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Processing, Mechanical and Nuclear Characterization of Boron Carbide Ceramics Consolidated by Spark Plasma Sintering

M. Cengiz[a], S.C. Ozer[a], B. Buyuk[b], A.B. Tugrul[b], O. Yucel[a], G. Goller[a] and F.C. Sahin[a,*]

[a]Istanbul Technical University, Metallurgical and Materials Engineering Department, Istanbul, Turkey

[b]Istanbul Technical University, Energy Institute, Nuclear Researches Division, Istanbul, Turkey

Boron carbide (B_4C) ceramics were produced by spark plasma sintering technique with 5, 10, 15, and 20 vol.% aluminum (Al) in order to improve sintering behaviours of B_4C ceramics. B_4C ceramics were produced, having square cross-section and $50\times50\times5$ mm^3 dimensions. The sintering process was carried out at different temperatures by applying 40 MPa of pressure with 100 °C/min under vacuum. The effects of various amounts of Al additive and sintering temperature on density, vickers hardness, fracture toughness and microstructure were examined. The hardness and fracture toughness of the samples were evaluated by the Vickers indentation technique. Microstructures of the samples were characterized by scanning electron microscopy technique. Fast neutron attenuation properties of the ceramics having highest density were also investigated.

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1. Introduction

B_4C is evaluated as an ideal material for nuclear applications, especially as control rods in reactors and shielding material in neutron shielding systems, due to its high hardness; being the third hardest material after diamond and cubic boron nitride, high flexural strength, low density, high wear resistance, chemical stability and thermal neutron cross-section value properties [1, 2].

In recent years, spark plasma sintering (SPS) technique has been used widely for manufacturing B_4C and B_4C containing ceramics because of its improvements on microstructural effects of said materials since it prevents grain coarsening [2]. With applying pulsed direct current, SPS enhances densification and the sintering process is completed at lower temperatures in shorter durations without grain growth compared to the traditional sintering techniques (pressureless sintering, hot pressing and hot isostatic pressing). These attributes make SPS a preferable candidate for producing boron carbide ceramics [3–5].

In this study B_4C ceramics with 5, 10, 15, and 20 vol.% Al addition were produced by using SPS method and physical, mechanical and nuclear characterization of those ceramics were performed.

2. Experimental

Commercial HS grade B_4C powders from German H.C. Starck Company, with an average particle size of 0.7 μm with 99.5% purity and metallic Al powder from Alpha Aesar Company with an average particle size of 5 μm with 99.5% purity were used in this study. Al additive was used as 5, 10, 15, and 20% volumetric in this experimental procedure. Suspensions were prepared by mixing B_4C and Al powder with Al_2O_3 balls in Merck quality ethanol medium by ball milling for 24 h. The slurry was then dried and granulated with screening. After screening, the dry powder was loaded in a graphite die with graphite sheets between the die and the powder for consolidation in SPS.

The samples were sintered by using the SPS apparatus (SPS-7.40MK-VII, SPS Syntex Inc.). After applying initial pressure as 10 MPa manually for compaction before sintering, 100 °C/min heating rate was used with 40 MPa pressure from room temperature to sintering temperature. An optical pyrometer was used for measuring the temperature of the die. All of the samples were subjected to 4 min soaking time. Whole process was carried out in vacuum and shrinkage, displacement, temperature, vacuum, current, and voltage for every 1 min was recorded. At the end of the process, sintered B_4C-Al compacts were obtained.

After the sintering process, the Archimedes method was used to determine the final densities and relative densities of the compacts. Specimens polished with a diamond paste having particle size of 1 μm were subjected to the hardness and fracture toughness tests at room temperature and were evaluated by the Vickers indentation technique at a load of 1 kg. The micrographs of all sample surfaces were observed by scanning electron microscopy (SEM; Model JSM 7000F, JEOL, Tokyo, Japan).

3. Results and discussion

Starting powder compositions, sample dimensions, and SPS process parameters along with the relative density

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[*] corresponding author; e-mail: `cinar@itu.edu.tr`

TABLE I

Density values of B_4C ceramics with different Al contents. Dimensions — 50×50 mm^2, thickness 5 mm, SPS parameters — 40 MPa and 4 min.

Starting powder	SPS temperature	Relative density
B_4C	1550 °C	97.9
B_4C +5%Al	1450 °C	98.1
B_4C +10%Al	1410 °C	97.9
B_4C +15%Al	1410 °C	97.9
B_4C +20%Al	1410 °C	98.3

TABLE II

Hardness and fracture toughness values of B_4C ceramics with different Al contents. SPS parameters — 40 MPa and 4 min.

Starting powder	SPS temperature	Hardness [GPa]	Fracture toughness [MPa m$^{1/2}$]
B_4C	1550 °C	31.0	2.95±0.3
B_4C+5%Al	1450 °C	29.7	3.38±0.3
B_4C+10%Al	1410 °C	29.6	3.73±0.3
B_4C+15%Al	1410 °C	28.9	4.10±0.3
B_4C+20%Al	1410 °C	28.3	4.45±0.3

values of the samples are given in Table I. All samples have 50×50 mm^2 square surface area and 5 mm thickness. 40 MPa pressure is applied under vacuum and the powders were heated with 100 °C/min heating rate and sintered for 4 min. The sintering temperatures were defined by checking the completion of the shrinkage amounts and decreased with increasing Al content. The reference sample without Al addition was sintered at 1550 °C whereas second sample with 5% Al addition was sintered at 1450 °C. Other samples were sintered at 1410 °C.

Maximum relative density values were achieved at the temperatures where the shrinkage is completed and the samples are kept constant at that temperature for 4 min. The reference sample (B_4C without Al) have 97.9% relative density whereas the other samples have higher relative densities. Some samples reached theoretical densities on their centres but since edges and the corners have lower densities, the overall densities of the samples are lower than theoretical density.

The hardness and fracture toughness values of the sintered ceramics are given in Table II. Hardness values of the B_4C ceramics without Al addition sintered at 1550 °C are obtained as 31.0 GPa, B_4C ceramics with 20% Al addition sintered at 1410 °C are obtained as 28.3 GPa. Hardness values decrease slightly with increasing Al content. The highest fracture toughness value were obtained as 4.45±0.3 MPa m$^{1/2}$ from the sample with 20% Al addition and sintered at 1410 °C for 4 min, whereas the reference sample has 2.95±0.3 MPa m$^{1/2}$.

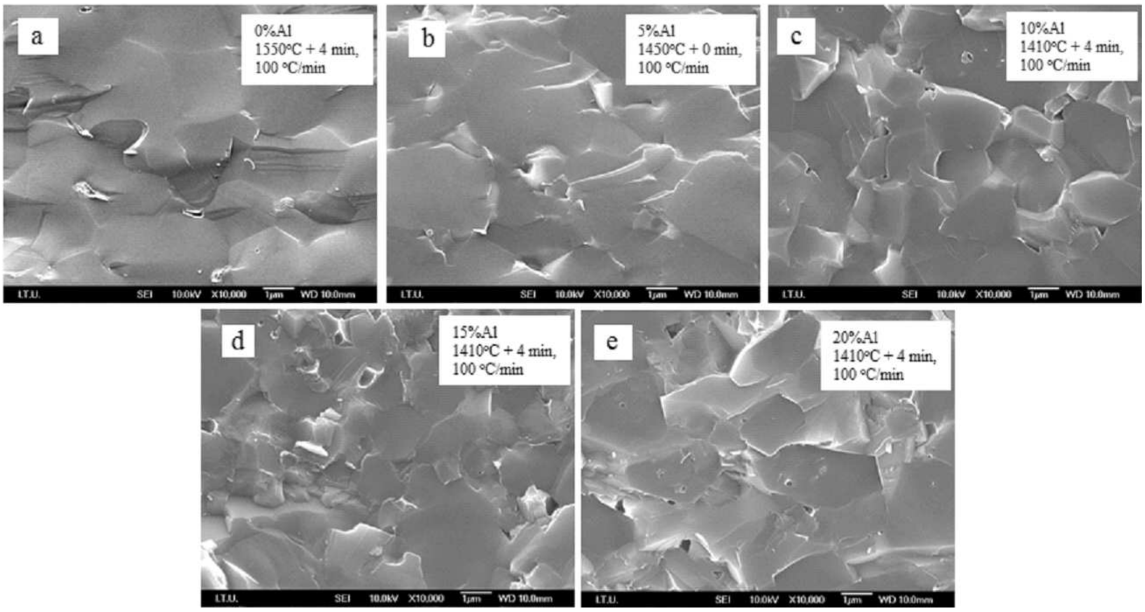

Fig. 1. SEM micrographs of a) B_4C sintered at 1550 °C, b) B_4C with 5% Al sintered at 1450 °C, c) B_4C with 10% Al sintered at 1410 °C, d) B_4C with 15% Al sintered at 1410 °C, and e) B_4C with 20% Al sintered at 1410 °C.

Fracture surface SEM images were given in Fig. 1, which provided the best result of relative density values. B_4C without Al addition and B_4C with 5% Al addition were observed to have 3–4 μm average grain size whereas B_4C with 10, 15, and 20% Al addition were observed to have 1–2 μm average grain size. The difference of the grain sizes between the samples are due to the sintering temperature difference. The sintered ceramics were ob-

TABLE III

The relative count-material thickness values of the B_4C–Al composites for Pu–Be neutron source.

x [cm]	Relative count [I/I_0]				
	B_4C +	5%Al	10%Al	15%Al	20%Al
0	1.0000	1.0000	1.0000	1.0000	1.0000
0.5	0.8544	0.8586	0.8561	0.8838	0.8980
1.0	0.8198	0.8308	0.8415	0.8445	0.8552
1.5	0.7727	0.8024	0.8241	0.8246	0.8267
2.0	0.7336	0.7550	0.7780	0.7782	0.7791

TABLE IV

Effective removal cross-section and half value layer values of the samples.

Material	Effective removal cross-sections [cm^{-1}]		Half value layers [cm]	
	Σ_{eff}	Std. dev.	HVL	Std. dev.
B_4C	0.158	0.008	4.386	0.051
B_4C+5%Al	0.148	0.008	4.682	0.054
B_4C+10%Al	0.136	0.010	5.095	0.073
B_4C+15%Al	0.134	0.009	5.171	0.0671
B_4C+20%Al	0.132	0.009	5.250	0.0681

served to have very few to no pores which are equal in size.

The shielding properties of the B_4C-Al ceramics were investigated against fast neutrons [6]. Effective removal cross-sections were carried out by using neutron transmission technique. Pu–Be neutron howitzer was used as a neutron source with 5 MeV average neutron energy and 1×10^5 n cm^{-2} s^{-1} neutron flux. The relative count-material thickness values were given in Table III. By using the values in Table III, neutron attenuation properties of the materials were drawn and given in Fig. 2.

The effective removal cross-sections were calculated by fitting the graphs according to Beer–Lambert's formula given below

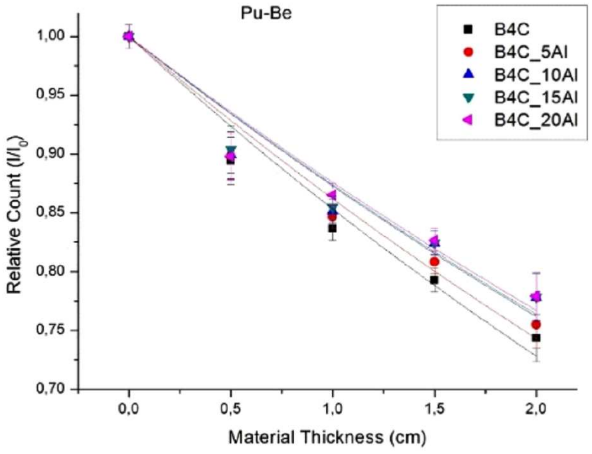

Fig. 2. Relative count-material thickness graphs for B_4C-Al composites.

$$I = I_0 \, e^{\Sigma_{\text{eff}} x}, \tag{1}$$

where I and I_0 are incoming and initial neutron counts, respectively. Σ_{eff} is effective removal cross-section of the material for the fast neutrons and x is the material thickness. Half value layer values ($0.693/\Sigma_{\text{eff}}$) of the materials for the fast neutrons were calculated. The effective removal cross-sections and half value layers (HVLs) of the B_4C-Al ceramics were given in Table IV.

From Table IV it can be seen that the effective removal cross-sections of the B_4C-Al composites were decreased with increasing Al ratio in the composites whereas the HVLs were increased. It means that reinforcing B_4C with Al causes a lower fast neutron shielding capability.

4. Conclusion

In this study, highly dense B_4C ceramics with Al additives and square cross-section were produced by SPS under vacuum with 40 MPa pressure, 100 °C/min and different sintering temperatures. Density values higher than 97% were obtained, theoretical densities were reached locally on the centres of the samples. The Vickers hardness of the samples ranged between 31.0 and 28.3 GPa. Fracture toughness values were measured between 2.95±0.3 and 4.45±0.3 MPa $m^{1/2}$. It is observed that the hardness values and sintering temperatures of the samples are decreased whereas the fracture toughness values increase with increase of Al addition.

The effective removal cross-section of the B_4C-Al ceramics were carried out for 5 MeV average neutrons. The results are compatible with the literature which is calculated as 0.149 cm^{-1} and 0.126 for B_4C and Al, respectively. It is concluded that adding Al to B_4C decreases the fast neutron shielding property of the samples and that B_4C has good thermal neutron absorption cross-section (755 barn). Therefore for both thermal and fast neutrons pure B_4C has higher shielding capability than B_4C-Al composites.

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