]

3.3. Results & Discussion

3.3.1. B₄C nano-particles & nano-flakes

Results from TGA/DTA, in Figure 20, shows that when boric acid and sucrose mixed and reacted to high temperature of up to 1500 °C, the mixture gone through several phase changes, in term of both its physical and chemical state, before finally resulted in the formation of B₄C nanostructures. To better appreciate the TGA/DTA result, we could combine the data analysis with the chemistry of boric acid and sucrose.^[118]

Figure 20 Thermo-gravimetry (blue solid line) and differential thermo-analysis (red dotted line) of boric acid and sucrose mixture when heated in Argon gas.

In first stage of heat treatment between 100 °C to 400 °C, dehydration and melting could be identified from the TGA/DTA curves. The TGA result shows three

dynamic chronological weight loss slopes resulting from dehydration of both boric acid and sucrose to form boron oxide and free amorphous carbon. DTA result also shows two distinct endothermic peaks due to the melting of both boric acid and sucrose.

Boric acid, also known as ortho-boric acid (H₃BO₃), at its initial state loses water around 130 °C at slow heating rate to form meta-boric acid (HBO₂). Further heating will dehydrate meta-boric acid into pyro-boric acid (H₂B₄O₇) and finally boron oxide.^[119] The complete dehydration process sequence of boric acid is listed below:-

Sucrose (C₁₂H₂₂O₁₁) like boric acid, experienced dehydration which results in the formation of residual carbon and water vapour at high temperature as shown below:-

However, in addition to the decomposition of boric acid and sucrose, interaction between the reactants occurred for boric acid and sucrose could lead to a coupled reaction at high temperature. Phang and Dollimore^[120] shows that at high temperature, dissociation of oxide would proceed spontaneously as Gibbs free energy (ΔG) of the reaction is negative. This is possible for the oxidation of carbon in the presence of oxygen at high temperature of more than 500 °C. Combining the boron trioxide dissociation together with the oxidation of carbon, the reaction will yield boron suboxide (B₂O₂) as shown in Equation (5) below. The coupled reaction would cause ΔG to be more negative which favours spontaneous reaction to occur at a lower temperature.

B₂O₂ formation is one of the vital ingredients in the synthesis of nanostructure boron carbide. The formation of B₂O₂ was also reported by Weimar et al., where volatile B₂O₂ yield at temperature above 1200 °C and could be synthesized at much lower temperature in an reducing environment.^[121] The transition from the decomposition of B₂O₃ to the formation of gaseous volatile B₂O₂ could be observed in Figure 20 between 400 °C to 1200 °C, the DTA curve observed a broad exothermic behaviour up to 700 °C followed by a broad endothermic behaviour beyond 700 °C. This shows a major change in the thermal behaviour of the mixture. However, the TGA curve shows a linear gradual decrease in mass which reflects minimum loss in mass during the change in thermal behaviour. A possible explanation for the bend in DSC curve would be the exothermic decomposition of sucrose that was gradually covered by the endothermic reduction of boron trioxide to boron suboxide. This is supported by the gradual weight lost due to CO gas escape.

In the later stage of the synthesis process above 1200 °C, rapid mass loss was observed with a steep exothermic behaviour which was attributed to the rapid sublimation of B₂O₃ gas. At temperature above 1400 °C, B₄C were formed which is indicated by the onset of strong endothermic reaction and decrease in the gaseous B₂O₂ loss due to solid boron carbide formation. The strongly endothermic process ($\Delta H=1812$ kJ/mol), was similarly observed by Thévenot.^[38]

Although, the intermediate production of B₂O₂ was not possible to be characterized from the synthesis process, the formation of boron carbide at a relatively

low temperature of 1400 °C provides a clue to B₂O₂ presence in the reaction for B₄C. B₂O₂ reaction with carbon could also be confirmed by analysing the mass loss with respect to the stoichiometry study in the chemical reaction. Assuming both boric acid and sucrose were fully dehydrated, the theoretical mass lost due to H₂O vaporization will be 48.4% which is close to the measured values. By assuming a complete further reduction of B₂O₃ by C to form B₂O₂ and CO, a successive theoretical mass loss of 15.1% due to the release of CO gas could be expected. However, the actual mass lost measured was 5-10% less than the calculated value which indicated that B₂O₃ was not fully reduced before sublimation occurred.

At temperature above 1430 °C, exothermic behaviour observed shows that the formation of B₄C was slow while vaporization continued to proceed even though excess free carbon was still present in the sample. This further reinforces the hypothesis whereby volatile B₂O₂ is the main reactant to free carbon at temperature below 1500 °C rather than B₂O₃. Furthermore, synthesis at high temperature of more than 1500 °C significantly accelerates the depletion of B₂O₃ due to sublimation and causes the reaction to terminate prematurely.

The presence of boron oxide (B₂O₃) could be identified from XRD pattern in Figure 21(a) as indicated by asterisks. Although boron carbide was reported to form at temperature as low as 1400 °C, the sublimation rate of B₂O₃ is still dependent on the several other heating parameters which include the heating rate, maximum temperature and quantity of precursor used. As sublimation of B₂O₃ would deplete the reactant, this would cause excessive unreacted carbon to stay within the final boron carbide product.

This effect could be seen in the XRD pattern of Figure 21(b), where free carbon (at $2\theta = 26^\circ$) is omnipresent with B₄C formation.

Figure 21: XRD pattern of synthesized B₄C (a) at 1500 °C, 10 min with B₂O₃ (ICDD #060297)^[122] indicated by asterisks, (b) 1500 °C, 60 min (c) Reference crystal database of B₄C (ICSD #81960).^[123]

By applying Rietveld refinement approach^[116] to analyse the XRD pattern, the crystallography of the B₄C nano-particles was found to fit with B₁₃C₂ phase or boron carbide with 13.3 at.% carbon. Boron carbide, although commonly known as B₄C, it has a wide range of solid solution, ranging from 9 to 20 at.% C.^[38] The super hardness of B₁₃C₂ phase was reviewed by Brahmin who reported a hardness value of 57 GPa.^[36] This is almost twice as hard as the typically known B₄C thus making it an important candidate for study in high performance material for extreme mechanical application.

FESEM image in Figure 22 shows the zero dimensional (0-D) and two-dimensional (2-D) nanostructure of B₄C. The particle size of the resultant B₄C nanoparticles is within the range of 80 to 100nm. This is consistent with the result achieved from Rietveld refinement of the XRD pattern. Apart from the volatile B₂O₂

reactant, another ingredient which is vital to the formation of nano-sized B₄C particles is sucrose. Several articles have reported the use of other carbon source which includes corn starch,^[121] citric acid,^[124] polyvinyl-alcohol,^[125] and etc, but rarely nanoparticles was achieved without complex equipment or nano-size precursors.^[126-128] A common characteristic that is often observed when sucrose decomposes is the dissipation of large quantity of H₂O vapour which accounts for 57.9% of its mass. The large amount of gas released from boric acid and sucrose caused the mixture to foam vigorously forming a sponge-like structure. As B₂O₃ is reduced to B₂O₂ vapour at high temperature, the reactive gaseous intermediate would deposit and react rapidly to the carbon network forming chains of boron carbide single crystals. Further heating would lead to the atomic migration and agglomeration to form nanoparticles.

B₄C nano-flakes as shown in Figure 22 (b) typically span around a few hundred nm wide and a few nm thick. When the boric acid and sucrose mix ratio increased from 2:1 to 10:1, the B₄C formation mechanism changed drastically. At high mix ratio, the carbon atoms are dispersed in a solution of liquid boron oxide instead of forming sponge-like carbon network. When the critical temperature is reached, it leads to the oxidation of carbon to form carbon monoxide gas which act as the intermediate reactant for B₄C formation. As the surface of the graphite crucible is highly porous, the reactive gaseous intermediate would deposit on to the graphite to form single crystal of boron carbide. As more B₂O₂ and CO absorbed on to the single crystal boron carbide, the molecules migrate and stack toward the corresponding plane to maintain the flakes shape.^[129] These processes are similar to a CVD process.

Figure 22 FESEM of B_4C (a) nano-particles (b) nano-flakes. ^[130]

To show that the graphite crucible was not involve in the reaction process, a controlled experiment was done by using only boric acid without sucrose and heat using same operating condition of the furnace. The product from the experiment shows that a solidified glassy pool of boron oxide that did not fully undergo the sublimation and no crystal was formed on the graphite crucible. Therefore, this shows that the graphite remain inert throughout the heating process.

TEM were used to characterise the B_4C nano-flakes morphology, atomic structure to understand its growth mechanism and inherent properties. TEM micrograph of the B_4C nano-flakes edge reveals high density of twinning present which was observed at atomic-scale as shown in Figure 23 (a) and (b) respectively.

Figure 23: (a) TEM micrograph of B₄C nano-flake, (b) HRTEM micrograph of nano-flake, (c) SAED in the $[1 \bar{1} \bar{1}]$ zone axis.^[130]

Surface energy play an important role in the formation of flakes when synthesize in a non-catalytic vapour-solid growth process.^[131] The degree of atomic coordination number could be used to deduce the surface energy of a particular crystallographic plane.^[132] It has also been proven that the probability for a low index crystal plane to nucleate and grow is higher due to lower surface energy.^[50] The surface energy minimisation principle is also consistent with earlier research where nanoparticles were driven by surface energy reduction to self-assemble into an extended ordered array.^[133] TEM micrograph shows the structural growth at the low surface plane of a nano-flake at atomic scale. Analysing the SAED image using Fast Fourier Transformation (FFT)

simulated diffraction pattern, the flakes were found to be projected in $[1\ \bar{1}\ \bar{1}]$ surface which is consistent with earlier finding where propagation of growth is prominent at low index plane. Planar defects were observed from micron to atomic scale as parallel dark lines in both Figure 23(a) and (b). These defects were also known to be (1 0 1) - type twins which are commonly observed after sintering.^[134,135] The inter-atomic spacing of (1 0 1) plane was identified in to be around 0.45 nm.

B₄C nano-flakes saturated with high concentration of twinning could be associated to the need to reduce the total high surface area induced by the strong anisotropic growth. These phenomena were often found in materials with the inclination to develop into an organized structure like whiskers,^[136] branching,^[137] and etc. Twins on the flakes were found to be parallel to the elongating direction $[1\ \bar{1}\ \bar{1}]$ which is in good agreement to the boron carbide flakes produce by Xu and Bando.^[50] Although twinning is known as defect in material structure, it has been reported to enhance both the strength and toughness.^[138,139] The mechanism of such enhancement is due to its crack arrest capabilities, which inhabit fracture and prevent further crack growth, resulting in an increase in fracture toughness. Therefore, B₄C nano-flakes with high concentration of twinning defect are essential for further characterization in its mechanical properties enhancement capabilities.

The close match of the synthesized boron carbide XRD pattern to B₁₃C₂ shows great potential as a superhard phase of nanostructure boron carbide. The most symmetric form of B₁₃C₂ is usually described in a rhombohedral unit cell (space group R-3m) that contains one 12-atoms icosahedra unit and one linear 3-atoms chain consisting of boron

and carbon atoms. The two most probable structure of $B_{13}C_2$ are firstly $B_{11}C(BBC)$, where $B_{11}C$ icosahedra is linked by B-B-C chains; and secondly $B_{12}(CBC)$, where boron icosahedra is linked by C-B-C chains.^[140] Density Functional Theory (DFT) calculation by Candra et al. shows that $B_{12}(CBC)$ structure to be the most stable of the two with larger binding energy (2.09 eV/cell) than the $B_{11}C(BBC)$.^[141] This was confirmed experimentally by Emin et al. using Carbon-13 Nuclear Magnetic Resonance (^{13}C NMR) spectroscopy.^[142]

Based on the HRTEM image of nano-flakes, the position of the 3-atoms-chain could not be confirmed as it is not obvious in the HRTEM image. By using a Multislice method^[114] to calculate the HRTEM image at $[1\bar{1}\bar{1}]$ zone axis, the observed HRTEM image matches the calculated image as shown in Figure 24 (b) and (c). Each of the bright spheres could be interpreted as B_{12} icosahedra while interconnects of C-B-C chain to the B_{12} icosahedra could be seen from the unit cell of $B_{13}C_2$ in Figure 24 (a).

Figure 24 (a) Simulated ball & stick diagram of $B_{13}C_2$ and (b) HRTEM micrograph with; (c) simulated HRTEM atomic arrangement of $B_{13}C_2$ in $[1\ \bar{1}\ \bar{1}]$ zone axis. (Boron atoms in cyan and Carbon atoms in grey).

3.3.2. B_4C nano-wires & nano-ribbons

By employing similar carbothermal reaction as the synthesis process for B_4C nanoparticles and nano-flakes, B_4C nano-wires and nano-ribbon were also successfully synthesized as shown in Figure 25 SEM image of the synthesized powder. SEM image also reveal an urchin-like formation similar to a ball with multiple spikes attached to the core. Observation on the growth pattern also shows changes in growth direction which could be likely due to twinning in the crystals, a common occurrence in the crystal structure of Boron-based compounds. The length of the nano-wire and nano-ribbons spans up to a few hundreds of micron with diameter ranging from tens of nanometre up to

5 micron. Using electron dispersive x-ray spectroscopy (EDS) mapping technique, in Figure 26, the image shows that the catalyst in red are mainly clustered at the core of the nano-wires and nano-ribbon. This suggests that the nickel catalyst plays a key role in the formation of the crystals. It can be deduced that, as the catalyst is saturated with the boron and carbon atoms, the wires and ribbon start to grow in various directions from the catalyst core.

Figure 25 SEM image shows B₄C nano-wires clusters.

Figure 26 Energy-dispersive x-ray spectroscopy mapping of nano-wires and ribbons cluster. Nickel in red and Boron in green.

Figure 27 shows the TEM and HRTEM image of a single boron carbide nano-wire. The TEM images indicate a long continuous wire with consistent diameter of around 200 nm. HRTEM reveal a highly crystalline structure of B₄C. Similar SAED pattern is observed compared to nano-flakes at zone axis $[1\ \bar{1}\ \bar{1}]$. The inter-atomic spacing of (1 0 1) plane was estimated to be 0.45 nm.

Figure 27 TEM images of a single boron carbide nano-wire.

From multiple attempts to control the morphology of the synthesized powder by varying the processing conditions, the nano-wires and nano-ribbon do not seem to be affected and exhibit random growth direction. It is, however, interesting to note that the

growth general favours in only one direction which could be employed in a fibre-reinforced composite material. Although various forms of nanostructured B₄C were synthesized in the current experiment, they contain a high amount of free carbon which impaired its ability to be sintered. This issue was similarly observed by Herth et al.^[143] As both B₄C and the free carbon shared similar constituent elements and physical properties, it is technically impossible to achieve to carbon-free B₄C.

Table 5 Summary on synthesized nano-structured B₄C, process conditions, pros and cons.

Nano-Particles and Flakes of Boron Carbide		Nano-Wires and Ribbons of Boron Carbide	
Condition: 1500 °C, 1 hr, Ar gas, no catalyst, mix ratio 2:1(particles), 10:1(flakes)		Condition: 1500 °C, 1 hr, Ar gas, with catalyst, mix ratio 10:1	
Pros	Cons	Pros	Cons
<ul style="list-style-type: none"> →Highly anisotropic structures →Controllable structure by varying of processing conditions →High twinning density improves toughness 	<ul style="list-style-type: none"> →High impurities (i.e. carbon) lead to poor sinter-ability →Poor packing of materials causes high porosity →Low yield 	<ul style="list-style-type: none"> →Highly anisotropic structures 	<ul style="list-style-type: none"> →High impurities (i.e. nickel) lead to poor sinter-ability →Poor packing of materials causes high porosity →Low yield

3.4. Summary

In conclusion, nano-particles, nano-wires, nano-ribbons and nano-flakes of B₄C were produced by using a carbothermal synthesis process with both non-catalytic and catalytic approaches. Characterisation and verification of nanostructured B₄C was done using SEM/EDS, XRD and TEM. Table 5 shows the summary of the process conditions and its respective advantages & disadvantages. The morphology of the nano-particles and nano-flakes was achieved by simply controlling the precursor boric acid and sucrose ratio from 2:1 to 10:1, which changes the mechanism of B₄C formation drastically. In addition, by adding nickel as catalyst to the synthesis process, nano-wires and nano-ribbons could be achieved. XRD refinement of the synthesized powder shows a closer match to B₁₃C₂, which is a superhard phase of boron carbide. Due to the surface energy minimisation principle, the B₄C nano-flake was found to grow with a $[1\ \bar{1}\ \bar{1}]$ projected surface. Analysis from HRTEM images collected from B₄C nano-flakes also shows high concentration of (1 0 1) type twinning which could potentially enhance the toughness of superhard material. HRTEM of the nano-wires also shown similar growth pattern as with the B₄C nano-flakes.

This is the first time synthesized B₄C was reported to show such great versatility to form various 0-D, 1-D and 2-D nano-structures using a single process with simple tuning of the processing conditions i.e. precursor mix ratio and catalyst used. The nano-structures B₄C shows great potential to be used as reinforcing agents in nano-composite material for extreme mechanical application.

CHAPTER 4: SYNTHESIS OF NANOSTRUCTURED B₆O

4.1. Introduction

In the recent years, boron suboxide (B₆O) has been internationally recognised as a novel high hardness material with values close to those of B₄C. Studies have shown B₆O, which shared similar crystal structure to B₄C, could form into various nanostructures such as nano-wires, nano-platelets and nano-films. As B₆O is known to be able to form star-shaped nano-wire, it could be hypothesized that star-shaped nano-plates of B₆O can also be produced by careful control of the processing conditions during the synthesis process. The star-shaped nano-plates of B₆O will closely resemble the platelets found in the nacreous layers of mollusc shell which is known for its toughening mechanisms.

In the current chapter, synthesis of a novel two dimensional, star-shaped nano-plates of B₆O will be shown. The novelty of the research is based on the complex morphology of star-shaped nano-plates B₆O synthesized which has not been shown in any earlier publication. The SPS sintering of the nano-structured B₆O could significantly attain both high hardness and high toughness as compared to its monolithic counterpart.

4.2. Experimental Procedures

B₆O was synthesized through a solid-liquid reaction between commercially available amorphous boron and boron oxide. The reaction process as shown in the Equation below:

Commercially available amorphous boron from Fluka (<0.1 μm, purity 95-97%) and boron oxide (B₂O₃) from Sigma-Aldrich (99.99%) were used. As B₂O₃ is known to undergo sublimation at 1500°C,^[119] most researchers usually add excess B₂O₃ in order to compensate for the B₂O₃ lost and achieve the stoichiometric balanced B₆O.^[144-146] In the current experiment, excess amount of B₂O₃ was added in the molar ratio of 10:1 or 37.5%. As B₂O₃ form a viscous flux above 450°C, amorphous boron were allowed to suspend within the viscous B₂O₃ flux throughout the reaction process. The precursors were milled using an agate mortar and pestle using ethanol as the solvent. Next, the mixed powders were poured into a BN crucible and placed in the furnace. The heat treatment process was carried out in a horizontal gas tube furnace (Elite Thermal Systems Ltd, UK) with continuous flow of inert argon gas at a maximum temperature of 1400°C and a holding time of 1 hour.

B₆O synthesized by the reaction of boron in excess B₂O₃ flux produced a transparent glassy solid embedded with fine particles of B₆O. As B₂O₃ dissolves fairly well in water, the solidified glassy-state B₂O₃ was dissolved in copious amount of deionised water at room temperature until all the particles were fully dislodge from the solid. Purification of the B₆O powder was carried out by repeated stages of centrifugation and dilution process. Filtration of the solid powder from the dissolved B₂O₃ solution was also tested and proven to work as well. Lastly, the wet powder was placed in a drying oven at 80°C for 12 hours until the dried brownish powder was collected.

X-Ray Diffraction (XRD) was measured using Bruker D8 Advance diffractometer (Germany), fitted with Cu-K α radiation source. The crystal structure of the boron suboxide was refined by Rietveld analysis using fundamental parameters approach in the TOPAS software.^[116] The boron suboxide crystallographic data for refinement was based on published X-ray diffraction pattern from the Inorganic Crystal Structure Database ICSD#73624.^[147] Field-Emission Scanning Electron Microscope (JEOL-FESEM7600, Japan) was used to study the morphology of the particles. Equipped with a Thermal Field Emission Gun, the FESEM was able to achieve a high resolution of 1.0 nm at 15 kV accelerating voltage. Transmission electron microscope (JEOL-TEM2010, Japan) was used to capture high resolution image and study the crystallography of the powder. Equipped with LaB₆ electron source and operating at 200 kV accelerating voltage, the TEM could achieve point resolution of up to 1.9 Å.

To sinter the synthesized power, the powder was loaded into the graphite die and punch unit for SPS processing. Graphite dies with inner diameters of 10 mm was used. The outer surface of the die was wrapped with graphite felt to homogenize the temperature distribution and reduce heat loss by radiation. Three different configuration of powder to graphite mould protection were tested to prevent cross reaction. In the first configuration, only graphite foil was used. In the second configuration, graphite foil coated with BN was used. Lastly, additional tantalum foils from Sigma-Aldrich (0.025mm thick, 99.9+% purity) was placed in between the powder and the mould.

SPS machine from Dr. Sinter, equipped with a 100 kN uniaxial press (Model SPS-1050, SPS-Syntex), was used for the sintering. The sinter process was conducted with

continuous flow of Argon gas. Three different uniaxial max pressures of 30, 60, and 80 MPa were applied. The samples were heated to 1800 °C at a heating rate of 110 °C/min, and the dwell time at this temperature was 1 min. Each specimen was gradually cooled to 600 °C at a rate of 100 °C/min and then naturally to room temperature with the furnace. The mould temperature was measured using an optical pyrometer.

4.3. Result and Discussion

4.3.1. Synthesis of nanostructured B₆O

FESEM micrograph of the B₆O powder in Figure 28 shows the agglomerated dried particles and particles size within the sub-micron range. Agglomeration of synthesized B₆O was also reported in several other literatures.^[148,149] Close analysis of the powder reveals the sharp angular edges of the particles. Energy-dispersive X-ray spectroscopy (EDS), in Figure 28 insert, shows strong signal at 0.18 keV and 0.52 keV indicative to the presence of elemental boron and oxygen respectively. A weaker signal at 0.27 keV was also detected, suggesting the presence of carbon likely from the carbon mounting tape. EDS quantitative point analysis of shows that the non-stoichiometric balanced B₆O_x where the oxygen occupancy, x, range from 0.842 to 0.869.

Figure 28 FESEM micrograph of synthesized sub-micron agglomerated B₆O powder with EDS analysis (insert).^[150]

It is known that stoichiometric balanced B₆O could only be formed through high pressure synthesis, whereas low or pressure-less pressure typically yields an oxygen-deficient state B₆O_x where x is less than 0.9.^[53] However, the synthesized B₆O holds a relatively high content of oxygen with reference to a pressure-less synthesis technique. This could be attributed to the excess B₂O₃ added into the precursors which favoured stoichiometric balanced B₆O formation.

FESEM micrograph of the powder in Figure 29 (a) shows multiple five-pointed star-shapes B₆O orientated at different angles. The result shows that the star-shape particles were not an isolated formation but a systematic controlled growth in significant quantity among the powder. Figure 29 (b) shows the high magnification image of a single five-pointed star. The star-shaped surface spans a few hundred nanometres across with a thickness estimated to be around 40 nm. The apex angles were measured with a

range from 68.7° to 70.9°. Re-entrant angles were measured with a range from 218° to 228°. The star-shaped particle also displayed near-symmetrical five-fold rotation symmetry along its core. Rough surfaces were also observed on the star-shaped surface characterized with nano-size bumps. The sharp angular edges of the B₆O particles could enhance the grain boundary density of the sintered material.

Figure 29 FESEM image of star-shaped boron suboxide. (a) Multiple star-shape particles observed in synthesized powder circle in red. (b) A single five-pointed B₆O star (coloured in red) observed under high magnification.^[150]

The key to the understanding of B₆O star-shaped formation lays in the study of its crystallographic properties. The crystal structure of B₆O belongs to a family of α -rhombohedral boron-rich compounds with space group $R\bar{3}m$ (no.166). Each vertex of the rhombohedral unit cell is occupied by one B₁₂ icosahedron which forms a rigid three-dimensional network.^[151] The atomic arrangement of B₆O is closely related to the crystal structure of B₁₃C₂ but with boron atoms in the icosahedra and oxygen atoms in the chain that is parallel to the trigonal axis.^[152] This configuration gives boron suboxide the composition B₆O. Earlier research on the crystal structure reveals the long inter-atomic distance between the oxygen atoms at non-bonding distance.^[153] Kobayashi et al. research has also shown that vacancies could occur at the oxygen positions in B₆O crystal.^[147] Therefore, the formula of the suboxide should more accurately be depicted as B₆O_x, where x will be less than 1. Hubert et al. have observed that the oxygen occupancy has direct correlation to the cell parameters.^[154] These findings were essential to determine the morphology of the crystal formation.

XRD of the powder obtained in Figure 30 shows that the diffraction pattern matched with the indexed B₆O crystallographic data from crystallographic database ICSD#73624.^[147] Refinement of the XRD by Rietveld techniques shows the cell parameter of $a = 5.363 \text{ \AA}$, $c = 12.328 \text{ \AA}$ and cell volume of $307.017 \text{ \AA}^3$. Estimation of the B₆O_x stoichiometry was done based on Hubert method^[154] which correlates the linear trend between the lattice parameters to the oxygen occupancy based on published experimental data. Calculation using the refined lattice parameters from the powder XRD shows that the estimated value of oxygen occupancy, x, was found to be between the range of 0.691 to 0.715. This calculated value was lower than what was recorded by EDS

of individual star-shaped particles. The result indicated that higher content of oxygen favours the formation of star-shaped particles whereas the powder diffraction data which consist of a mixture of star and non-star shaped particles have relatively lower oxygen content. This phenomenon could be explained from the lattice parameters variation due to the amount of oxygen interstitial atoms.

Figure 30 X-Ray diffraction of synthesized boron suboxide powder (red) indexed by ICSD#73624 (blue).^[150]

TEM image of the B₆O particle in Figure 31 (a) shows that the agglomerated B₆O with a single star shaped particle. One vertex of the star was measured with an angle of 71.8°. This matches the dihedral angle between the twinning planes of the stoichiometry B₆O_{0.87} rhombohedral unit cell reported by Jiang et al.^[59] SAED of the particles, insert of Figure 31 (a), shows that the particle can be indexed to the [100] zone axis of B₆O

crystal. Figure 31 (b) shows the proposed close packing of rhombohedral unit cells with cyclic twinning to form the star-shaped particles. The top view of the illustration shows the symmetrical 5-fold rotational cyclic twinning. The side view shows the growth in two-dimensional perpendicular to the c-axis. It is interesting to note that the rough surfaces of the star shape surface illustrated in Figure 31 (b) coincided with observation in the SEM image of the star in Figure 29 (b).

Figure 31 (a) TEM image shows an agglomerated B₆O particle with a single star and indexed SEAD (insert). **(b)** Graphical representation (top and side view) of the proposed cyclic twinning in the star-shaped crystal. **(c)** Unit cell of B₆O shows the dihedral angle of 71.8° perpendicular to the c-axis. ^[150]

Although the dihedral angle of 71.8° between the twinning planes shown in Figure 31 (c) resulted in a 1° misfit, it was still able to form a near-symmetrical five-pointed star shape. Earlier report has also shown that it is possible for similar cyclic twinning structured material to achieve close packing with misfit as high as 7.5°. ^[155]

However, the misfit could have resulted in the formation of non-symmetrical irregular shaped stars and stacking fault may occur during the growth process. The preferential growth patterns in B₆O crystals are still not well-understood. However, the reaction conditions used would most probably favour a kinetically-controlled crystal growth due to the short reaction time and temperature of 1400°C, much lower than the crystal melting point.^[156] Similar technique of manipulating crystal morphology by controlling the processing condition has also been applied in the synthesis of B₄C nano-particles and nano-flakes.^[130] In-depth study has to be done to better understand the crystal growth mechanism between B₆O icosahedral particles,^[63] B₆O star-shaped nanowires,^[59] B₆O platelets^[60] and the current nanoplates star-shaped B₆O.

4.3.2. Spark plasma sintering of B₆O

Synthesized B₆O powder was subjected to SPS under the same processing conditions with different sample protection configuration. The sintering conditions and properties of the samples are given in Table 6 Sintering condition and properties of SPS B₆O materials.^[157] The sintered pellets using different types of protection have very similar relative density. However, the samples sintered with only graphite foil and graphite foil with the BN coating have better fracture toughness than the sample sintered with Ta foil. The differences in properties are likely due to the porosity which correlates to the relative density when different protective mediums were used.

Table 6 Sintering condition and properties of SPS B₆O materials. ^[157]

Sample ID	Sintering conditions				Properties of samples		
	Temperature, °C	Time, min	Pressure, MPa	Remarks	Relative density, %	Hardness, GPa	Fracture toughness, MPa·m ^{1/2}
30B ₆ O-G	1800	1	30	Graphite die	93.8	31.7 ± 0.9	5.0 ± 0.2
30B ₆ O-BN	1800	1	30	BN coating	93.7	31.5 ± 0.7	4.9 ± 0.2
30B ₆ O-Ta	1800	1	30	Tantalum foil	94.1	32.2 ± 0.8	4.3 ± 0.1
60B ₆ O-Ta	1800	1	60	Tantalum foil	96.1	33.5 ± 0.8	4.2 ± 0.1
80B ₆ O-Ta	1800	1	80	Tantalum foil	98.3	34.8 ± 1.0	4.0 ± 0.1

According to the XRD analysis as shown in Figure 32, both B₆O protected by graphite foil and BN contain impurities such as boron oxide, boron carbide and free carbon. This is likely due to carbon diffusion from the graphite mould, follow by reaction with the sintered powder. However the sintered powder with tantalum foil protection shows a higher hardness of 32.2 GPa as compared to the two others sample sintered at 30 GPa. This could due to the presence of impurity which resulted in an overall decrease in hardness. It is also noteworthy that the tantalum does not have any cross reaction with the powder or the graphite mould as shown in the XRD diagram of Figure 32.

Figure 32 XRD patterns of B₆O material fabricated via SPS at 1800°C for 1min under uniaxial pressure of 30MPa using different protective layers. ^[157]

From table 6, it can be seen that the samples prepared by SPS at a temperature of 1800°C with a holding time of 1 min and a pressure of 30 MPa shows a high relative density of 94.1% with reasonable hardness and fracture toughness. To further improve the sintering of the synthesized B₆O, higher uniaxial pressure of 60 and 80 GPa were used. The trend of the increased sintering pressure could be observed in Table 6. The highest relative density and hardness recorded were found to be 98.3% and 34.8 GPa respectively. A slight decrease in fracture toughness was also observed for the sample sintered at 80 GPa, however, the drop was fairly low within 0.2 to 0.3 MPa.m^{1/2} which is not very significant. Nevertheless, the high hardness of 34.8 GPa and fracture toughness of 4.02 MPa.m^{1/2}, are some of the highest values reported for sintered B₆O.^[54,57,146,158] This could be attributed to toughening effect of nano-structured B₆O in the sintering process.

4.4. Summary

In summary, the star-shaped of B₆O nano-plates were formed through a liquid-phase reaction of amorphous boron and boron oxide. SEM images have shown that the particles have regular five-pointed vertices that span a few hundred nm across with thickness of around 40 nm. Analysis has also confirmed that the formation of the five-pointed star-shaped nano-plates was possible owing to the dihedral angle of 71.8° in B₆O rhombohedral unit cell and the cyclic twinning with 1° misfit.

In addition, EDS quantitative analysis shows that the oxygen-deficit B₆O_x where the oxygen occupancy, x, range from 0.842 to 0.869, contributed to the unique crystal growth process. SPS consolidation of B₆O star-shaped particles was performed and high

hardness of 34.8 GPa and fracture toughness of 4.0 MPa.m^{1/2} were achieved. These values were some of the highest values recorded for sintered B₆O as compared to earlier literature. The unique structure and excellent mechanical properties of B₆O would make it as a potential candidate for high hardness, high toughness structured composite material.

CHAPTER 5: CORE-SHELL B₄C-BN COMPOSITE

5.1. Introduction

One approach to enhance the mechanical properties of conventional composite material is to mimic the biological material structured hard and soft system. This allows efficient stress transfer, energy dissipation and enhances crack resistance in the structured composite. The hypothesis of this research is to prove that, based on the hard core and soft matrix design, reactive SPS of B₄C particles in nitrogen gas could form a unique core-shell structure composite that would simulate the toughening mechanisms in structured biological material and achieved significant enhancement of the mechanical properties.

In the current study, the Vickers hardness indentation test and Split-Hopkinson Pressure Bar (SHPB) test conducted on the core-shell structure of B₄C-BN will be presented in this chapter. Three different sintering pressures will also be tested to study the effect of on the microstructure and toughness enhancement mechanisms. Based the ‘hard’ and ‘soft’ design principle, structured B₄C-BN is expect to achieve significance enhancement in the toughness with potential to form a high impact-resistant composite. The unique hard and soft core-shell composite material design could similarly be utilised as a template for other material combination to achieve high hard and toughness properties.

5.2. Experimental Procedures

Commercial boron carbide powder (1.5micron, 89-92% purity) from Sinopharm Chemical Reagent Co. Ltd. (China) was used in the current study to form a core-shell structure of B₄C-BN. The chemical reaction process illustrated in the Equation below shows the reaction between B₄C and N₂ gas to form BN and free carbon. Zhang et al. [159] demonstrated that reaction between B₄C and N₂ was exothermic and was thermodynamically favourable to proceed:-

The commercial B₄C powder was loaded into graphite die set for SPS consolidation. The graphite dies have an inner diameter of 10 mm and wrapped with 5 mm thick graphite felt to regulate the temperature distribution and reduce the heat loss by radiation. The SPS machine produced by Sumitomo Coal Mining Co. Ltd (DR SINTER series SPS-1050, Japan) was equipped with a 100 kN uniaxial press with the use of pulsed electric current to achieve densification. The sintering procedure was conducted with continuous flow of N₂ gas at 2 L/min. Pressure was gradually applied uniaxially from 25 MPa to 120 MPa during sintering. After an intermediate heating of 900 °C for up to 40 min, the samples were further heated at elevating rates from 5 to 500 °C/min up to 1800 °C with a dwell time of 10 min. Each specimen was gradually cooled down to 600 °C at a cooling rate of 20 °C/min and subsequently furnace-cooled to room temperature.

Figure 33 Schematic of core shell B₄C-BN before and after sintering

For comparative study, B₄C added with 0.5-25 %wt of hexagonal boron nitride powder, produced by Wako Pure Chemicals Industries Ltd. (Japan), were processed by SPS under vacuum at 5 Pa. Ethanol was used as a mixing medium. Homogenization was performed using ultrasonic apparatus fitted with a titanium probe tip for 10 - 40 min until the slurries were dried under stirring conditions. A max temperature of up to 1800°C was similarly applied during sintering with 10 min of dwell time.

Vickers indentation tests were applied with 1 kg load and holding time of 10 sec (Future- Tech FM-300e, Japan). Ten measurements were collected and results are averaged out to get an accurate reading. Static fracture toughness, K_{Ic} , was calculated^[160] as below:-

$$K_{Ic} = 0.016 \frac{P}{c^{3/2}} \left(\frac{E}{H_v} \right)^{1/2} \quad (8)$$

Where P = applied load in Newton; c = crack length from the centre of the indentation impression to the crack tip, in metre; E = Young's modulus, in GPa; and H_v = Vickers hardness, in GPa.

Quasi-static compressive tests were also carried out by using a hydraulic test machine (Instron 5567, USA). A pair of hardened steel plates was used to sandwich specimen to protect the load cell from potential damage due to indentation by the hard specimen. Dynamic compression testing on B₄C-BN samples at high strain rates of 1000s^{-1} were conducted using a Split Hopkinson Pressure Bar (SHPB) system. Schematic of the SHPB equipment layout is shown in Figure 34. The SHPB equipment consists of a 20 mm diameter, 400mm long YAG300 maraging steel striker and 20 mm diameter, 1200 mm length incident and 20 mm diameter, 1200 mm length transmitted bars. Both incident and transmitted bars were fitted with TML strain gauges (Tokyo Sokki Kenkyujo Co. Ltd., Japan, with a gauge factor of 2.11). The stress and strain were calculated based on the electric signals from the strain gauges using elastic bar wave theory.^[161]

To ensure consistency and protection to the equipment, high strength hardened steel plates, with impedance close to the bars, were used to sandwich between the bars and samples to prevent damage to the bars.^[162]

Figure 34 Schematic of a compression Split-Hopkinson Pressure Bar (SHPB)

Nitrided B₄C sample for SHPB testing were prepared by using three different maximum pressures of 30, 60 or 100 MPa, denoted as sample A, B and C respectively. Other SPS conditions were fixed for nitrogen atmosphere, heating duration of 25 min and up to a maximum temperature of 1800°C. Graphite moulds with inner diameter of 10 mm were used. Height of each sintered pellets were fixed at 6 mm after surface polish and grinding. Two identical samples were sintered for each sintering pressure for consistency check.

The reactive SPS sintered sample and fragments from the SHPB testing were observed using SEM (JEOL JSM-7600F, Japan) equipped with energy dispersive system (EDS). TEM microscopy (JEOL JEM2100F, Japan) was also used to check the distribution of B₄C and BN. Stereo microscopy (Leica MZ6, Germany) was used to observe the sample after destructive testing. XRD was measured using Bruker AXS (D8 Advance, Germany) with a Cu K α radiation source. Rietveld analysis was done using TOPAS software. Density of the sintered samples was measured by the Archimedes technique.

5.3. Results & Discussion

5.3.1. Characterisation of core-shell B₄C-BN

SEM of the cross section of the core-shell structure B₄C-BN, in Figure 35, shows the textured layering after SPS. The lighter grey observed in the SEM is indicative of the sintered boron carbide. The darker is indicative of porosity which is likely due to the displacement of the 'softer' BN phase during sample preparation process, which involves

surface grinding with diamond lapping disk with water medium. The layered structure of the composite is expected and matches the schematic of compressed core-shell B₄C-BN as shown in Figure 33.

Figure 35 Cross-section SEM image of sintered core-shell B₄C-BN after SPS consolidation with arrows indicating the press direction.

The samples density measured by Archimedes technique shows that all samples have a relative densities of 96-98%. XRD patterns from Figure 36(a) shows the formation of BN phase from B₄C powder after nitridation in N₂ gas atmosphere as represented in the Equation below:

Apart from B₄C, XRD of the initial commercial powder had shown the presence of B₂O₃ phase which is a common residue of the precursor during B₄C synthesis process. The B₂O₃ peak after nitridation appears to be significantly reduced which could be

attributed to two possible explanations. The first reason is the sublimation of B₂O₃ above 1500°C [119] where solid B₂O₃ was vaporised and removed by the flow of nitrogen gas. Second reason is due to carbothermal reaction between B₂O₃ and simultaneous nitridation to form BN as shown in the Equation below. [163,164]

The latter was most likely the dominant process as earlier research has shown that the reaction between B₂O₃ and free carbon could proceed at relatively lower temperature from 1400°C [130]. This was also supported by Bartnitskaya [164] work in the synthesis of boron nitride between the temperature of 1000 to 1450°C using the same reaction process. Although B₂O₃ was known to form both B₄C and BN, the bulk of the BN observed in the XRD was formed by the reacting B₄C powder as the amount of B₂O₃ will not have been sufficient to account for the BN formed during the extensive heating duration. As both BN and graphite shared very similar crystal structure, it is often difficult to identify the exact composition of each component from the XRD peaks. SEM image of the sintered composite, as shown in Figure 36(b), reveals an almost fully dense materials. Elemental analysis by EDS revealed strong signal of nitrogen in the reactive-sintered composite, lending support to the successful reaction of B₄C to form BN with obvious drop in B₂O₃ content from the commercial powder before nitridation.

Figure 36(a) XRD patterns of B₄C powder before and after nitridation in N₂ gas. **(b)** SEM image of sintered B₄C in N₂ gas with EDS analysis insert (bottom right)^[165]

TEM image from Figure 37 (a, b) show the B₄C powder after nitridation. Layers of BN shell were found to encapsulate individual B₄C grains. In addition, the size of B₄C grains was found to be in the submicron range, which was smaller than the initial powder size of 1.5 micron. This result was consistent with earlier research where the crystallite size of B₄C was found to decrease rapidly at the early stage of the nitridation process^[166]. Crystallite size of BN determined by Rietveld refinement of the XRD pattern was found to be fairly constant at 30-50 nm for specimens with more than 3 %wt of BN.

TEM image from Figure 37 (c, d) shows the cross section of the reactive-sintered B₄C in N₂ gas that was cut using Focused Ion Beam (FIB). Energy filtered TEM of SPS

sintered B_4C -BN at triple grain boundary in Figure 38 also shown that the newly synthesized BN was found to be located along the grains boundaries forming a continuous 3-D matrix in the composite. The BN layer in the composite could potentially provide a transitional region for stress redistribution, thus mitigate brittle-failure and increase fracture toughness.

Figure 37 TEM image of (a-b) nitrided B_4C powder and (c-d) cross section of sintered B_4C in N_2 gas cut by FIB. ^[165]

Figure 38 Energy filtered TEM of SPS sintered B₄C-BN at triple grain boundary.^[166]

5.3.2. Indentation test of core-shell B₄C-BN

Indentation hardness comparison was done between the mechanically-mixed B₄C and BN and core-shell structured B₄C-BN as shown in Figure 39. For the SPS of mechanically-mixed B₄C and BN powders (B₄C+BN), the %wt of BN was the amount of commercial BN used in the mixture. For the core-shell B₄C-BN, reactive-SPS was employed to allow B₄C to react with N₂ (B₄C+N₂), the %wt of BN was the estimated value from the XRD Rietveld refinement analysis.

The highest averaged hardness value for Vickers and Berkovich indentation achieved were 39.3 GPa and 56.0 GPa respectively at 0.4%wt of BN. These results show that an optimum amount of up to 3% BN is desirable to achieve an even redistribution of stress to the material structure. However, excessive amount of BN deteriorate the hardness due to grain boundary shearing as observed in simulated and experimental materials studied by other researchers.^[167,168] Other reported hardness values of similar SPS of B₄C-based composites typically range from 32 to 41.8 GPa.^[109,169,170]

The results from the indentation test have shown that the micro-hardness value does not have substantial difference with nitrided-B₄C when using a Vickers hardness tester. However, more significant result was achieved from the localised nano-hardness measured by Berkovich indenter tip. It have been verified that the high values registered was not due to indentation size effect as the hardness of mechanically-mixed B₄C-BN has comparatively lower value using the same Berkovich indenter tip. This high hardness observed by the Berkovich indentation of core-shell structured B₄C-BN could be attributed to the presence of superhard phase of boron suboxide as observed in earlier research.^[166]

Figure 39 Vickers/Berkovich hardness vs content of the BN in composite ^[166].

5.3.3. Quasi-static and dynamic compressive test

Quasi-static compression testing was used to determine the mechanical properties of the SPS specimens at low strain rate on the order of 10^{-3} s^{-1} . The stress-strain curve in

Figure 40 shows that SPS-sintered pure B₄C pellet achieves a high compressive strength of 3100 MPa, which compares favourably to the reported values of 2854 MPa from the literature^[171] and also the commercial hot pressed B₄C of 2746 MPa.^[172] The result shows strong capability of SPS to achieve nearly full dense boron carbide. Figure 40 also shows that 50% B₄C - 50% BN composite is tougher than the sintered pure B₄C. It can withstand high loading up to the limit of the load frame at 140 MPa and still remains elastic, exhibiting both strength and ductility and a toughness of approximately 300 MJ/m³, three times higher than that of the pure B₄C. This can be attributed to the soft BN of which acts as a sacrificial bond for cracks to mitigate through a tortuous path running along the hard granular B₄C. This also satisfies the fundamental requirement of armour materials in having a soft matrix to promote load transfer and stress redistribution, resulting in significant energy absorption.

Figure 40 Stress-strain curve from quasi-static compressive test of SPS sintered B₄C and mechanically-mixed B₄C-BN composite

Dynamic compressive behaviour of the pure B₄C and B₄C with varying ratio of BN was characterized through Split-Hopkinson Pressure Bar (SHPB) technique, which impacts the samples at high strain rate on the magnitude of 10^3 - 10^4 s⁻¹. Figure 41 show that pure boron carbide has high compressive strength of 2900 MPa, which is close to the value found in quasi-static test. However, the value is lower than expected because it is known that fracture strength increases at higher strain rate. For example, at strain rate of 10^3 s⁻¹, the dynamic fracture strength of brittle ceramics like aluminium nitride is 87% higher than that measured at a strain rate of 10^{-2} s⁻¹.^[173] Possible reason for the lower than expected fracture strength could be due to the premature edge fracture of the sample. This was supported by evidence from the stress-strain curve as the trend plateau prematurely at 2200MPa indicative to a fracture. As the stress is calculated by dividing the loading force with the surface area of contact, the fracture of the sample edge will cause a rapid raise in the material stress which resulted in a premature failure.

The results, in Figure 41, shows that those specimens with BN mix generally were impacted up to stresses of 700 MPa, which are probably due to sample dimension limitation. It was recommended that the sample's length-to-diameter ratio to be maintained at 0.5 to 1 to minimize the errors. However, the sintered B₄C have an L/D ratio of 0.425 while the B₄C-BN composite samples' have L/D ranges of only from 0.042 to 0.069, which have even more prominent error as compared to pure B₄C. This causes high radial inertia in the samples which in turn resists them from fracture into columnar fragments by axial splitting. Nevertheless, the composites shows a relatively slow rising trend on the modulus of resilience with the increase in the content of boron nitride, ranging from 25 J/m³ for 20% boron nitride to 60 J/m³ for 35% boron nitride to 120 J/m³

for 65% boron nitride-boron carbide composite. The result also shown B₄C generally performed better than B₄C-BN composite (where BN >20%), which experienced significant lost in strength. From the result, it shows that by adding BN powder in high ratio does not help in improving the overall properties but trade off strength with slight improvement in the toughness.

Table 7 Mechanically-mixed B₄C-BN SPS-sintered samples composition, dimensions and L/D ratios.

Samples	Average Thickness (mm)	Standard Deviation	Area (mm ²)	Approx. Diameter (mm)	L/D ratio
Pure B ₄ C	1.965	0.029	16.790	4.624	0.425
B ₄ C - 20% BN	0.694	0.032	79.304	10.049	0.069
B ₄ C - 35% BN	0.438	0.046	85.455	10.431	0.042
B ₄ C - 65% BN	0.562	0.076	85.833	10.454	0.054

Figure 41 Dynamic stress-strain curve of (a) B₄C (b) B₄C -20%BN composite (c) B₄C -35%BN composite (d) B₄C -65%BN composite.

With reference to Figure 42, the increase of sintering pressure from 30 to 60 MPa significantly increases the SHPB toughness, $S_{\max}$. This is accompanied by noticeable increase in hardness, fracture toughness and also the relative density. However, the increase of maximum strain, $\epsilon_{\max}$, is rather low when compared to increase for sample sintered at 100 MPa. With reference to Figure 43, from sintering pressure of 30 to 100 MPa, dynamic toughness versus SPS pressure increases shows a upward parabolic trend which is represented in the Equation below:-

$$S = 0.0023P^2 + 0.0496P + 2.96 \quad (11)$$

Such relationship between the sintering condition and dynamic toughness is due to a stronger increase of $\epsilon_{\max}$ than that of $S_{\max}$ at higher sintering pressure. Sample sintered at 100 MPa shows the highest relative density of 98.0%. From 60 to 100 MPa sintering pressure, the hardness does not change significantly, whereas K_{Ic} continues to increase at a higher rate.

Table 8 Core-shell B₄C-BN SPS sintering conditions, mechanical properties and optical microscopy observation of fragment after Split-Hopkinson Pressure Bar (SHPB) test. ^[174]

S	Pressure, P [MPa], (atmosphere) and SPS time [min]	HV [GPa]	K_{Ic} [MPa.m ^{1/2}]	SHPB max stress, $\sigma_{\max}$ [MPa]	SHPB max. Strain $\epsilon_{\max}$	SHPB toughness from area S [MJ/m ²]	Observations from the optical microscopy after SHPB test
A1	30/(N ₂) 25 min	27.4	3.17	713	0.0134	6.52	Relatively uniform fraction of middle size fractured pieces
A2	30/(N ₂) 25 min	–	–	723	0.0124	5.77	
B1	60/(N ₂) 25 min	35.6	4.18	925	0.0209	12.95	Two fractions very different: 1. Few very large pieces 2. Fraction of small pieces
B2	60/(N ₂) 25 min	–	–	1185	0.0199	14.22	
C1	100/(N ₂) 25 min	34	5.31	1014	0.0598	29.83	Two fractions very different: 1. Needle-like pieces 2. Significant fraction of very small pieces.
C2	100/(N ₂) 25 min	–	–	1270	0.0593	30.93

Figure 42 Stress-strain curve of core-shell B₄C-BN tested by SHPB with a strain rate of 1000s^{-1} .

Figure 43 Dynamic toughness (S) vs. max SPS sintering pressure used (P) at 30, 60 and 100MPa. ^[175]

The porosity observed in samples A and B is a strong determining factor of the fracture pattern as shown in Figure 44. For example, in Figure 44(c), the crack can be observed to travel along a path of closed pores. Straight lines cracks usually indicate a brittle intra-granular fracture path; however the presence of pores could potentially alter the pattern and deflect the cracks. Elemental mapping on the fracture surface reveals the distribution of nitrogen and oxygen that generally segregate close to the pores as shown in Figure 44(b and d, in yellow circles). Some of the segregation, however, was found in the grain boundary and sometimes in the absence of any porosity as shown in Figure 44(b and d, in yellow rectangles). It was also observed that nitrogen attached more closely to the pores as compared to oxygen atoms. The presence of nitrogen cluster near the pores could be due to the trapping of nitrogen gas during the SPS sintering process as the grains boundary merges together enclosing the pores.

Quantitative area analysis of the nitrogen content shows a concentration of 1 to 4 wt% for sample A, B and C. It is useful to note that EDS may not be the most accurate analysis technique in the detection of light elements. Therefore, it will be more useful to use the value as a relative comparison to the current sample rather than an absolute value of the actual composition. One important criterion for the pore to deflect the crack is its shape. As shown in Figure 44 (a, b, c and d), the shape of the pores are mainly triangular or rectangular, which could potentially act as strain concentrators. The closing up of the pores when a high sintering pressure is used were also observed for Sample C as shown in Figure 44 (e and f). The change in the size and shape of the pores could have induced different toughening mechanisms in the composite.

Figure 44 SEM micrograph and corresponding overlay of EDS element mapping of sample fragment sintered at 30 MPa (a & b), 60 MPa (c & d) and 100 MPa (e & f). (red dots indicate nitrogen and green dots indicate oxygen) ^[174]

Figure 45 shows the SEM images of the fragments of sample a, b and c at three different magnification. The fracture surface shows significant differences where higher pressure sintered samples tend to exhibit a pullout-like mechanism. There is, however, insufficient data on how the pores characteristics influence the mechanical properties.

Figure 45 SEM images at different magnifications, x25, x50 and x500, for samples A (40 MPa), B (60 MPa) and C (100 MPa) fragments after SHPB testing. Arrow in (c) shows a particle dislodged by pullout mechanism. [\[174\]](#)

5.4. Summary

In conclusion, B₄C nitrided through a reactive-SPS process produced a unique core-shell structured composite consisting of both B₄C and BN. Characterisation of the B₄C-BN composite shows that the BN located between the boundaries of B₄C grains forming a continuously 3-D matrix in layered formation. The highest hardness values measured, at an optimum content of 0.4%wt of BN, by both Vickers and Berkovich indentation were 39.3 GPa and 56.0 GPa respectively. Superior localised hardness by

nano-indentation was observed in nitrided B₄C but not in mechanically-mixed sintered B₄C-BN. The possibility of a superhard boron suboxide phase was credited for the high localised hardness.

This structured composite was made possible by the fast sintering process of SPS with the use of pulsed electric current. The BN matrix provided a transitional region for effective redistribution of the stress, thus it could mitigate brittle-failure and increase toughness of the composite. The reactive SPS technique used to form the nano-layers of nitride-based composite could be applied in other combination ceramics materials and create a new class of mechanical properties-enhanced structured B₄C-BN like composite material.

The research has indicated that dynamic mechanical properties of sintered B₄C could be controlled by designing B₄C composites in which the grain boundaries between particles are modified. Fracture analysis after SHPB testing has given clues on mechanisms that lead to higher toughness, such as crack deflection and also pull-out fracture mode. This provides the means for further developments toward higher toughness B₄C ceramic composite materials.

CHAPTER 6: CONCLUSION & FUTURE WORK

6.1. Conclusion

Nano-particles, nano-wires, nano-ribbons and nano-flakes of B_4C were produced through a carbothermal synthesis using both catalytic and non-catalytic approach. Characterisation of the nanostructured B_4C was done using SEM/EDS, XRD and TEM. As both B_4C and the free carbon shared similar constituent elements and physical properties, it is technically impossible to achieve to carbon-free synthesized B_4C . The research for the first time has shown that the various morphologies of the nanostructured B_4C could be achieved by simply controlling the processing conditions such as the precursor mix ratio and the use of catalyst material. This technique could be emulated in the synthesis process of other superhard nano-structured materials.

A novel star-shape nano-plate of B_6O was formed through a liquid-phase reaction between amorphous boron and boron oxide. This is the first time such complex morphology of B_6O has been achieved. Analysis have shown that the formation of the five-pointed star-shaped crystal structure was possible due to the dihedral angle of 71.8° in B_6O rhombohedral unit cell and the cyclic twinning with 1° misfit. Moreover, EDS quantitative analysis clarified that the oxygen-deficit B_6O_x where the oxygen occupancy, x , range from 0.842 to 0.869, contributed to the unique star-shaped crystal growth process. SPS consolidation of the synthesized B_6O powder was performed and bulk ceramic with high hardness of 34.8 GPa and fracture toughness of $4.0 \text{ MPa.m}^{1/2}$ were obtained. This was one of the highest reported values for sintered B_6O and such

high hardness and toughness structured composite would not have been possible through conventional sintering processing.

A unique core-shell structured of B_4C -BN was produced through a reactive-SPS process of B_4C . Characterisation of the sintered composite shows that the BN located between the boundaries of B_4C grains forming a continuously 3D matrix in a layered formation. High localised hardness of 56.0 GPa was registered using Berkovich indentation technique which was attributed to the presence of superhard phase of boron suboxide was observed in earlier study. The result also shows that an optimum amount of BN of up to 3% is desirable to achieve an even redistribution of stress to the load-bearing material structure. Result from the quasi-static testing of B_4C -BN composite shows that the role of BN acted as sacrificial bond for cracks to mitigate through a tortuous path running along the hard granular B_4C . This softer BN matrix is able to promote load transfer and stress redistribution, resulting in significant energy absorption.

Dynamic testing of the core-shell B_4C -BN shows that the sintering pressure has significant effect on toughness of the composite. Increasing sintering pressure from 30 to 90 MPa shows a parabolic increasing trend of toughness. The increased toughness was attributed to the nitrogen and oxygen content in the composite, which control the pores which act as strain concentrators. This finding could also be used to optimise other boron-based composite materials.

6.2. Recommendations for Future Work

Future work to be done for the 0D, 1D and 2D nanostructured B_4C will be to look into the purification of excess free carbon from the synthesis process. As B_4C similarly hold carbon in its crystal structure, chemical approach to remove the excess carbon without affecting the B_4C is highly challenging. In addition, graphite has very close density and grain size to the synthesized B_4C which also make it harder to remove by physical means. However, there are still much characteristic differences between B_4C and free carbon which are yet to be explored. In-depth study on the thermodynamic such as the Gibbs free energy of formation could be done to optimise the crystal growth. One alternative approach is to convert free carbon into diamond-like phase to form a superhard boron carbide - diamond nanocomposite particulate materials for armour application.

Another interesting field of research to look into will be the alignment of nanostructured material to achieve anisotropic mechanical properties within a bulk material. Such properties will reveal the material greatest potential in a specific orientation where it is needed most. One of such technique is by using a strong electromagnetic field to orientate the crystal particles to a desired position during the sintering process. This material properties enhancement design coincide with the mechanical properties enhancement principles which are commonly found within biological materials.

Fracture toughness measurement done in the current work was based on Vickers indentation technique instead of ASTM Standard Test Method for Measurement of

Fracture Toughness due to the limitation of time and the resources to produce the number of samples required to conduct the test. The calculated value is recommended to be used only on comparative basis rather than an absolute value. As ASTM standard is a better quantitative approach to appreciate fracture toughness, based on the result achieved in the current work, the best consolidation condition could be focused and samples could produce in larger quantity for testing in accordance to ASTM standard for future study.

Last but not least, the study of the porosity effect on mechanical properties such as the toughness and flexure strength in advanced ceramic and composite materials could be further extended. It is shown from the core-shell structure of B_4C -BN that the presence of pores alters the toughening behaviour through crack deflection. However, it is also a common knowledge that high porosity weakens the mechanical properties of advanced ceramic materials. Therefore, in-depth study should be carried out to understand the role of porosity in mechanical properties enhancement.

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APPENDIX A: SELECTED CRYSTALS DIFFRACTION

DATA FROM CRYSTALLOGRAPHIC DATABASE

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*data for      ICSD #81960
CopyRight     ©2013 by Fachinformationszentrum Karlsruhe, and the U.S. Secretary
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Coll Code     81960
Rec Date     1997/11/10
Mod Date     2012/02/01
Chem Name     Boron Carbide (0.8/0.2)
Structured    B12 (B C2)
Sum          C2 B13
ANX          N2013
D(calc)      2.5
Title         Structures of the boron-rich boron carbides from neutron powder
              diffraction: implications for the nature of the inter-icosahedral
              chains
Author(s)     Kwei, G.H.; Morosin, B.
Reference     Journal of Physical Chemistry
              (1996), 100, 8031-8039
Unit Cell    5.5973(6) 5.5973(6) 12.0642(13) 90. 90. 120.
Vol          327.33
Z            3
Space Group  R -3 m H
SG Number    166
Cryst Sys    trigonal/rhombohedral
Pearson      hR15
Wyckoff      h2 c b
R Value      0.017
Ref Cell     RH 5.158 5.158 5.158 65.705 65.705 65.705 109.11
Trans Red    0.333 -0.330 -0.330 / -0.660 -0.330 -0.330 / 0.333 0.667 -0.330
Comments     Sample from Cu-melt-grown crystals
              The structure has been assigned a PDF number (calculated
              powder diffraction data): 01-086-1128
              Rietveld profile refinement applied
              Temperature in Kelvin: 12
              Temperature factors available
              Structure type : B13C2
              X-ray diffraction (powder)
              At least one temperature factor is implausible or
              meaningless but agrees with the value given in the paper.

Atom #  OX  SITE      x          y          z          SOF      H
ITF(u)
B 1 +0  18 h  0.83696(24) 0.16304(24) 0.35832(19)  1.      0
0.0016(4)
B 2 +0  18 h  0.89270(24) 0.10730(24) 0.11396(23)  1.      0
0.0040(5)
B 3 +0  3 b  0          0          0.5          0.99    0
0
C 4 +0  6 c  0          0          0.3812(4)    0.99(3)  0
0
Lb1 Type  U11      U22      U33      U12      U13      U23
B3 B0+  0.0029(17) 0.0029(17) 0.008(3)  0.0014(9) 0      0
c4 C0+  0.0009(10) 0.0009(10) 0.0098(20) 0.0005(5) 0      0

Std. Notes   Transformation Method: Tidy
              TRANS Origin 0 0 1/2
Std. Cell    5.5973 5.5973 12.0642 90 90 120
Std. Vol.    327.33
Std. Z       3
Std. SG      R3-MH
Std. Atom

Atom #  OX  SITE      x          y          z          SOF
B 1 +0  18 h  .50363    .49637    .19165    1.
B 2 +0  18 h  .44063    .55937    .05271    1.
B 3 +0  3 a  0          0          0          .990
C 4 +0  6 c  0          0          .11880    .990
*end for      ICSD #81960

```

```

#####
###      Entry exported from ICDD PDF Database by Match!      ###
#####
###      PDF Entry No.: 00-006-0297      ###
#####
###      Copyright International Centre for Diffraction Data (ICDD)      ###
###      12 Campus Boulevard, Newtown Square, PA 19073-3273, U.S.A.      ###
#####

***** Phase Classification *****
Formula sum   : B2 O3
Pearson symbol: cP80
Quality       : O (doubtful)
Reference     : Senkovits, Hawley, North American Aviation Incorporated, Downe
                y, California, USA, Private Communication, ()
***** Crystal Structure *****
Published crystallographic data:
Space group   : P -
Crystal system : cubic
Cell parameters : a=      10.0550 A
Cell volume    : 1016.59
Formula units (Z): 16
***** Diffraction Data *****
Published diffraction lines:
Wavelength used for calculation of 2theta values: lambda = 1.541874 A
  d      2theta      Int.      h      k      l      Remark
  6.0800   14.5693    35.00      3      1      0      hkl generated by input software.
  3.2100   27.7928   100.00      2      2      2      hkl generated by input software.
  2.9200   30.6174    12.00      4      0      0      hkl generated by input software.
  2.6000   34.4967    10.00      5      1      0      hkl generated by input software.
  2.4900   36.0718    10.00      5      2      0      hkl generated by input software.
  2.2600   39.8906    14.00      6      0      0      hkl generated by input software.
  1.9800   45.8296     8.00      6      2      0      hkl generated by input software.
  1.8800   48.4188     6.00      7      1      1      hkl generated by input software.
  1.6800   54.6311     4.00      6      6      4      hkl generated by input software.
  1.6000   57.6107     4.00      10     3      2      hkl generated by input software.
  1.4100   66.2906     4.00
  1.0700   92.1919     4.00
  0.9460  109.1636     6.00
  0.8660  125.8037     6.00
***** Experimental *****
Physical properties:
Meas. density :      1.8050
Calc. density :      1.8190
***** Remarks *****
General: Analysis: Sample was over 99% pure, with water as impurity.
General Comments: High pressure phase.
Melting Point: 567 K.
Reason O Quality Was Assigned: O assigned because average 2 is 0.223.
Unit Cell: Hexagonal form: a=4.334, c=8.334, C=1.923, S.G.=`P312`; Z=3 (reference:
Berger, Acta Chem.
Scand., 7 611 (1953)).
Unit Cell Data Source: Powder Diffraction.

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*data for      ICSD #73624
CopyRight     ©2014 by Fachinformationszentrum Karlsruhe, and the U.S. Secretary
of            Commerce on behalf of the United States. All rights reserved.

Coll Code     73624
Rec Date     1994/06/30
Chem Name    Boron Oxide (6/0.8)
Structured   B6 00.76
Sum          B6 00.76
ANX          N5036
D(calc)      2.5
Title        Structure of B6O boron suboxide by Rietveld refinement
Author(s)    Kobayashi, M.; Higashi, I.; Brodhag, C.; Thevenot, F.
Reference    Journal of Materials Science
              (1993), 28, 2129-2134
Unit Cell    5.367(1) 5.367(1) 12.328(2) 90. 90. 120.
Vol          307.53
Z            6
Space Group  R -3 m H
SG Number    166
Cryst Sys    trigonal/rhombohedral
Pearson      hR14
Wyckoff      h2 c
R Value      0.028
Red Cell     RH 5.146 5.146 5.146 62.853 62.853 62.853 102.51
Trans Red    0.333 -0.330 -0.330 / -0.660 -0.330 -0.330 / 0.333 0.667 -0.330
Comments     The structure has been assigned a PDF number (calculated
              powder diffraction data): 01-081-2192
              Rietveld profile refinement applied
              Temperature factors available
              Structure type : PB6
              X-ray diffraction (powder)

Atom #  OX  SITE      x      y      z      SOF      H
ITF(B)
B 1 +0  18 h  0.156(2)  0.844(2)  0.641(1)  1.      0
2.4(5)
B 2 +0  18 h  0.223(1)  0.777(1)  0.781(1)  1.      0
1.5(5)
O 1 +0  6 c   0      0      0.625(1)  0.76(6)  0
0.1(7)
Std. Notes   Transformation Method: Tidy
              TRANS Origin 0 0 1/2
Std. Cell    5.367 5.367 12.328 90 90 120
Std. Vol.    307.53
Std. Z       6
Std. SG      R3-MH
Std. Atom

Atom #  OX  SITE      x      y      z      SOF
B 1 +0  18 h  .51067  .48933  .19233  1.
B 2 +0  18 h  .44367  .55633  .05233  1.
O 1 +0  6 c   0      0      .12500  .760
*end for     ICSD #73624

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*data for      ICSD #654971
CopyRight     ©2014 by Fachinformationszentrum Karlsruhe, and the U.S. Secretary
of            Commerce on behalf of the United States. All rights reserved.

Coll Code     654971
Rec Date      2008/07/07
Mod Date      2011/02/01
Chem Name     Boron Carbide (4/1)
Structured    B4 C
Sum           C1 B4
ANX           NO4
D(calc)       2.51
Title         The crystal structure of boron carbide
Author(s)     Clark, H.K.;Hoard, J.L.
Reference     Journal of the American Chemical Society
              (1943), 65, 2115-2119
Unit Cell     5.60 5.60 12.12 90.0 90.0 120.0
Vol           329.16
Z             9
Space Group   R -3 m H
SG Number     166
Cryst Sys     trigonal/rhombohedral
Pearson       hR15
Wyckoff       h2 c b
Red cell      RH 5.174 5.174 5.174 65.519 65.519 65.519 109.721
Trans Red     0.333 -0.330 -0.330 / -0.660 -0.330 -0.330 / 0.333 0.667 -0.330
Comments      B1 Z[-Z]; B2 Z[-Z]
              Cell and Type only determined by the author(s). Coordinates
              estimated by the editor in analogy to isotypic compounds.
              Metals formula record: B4 C (z = 3) R3-M
              Metals Sdata Record: INT= film; RAD= Cu; APP= Weissenberg
              Metals structure type B4 C
              Standard deviation missing in cell constants
              Structure type : B13C2
              No R value given in the paper.
              At least one temperature factor missing in the paper.

Atom # OX SITE x y z SOF H
B 1 +0 18 h -.1667 0.1667 0.360 1 0
B 2 +0 18 h -.106 0.106 .113 1 0
C 1 +0 6 c 0 0 0.385 1 0
C 2 +0 3 b 0 0 0.5 1 0

Std. Notes Transformation Method: Tidy
TRANS Origin 0 0 1/2
Std. Cell 5.6 5.6 12.12 90 90 120
Std. Vol. 329.16
Std. Z 9
Std. SG R3-MH
Std. Atom

Atom # OX SITE x y z SOF
B 1 +0 18 h .49997 .50003 .19333 1.
B 2 +0 18 h .43933 .56067 .05367 1.
C 1 +0 6 c 0 0 .11500 1.
C 2 +0 3 a 0 0 0 1.

*end for      ICSD #654971

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*data for      ICSD #35538
CopyRight     ©2014 by Fachinformationszentrum Karlsruhe, and the U.S. Secretary
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              Commerce on behalf of the United States. All rights reserved.
Coll Code     35538
Rec Date      1980/01/01
Mod Date      2010/08/01
Chem Name     Boron Nitride
Structured    B N
Sum           B1 N1
ANX           AX
D(calc)       2.26
Title         An X-ray examination of the structure of boron nitride
Author(s)     Brager, A.
Reference     Acta Physicochimica (USSR)
              (1937), 7, 699-706
Unit Cell     2.51 2.51 6.69 90. 90. 120.
Vol           36.5
Z             2
Space Group   P 63/m m c
SG Number     194
Cryst Sys     hexagonal
Pearson       hP4
Wyckoff       d c
Red cell      P 2.51 2.51 6.69 90 90 119.999 36.501
Trans Red     1.000 0.000 0.000 / 0.000 1.000 0.000 / 0.000 0.000 1.000
Comments      Given space group was P6-, shifted by 1/3 2/3 1/4
              AE: B: 3l N3; N: 3l B3 (+6N)
              The structure has been assigned a PDF number (calculated
              powder diffraction data): 01-085-1068
              The structure has been assigned a PDF number (experimental
              powder diffraction data): 45-896
              Standard deviation missing in cell constants
              Structure type prototype : BN
              Structure type : BN
              X-ray diffraction (powder)
              No R value given in the paper.
              At least one temperature factor missing in the paper.
Atom # OX SITE x y z SOF H
B 1 +3 2 c 0.3333 0.6667 0.25 1. 0
N 1 -3 2 d 0.3333 0.6667 0.75 1. 0
Std. Notes Transformation Method: Tidy
              Multiple transformations possible, first one selected
Std. Cell     2.51 2.51 6.69 90 90 120
Std. Vol.     36.5
Std. Z        2
Std. SG       P63/MMC
Std. Atom
Atom # OX SITE x y z SOF
B 1 +3 2 c .33333 .66667 .25 1.
N 1 -3 2 d .33333 .66667 .75 1.
*end for      ICSD #35538

```