Homogeneity enhancement of oxide additives in boron carbide by precipitation method

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Abstract

This study aims the use of the precipitation method to enhance the uniformity of oxide additives in boron carbide ceramics. Achieving a homogeneous distribution of additives is critical, as higher additive content tends to degrade the mechanical properties of boron carbide. In this research, yttrium and aluminium hydroxide salts were dispersed and incorporated into boron carbide slurry under highly alkaline conditions. The mixture was aged and subsequently calcined to produce metal oxide layers around the boron carbide particles. The additive-to-boron carbide ratio and calcination conditions were systematically varied and the resulting powders were characterized using SEM, EDX and zeta potential analyses. The precipitation method effectively improved additive dispersion, achieving a uniform distribution. Furthermore, samples processed through precipitation exhibited higher densities compared to conventional benchmark samples.

Keywords*: powders, carbides, precipitation, synthesis*

I. Introduction

Boron carbide (B_4C) is recognized as the third hardest material known, following diamond and cubic boron nitride. Its strength-to-density ratio is notably higher than most materials, making boron carbide highly desirable for extreme environments due to its low density and exceptional hardness [1,2]. However, sintering boron carbide is challenging because of its high melting point, strong covalent bonding and the presence of a thin oxide film around the powder particles. These challenges limit its applications. In order to overcome these limitations, research efforts has focused on reducing the sintering temperature and improving fracture toughness by introducing secondary phases and additives such as carbon, metal oxides and pure metals [3–5].

Sintering aids like carbon, elemental boron, oxide ceramics and metallic additives are commonly used to lower the sintering temperature of boron carbide, though they often compromise its mechanical properties. Carbon is the primary secondary phase in dense boron carbide [6–8]. While metallic oxide additives can reduce the sintering temperature, they often result in the formation of brittle secondary phases such as aluminium borides and carbides, which degrade the mechanical properties of boron carbide. Alumina-rare earth additive combination was often used for sintering silicon carbide (SiC) samples, since they can lower the sintering temperature through liquid phase sintering and improve mechanical properties due to higher final densities [9–12].

Appropriate selection of additive is important, but it is also crucial to limit their amount and ensure their homogeneous distribution to maximize mechanical properties. Several methods, including high-energy milling, liquid processing and spray drying, have been explored to enhance additive dispersion [13–19]. The precipitation method has shown promise in ceramic powder processing, enhancing homogeneity. Various factors, such as pH, calcination time and temperature, affect the precipitation process. Studies on synthesizing yttrium aluminium garnet (YAG) powders using precipitation methods have demonstrated that nanosized powders with improved homogeneity can be produced [20–25].

This study aims to improve additive homogeneity using the precipitation method and reduce the sintering temperature by leveraging the Y_2O_3-Al_2O_3 eutectic point. The method has been successfully employed, resulting in improved homogeneity compared to ball-milled samples.

II. Experimental

Submicron boron carbide powder (H.C. Starck GmbH, 3000F) was used in this study. The

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precipitation method was employed to achieve homogeneous dispersion of additives around boron carbide particles. Aluminium nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, Carlo Erba, RE3120) and yttrium nitrate hexahydrate ($Y(NO_3)_3 \cdot 6H_2O$, ABCR, AB122290) were dissolved in ethanol (Tekkim, TK120320) and stirred until a stable solution was reached, as shown in Fig. 1. The solutions were also sonicated in a bath for 15 min to improve homogeneity. The required amounts of salts were calculated to be 5–10% and yttria-alumina ratio of 40–60% was used since it corresponds to one of the eutectic points of the system. Two set of samples were prepared: i) samples with 5% additives (named 3A-2Y), representing 3% yttria and 2% alumina and ii) samples with 10% additives (named 6A-4Y), representing 6% yttria and 4% alumina [26]. In a separate container, the precursor boron carbide powder was dispersed in deionized water and the pH was increased to 9.5 using ammonia (25% RPE, Carlo Erba 419993), determined by preliminary studies. The aluminium and yttrium salt solution was fed into the boron carbide dispersion at a constant pH monitored by a pH meter (Hanna Instruments). This process led to the co-precipitation of yttrium and aluminium additives with boron carbide powders. The dispersion was aged and then dried overnight at 90 °C. The dried powders were calcined in a tube furnace (Protherm) under oxidizing and inert atmospheres at 500 °C for 1 h. Reference samples were prepared using traditional ball milling (24 h at 100 rpm) of the boron carbide powder with aluminium oxide (ABCR, AB210700) and yttrium oxide (ABCR, AB111934) powders, for comparison. The obtained powders were compacted into 10 mm steel dies to produce green bodies, which were pressureless sintered under constant argon flow at 1750 and 1800 °C in a high temperature furnace (Carbolite, HTF1800).

Zeta potential measurements (Malvern Zetasizer) were conducted to determine the surface properties of the prepared particles. For each powder, 0.05 g was dispersed in 200 ml distilled water, with 0.1 M HCl or 0.1 M KOH added to adjust the pH. Isoelectric points were determined where zeta potential values equaled zero. X-ray diffraction analysis (XRD, Philips X'Pert) were conducted to observe phases. The powders and dense samples were examined using scanning electron microscopy (SEM, Zeiss Sigma) and energy dispersive spectroscopy (EDS) to observe particle size, surface characteristics and additive dispersion. The densities of the sintered samples were determined using the Archimedes immersion testing and estimated from SEM images.

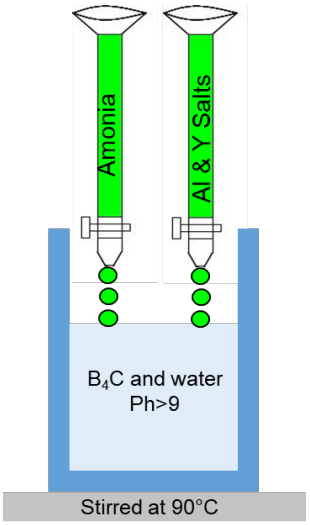

Figure 1. Illustration of precipitation setup

III. Results and discussion

Figure 2 shows the X-ray diffraction (XRD) pattern and SEM image of the as-received boron carbide powder used in this study. The average particle size, determined from SEM images, was 1.5 µm. Small amounts of free carbon and oxidized B_2O_3 form were detected in the powder, and these types of impurities were expected in boron carbide samples as reported in the literature.

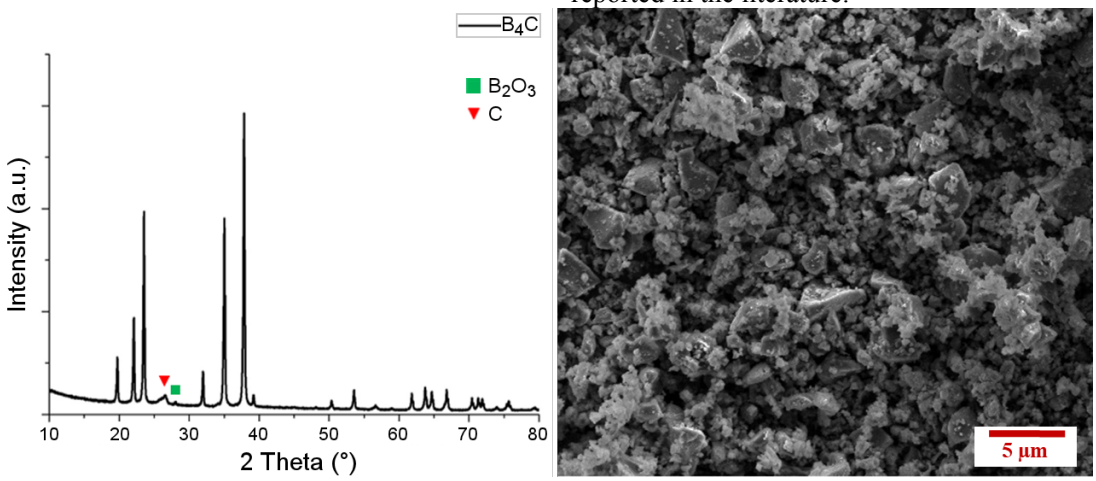

Figure 2. XRD pattern and SEM image of the as-received B_4C powder

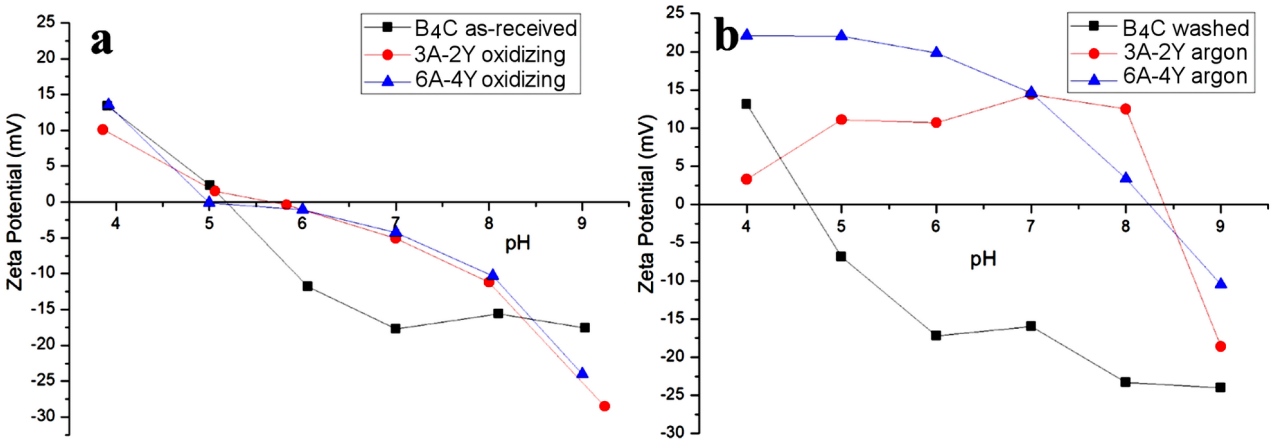

Figure 3. Zeta potatial measurement of B_4C powders and precipitated samples under: a) ambient and b) argon atmosphere

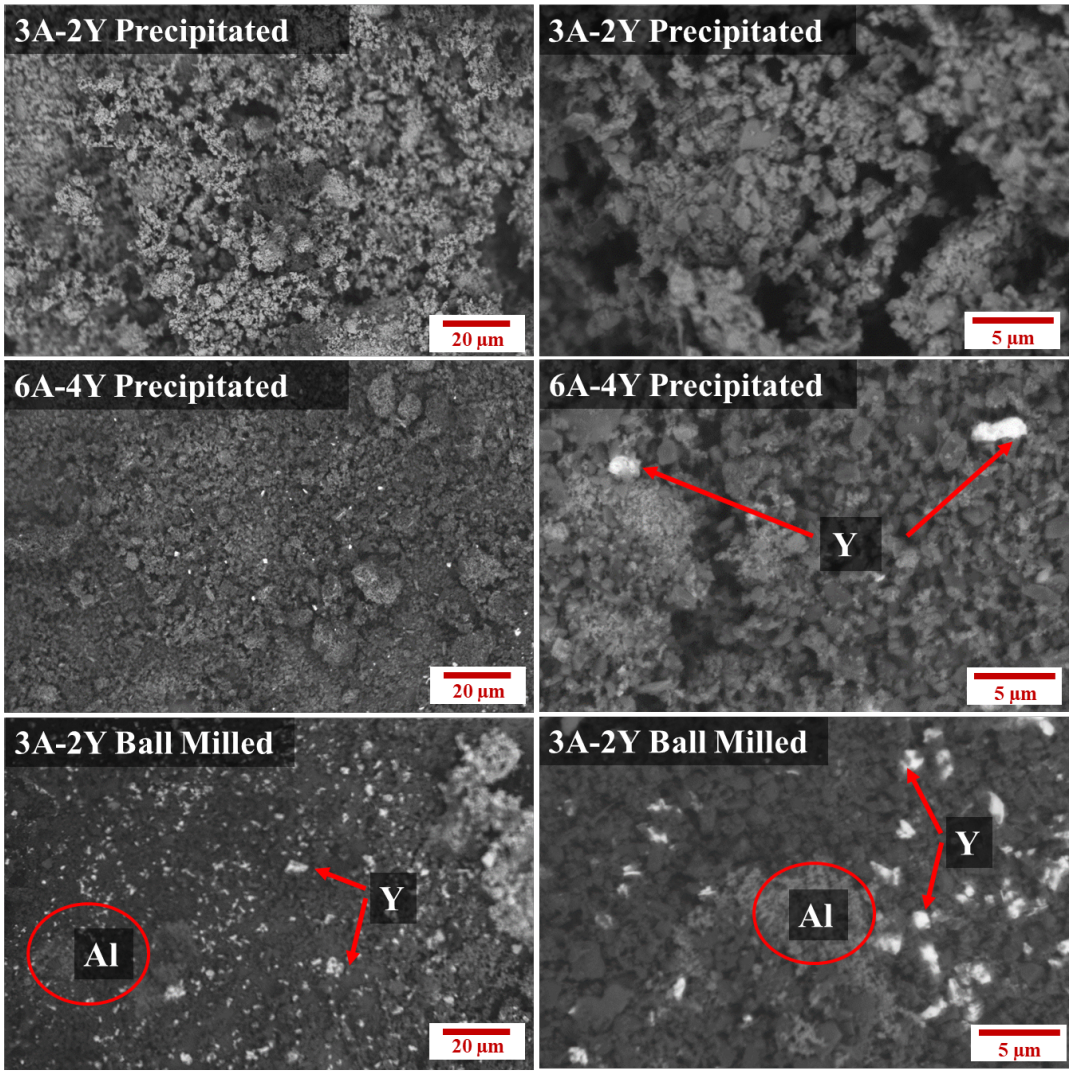

Figure 4. SEM images of precipitated and ball milled powders

The zeta potential measurements, presented in Fig. 3a, indicate that there is no significant difference between the as-received and precipitated boron carbide powders. Both the as-received boron carbide and the precipitated powders (calcined in an oxidizing atmosphere) exhibited similar isoelectric points,

comparable to the isoelectric point of boron oxide [27]. This suggests that surface oxidation of boron carbide particles occurred during calcination under ambient atmosphere, preventing changes in surface characteristics. After washing with methanol, the isoelectric point of the as-received boron carbide shifted to lower pH values (Fig. 3b), which is characteristic of carbide powders [28,29]. In contrast, the isoelectric points of the precipitated samples, calcined under an argon atmosphere, shifted to higher pH levels compared to the previous samples calcined under an oxidizing environment. This suggests that oxidation (and formation of B_2O_3 surface layer) was prevented by utilizing argon, and the isoelectric points shifted to higher pH levels typical of metal oxide powders [30,31]. This shows that surface modification was successfully achieved through precipitation and calcination under argon atmosphere.

Figure 4 shows SEM images of the precipitated powders (calcined under argon) and ball-milled powders. The ball-milled powder exhibited agglomerations and heterogeneous additive dispersion, while the 3A-2Y sample showed homogeneous powder morphology with no agglomerations. Although some agglomerations containing yttrium were observed in the 6A-4Y sample, it exhibited lower inhomogeneity compared to the ball-milled samples.

Density result of the samples sintered at 1750 and 1800 °C is given in the Table 1. The ball milled samples with additives yielded higher densities compared to the pure boron carbide samples. However, the precipitated samples yielded even higher densities compared to the ball milled counterparts. Thus, the precipitated samples yielded almost 10% higher densities compared to the pure boron carbide sample and 5–6% higher densities compared to the ball milled samples. There was no significant difference between the 3A-2Y and 6A-4Y samples.

SEM images of the sintered pure boron carbide and 3A-2Y samples at 1750 °C for 1 h are shown in Fig. 5. The pure boron carbide exhibited lower densification with slight necking and no pore closure, indicating that it was in the intermediate stage of sintering. In contrast, the precipitated sample showed powder coalescence and some pore closure, indicating that it was in the final stage of sintering and achieved higher densities.

Table 1. Sintering studies and density results; (P) – precipitated, (BM) - ball milled

Sample	Density	Sintering conditions
Pure boron carbide	75%	1750°C, 1 h
3% Al_2O_3-2% Y_2O_3 (P)	86%	
6% Al_2O_3-4% Y_2O_3 (P)	86%	
3% Al_2O_3-2% Y_2O_3 (BM)	81%	
6% Al_2O_3-4% Y_2O_3 (BM)	80%	
Pure boron carbide	78%	1800°C, 1 h
3% Al_2O_3-2% Y_2O_3 (P)	88%	
6% Al_2O_3-4% Y_2O_3 (P)	89%	
3% Al_2O_3-2% Y_2O_3 (BM)	83%	
6% Al_2O_3-4% Y_2O_3 (BM)	83%	

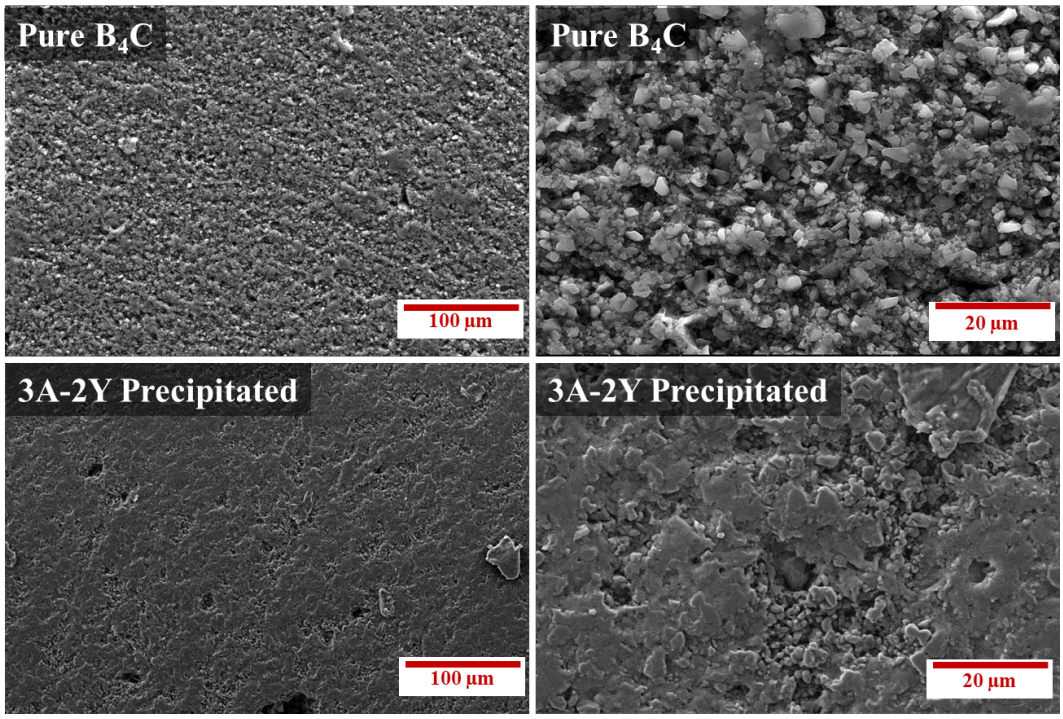

Figure 5. SEM images of pure and precipitated (3A-2Y) B_4C at 1750°C for 1 h

Analysis of the samples sintered at 1800 °C (Fig. 6) showed slight density improvements compared to those sintered at 1750 °C. The pure boron carbide remained in the intermediate stage of sintering, with no significant pore closure and limited necking. The ball-milled samples were in the final stage of sintering, similar to the precipitated samples. Powder coalescence and pore closure were observed in the ball-milled samples, however, densities were lower due to inhomogeneous distribution. Al- and Y-rich agglomerations were present in the microstructure of the ball-milled samples, as shown in Fig. 6. The precipitated samples achieved nearly 90% density at relatively low temperatures compared to the literature. Although these density results were insufficient for meaningful hardness testing, they showed promising improvement relative to both the literature and the counterpart samples.

Since agglomerations and secondary phases were not observed in all precipitated samples, area analysis and EDS map and area scans was conducted on 3A-2Y sample. Figure 7 showed homogeneous distribution of Al, Y and O throughout the scanned area.

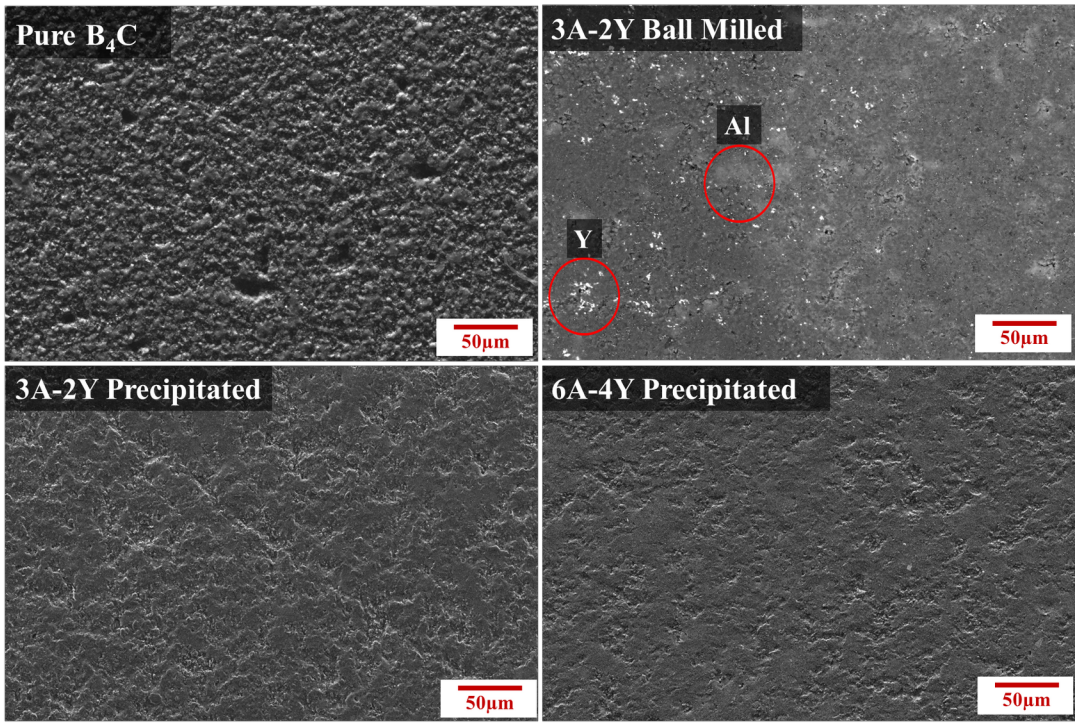

Figure 6. SEM images of pure, ball milled and precipitated B_4C at 1800°C for 1 h

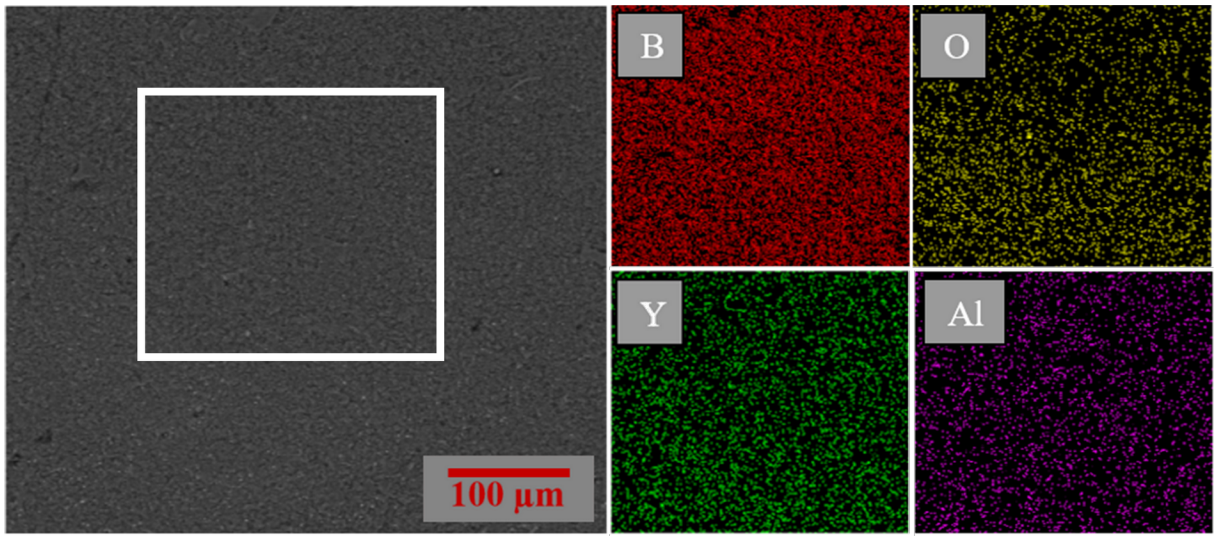

Figure 7. Elemental mapping of 3A-2Y precipitated sample sintered at 1800 °C

IV. Conclusions

The study demonstrates that the precipitation method significantly improves the homogeneity of oxide additives in boron carbide powders compared to traditional ball milling. This improved homogeneity, confirmed by SEM and EDS analysis, results in higher densities of the sintered samples, i.e. the pure boron carbide samples showed nearly 10% low densification than the precipitated samples. The study concludes that using the precipitation method for oxide additive dispersion in boron carbide is effective and recommends further research on mechanical properties and different oxide combinations to optimize sintering behaviour and performance.

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