



## Short Communication

Low temperature densification of B<sub>4</sub>C ceramics with CaF<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub> additivesChangming Xu<sup>a,b,\*</sup>, Katarina Flodström<sup>b</sup>, Saeid Esmailzadeh<sup>b</sup><sup>a</sup> State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 200050, Shanghai, P.R. China<sup>b</sup> Department of Materials and Environmental Chemistry, Arrhenius Laboratory, Stockholm University, SE-10691 Stockholm, Sweden

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## ABSTRACT

This study deals with low temperature densification of boron carbide (B<sub>4</sub>C) ceramics with combined employment of CaF<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub> sintering additive and Spark Plasma Sintering (SPS) technique. It demonstrates that a small amount addition of CaF<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub> has strong effect on the densification of B<sub>4</sub>C ceramics. With 0.5–1 wt.% CaF<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub> addition, nearly full-densification up to 99.1% of B<sub>4</sub>C ceramics can be attained at a temperature as low as 1700–1750 °C.

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## 1. Introduction

Boron carbide (B<sub>4</sub>C) has a low density, high melting point, high neutron absorption cross-section, and excellent chemical resistance at room temperature. It has been widely used for abrasive and wear resistant applications, e.g., as blast nozzles, wheel dressing tools, light weight armor plates, and nuclear reactor controlling rod application [1–3].

However, the sintering of pure B<sub>4</sub>C ceramic has been proven quite difficult, mainly due to its rigid covalent bonds of B–C, which are responsible for its intrinsically extremely low self-diffusion coefficient and high vapor pressure [4]. Pure B<sub>4</sub>C without sintering aid addition normally reveals highly porous interconnected structure with rapidly grown grains at over 2000 °C [5]. This intrinsic characteristic makes B<sub>4</sub>C ceramic impossible to be fully densified without external pressure or sintering additive added.

Normally, pure B<sub>4</sub>C ceramic can be sintered to a densification level of 79–95% at 2050–2150 °C with pressure 5–40 MPa, up to the starting powder used and the sintering conditions applied [6–9]. With sintering additive used, the densification temperature can effectively be lowered down by activating ceramic particle surface through chemical reaction and/or by promoting mass transportation and particles rearrangement via liquid phase sintering, etc. It is reported that by adding solid-dissolved carbide additive (W,Ti)C with amount as high as 10–50 wt.% can lower down the sintering densification temperature of B<sub>4</sub>C ceramics to 1850 °C [9]. Fewer amounts, 10–25 wt.%, of TiC/Mo [10], CrB<sub>2</sub> [11], and Al<sub>2</sub>O<sub>3</sub>/TiC [12],

similar densification can be achieved as well; however, a higher temperature of 1950 °C is in return required.

Spark plasma sintering (SPS) is a sort of relatively novel sintering technique that has been proven to be a powerful and effective tool to lower down the sintering temperature of a wide range of materials meanwhile with fairly limited grain growth within minutes time [4,5]. With SPS technique, pure B<sub>4</sub>C ceramics with a relative density of 95% can be reached at 1850–2050 °C with 32–40 MPa pressure [13,14]. Ghosh et al. consolidated submicrometer-sized commercial B<sub>4</sub>C powder to near theoretical densities at 1750 °C with 88 MPa pressure; however, rather limited sintering study is available from the literature [15].

In the present study, the effect of using binary additive of CaF<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub> on the densification of B<sub>4</sub>C ceramics together with the employment of SPS sintering technique is studied.

## 2. Experimental

Boron carbide powder (grade HS, H. C. Starck, Berlin, Germany) was used in the present study as received. According to the supplier's data, the powders have an average particle size of 1 μm. The additives used in this work were CaF<sub>2</sub> (ABCR, Germany) and Y<sub>2</sub>O<sub>3</sub> (grade C, H. C. Starck, Berlin). These materials were added to B<sub>4</sub>C to give a combined weight percentages of 5, 3 and 1 and also 0.5 wt.% CaF<sub>2</sub> was added for comparison. By using de-ioned water as medium, the powders were blended together in a planetary ball mill (Retsch, PM 100, Germany) and ball milled at a rotary speed of 300 rpm for 1 h. The slurry was dried at ~95 °C in air for 24 h to evaporate all the water. The mixture powders were then sieved through ~200 grit sieve.

All the powders, each of mass about 1.2 g, were filled into a graphite die with an inner diameter of 12 mm. The starting pressure loaded on the powders was 50 MPa and manually kept constant at ~58 MPa

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before sintering starts at approximately 1550 °C. Consequently, the pressure goes down naturally as sintering proceedings not only to allow the releasing of gaseous products during sintering but also to avoid the breaking of the die under fast heating (200 °C/min) condition, and then increased to 50 MPa in 1 min when the temperature reaches the designated soaking temperature (1700, 1750 and 1800 °C, respectively). The soaking time was 5 min in all cases. The density of the sintered bodies was measured by the Archimedes principle. The microstructure of the fracture surface was investigated by using scanning electron microscopy (SEM, JSM-7000F, JEOL, Tokyo, Japan). The phase composition was determined by powder x-ray diffraction (XRD, PIXcel, X'Pert PRO, PANalytical, Tokyo, Japan).

### 3. Results and discussions

#### 3.1. Sintering behavior

Fig. 1 shows typical loading pressure and temperature profiles for B<sub>4</sub>C ceramics added with different amount of CaF<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub> (0, 1, and 5 wt.%, respectively) sintered at 1800 °C under pressure of approximately 5.6 kN (corresponding to 50 MPa). For the B<sub>4</sub>C samples with CaF<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub> added, a slight ramp in the temperature range of 1150–1450 °C can be found, which can be attributed to the formation of transient liquid phase [16]. This liquid formation could be assigned either to the melting of CaF<sub>2</sub> (with melting point of ~1420 °C) or to the formation of eutectic mixture of Y<sub>2</sub>O<sub>3</sub> and CaF<sub>2</sub>. The loading pressure starts to drop off naturally at ~1550 °C in all cases, indicating the occurrence of sintering. With the loading pressure increased to 50 MPa (approximately same rate in all cases), the B<sub>4</sub>C samples with addition of CaF<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub> reveal rapid densification in contrast to pure B<sub>4</sub>C sample. The rapid densification process can be completed even within the first 2 min when soaking at 1800 °C.

Fig. 2 shows the influence of both additive amount sintered at different temperatures and consolidating pressure at 1700 °C on the densification of B<sub>4</sub>C ceramics. Fig. 2(a) shows that a small amount of 0.5–1 wt.% CaF<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub> can remarkably improve the relative density to 99.4% at 1750–1800 °C, whereas decreased with the increasing additive amount. This result is in accordant with the sintering behavior as indicated in Fig. 1. When the temperature is as low as 1700 °C, the maximum relative density is merely as high as 91.2%.

Fig. 2(b) shows that, by loading 70 MPa pressure at 1700 °C, a near-fully densification of 98.5% can be achieved for the B<sub>4</sub>C sample added with 1 wt.% CaF<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub>. A slightly lower introduction, 0.5 wt.%, of CaF<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub> into B<sub>4</sub>C ceramic requires a higher pressure of 80–90 MPa to reach maximum densification (around 98.7%). However, an over-high pressure results in a remarkable declining tendency of densification when the pressure regardless the CaF<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub> amount added.

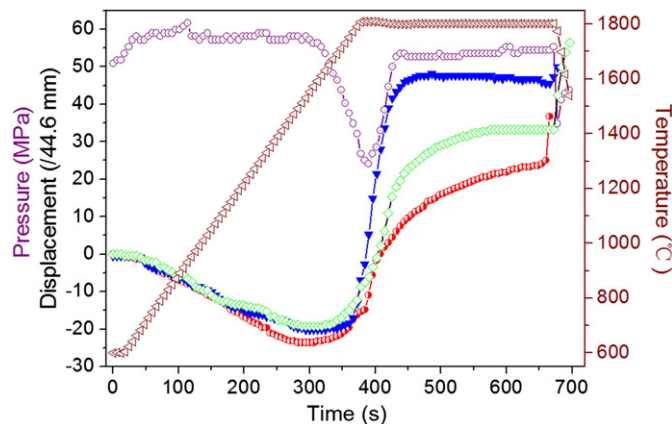


Fig. 1. Sintering profiles for B<sub>4</sub>C ceramics with various CaF<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub> additions.

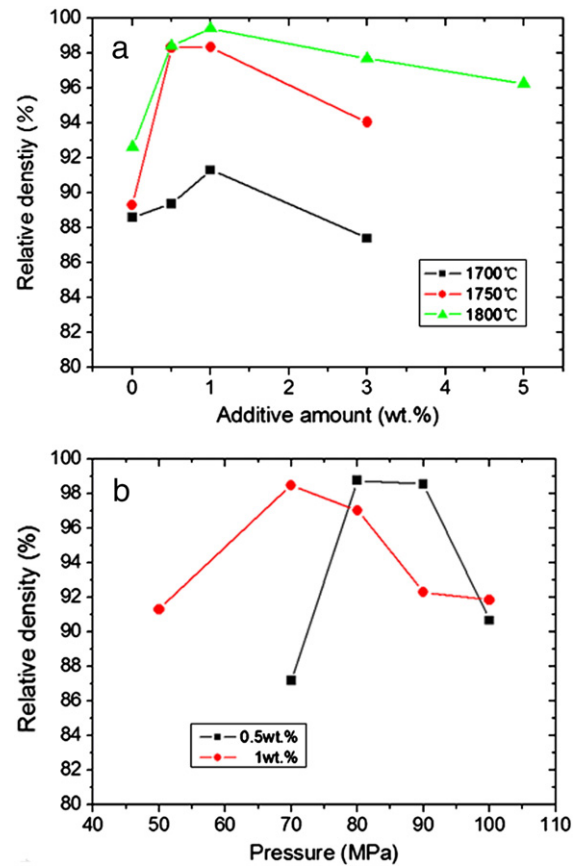


Fig. 2. Relative density as a function of (a) CaF<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub> additive amount sintered at various temperatures with pressure of 50 MPa, and (b) the loading pressure for B<sub>4</sub>C ceramic sintered at 1700 °C with CaF<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub> addition of 0.5 wt.% and 1 wt.%, respectively.

#### 3.2. Phase composition

Fig. 3 shows the phase composition of the B<sub>4</sub>C sample with 5 wt.% addition of CaF<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub> addition before and after sintering at 1800 °C. YBO<sub>3</sub>, CaC<sub>2</sub>, and yttriofluorite ((CaF<sub>2</sub>)<sub>0.85</sub>(YF<sub>3</sub>)<sub>0.15</sub>) are identified as the main newly formed phases in B<sub>4</sub>C ceramics after sintering. Actually, a white gray mass layer can also be found on the graphite die and graphite spacers in the SPS chamber after the sintering process, indicating gas releasing and subsequently depositing that occurred during the sintering process. This gaseous product could be determined as YF<sub>3</sub> and/or BF<sub>3</sub>, originating either from the reaction between B<sub>4</sub>C and Y<sub>2</sub>O<sub>3</sub> or from the reaction between B<sub>4</sub>C and CaF<sub>2</sub>. Obviously,

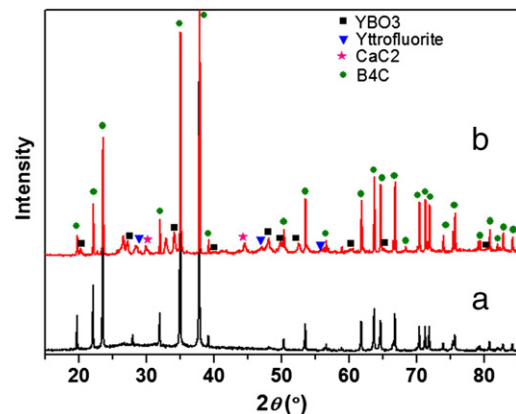


Fig. 3. XRD patterns for B<sub>4</sub>C ceramics: (a) without and (b) with 5 wt.% CaF<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub> addition sintered at 1800 °C with 50 MPa pressure, respectively.

increasing  $\text{CaF}_2/\text{Y}_2\text{O}_3$  additive amount could result in an increased gas releasing level as more reactants were included.

During sintering process, decreasing pressure loaded on  $\text{B}_4\text{C}$  samples allows the releasing of gas(es) generated during sintering, which normally favors the driving-off of the pores from inside and thereby promoting the densification of  $\text{B}_4\text{C}$  ceramics. When sintered at  $1700^\circ\text{C}$ , an appropriate pressure of 70–90 MPa helps to attain maximum relative density. However, the in situ formed gas could be entrapped in the  $\text{B}_4\text{C}$  sample with closed surface cladding with an over-high pressure applied. Similar behavior regarding the influence of mechanical pressure on the densification of  $\text{B}_4\text{C}$  ceramics during the SPS sintering process has also been reported [17].

### 3.3. Microstructure

Fig. 4 shows typical fracture surface observation on the  $\text{B}_4\text{C}$  samples added with various amounts of  $\text{CaF}_2/\text{Y}_2\text{O}_3$  sintered at  $1800^\circ\text{C}$  with a pressure of 50 MPa. In good agreement with the relative density results as shown in Fig. 2, pure  $\text{B}_4\text{C}$  sample without  $\text{CaF}_2/\text{Y}_2\text{O}_3$  addition showed undensified microstructure (Fig. 4a). When the additive amount was increased to 1 wt.% (Fig. 4b), it became fully dense and the additive distributed separately throughout  $\text{B}_4\text{C}$  matrix. However, an excellent wetting between the additive and  $\text{B}_4\text{C}$  grains can be deduced according to the close contact of the white phase ( $\text{CaF}_2/\text{Y}_2\text{O}_3$ ) and gray phase ( $\text{B}_4\text{C}$ ), as pointed out by the white arrows in Fig. 4b. Due to the transgranular fracture nature of  $\text{B}_4\text{C}$  ceramic, it is a little bit difficult to recognize separated  $\text{B}_4\text{C}$  grain from its adjacent ones.

Among most of metal ions, the radius of calcium and yttrium cations ( $\text{Ca}^{2+}$  and  $\text{Y}^{3+}$ ) is among the smallest class that is fairly close to that of B and/or C atoms. Although the diffusion ability of B and C in  $\text{B}_4\text{C}$  ceramic is rather low, the excellent wetting between  $\text{CaF}_2/\text{Y}_2\text{O}_3$  and  $\text{B}_4\text{C}$  allows excellent contact between  $\text{CaF}_2/\text{Y}_2\text{O}_3$  and  $\text{B}_4\text{C}$ , which enables much high possibility for the inter-substitution or inter-diffusion of  $\text{Ca}^{2+}/\text{Y}^{3+}$  ions with B/C atoms. The penetration of  $\text{Ca}^{2+}/\text{Y}^{3+}$  ions into  $\text{B}_4\text{C}$  lattice at atomic/ionic level would induce the local distortion of

$\text{B}_4\text{C}$  lattice and the consequent activation of outer fraction of  $\text{B}_4\text{C}$  grains. Subsequently, this process favors the outer transportation of B/C atoms and hence promoting the Ostwald ripening process and the sintering densification. As pointed out by the white arrows in Fig. 4d,  $\text{B}_4\text{C}$  grains show slightly rounder morphology with 3–5 wt.%  $\text{CaF}_2/\text{Y}_2\text{O}_3$  compared with those with less  $\text{CaF}_2/\text{Y}_2\text{O}_3$  addition. This agrees well with the deduced conclusion that liquid phase was deduced to form in a low temperature range in the samples added with  $\text{CaF}_2/\text{Y}_2\text{O}_3$ , as indicated in Fig. 1. The reaction between fluorine ion and/or oxygen ion ( $\text{F}^-/\text{O}^{2-}$ ) with  $\text{B}_4\text{C}$  and the consequent reaction heat in local area and vaporization of fluoride gas(es) could promote the proceeding of the process mentioned above.

In addition, as the radius of aluminum ion ( $\text{Al}^{3+}$ ) is comparable with or even smaller than  $\text{Y}^{3+}$  ion,  $\text{Y}_2\text{O}_3$  could be replaced by  $\text{Al}_2\text{O}_3$  and be expected to show similar or better effect in regard with the sintering densification. Actually, this has been confirmed by our unpublished.

With the additive amount increasing to 3–5 wt.%, morphology of relatively separated grains in the  $\text{B}_4\text{C}$  matrix was presented (Fig. 4c–d). During sintering, this close contact of  $\text{CaF}_2/\text{Y}_2\text{O}_3$  additive around  $\text{B}_4\text{C}$  particles could reduce the direct contact within  $\text{B}_4\text{C}$  particles and thereby restrain the mass transportation from a  $\text{B}_4\text{C}$  particle to its adjacent ones. As a result, the densification of  $\text{B}_4\text{C}$  ceramics could be restrained. What is more, the degassing induced by the reaction between  $\text{CaF}_2/\text{Y}_2\text{O}_3$  and  $\text{B}_4\text{C}$  or the vaporization of fluorides ( $\text{BF}_3$  or  $\text{YF}_3$ ) or  $\text{CaF}_2/\text{Y}_2\text{O}_3$  during sintering would leave pores inside  $\text{B}_4\text{C}$  samples, remaining close to the  $\text{CaF}_2/\text{Y}_2\text{O}_3$  additive, as pointed out by the white arrows in Fig. 4d. This process results in a declining of the densification. That could also be the reason why the sintering curve of the  $\text{B}_4\text{C}$  sample added with 5 wt.% plotted in Fig. 1 remains horizontally steady in the last 2 min at the soaking stage however with incomplete densification.

Fig. 5 represents the fracture surface of the  $\text{B}_4\text{C}$  ceramics added with 0.5 wt.% and 1 wt.%  $\text{CaF}_2/\text{Y}_2\text{O}_3$ , respectively and sintered at  $1700^\circ\text{C}$  with different pressures loaded. It can be seen that, regardless of the additive amount used,  $\text{B}_4\text{C}$  ceramic can anyhow be densified by employing

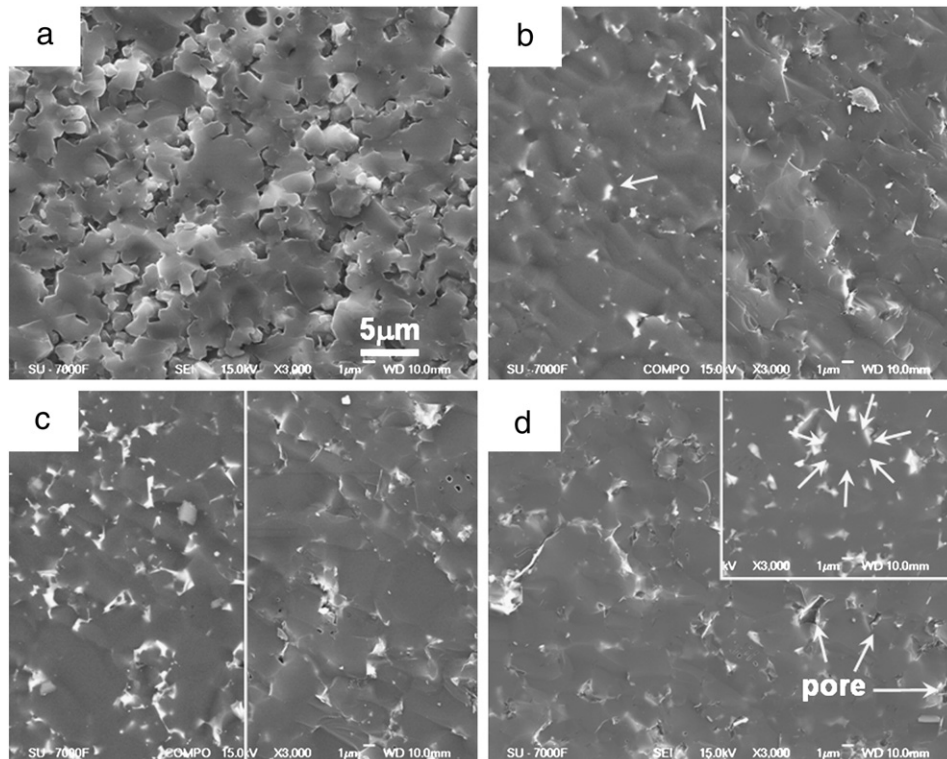
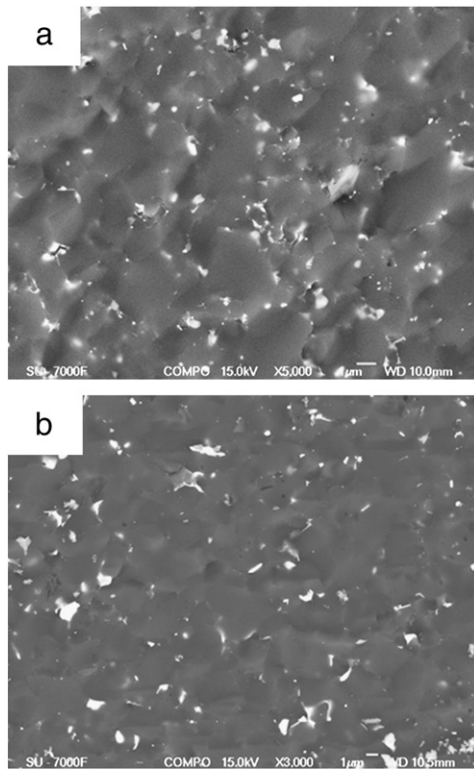


Fig. 4. Typical fracture surface of  $\text{B}_4\text{C}$  samples added with different amount of  $\text{CaF}_2/\text{Y}_2\text{O}_3$  sintered at  $1800^\circ\text{C}$  with 50 MPa pressure: (a) pure  $\text{B}_4\text{C}$ , (b) 1 wt.%  $\text{CaF}_2/\text{Y}_2\text{O}_3$ , (c) 3 wt.%  $\text{CaF}_2/\text{Y}_2\text{O}_3$ , and (d) 5 wt.%  $\text{CaF}_2/\text{Y}_2\text{O}_3$  (for (b–d): the left side is back scattering image (BSI) and the right side is scanning electron image (SEI)).



**Fig. 5.** Typical fractured surface of the  $B_4C$  ceramic sintered at  $1700\text{ }^\circ\text{C}$ : (a) 0.5 wt.%  $\text{CaF}_2/\text{Y}_2\text{O}_3$  addition with pressure of 80 MPa and (b) 0.5 wt.%  $\text{CaF}_2/\text{Y}_2\text{O}_3$  addition with pressure of 70 MPa.

pressure of 70–80 MPa. Compared to the samples sintered at  $1800\text{ }^\circ\text{C}$  (shown in Fig. 3), the sample sintered at  $1700\text{ }^\circ\text{C}$  in general shows a smaller grain size.

#### 4. Conclusions

A small amount of  $\text{CaF}_2/\text{Y}_2\text{O}_3$  is found to have a rather strong effect in regard with the densification of  $B_4C$  ceramics even at the temperature as low as  $1700\text{--}1750\text{ }^\circ\text{C}$ , combining with the employment of SPS sintering technique. Excellent wetting between  $\text{CaF}_2/\text{Y}_2\text{O}_3$  and  $B_4C$  allows the easy and fast diffusion of  $\text{Ca}^{2+}/\text{Y}^{3+}$  ions with small radius

into  $B_4C$  grains which could promote the mass transportation within  $B_4C$  grains. Thereby, the sintering densification could be greatly promoted. Both the reaction between  $\text{CaF}_2/\text{Y}_2\text{O}_3$  and  $B_4C$  and the Ostwald ripening process induced by the liquid phase formation favors this process as well.

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