



## POWDER PROCESSING AND BINDER REMOVAL STUDIES FOR THE FABRICATION OF DEFECT FREE BORON CARBIDE PELLETS

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(Received November 11, 2008 and accepted in revised form December 18, 2008)

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Compaction behaviour of boron carbide ( $B_4C$ ) has been studied by pressing the powder at different load with and without the lubrication of powder and die walls. The study was mainly focused on the optimization of powder processing, compaction, binder removal and sintering conditions. The results clearly suggest that the binder removal rate during the sintering caused the formation of cracks and pores. However, these defects have been eliminated by removing the binder before sintering. The endcapping problem of pellets was controlled by lubricating the powder and die walls.  $B_4C$  pellets with required dimensions were produced using uniaxial die-compaction and pressureless sintering technique.

**Keywords:**  $B_4C$ , Uniaxial die compaction, Binder removal, Pressureless sintering

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### 1. Introduction

Boron Carbide is one of the hardest materials known, ranking third behind diamond and cubic boron nitride [1]. Combined with its low weight (theoretical density:  $2.52 \text{ g/cm}^3$ ) and excellent abrasion resistance it is the premier material for personal armor, nozzle material for slurry pumping and grit [2]. Its ability to absorb neutrons without forming long lived radionuclides make the material attractive as an absorbent for neutron radiation arising in nuclear power plants. For nuclear application it is used in the form of pellets in control rods and shut down rods for controlling the power of nuclear reactor. The  $B_4C$  powder is further processed by powder metallurgy route and ultimately sintered to obtain the pellet of desire shape and dimension [2, 3]. Boron carbide is a difficult material to process to obtain pellet because of high hardness. Its powder does not easily compact, resulting in poor green density. The formation of a green (unfired) body is an essential prerequisite to the sintering process. High green densities are advantageous because they incur less shrinkage on firing and usually impart high green strength. In addition, the material must be as homogeneous (same size of powder particles) as possible in terms of both physical and chemical properties to ensure that an even shrinkage takes place without cracking. Binder is usually added in powder to enhance the green strength/density. The granulation of powder is normally conducted

before compaction to enhance the flowability and die filling properties of the powder. The granules so obtained are spheroidized to round off the sharp edges and to obtain a free flowing feed material for die pressing. Both powder and die are lubricated before pressing to ease the process of ejection of pellet from the die. Powders are lubricated with some organic acid (stearic acid) and die with zinc stearate. These lubricants reduce the friction within the powder particles and also friction between powder & die wall, which reduces the tendency of endcapping (cracks at the edges) in the final product [4-6]. The process of powder compaction can generally be divided into three distinct stages such as die filling, compaction and ejection. The powder behaviour during the above three stages all determine the properties of final compacts. Therefore, understanding the mechanical behaviour of powders during each stage is very important. Proper tooling for the compaction also need the careful attention in respect of dimensions accuracy and desire shape of pellets. The green bodies should have high strengths, thus, facilitating handling before sintering. Binder removal is also important step before sintering otherwise it may produce cracks in the final sintered product. After compaction sintering is the next step, which is essentially a removal of the pores between the starting particles (accompanied by shrinkage of the component), combined with growth together and strong bonding between the particles by diffusion.

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Pressure and pressureless sintering methods are used to produce the final product from green pellets.

B<sub>4</sub>C powder are typically hot-pressed (pressure method) at ~2100°C and 30-40 MPa to obtain dense articles (small size) [7, 8]. Vasilos and Dutta [9] hot pressed B<sub>4</sub>C up to 98% of theoretical density at 1750°C under 0.167 MPa. Although, it is possible to produce simple shapes with near to theoretical density but these methods do not produce bodies of large size and complex shape. Therefore pressureless sintering of B<sub>4</sub>C is usually preferable in order to avoid expensive diamond machining for complex shapes. However, in pressureless sintering process, various additives (sintering aids) are used to enhance the sintered density without pressure, e.g. Al<sub>2</sub>O<sub>3</sub>, TiB<sub>2</sub>, AlF<sub>3</sub>, W<sub>2</sub>B<sub>5</sub> etc.

The present research work deals with the preparation of B<sub>4</sub>C pellets with diameter of 26.0-26.8 mm and length of 31.0-32.0 mm. The objective was to produce defects free sintered pellets of sintered density  $\geq 1.65 \text{ g/cm}^3$  with desired dimensions using uniaxial die-compaction and pressureless sintering technique. The study was mainly focused on the optimization processes such as mixing of binder & B<sub>4</sub>C powder, granulation of powder mixture, percentage and type of lubricants, pressing conditions, binder removal and sintering.

## 2. Experimental Procedures

### 2.1. Powder processing and sintering

Fine B<sub>4</sub>C powder with average particle size  $\leq 3 \mu\text{m}$  and surface area  $8.26 \text{ m}^2/\text{gm}$  was used as starting material. Polyethylene glycol (PEG) 3 wt% was used as binder. The PEG was dissolved in water and then was mixed with boron carbide powder. The mixture was ball milled for 2 hours by adjusting the powder to ball ratio 1:2. After ball milling mixture was dried in oven at 80°C. The dried cake was then passed through the granulator. The granules thus obtained were spherodized for about 2 hours to round off the sharp edges.

The pellets of spherodized powder were pressed at different pressures (39, 52 and 65 MPa) by using hydraulic press. After visual inspection of the pellets, the pressure 39 MPa was selected for further pressing the pellets. Some pellets were compacted after mixing lubricant (1% stearic acid) in the powder particles. The die walls were lubricated by applying thin slurry of ethanol and

zinc stearate in each case. After having experience with different compaction and sintering conditions, finally three pellets (1, 2 and 3) from powder containing binder were pressed at pressure of 39 MPa, the other conditions for these pellets were:

- Pellet 1: Pressed without lubrication of both powder & die walls and binder was not removed before sintering
- Pellet 2: Pressed with lubrication of die walls only and binder was removed before sintering
- Pellet 3: Pressed with lubrication of both powder & die walls and binder was removed before sintering

For binder removal treatment of pellets 2 and 3, these were placed in furnace in argon environment. The pellets were heated up to 250°C with the heating rate of 0.5 °C/min and dwelled at this temperature for 4 hours. Then heated up to 450°C with heating rate of 0.5 °C/min and dwelled at this temperature for 4 hours. Further heated up to 600°C with heating rate of 1°C/min and dwelled at this temperature for 4 hours.

The pellets were sintered at 2250°C for 2 hours in argon atmosphere. Firstly the pellets were heated at 1000°C with the heating rate of 10°C/min then up to 1600°C with the heating rate of 6°C/min. Finally heated up to 2250°C with the heating rate of 3°C/min for 2 hours and then furnace off and allowed the pellets to cool within the furnace.

### 2.2. Characterization

Green and sintered pellets were characterized in terms of dimensions, density and defects. For green pellets the density was measured by using geometrical method and soundness of the pellets was examined by visual inspection. The sintered density was measured by both geometrical and immersion method. The soundness of the sintered pellets was studied by visual inspection. Density of sintered pellet was measured by penetration immersion method according to procedure given in ASTM Standard C 373. In this method dry mass of the pellet (D) was determined to the nearest 0.01 g. Pellet was placed in a beaker of distilled water, boiled for 5 hours and then allowed to soak for additional 24 hours. Impregnated pellet was suspended in water and its suspended mass (S) was determined to the nearest 0.01 g. After this pellet was taken out of water, excess water from the surface was removed by blotting operation using a wet cloth of cotton and its saturated mass (M) was determined to the nearest 0.01 g. Exterior volume (V) in cubic centimeters, was calculated as follows:

$$V = M - S$$

and the bulk density of the pellet (B) in  $\text{g/cm}^3$  was determined by:

$$B = D/V$$

The apparent porosity (P) as percentage of the exterior volume of the pellet was calculated as follows:

### 3. Results and Discussions

#### 3.1. Compaction behavior of $B_4C$ powder mixture

In the pellets compacted at 52 and 65 MPa pressure, it was found that the endcapping was present in the green pellets. Figure 1 clearly shows the endcapping in green pellet pressed at 65 MPa. However, endcapping was not observed in the pellets (Pellet 1, 2 & 3) compacted at 39 MPa and the green density of these pellets was around  $1.26 \text{ g/cm}^3$  (50% of the theoretical density). Since  $B_4C$  particles do not plastically deform during the compaction, the green strength of the green pellets is due to the binder added in the powder. This binder works as glue between the particles and provides the green strength [6]. Thus, in compaction, the powder undergoes high shear and compressive strains, which lead to consolidation and densification. However, when maximum ram pressure has been reached and rams pullback starts, the compressive stresses start to relax and the material goes abruptly from plastic to pure elastic. If stressed beyond their elastic limit, they break. Therefore, green ceramic bodies are classified as brittle elastic solids after the maximum compaction force has been reached. With this fact in mind, consider a pellet in a die with the ram being withdrawn (the initiation of ejection). The pressure on the pellet's top is being reduced, because of the pullback of ram, while its side and bottom the rigid die walls maintaining their hold. These situations are ripe for some kind of tensile and shear stress build up in the region of the ram. As a result, since the material can no longer deform plastically, a crack may be initiated [10, 11]. Ram pullback and pellet ejection are therefore, could be chosen the reasons for the endcapping in the pellets compacted at 52 and 65 MPa pressure.

#### 3.2. Binder removal and sintering studies

Two biggest challenges encountered during sintering are crack and distortions. Cracks are mostly due to the non-uniform density distribution

induced from the compaction process and the temperature gradient [12]. Considering the size of green pellets, to avoid the sintering defects, sintering conditions were selected as recommended by Taylor et al. [13].

$$P = [(M - D)/V] \times 100$$

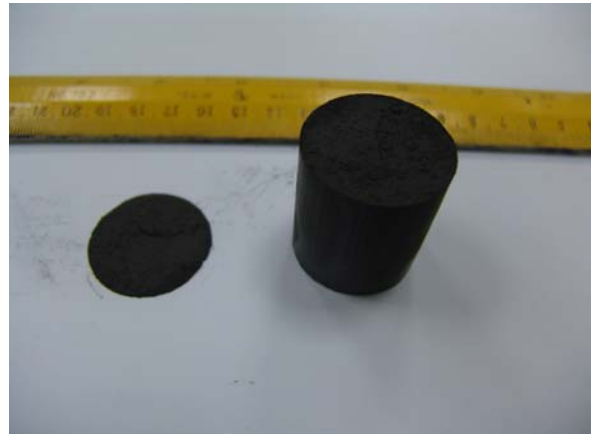
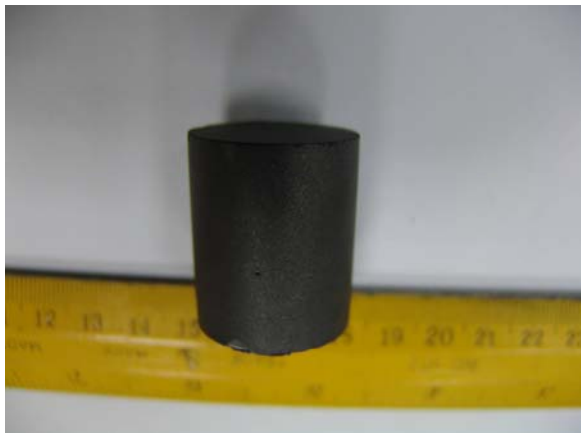


Figure 1. Green pellet compacted at 65 MPa showing endcapping (upper surface detached and placed on the side),

In case of Pellet 1, after sintering at  $2250^\circ\text{C}$  endcapping and cracks were found, Fig. 2a. There were also pores formed on the surface of the pellet. The endcapping is a defect which appears during compaction. Although, in the visual inspection of green Pellet 1, endcapping was not observed. It has been observed that the endcapping is caused by the differential strain recovery during the ejection. The addition of the lubricant reduces the inter-granular and powder/die-wall friction, and thus reduces tendency for end caps to form [6, 10, 14 & 15]. As far as the cracks and pores are concerned that may appear during the sintering. This pellet (Pellet 1) was directly sintered from green state and no binder (PEG) removal treatment was performed before sintering. The PEG is an organic compound with low boiling point and in inert atmosphere it decomposes into monomers, which are highly volatile. At higher temperatures a high vapor pressure is developed which may lead to cause cracks during sintering. The dimensions of the green pellet play a very vital role in the removal of the binder. The ceramics pellets with the dimensions similar with pellets under study, it is recommended that prior to sintering, binder must be removed slowly so that binder can leave the pellet without causing cracks. Sintering is done in stages with the heating rate 3 to  $10^\circ\text{C}/\text{min}$  and for

binder removal the heating rate of 0.5°C/min is recommended [6, 16-18].



(a) Pellet 1



(b) Pellet 2



(c) Pellet 3

Figure 2. The pellets sintered at 2250°C (a) Pellet 1: Endcapping and cracks, (b) Pellet 2: Endcapping and (c) Pellet 3: Defect free.

These results revealed that endcapping defect was produced during the green pellet formation

due to absence of lubricants and the cracks & pores are formed due to the fast rate of binder removal during sintering. So, it is deduced that the binder should be removed before sintering with slow heating rate as mentioned in experimental procedure.

As mentioned earlier that for Pellet 2, binder was removed before sintering, however powder was not lubricated with stearic acid before compaction.

After the sintering of Pellet 2, endcapping was observed on the top end of the pellet, Fig. 2b. No surface cracks and pores were observed. It shows that binder removal treatment performed on this pellet eliminated the cracks and pores formation during sintering. But the endcapping was still present because it is the defect which is developed during the compaction and was appeared during sintering.

If we compare Pellets 1 and 2 both have the same powder processing conditions. However, binder removal treatment was only performed for Pellet 2 prior to sintering. It was observed that after sintering both pellets showed endcapping. This defect was present in the green state but revealed during sintering. In addition to endcapping cracks and pores were formed on the surface of Pellet 1, which did not appear in Pellet 2 due to the binder removal before sintering as discussed before.

For Pellet 3, binder was removed before sintering and powder was also lubricated with stearic acid before compaction. In this pellet, it was observed that no cracks and endcapping appeared after the sintering, Fig. 2c. As mentioned before that 1 wt% stearic acid was added to the granules before compaction. Stearic acid used for internal lubrication of granules resulted in the reduction in the coefficient of friction of granules and die-walls/pellet system. Which reduced the stresses generated during ejection and green pellet was fabricated without endcapping. The binder removal treatment before sintering has eliminated the formation of cracks and pores during sintering as in the case of Pellet-2.

Binder is removed by thermal degradation in an inert atmosphere (Argon). Thermal debinding of binder in an inert atmosphere can be roughly divided into three stages.

Table 1. Sintered density, dimensions and condition of Pellets 1, 2 &amp; 3.

Pellet No.	Dimension (mm)		Density (gm/cm <sup>3</sup> )	% Theoretical Density	Pellet condition
	Length	Diameter			
1	29.35	26.95	1.74	69	Endcapping & cracks
2	29.73	26.6	1.70	67.4	Endcapping
3	29.42	26.78	1.76	70	Defect free

Stage 1 involves initially heating the binder to the point it softens, e.g.,  $\approx 150-200^{\circ}\text{C}$ . This softening is responsible for the deformation of pellet. This adverse effect of softening can be minimized by heating the green compact at lower heating rate. Therefore, in the present study the heating rate during this temperature ( $150-200^{\circ}\text{C}$ ) was kept  $0.5^{\circ}\text{C}/\text{min}$ .

In stage 2, temperature range  $\approx 200-400^{\circ}\text{C}$ , most of the binder is removed by evaporation and chemical decomposition. Appreciable capillary flow can accompany the evaporation process. The polymer undergo the thermal degradation by chain scission at random points in the main chain to form smaller chain segments. The formation of smaller chain segments leads to a reduction in the polymer viscosity. With continuous thermal degradation, the chain segments become small enough (i.e., their volatility increases) that evaporation is promoted. The high heating rate during this stage of debinding can cause the formation of cracks. In our debinding experiment again heating rate at this stage was kept  $0.5^{\circ}\text{C}/\text{min}$ .

In stage 3, the small amount still remaining in the body is removed by evaporation and decomposition at temperatures above  $\approx 400^{\circ}\text{C}$ . The highly porous nature of the body facilitates the removal of the binder. Therefore, the heating rate during this stage was kept  $1^{\circ}\text{C}/\text{min}$ . This is higher than the heating rates in the first and second stage.

These results clearly suggest that the binder removal rate during the sintering of pellet 1 was higher and it caused the formation of cracks and pores.

The sintered density, % theoretical density, dimensions and final conditions of pellets 1, 2 & 3 are given in Table 1.

#### 4. Conclusions

- Endcapping in green pellet can be avoided by applying an optimum compaction pressure and with lubrication of both die walls & powders.
- The binder Polyethylene glycol (PEG) should be removed before sintering with slow heating rate to prevent the formation of cracks/defects in the sintered pellet.
- Stearic acid is suitable for internal lubrication of granules, which resulted in the reduction in the coefficient of friction of granules and die-walls/pellet system.
- A green density of about 50% of TD gives desired sintered density and dimensional control of pellets.
- A sintering temperature of  $2250^{\circ}\text{C}$ , time 2 hrs and atmosphere argon are suitable to attain the desired density.

#### Acknowledgements

The authors are grateful to Director General, PINSTECH for his interest and financial support for this work. The authors also acknowledge technical staff of the Group for their efforts and cooperation in carrying out this work.

#### References

- [1] J. F. Shackelford and W. Alexander, CRC Materials Science and Engineering Handbook, CRC Press, Boca Raton, Fl., 1991.
- [2] F. Thevenot, J. Euro. Ceram. Soc. **6** (1990) 205.

- [3] R.A. Murgatroyd and B.T. Kelly, Atomic Energy Rev. **15** (1977) 1.
- [4] R.M. German, Powder Metallurgy Science, Metal Powder Industries Federation Princeton, New Jersey, 1984.
- [5] R.M. German, Powder Metallurgy and Particulate Materials Processing, Princeton, New Jersey, 2005.
- [6] M. N. Rahaman, Ceramics Processing and Sintering, Marcel Dekker, New York, 1995.
- [7] W. Weimer, Thermochemistry and Kinetics, in Carbide, Nitride and Boride Materials Synthesis and Processing, Edited by Chapman and Hall, New York, 1997.
- [8] R. Angers and M. Beauvy, Ceramics Int. **10** (1984) 49.
- [9] T. Vasilos and S. K. Dutta, Am. Ceram. Soc. Bull., **53** (1974) 453.
- [10] Robert A. Thompson, Ceramics Bulletin **60** (1981) 244.
- [11] C.-Y. Wu, et al., Powder Technology **152** (2005) 107.
- [12] R.M. German, Sintering Theory and Practice, first ed., Wiley, New York, 1996.
- [13] Taylor et al., U.S. Patent No. 5720911.
- [14] Peng Chen, Gap-Yong Kim and Jun Ni, J. Mater. Processing Tech. **190** (2007) 243.
- [15] David C. Zenger and Haimain Cai, The Int. J. Powder Metall. **34** (1998) 33.
- [16] M. J. Edirisinghe, J. Mater. Sci. Lett. **10** (1991) 1338.
- [17] J. Woodthorpe, M. J. Edirisinghe and J. R. G. Evans, Polymer Removal **24** (1989) 1038.
- [18] J. Wang, S. H. P. Li and R. Stevens, J. Mater. Sci. **27** (1992) 63.