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BORON CARBIDE BASED CERAMIC COMPOSITES HOT PRESSED WITH ALUMINIUM ADDITIVE

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ABSTRACT

Ceramic composite materials consisting of B_4C matrix and $Al_8B_4C_7$ secondary phase were prepared by in situ reactive sintering of the initial powder mixture B_4C-Al with concentration from 5 to 25 wt.% Al sintering additives. The composite samples were hot pressed at the temperature of 1850 °C, pressure of 35 MPa, for 15 min in a vacuum atmosphere. The portion of $Al_8B_4C_7$ secondary phase increased from 3.3 to 22.1 wt.% when increasing the concentration of Al sintering additive from 5 to 25 wt.% Al. Significant improving of densification and mechanical properties was measured at increasing of Al sintering additive concentration from 5 to 10 wt.% Al. The highest average hardness of 28.74 GPa was achieved when adding 15 wt.% Al sintering additive. The fracture toughness increased with concentration of Al sintering additive in whole concentration range with the highest average value of 5.92 MPa.m$^{1/2}$ at 25 wt.% Al sintering additives.

Keywords: boron carbide, ceramic composite, secondary phase, hardness, fracture toughness

INTRODUCTION

Boron carbide (B_4C) based ceramic materials have been intensively studied, because of their excellent properties [1-3]. Due to its prevailing covalent bonding the boron carbide based ceramic materials are extremely hard. The high hardness, above 30 GPa, places it on the third place between hardest materials after diamond and cubic boron nitride [4-6]. B_4C is corrosion and wear resistant and ambient and elevated temperatures [7-8]. Boron carbide is characterized by high melting temperature of 2450 °C, it has low density of 2.52 g.cm^{-3}, high Young's modulus of 460 GPa and high cross-section for absorption of neutrons [4, 10-12]. Difficult sinterability of B_4C is one of the main problems of reliable compacts preparations. Hinder sinterability causes closed rest porosity in the sintered compacts, which is irremovable [7, 9, 10 12]. This stems from small coefficients of self-diffusion in B_4C. Full density of B_4C cannot be achieved at pressureless sintering without sintering additives. B_4C compacts with near full density of 2.52 g.cm^{-3} can be prepared by hot pressing at temperatures above 2300 °C. However, the sintering at temperatures above 2000 °C causes the particle coarsening in ceramic compacts [5, 13]. Using fine powder, adding of sintering additives and application of pressure at sintering allows decreasing of sintering temperature [12, 14-19].

One of the major disadvantages of B_4C is its low fracture toughness, which have to be improved for successful applications of boron carbide based ceramics [17, 20]. An increase of fracture toughness of samples can be solved through sintering of ceramic composite systems, which enables decreasing of sintering temperature too. Choosing of suitable composite systems permits creation of new phases in situ during sintering. Sintering additives in form of some elements (such as Al, Hf, Ti, B, C), and compounds (such as Al_2O_3, HfO_2, TiO_2, ZrO_2, Si_3N_4, TiC, W_2B_5) are used at fabrication of in situ sintered B_4C based ceramic composite materials [4, 14, 15]. They improve densification and influence the microstructure and mechanical properties of sintered compact because of creation of new secondary phases. Secondary phases are essential mainly for enhancing of fracture toughness, which is critical for boron carbide based ceramic materials, because it achieves values only from 2 to 3 MPa.m$^{1/2}$. The composite hardness can decrease, as phases with smaller hardness in comparison to B_4C are created [15].

Sintering of B_4C based ceramic composite with Al additive is interesting because of its low density [14, 20]. It is possible to densify the system at pressureless sintering, hot pressing and plasma spark sintering. Porous B_4C skeleton can be infiltrated with molten aluminium. Al sintering additive is used at pressureless sintering of B_4C-Al system. Achieved structure is similar to boron carbide with some changes in elementary lattice cell. Compacts with the density from 95 to 99 % are possible to prepare at sintering temperatures from 2100 to 2200 °C. Hot pressing can be used for increasing of densification when the sintering temperature decreases to 1600 °C. Final composite is very dependent on the composition of powder mixture, densification value and sintering temperature. Sintering pressure has a positive effect on density and mechanical properties. Al additive enables sintering with in situ reactions and creating of composite consisting of B_4C matrix reinforced with $Al_8B_4C_7$ secondary phase. $Al_8B_4C_7$ secondary phase can function as sintering additive to improve the sintering property of B_4C based ceramic which could result in higher relative density, lower shrinkage rate and better mechanical properties compared to that without $Al_8B_4C_7$ secondary phase. $Al_8B_4C_7$ secondary phase can be used as high temperature construction material since it possesses density of 2.69 g.cm^{-3}, which is close to density of B_4C (2.52 g.cm^{-3}) [19-21].

USED MATERIALS AND EVALUATION METHODS

Densities, microstructures and mechanical properties of B_4C based ceramic composite materials were studied on compacts prepared using hot pressing process of the initial powder mixture composed of B_4C powder with different concentration of Al sintering additive. The initial B_4C-Al powder mixture contained 5, 10, 15, 20 and 25 wt.% Al sintering additive. Their homogenisation was accomplished using wet mixing in horizontal mill with Teflon container and B_4C mill balls in isobutyl alcohol lubricant. The green samples were die pressed in simple tool with floating die of cylindrical shape with diameter of 8 mm at pressure of 140 MPa. All samples were consequently hot pressed in graphite die with floating matrix of cylindrical shape at the temperature of 1850 °C, pressing time of 15 min and pressure of 35 MPa in a vacuum atmosphere with final vacuum value about 10 Pa.

The densities of hot pressed samples were measured using Archimedes method. The microstructures were studied with Axiovert 40 MAT microscope and JEOL JSM-IT300 scanning electron microscope. The phase analysis was done using X ray diffraction method with Philips PW 1710 diffractometer. Volume portion of phases was estimates using image analysis with software of AxioVision, module Mutiphase. The hardness and fracture toughness of ceramic composite materials were measured using Vickers indenter Buehler IndentaMet 1100 with load of 49.03 N and indentation time of 10 s.

RESULTS AND DISCUSSION

Densification of B_4C-Al initial powder mixture

The average densities of ceramic composites prepared by hot pressing of the initial powder mixture B_4C with different concentration of Al are summarised in tab. 1. Their densities increased from 93.90 to 98.85 % when increasing the Al sintering additive concentration from 5 to 10 wt.% Al. Small differences in the

densities, in the interval from 98.85 to 98.89 %, were measured for samples with the initial concentration in the interval from 10 to 25 wt.% Al. These differences were lower than scatter of measured values, but the highest average density of 98.89 % was measured for sample with the initial concentration of 15 wt.% Al.

Table 1 Effect of Al concentration on density and portion of phases in B_4C-$Al_8B_4C_7$ composite

Al concentration (wt.%)	Density (%)	B_4C portion (vol.%)	$Al_8B_4C_7$ portion (vol.%)
5	93.90	96.7	3.3
10	98.85	94.8	5.2
15	98.89	92.8	7.2
20	98.74	86.3	13.7
25	98.84	77.9	22.1

Microstructure of B_4C-$Al_8B_4C_7$ ceramic composite

Microstructure of ceramic composite materials with the initial concentration of 5 and 10 wt.% Al sintering additives are depicted in Figs. 1 and 2. The microstructures contain three phases with different colours. The microstructures consist of grey matrix of boron carbide (B_4C) phase, light areas of aluminium boron carbide ($Al_8B_4C_7$) phase and small portion of dark areas which represent rest porosity of samples. All samples had similar microstructure but with different portion of observed phases. The portion ratio of $Al_8B_4C_7$ secondary phase increased and the portion of rest porosity decreased with increased concentration of Al sintering additive in the initial powder mixture.
The identification of phase composition was realised by X ray diffraction analysis. All composites had similar XRD records with major portion of B_4C phase which corresponds with grey areas in Fig. 1 and 2 and minor portion of $Al_8B_4C_7$ phase and it corresponds with light areas in Fig. 1 and 2. The formation of $Al_8B_4C_7$ phase was in good agreement with theoretical background.

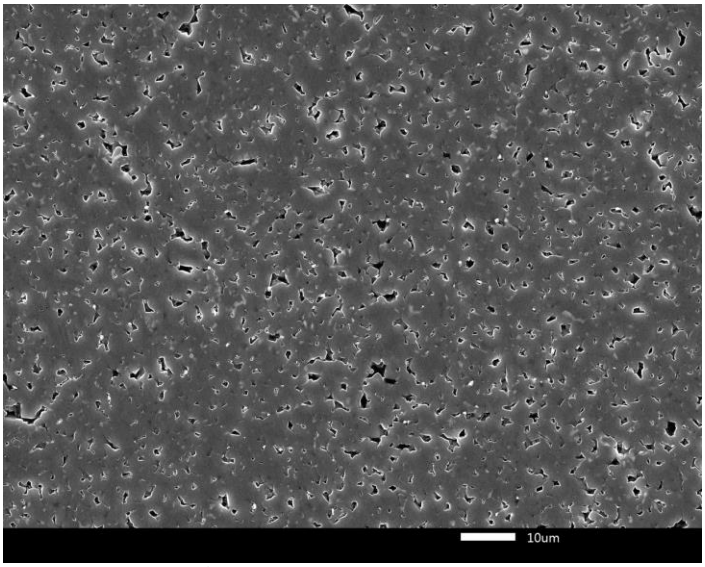

Fig. 1 Microstructure of B_4C based composite sintered with 5 wt. % Al

The effect of Al concentration on the portion of observed phases measured using the image analysis is given in Table 1. The portion of $Al_8B_4C_7$ phase was 3.3 vol.% for sample in fig. 1 which was hot pressed from the initial powder mixture B_4C with 5 wt.% of Al sintering additive.
The image analysis showed a positive effect of Al sintering additive on portion of $Al_8B_4C_7$ secondary phase in B_4C-$Al_8B_4C_7$ composite. The image analysis of composite microstructures showed that the portion of the $Al_8B_4C_7$ secondary phase increased from 3.3 to 22.1 vol. % $Al_8B_4C_7$, but he portion of B_4C matrix decreased from 96.7 to 77.9 vol.% B_4C when increasing the concentration of Al sintering additives from 5 to 25 wt.% of Al sintering additive. The increase of $Al_8B_4C_7$ secondary phase portion with the increase of Al sintering additive concentration can be related to the larger extent of the in-situ reaction at higher concentration of Al.

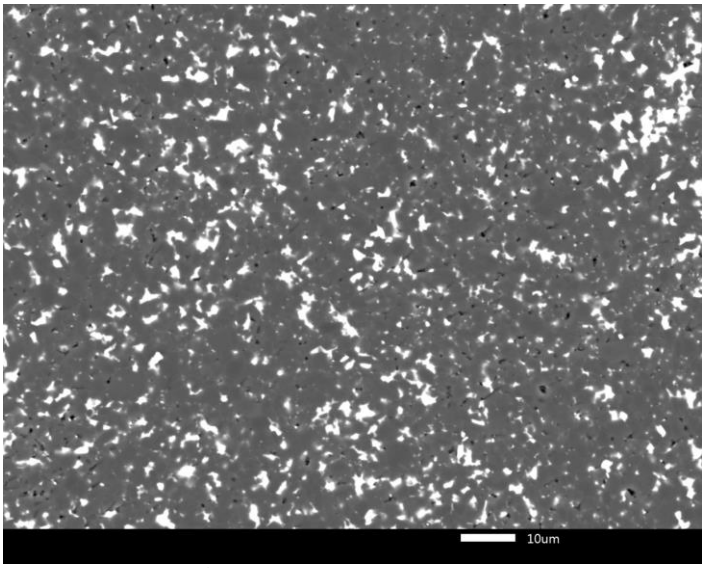

Fig. 2 Microstructure of B_4C based composite sintered with 10 wt. % Al

Mechanical properties of B_4C-$Al_8B_4C_7$ composite

The effects of Al sintering additive concentration in the B_4C-Al initial powder mixture on the hardness and fracture toughness of B_4C-$Al_8B_4C_7$ ceramic composite materials are plotted in Figs. 3 and 4.

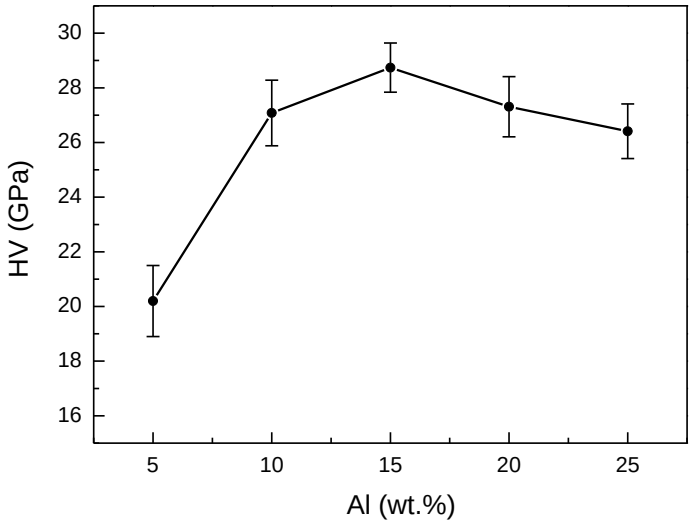

Fig. 3 Effect of Al on hardness of B_4C based ceramic composite

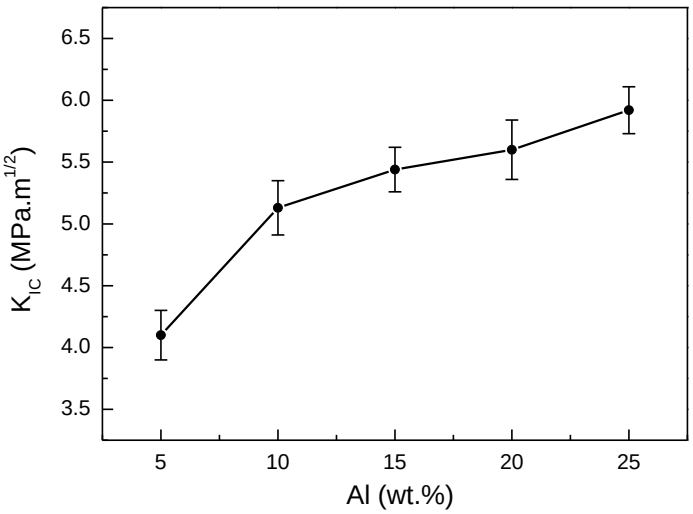

Fig. 4 Effect of Al on fracture toughness of B_4C based ceramic composite

The effect of Al sintering additive on the hardness of B_4C-$Al_8B_4C_7$ ceramic composite presented in fig. 3 can be divided to two sections. Average hardness of B_4C-$Al_8B_4C_7$ ceramic composite increased from 20.20 GPa to 28.74 GPa in the concentration interval from 5 to 15 wt. % Al sintering additive because of better densification of composite and larger extent of in situ reaction with increased concentration of Al. Average hardness of B_4C-$Al_8B_4C_7$ ceramic composite slightly decreased from 28.74 GPa to 26.41 GPa in the concentration interval from 15 to 25 wt. % Al because of creation of large portion of secondary phase $Al_8B_4C_7$ with lower hardness compared to B_4C matrix. The highest hardness of 28.74 GPa was achieved when adding 15 wt.% Al sintering additive.

Addition of Al into B_4C powder had the positive effect on the increase of fracture toughness in whole studied Al concentration range (see fig. 4). Average fracture toughness of B_4C-$Al_8B_4C_7$ composite increased from 4.10 to 5.92 MPa.m$^{1/2}$ with the increase of Al sintering additive concentration from 5 to 25 wt.% Al. The highest average fracture toughness of 5.92 MPa.m$^{1/2}$ was measured at composite with the highest concentration of 25 wt.% Al sintering additives. The fracture toughness increased by 44 % at the composite sintered with the highest concentration of sintering additive (25 wt.% Al) compared to the composite with the lowest concentration of sintering additive (5 wt.% Al). This effect can be explained by both toughening effect of $Al_8B_4C_7$ secondary phase and higher fracture toughness of $Al_8B_4C_7$ compared to B_4C matrix.

CONCLUSIONS

Ceramic composite material consisting of boron carbide B_4C matrix and aluminium boron carbide $Al_8B_4C_7$ secondary phase was prepared by hot pressing of the initial powder mixture B_4C-Al with concentration from 5 to 25 wt.% Al. The composite samples were hot pressed at the temperature of 1850 °C, pressure of 35 MPa, during hot pressing time of 15 min in vacuum atmosphere about 10 Pa.

Significant improving of average density of B_4C based ceramic composite material from 93.90 to 98.85 %. was reached at increasing of Al sintering additive concentration from 5 to 10 wt.% Al. The highest average density of 98.89 % was measured for composite with the initial concentration of 15 wt.% Al sintering additive.

The portion of the $Al_8B_4C_7$ secondary phase increased from 3.3 to 22.1 vol.% $Al_8B_4C_7$ when increasing the concentration of Al sintering additives in the initial B_4C-Al powder mixture from 5 to 25 wt.% of Al sintering additive.

The hardness of B_4C-$Al_8B_4C_7$ ceramic composite increased from 20.20 GPa to 28.74 GPa in the concentration interval from 5 to 15 wt. % Al sintering additive because of better densification of composite and larger extent of in situ reaction with increased concentration of Al sintering additive.

Addition of Al into B_4C powder had the positive effect on the increase of fracture toughness in whole studied Al concentration range. Average fracture toughness increased from 4.10 to 5.92 MPa.m$^{1/2}$ in B_4C-$Al_8B_4C_7$ composite with increase of concentration of Al sintering additive from 5 to 25 wt.% Al.

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