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ORIGINAL ARTICLE

Modification of commercial boron carbide powder using Rapid Carbothermal Reduction

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Abstract

Non-uniform morphology and existence of free carbon are two main problems for commercial boron carbide powders. This work proposes a method for eliminating free carbon and changing the morphology of commercial powders using Rapid Carbothermal Reduction (RCR) process. Free carbon is eliminated from commercial boron carbide powders and morphology is evolved to less angular shapes with limited particle size growth. Commercial and modified powders were densified by Spark Plasma Sintering at 1900°C with 0, 5, and 20 minutes dwell. Despite the particle size growth, modified boron carbide powders reached >99% TD with shorter dwell times compared with commercial starting powders. Improved microhardness observed with dense modified samples as a result of enhanced morphology and increased twinning.

1 | INTRODUCTION

Boron carbide is the third hardest engineering material and has noticeably higher strength-density ratio than most materials. Extra high hardness values and low density make boron carbide very desirable for extreme environments. Knoop hardness of boron carbide is reported to be 28.5-30.5 GPa with a 100 g indentation load (HK_{100}).[1–3] There is a direct relationship among powder quality and mechanical properties of dense materials. Powder attributes, green body properties, and sintering methods are the major factors that affect the final microstructure. Mechanical properties are affected by grain size, porosity, homogeneity, inclusions, and secondary phases.[4–7]

Commercial boron carbide powders are produced by the carbothermal reduction method since it is relatively low cost and scalable process. Wide particle size distribution and uneven morphology is observed due to extensive milling processes and free carbon is commonly found in the final product even after the purification processes.[8–11] Rapid Carbothermal Reduction (RCR) is a method which yield submicrometer boron carbide particles with narrow particle distribution. RCR process depends on feeding boron oxide-carbon precursor to the system at high temperature to decrease boron loss and prevent existence of free carbon.[12,13]

Sintering of boron carbide is another challenge due to high melting temperature and low plasticity. Hot pressing is widely used to sinter boron carbide without additives, but temperatures higher than 2100°C and long dwell times are often necessary.[14–17] Spark Plasma Sintering (SPS) is an alternative method which successfully produce highly dense boron carbide articles. Neck formation and diffusion starts at early stage of heating cycle and densification is completed at lower temperatures. Reported sintering temperatures for fully dense samples are as low as 1700°C with limited grain growth. Because of differences in sample size and temperature measurement techniques comparing SPS experiments are challenging given the uncertainty in the true temperature of the sample.[18–21]

In this work, commercial boron carbide powders with high purity are used for modification. SPS is well established and successful sintering method for boron carbide and samples with enhanced mechanical properties have been reported. The aim of this study was to enhance sintering behavior and final properties of boron carbide by changing the powder morphology and eliminating the free carbon. Modified boron carbide powders exhibit enhanced

sintering behavior and hardness results of sintered articles are higher than counterparts.

2 | EXPERIMENTAL PROCEDURE

Two commercial boron carbide powders from various suppliers (UK Abrasives, Northbrook, IL; H.C. Starck, Munich, Germany) were used for this study. Boron carbide powder was dispersed in methanol with constant stirring and heating and boric acid (US Borax, Chicago, IL) was added into dispersion. Mixture heated to evaporate excess liquid to form boron carbide-boric acid paste which is placed into the drying oven for at least 12 hours at 120°C. Dried product was placed into an electric tube furnace and calcined at 600°C under constant argon flow. Calcined chunks were placed into a mortar and crushed and only particles between 125 and 425 μm were used for RCR feeding. Precursor was put into sealed hopper and kept at room temperature until furnace was heated to 1825°C and stabilized. B_4C–B_2O_3 mixture was fed into the reactor at this temperature with 6 g/min feeding rate. Reacted powder accumulated in the crucible and the produced gas byproducts left the system through the exhaust line (Figure 1).

Carbon analyses (LECO CS-230, St. Joseph, MI), oxygen analyses (LECO TC-600), boron titration (ASTM C-791, West Conshohocken, PA) analyses were completed for every boron carbide powder. FESEM (Zeiss-Sigma, Oberkochen, Germany) and X-ray diffractometry (PANanalytical X'Pert, Amelo, Netherlands) were used to characterize these powders and the results were compared with two commercial powders (H.C. Starck, Grade HD20 and UK Abrasives F1500). *B*/*C* ratios and existence of free carbon were estimated from x-ray diffractometer (XRD) patterns (a and c lattice parameters) and carbon/oxygen analyses.[22,23]

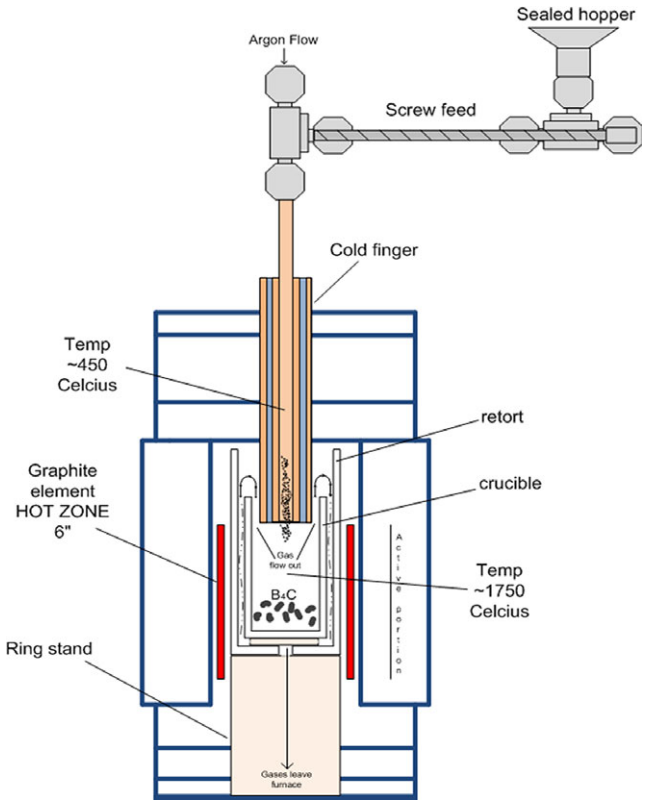

FIGURE 1 Schematic of Rapid Carbothermal Reduction process [Color figure can be viewed at wileyonlinelibrary.com]

To achieve dense boron carbide samples, powders were densified with SPS furnace (Thermal Technology 10 Series, Santa Rosa, CA) under argon atmosphere with 50 MPa applied pressure and a heating ramp rate of 300°C/min. To produce similar size samples, approximately 4 g of powders were placed into 20 mm diameter graphite die. Temperature measurements were taken from a hole on

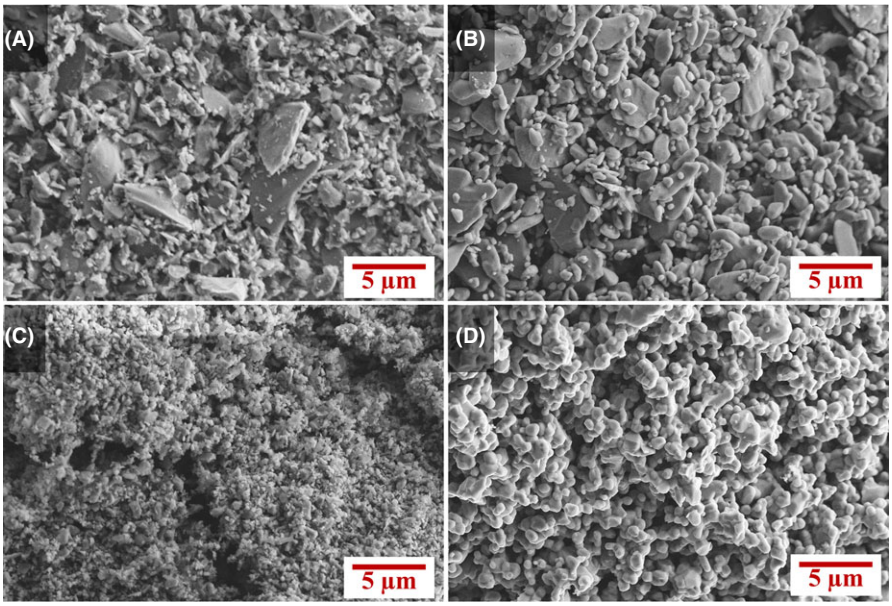

FIGURE 2 SEM images of UK powder (A) before, (B) after RCR processing at 1825°C. (C) Starck powder before (D) after RCR processing at 1825°C [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Characterization of boron carbide powders before and after Rapid Carbothermal Reduction processing

Name	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)	Free C (%)	C (%wt)	O (%wt)	*B/C*
UK powder	0.30	1.27	2.60	2.50	20.98	3.61	4.41
UK modified	0.90	2.05	3.05	0.00	20.88	0.47	4.20
Starck powder	0.10	0.50	0.85	1.50	22.16	1.58	4.04
Starck modified	0.61	0.93	1.45	0.00	20.88	0.27	4.40

B/C ratio is added.

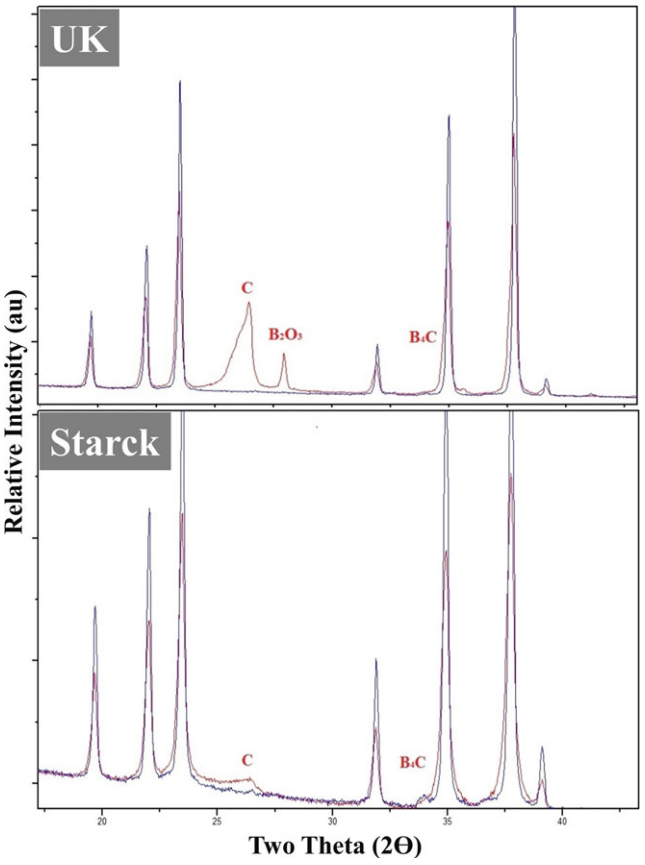

FIGURE 3 XRD pattern of commercial and modified UK (top) and Starck (bottom) powders. Elimination of free carbon is evident after modification process. Typical carbon peak is between 2θ values of 24.5° and 26 [Color figure can be viewed at wileyonlinelibrary.com]

the side of the die using high temperature pyrometer. Sintering temperature was 1900°C with 5, 10, and 20 minutes dwell.

Densities of sintered samples were determined using Archimedes immersion testing. Samples were cut along cross sections and polished to an optical finish. Knoop microhardness was taken at 100, 300, 500, and 1000 g loads with 10 measurements for each load (Leco M400 Microhardness Tester). Samples were etched by electrolytic method using 0.1% KOH solution and 5V applied for approximately one minute. Grain size measurements were taken from linear intercept analyses from the FESEM images using computer software Lince (by Technische Universität Darmstadt, Darmstadt, Germany).

3 | RESULTS AND DISCUSSIONS

3.1 | Powder synthesis and characterization

Scanning electron microscopy (SEM) analysis of starting and modified powders are shown in Figure 2. Commercial powders are characterized by fracture surfaces as a result of extensive milling. RCR processing changed the morphology of the powder and eliminated all the small particles. Thus, particle size distribution of processed powders is narrower compared to commercial powders. Table 1 shows the analysis results of powders used and produced in this study. Particle size analysis results show that d_{10} values are significantly increased due to elimination of small particles. On the other hand increase in d_{90} values is not significant. This particle size growth was expected due to residence time at high temperature. XRD analysis of the samples also revealed free carbon peak is eliminated from all commercial powders as a result of RCR process (Figure 3). XRD peaks also did not show significant change in the peak positions which indicates small or none stoichiometry change in the boron carbide powders. Small particles present in UK powder were eliminated after feeding through RCR furnace. Thermodynamically, small particles are more reactive so change in d_{10} and d_{50} was more significant compared with d_{90}; Figure 2 illustrates the change in morphology and particle size before and after the RCR process. Morphology of the powder also evolved to be less angular which was observed qualitatively from SEM images. This physical change was more apparent with smaller particle. Free carbon prior to this treatment was 2.50 wt% and after treatment there was no evidence of free carbon. The assumption is that all of the free carbon reacted with added boron and converted to boron carbide. Stoichiometry of the powders were slightly changed after the modification process but remained in the carbon rich side according to literature.[24,25] Starck powder was affected more in terms of particle size change since it had the smallest starting average particle size. Particle size (d_{90}) increased to 1.45 μm which was corresponding to 70% increase as compared to starting powder. Neck formation was observed throughout the powder as reflected in SEM images. Free carbon was reduced below detection limit which was 1.00 wt% before the process.

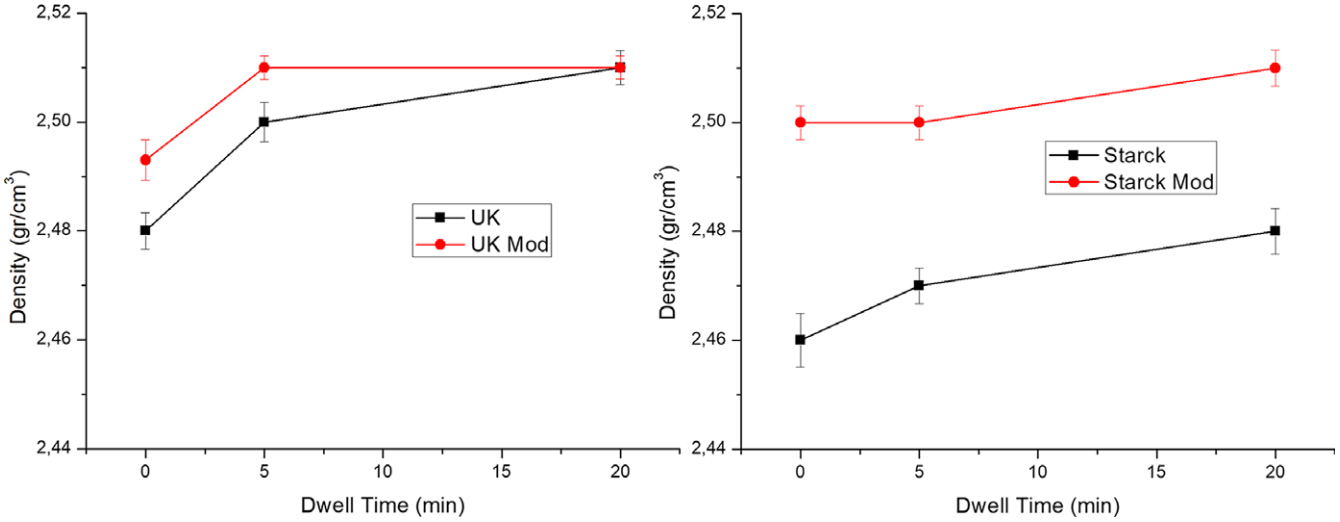

FIGURE 4 Densities of commercial and modified boron carbide samples with various dwell times at 1900°C under 50 MPa load [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Grain size measurements of boron carbide samples (all results are μm)

Name	1900°C	1900°C, 5 min	1900°C, 20 min
UK	2.64	3.03	3.79
UK modified	3.06	3.40	3.78
Starck	1.25	1.43	2.19
Starck modified	1.37	1.81	2.39

Processed powders reached to full densities earlier than commercial powders despite the increased particle size. This proves that morphology of the powder is critical to reach full densities and less angular morphology promotes the densification. Figure 4 compares density profiles of the modified samples with original commercial samples. Densities of modified samples were slightly higher than that of commercial samples. Modified and starting Starck samples had the higher density differences since amorphous carbon was removed completely.

Grain size measurements were carried out and these analyses also did not show any grain size coarsening. Initially, modified boron carbide samples resulted in larger grain sizes as a result of the larger average particles size for the modified boron carbide powders. Grain size changes of modified boron carbide samples were compared to corresponding commercial samples and are given in Table 2. Modified samples had larger grain sizes until 20 minutes dwell and grain sizes are the same at 20 minutes dwell time. Commercial samples yielded

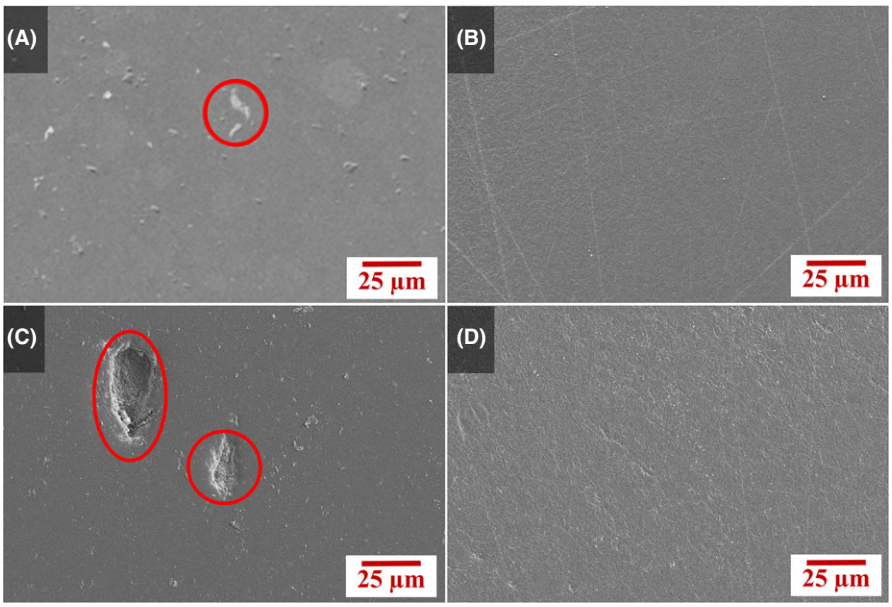

FIGURE 5 SEM images of sintered boron carbide samples with 20 min dwell at 1900°C (A) commercial UK, (B) modified UK, (C) commercial Starck and (D) modified Starck. Carbon inclusions are completely removed with RCR processing [Color figure can be viewed at wileyonlinelibrary.com]

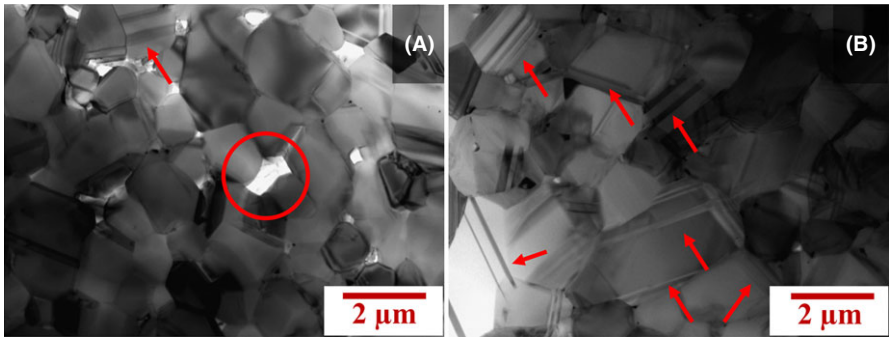

FIGURE 6 A, TEM images of Starck 20 min sample with limited twinning (arrows), intragranular pores (circle) and some large grains. B, TEM images of Starck Modified 20 min sample with high twin density (arrows) and some larger grains [Color figure can be viewed at wile yonlinelibrary.com]

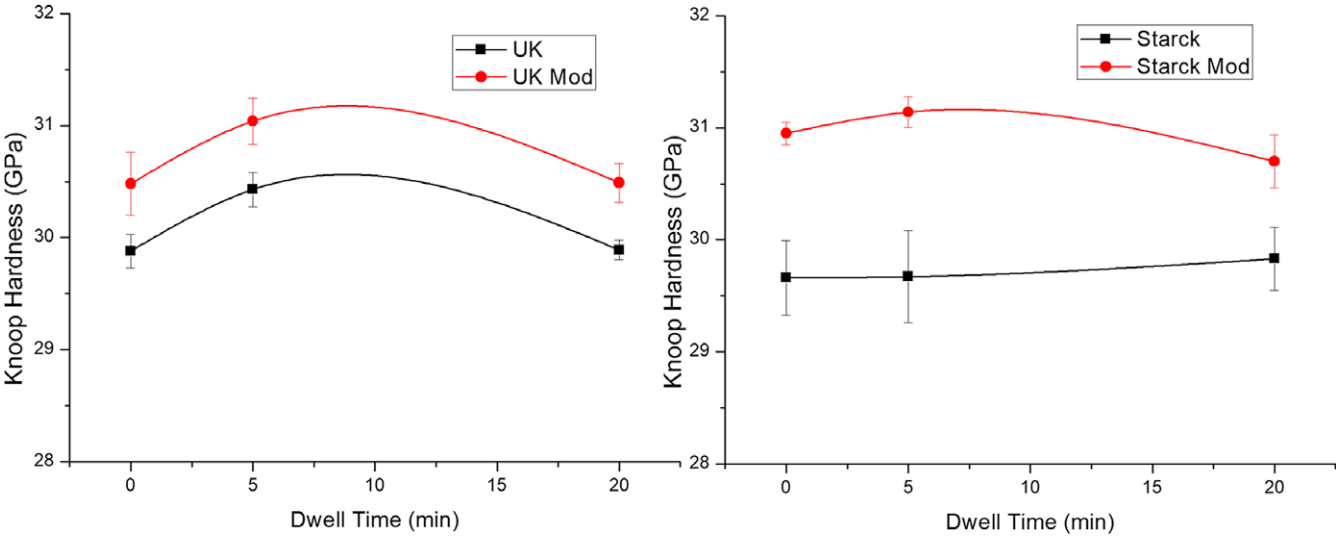

FIGURE 7 HK_{100} values of modified boron carbide samples comparing the commercial samples with 0, 5, and 20 min dwell at 1900°C [Color figure can be viewed at wileyonlinelibrary.com]

some carbon inclusion after the sintering which were removed with modification and density was enhanced (Figure 5).

Transmission electron microscopy (TEM) analysis is completed for sintered commercial and modified Starck samples. Modified sample had higher twin concentration comparing to commercial sample. Twins were placed on the grain edges, as seen in Figure 6, which indicated modification generated twins around the particles. This is an agreement from previous work which showed RCR synthesized powders has higher twin density and existed twins increased the hardness of boron carbide.[26–28] Modification of commercial boron carbide improved hardness results by removing free carbon, changing the morphology and introducing more twin structures to dense samples, despite increased particle size. Effect of the stoichiometry change is limited, since samples remained in the carbon-rich side after the RCR process. Starck samples had the most significant change with modification and its hardness. Figure 7 shows hardness results of modified boron carbide samples with five minutes dwell which were the peak hardness results.

4 | CONCLUSIONS

Free carbon was reduced to trace amounts with limited increase in particle size. Particle size distribution was narrower compared to original starting powders. Morphology was changed and particles were less angular. Particle size increase is inevitable due to residence time at high temperature. Modified powders reached high densities faster than original starting counterparts and resulted higher hardness values, despite the increased particle size. This shows the morphology of the powder is critical for the sintering processes and round-shaped particles have better sinterabilty. Higher hardness results are reached due to introduced twins and decreased free carbon content of the powder.

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