Synthesis of B_4C/YTZP Composite Powder and Studying Effect of its Addition on Mechanical Properties of B_4C

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ABSTRACT

In this research B_4C powder have been coated with yttria stabilized tetragonal zirconia polycrystalline (YTZP) (ZrO_2 – 6wt% Y_2O_3) by using sol-gel method in order to obtain on composite powder (B_4C core/ YTZP shell, 1/1 wt%). Zirconium oxychloride ($ZrOCl_2.8H_2O$) and yttrium nitrate ($Y(NO_3)_3.6H_2O$) were used as the precursors for synthesis of the YTZP compound. The coated B_4C powder was then used as additive powder to B_4C. It was mixed with different percentages for making ceramic–ceramic composite samples. The YTZP weight percentages added to the B_4C were in the range (0–12.5) wt%. The samples sintered by using spark plasma sintering technique at 1800 and 1900°C for 5 min. Density and mechanical properties (Vickers microhardness, fracturetoughness and fracturestrength) for the sintered samples were measured. The results show that the best YTZP additions to the B_4C that have good mechanical properties were ranged 5 – 7.5 wt%.

Keyword: B_4C/YTZP composite powder, sol-gel, microhardness, fracture strength, fracture toughness.

تصنيع مسحوق مركب من $YTZP\backslash B_4C$ ودراسة تأثير إضافته على الخواص الميكانيكية لكاربيد البورون

الخلاصة:

في هذا البحث تم طلاء مسحوق كاربيد البورون (B_4C) بالزركونيا المثبتة جزئيا باليتيريا (YTZP) (ZrO_2 – 6 wt% Y_2O_3) باستعمال طريقة السائل الهلامي للحصول على مسحوق متراكب (B_4C القلب/YTZP القشرة, 1/1 نسبة وزنية). استعمل اوكسي كلوريد الزركونيوم ($ZrOCl_2.8H_2O$)ونترات اليتريوم ($Y(NO_3)_3.6H_2O$) كمواد اوليةلإنتاج المركب YTZP. بعدها استعملمسحوقكاربيد البورون المطلي كمسحوق مضاف الى كاربيد البورون. حيث خلط عند نسب مختلة لعمل نماذج متراكبة سيراميكية. ان النسب الوزنية لمركب YTZP المضافة الى B_4Cكانت بين (0 – 12.5)%. تم تلبيد النماذج بتقنية التلبيد بالبلازما بدرجة حرارة (1800 و 1900) درجة مئوية لمدة خمسة دقائق.تمقياس الكثافة والخواص الميكانيكية(الصلادة المجهرية

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بطريقة فيكرز, متانة الكسر ومقاومة الكسر) للنماذج الملبدة.وأظهرت النتائج أن أفضل الإضافات منYTZPإلى B_4Cوالتي تضمنت خصائص ميكانيكية جيدة تراوحت بين 5 – 7.5 نسبة وزنية.

INTRODUCTION

Boron carbide (B_4C) is known as an important hard materialdue to its interesting properties such as low density (2.52 g/cm^3),high melting point (2450°C), good wear resistance, high hard nessand elastic modulus, p-type semiconductor, good chemicalstability as well as high neutron absorption cross section. The combination of these properties makes boron carbide acandidate material for a variety of structural applications [1,2].

The main problem associated with the use of this materialis its low sintering ability. The low self-diffusionco efficient of B_4C, which results from the strong covalent bonding between atoms, lowplasticity, high resistance to grain boundary sliding and lowsurface tension in the solid state altogether make powders sintering a difficult task [3,4]. Therefore, many researchers are concentrated on finding newtechniques for improving the sinter ability and fracture toughnessof boron carbide at less demanding conditions. Spark plasmasintering (SPS) has become a popular technology that has the advantage of higher heating rates, lower sintering temperaturesand shorter dwell times in comparison with conventional hotpressing [5].

It has been frequently observed that small amounts of oxides are very effective in improving the sinter ability of nonoxide ceramics. Baharvandiet al.Investigated on addition of (0–30) wt% ZrO_2 – 3 mol% Y_2O_3 powder onsintering behavior and mechanical properties of B_4C. It was found that the B_4C sintered densities were increased from 75% to 98.5%ρ_{th}.As a result of density improvement, mechanicalproperties such as hardness, strength and fracture tough nesswere increased remarkably. However, when the amount of ZrO_2–3% Y_2O_3 exceed 20wt%. Hardnessstarted to reduce [3].Goldstein et al. reported that heating of B_4C–YTZP (YttriaStabilized Zirconia Polycrystals) mixtures to temperature of ~2000°C yielded B_4C–ZrB_2 composites with better densificationthan monolithic B_4C [6].Subramanian et al. have reported the effect of zirconia with varying additions of (ZrO_2: 0–30 wt%) on pressureless sintering of boron carbideat 2275°C. Samples prepared with the addition of ≥5 wt% ZrO_2 showed higher densities in the range of 93–96% ρ_{th}, compared to 86.63% ρ_{th} for boron carbide only. Also, addition of ZrO_2 was found to increase the hardness of sintered samples and regardless of ZrO_2content, the hardness values ranged between 30 and 31.5 GPa [7].

The present work was aimed at developing a suitable process for the production of dense boron carbide pellets with high fracture strength. B_4C/YTZP core/shell composite powder (CP) has been synthesized by usingsol-gel method. Then, fabricatedcomposites from B_4C and CP by using SPS technique.

EXPERIMENTAL PART

Boron carbide powder with average particle size around 0.46 µm were used as the starting material. Zirconium oxychloride ($ZrOCl_2.8H_2O$) and yttrium nitrate ($Y(NO_3)_3.6H_2O$) were used as the precursors for preparation of YTZP compound. The following steps were carried out for synthesis of composite powder (CP):

Dispersed appropriate amount of B_4C powder in a mixed solution containing of (61.94 wt% deionized water, 36.65 wt% ethanol, 0.14 wt% CTAB (cetyltrime thylammonium bromide, $C_{19}H_{42}BrN$), and 1.27 wt% ammonia) and stirring the mixture by using magnetic stirrer at 50°C and (250 rpm) for 30 min.
Dissolved $ZrOCl_2.8H_2O$ and $Y(NO_3)_3.6H_2O$ separately in minimum volume of deionized water with concentration 1.8 M and 0.2 M, respectively. The two solutions are then mixed with (ZrO_2–6wt% Y_2O_3) (YTZP) and then stirring the mixture solution by using magnetic stirrer at 50°C and (200 rpm) for 30 min.

The formed YTZP solution was added drop-wise to the B_4C mixture solution with (B_4C:YTZP = 1:1, wt/wt) and then the total mixture was mixed by using magnetic stirrer at 80°C and (250 rpm) for 6 hours.

Addition of ammonium hydroxide drops to the total mixed solution until the gray colored gel bed was formed. The gel formation begins at (pH=5).
Filtrating the mixed solution with filter papers to get out the gel.

To remove the effect of surfactant (CTAB), the obtained gel was collected and washed repeatedly with ethanol and deionized water (1/1, V/V ratio), after that the gel was dispersed in acetone with (gel:acetone = 1:2, V/V ratio) and stirring the solution of gel and acetone by magnetic stirrer at 80°C and (250 rpm) for 3 hours in order to remove any possibility of the pore in the formed YTZP shell. The gel was then washed and stirred with deionized water for separated the coated B_4C particles from the agglomerations.

Filtrating the washed gel with filter papers to get out the gel.
The filtered gel has been dried at temperature 80°C for 6 hours in electric oven.
The gel was crushed by mortar and pestle. Finally, white to light gray colored powder was obtained; this indicates that the boron carbide particles were coated by YTZP to form composite powder (B_4C core/ YTZP shell).

The synthesized composite powder was mixed with uncoated B_4C powder at different percentages (0, 5, 10, 15, 20 and 25) wt% CP. These weight percentages of CP can be expressed as YTZP wt% to becomes (0, 2.5, 5, 7.5, 10 and 12.5) wt% YTZP, because CP consisted of B_4C+YTZP with 1:1 wt%. Spark plasma sintering is used for sintering the ceramic powders to overcome the problem of oxidation during conventional sintering also advantages of SPS in fast sintering and higher sintered density. The sintering procedure was conducted in two temperatures (1800 and 1900)°C at a heating rate of 100°C/min and the applied pressure was 80 MPa uniaxial press. The holding time at the highest temperatures was 5 minutes. After sintering at the desired temperature, the pressure was relaxed and the specimens were cooled at 100°C/min in the chamber. The sintered samples were typically 15 mm in diameter and 5 mm in thickness.

X-ray diffractometry (PANalyticalX'Pert Pro diffractometer)was used to analyze the structural changes of the sintered samples. The relative density of the sintered samples was measured by the Archimedes method, using distilled water as the immersionliquid. The hardness was determined using a Vickers microhardnesste sting machine(MitutoyoHM 122) with pyramidal diamondindenter and a load of 9.81 N for 15 s, and 4 indentations were made on each sample. Crack lengths and indentation diagonallengths extending from the corners of the Vickers indentations were measured by optical microscopy for fracture toughness(K_{1C}) determinations. The fracture toughness was calculated using equation (1) [8].

$$K_{Ic} = 0.0319 \frac{P}{a.l^{1/2}} \quad \ldots (1)$$

Where: K_{1c} = fracture toughness ($MPa.m^{½}$), P = applied load (N), a = diameter of the Vickers indent (m) and l = crack length (m).

Brazillian test is used to determine the fracture strength using equation (2) [9]:

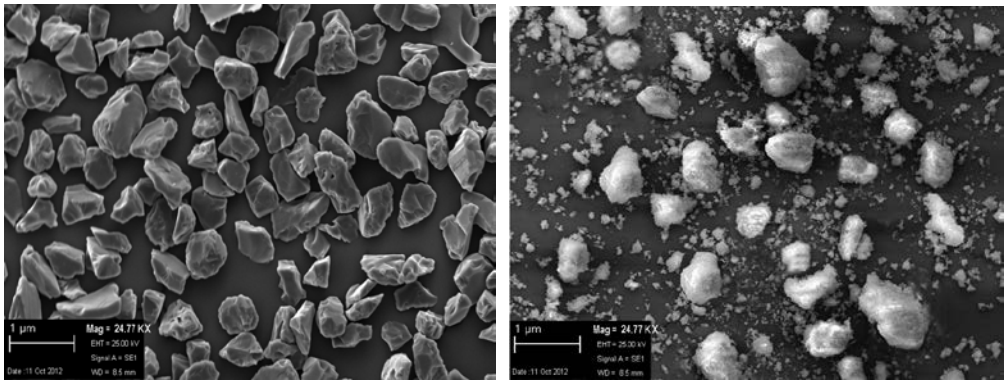
$$\sigma = \frac{2P}{\pi d t} \quad \ldots (2)$$

Where: σ = fracture strength, P = applied load (N), d = diameter of the disc (mm) and t = thickness of the disc (mm).

RESULTS AND DISCUSSION

SCANNING ELECTRON MICROSCOPE (SEM)

Figure (1-a and b) show the SEM images of the starting B_4C powder (before coating) and the composite powder (B_4C core/ YTZP shell), respectively. It is clear from figure (1-b), successfully coating of B_4C particles with YTZP compound at low temperature via sol gel method. Also, it is shown there are some nanoparticles of shell material spread between the composite powder. This may be due to happen some friction between the composite powder that leads to fragile the shell during the transport of the powders.



(a) **(b)**

Figure (1) SEM image of the: (a) starting B_4C powder and (b) synthesized composite powder (B_4C core/ YTZP shell).

In order to monitor microstructure development for the sintered samples; the SEM micrographs for the surface of B_4C samples with different YTZP additions and sintered at 1900°C are presented in Figure (2). The microstructure displays irregular (non-equiaxed) fine-grain microstructure with average grain sizes are slightly larger than the raw B_4C powder particle size. The addition of YTZP to B_4C changes the microstructure considerably because it is added as composite powders, so the formed ZrB_2 phase appears like circular within B_4C matrix. The black and dark grey regions correspond to pores and B_4C, respectively. Lighter areas are ZrB_2 phase. These contrasts in regions are clearly shown in the high magnification SEM micrograph of selected region as in Figure (2-d). Furthermore, it is clear that by increasing YTZP

amount the porosity decreased and denser materials are obtained this due to increasing the densification by formation ZrB_2 phase that filled the pores.

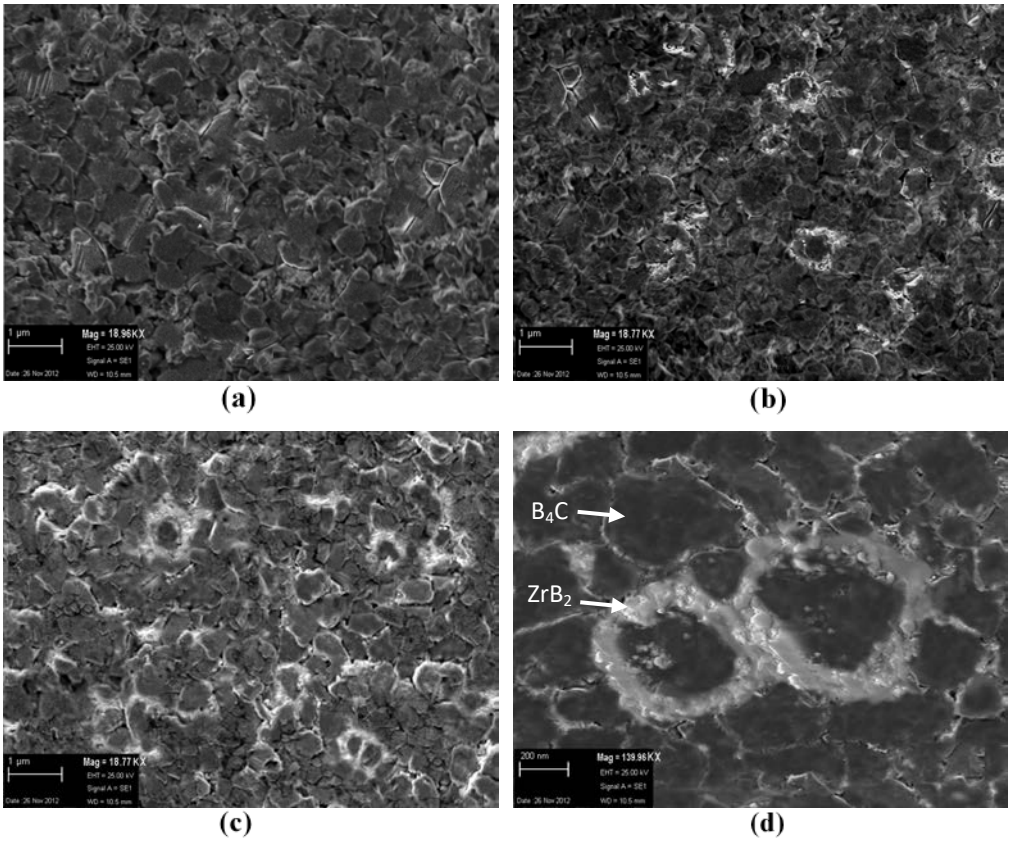


Figure (2) SEM micrographs of sintered B_4C samples at 1900°C with different YTZP additions: (a) 0 wt%, (b) 5 wt%, (c) 12.5 wt% and (d) high magnification SEM micrograph of selected region ofB_4C–7.5 wt% YTZP sintered at 1900°C.

X-RAY DIFFRACTION (XRD)

The mixture powder samples from B_4C with composite powder are sintered at (1800 and 1900)°C by SPS with 100°C/min heating rate for 5 minutes holding time. The heating of B_4C–ZrO_2 mixtures, under an argon or vacuum atmospheres, generates B_4C–ZrB_2 composites, because of a low temperature (<1500°C) carbide–oxide reaction [3]. The possible reaction between B_4C and ZrO_2 to form ZrB_2 is as follows [10]:

$$7ZrO_2 + 5B_4C \rightarrow 7ZrB_2 + 3B_2O_{3(l)} + 5CO_{(g)} \quad \ldots(3)$$

$$2ZrO_2 + B_4C + 3C \rightarrow 2ZrB_2 + 4CO_{(g)} \quad \ldots(4)$$

Carbon for the reaction (4) was taken, as that present in boron carbide as free carbon. When any of these reactions occurs, weight of the specimen will decrease as a result of the evaporation of CO gas [7]. X-ray diffraction patterns for 7.5 wt% YTZP that sintered at 1900°C and 12.5 wt% YTZP that sintered at (1800 and 1900)°C are chosen in this test as shown in figures (3to 5). As shown from these

figures, aftersintering the powder samples, however, strong hexagonal ZrB_2 peaks were detected in addition to B_4C peaks. The strongest diffraction peaks of ZrB_2 are observed at 2θ = 25.2° (001), 32.6° (100) and 41.6° (101). All ZrB_2 peaks are coincide with JCPDS card No. (34-0423). While the strongest diffraction peaks ofrhombohedral B_4C are observed at2θ =19.7° (101), 23.4° (012), 34.9° (104) and 37.8° (021), corresponds to JCPDS card No. (35-0798).

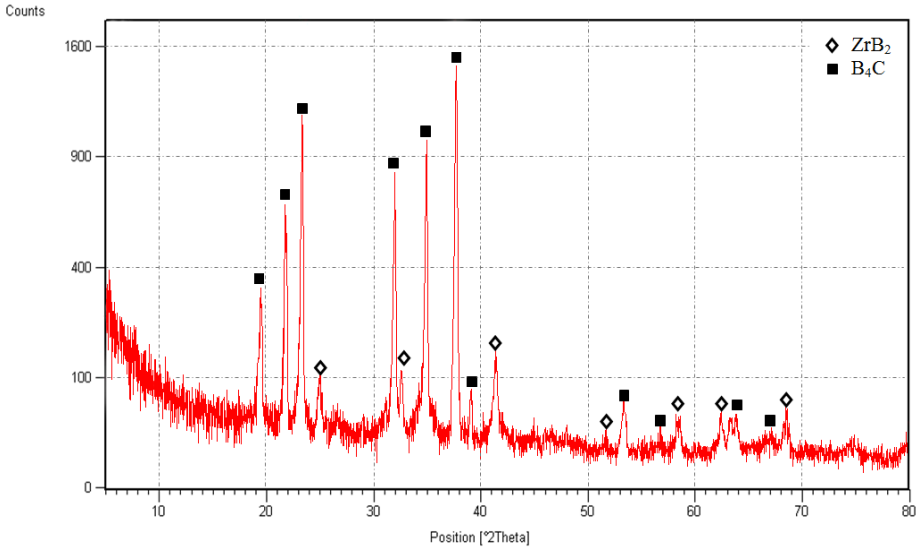


Figure (3) XRD pattern of sample from B_4C - 7.5 wt% YTZP sintered at 1900°C.

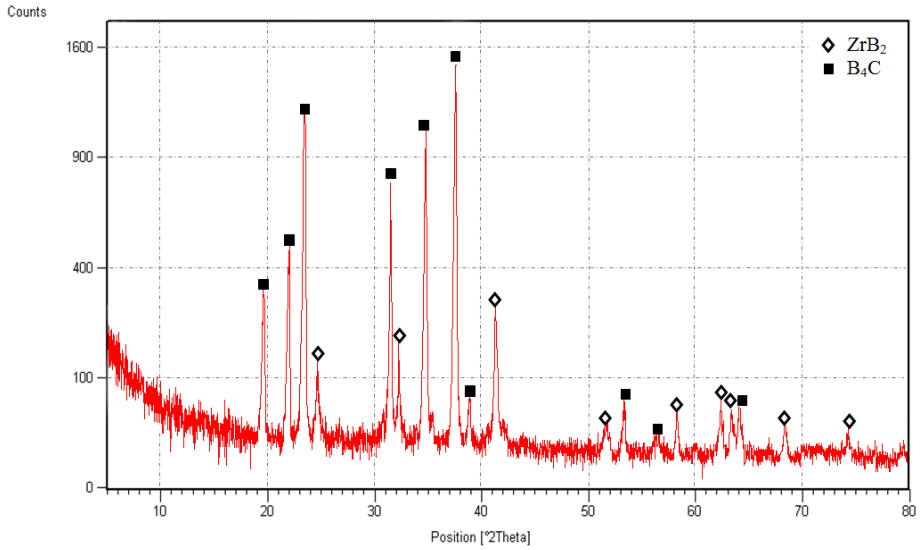


Figure (4) XRD pattern of sample from B_4C - 12.5 wt% YTZP sintered at 1900°C.

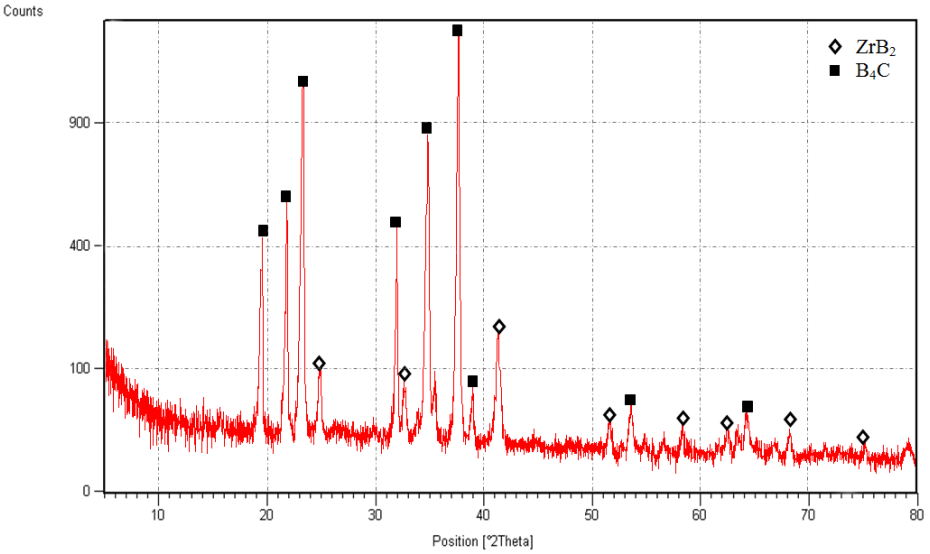


Figure (5) XRD pattern of sample from B_4C - 12.5 wt% YTZP sintered at 1800°C.

The diffraction peaks of sintered samples especially of ZrB_2 show sharp peak intensities and clean profiles, indicating that the composite samples (B_4C–YTZP) after sintering process have high crystallinity. Furthermore, it was found from these XRD patterns, the diffraction peaks intensities of ZrB_2 increased with increasing YTZP content from 7.5 to 12.5 wt% YTZP, and that due to increase the reaction between B_4C and ZrO_2. The yttrium existing in the YTZP compound essentially overlaps that of zirconium, which suggests that Y^{3+} ions are included in ZrB_2 [6].

DENSITY

Figure (6) shows the percent relative densities (% ρ_r) of sintered samples with varying addition of YTZP to B_4C that sintered at 1800 and 1900°C. It is found that, the samples sintered at 1800°C, the relative density at 0 wt% of YTZP showed a density of 94.02 %ρ_r, which increased with the addition of YTZP to reach 98.8 %ρ_r at 12.5 wt% YTZP. The enhanced on sintering of B_4C by YTZP additions may be attributed to the carbide-oxide reaction that leads to formation two phase composite consisting of ZrB_2 and B_4C as showed in XRD analysis of the sintered samples figures (3 to 5). The addition of YTZP is beneficial in lowering the sintering temperature of boron carbide, consequently accelerating densification via enhanced grain boundary diffusivity. Diffusion processes in B_4C are very slow and densification is extremely difficult due to the fully covalent bonding prevailing in this compound [3,7].

From this figure also, it has been shown that the relative density of the samples are increased when increasing the sintering temperature to 1900°C. Sintering at high temperature caused to high diffusion rates and higher densification. It is seen that relative density at 0 wt% YTZP was 95.95 %ρ_r and increased to reach the maximum value 99.96 %ρ_r at 7.5 wt% YTZP. A slight density decreases of the samples after addition 10 and 12.5 wt% YTZP. The relative density at 12.5 wt% of YTZP showed

a density of 99.77 $\%\rho_r$. Increasing YTZP additive amount in B_4C leads to increase the reaction between B_4C and ZrO_2 this could result in weight loss as a result of the evaporation of CO gas and the porosity increased obviously [11,10]. Because the sintering process was done in the SPS at high temperature (1900°C), high heating rate 100°C/min and high applied pressure (80 MPa), all these parameters caused to arrest the formed gases during the reaction inside the sample to form close pores. So, decreasing pressure loaded on B_4C samples, during sintering process, allows the releasing of gases generated during sintering, which normally favors the driving-off of the pores from inside and thereby promoting the densification of B_4C ceramics [12].

The behavior of the density curve in this work like as showed in the previous literatures but hear higher density value can obtained with less amount of YTZP due to the YTZP compound has been added as composite powder form that did to form new distribution of YTZP more like nano-flaky imbedded in B_4C matrix. The maximum relative density of B_4C in this work was 99.96 %ρr when addition 7.5 wt% YTZP during sintering at 1900°C, while in the previous literatures the maximum relative density obtained with amount of YTZP or ZrO_2 addition were: 97 %ρr, 15 wt% YTZP during sintering at 2150°C [3], 95.82 %ρr, 25 wt% ZrO_2 during sintering at 2275°C [7], 91 %ρr, 15 wt% YTZP during sintering at 2130°C [6]. Hence, the reduction of YTZP content in B_4C is beneficial for producing B_4C products have less weight possible with high density and produced at low temperature.

Figure (6) relative density of sintered B_4C samples as a function of YTZP content that sintered at 1800°C and 1900°C.

VICKERS MICROHARDNESS

The microhardness of a material is an important mechanical property because it relates how much the material will inelasticly deform when a surface load is applied. Because, the indentation diameters of micro Vickers tester for sintered specimens are very small and does not appear in Vickers tester instrument. The light optical

microscope with computer programused for analysis of images and calculate the micro hardness. The Vickers microhardness value of the B_4C samples that sintered at 1800°C and 1900°C as a function of YTZP content is shown in figure (7). It is clear that the hardness of specimens increased with increasing YTZP content, apparently because of the improvement in density. However, when more increasing of YTZP content in B_4C, the hardness decreased. This is due to the formation of less hard ZrB_2 composition[3].

The hardness value is also depending on sintering temperature. This figure also shows that the hardness values rise together with sintering temperature increases. Because the hardness values are highly correlated with density and porosity. So reducing the number of defects in a specimen is a common way of increasing its microhardness [13]. The hardness has a maximum value of 34.8 GPa when 5 wt% YTZP content and 1900°C sintering temperature.

Figure (7) The effect of YTZP addition on Vickers microhardness of B_4C samples sintered at 1800°C and 1900°C.

FRACTURE TOUGHNESS

Figure (8) demonstrates the effect of YTZP addition on fracture toughness of B_4C samples that sintered at (1800 and 1900)°C. From the figure, it is obvious that by increasing the YTZP content, the fracture toughness of the specimens increases. This increasing in toughness is attributed to increase presence of ZrB_2 second-phase in the microstructure of such samples. ZrB_2 phase inclusions can increase fracture toughness of sintered B_4C by two mechanisms [14,15]: (a) toughening due to crack bridging of ZrB_2 second-phase; (b) toughening due to thermal residual stress. In the present situation the reason for toughness increase seems to be the interaction of cracks with tougher ZrB_2 phase (4 – 5 $MPa.m^{1/2}$,ZrB_2 fracture toughness [16]) or crack deflection by microcracks around ZrB_2 compounds phases as shown in figure (9). Due to thermal expansion mismatch between ZrB_2 and B_4C, microcracking can be supposed around ZrB_2 phase. This overall deflection process results in a jagged fracture surface on the specimen because the change in orientation of the crack plane during deflection leads to a reduction of the crack extension force [17].

Fracture toughness of B_4C specimens which content 12.5 wt% YTZP, increased by more than 30 % above of the pure B_4C specimen. Furthermore, increasing the sintering temperature from 1800 to 1900°C, the toughness of the samples increases. This can be related to the lower amount of porosity and higher densification.

Figure (8) The effect of YTZP addition on fracture toughness of B_4C samples sintered at 1800°C and 1900°C.

Figure (9) SEM micrograph of B_4C–7.5 wt% YTZP shows the crack deflection by ZrB_2 phase through Vickers hardness test.

FRACTURE STRENGTH (BRAZILIAN TEST)

Figure (10) shows the effect of the YTZP additions on the fracture strength of the B_4C samples which are sintered at 1800 and 1900°C. It is found that the YTZP addition has highly improving the fracture strength of the B_4C sample. The increasing in the fracture strength of B_4C with increasing YTZP content as well as with increasing sintering temperature this is due to the density improvement with less porosity which leads to increase the particles bonding. The strength increased from 76.1 to 91.7 MPa with the addition of 10 wt% YTZP for B_4C samples sintered at 1800°C, while the B_4C samples that sintered at 1900°C the strength increased more

to reach the maximum value 100.9 MPa with the addition of 7.5 wt% YTZP. With further additions of YTZP, the strength decreased this may be due to the presence of residual porosity in the B_4C sintered samples may account for part of the decrease in the fracture strength values. Residual stresses in the sintered composite samples are another factor that may have contributed to the reduction in fracture strength. Since ZrB_2 has an average thermal expansion coefficient of 5.9 10^{-6}/°C [18], which is higher than that of the B_4C matrix (4.510^{-6}/°C). This mismatch in the thermal expansion coefficient between B_4C and ZrB_2 could produce residual stresses near ZrB_2–B_4C grain boundaries, which could also result in microcracking which lower in the strength values [19].

Figure (10) The effect of YTZP addition on fracture strength of B_4C samples sintered at 1800°C and 1900°C.

CONCLUSIONS

1. Successfully coating of B_4C particles with YTZP compound at low temperature via sol-gel method for producing composite powder (B_4C core/ YTZP shell).
2. High dense boron carbide specimens were fabricated by SPS technique at a temperature 1900°C for 5 min, and nearly full-densification up to 99.96% of theoretical density obtained when addition 7.5 wt% YTZP.
3. Addition of YTZP as composite powder form has remarkable effect on sintering and mechanical properties of B_4C composition due to its lead to form a new and good distribution within B_4C matrix composite and high densification of B_4C can be achieved with less amount of YTZP comparing with previous literatures.
4. The best YTZP additions to B_4C that has good mechanical properties were ranged 5 to 7.5 wt% and with an increase in the YTZP content more that, the most properties will reduce as a result of the residual pores.

REFERENCES

[1] Ma Q. C., Zhang G. J., KanY. M., Xia Y. B. andWang P. L., "Effect of Additives Introduced by Ball Milling on Sintering Behavior and Mechanical Properties of Hot-Pressed B_4C Ceramics", Ceramics International, Vol. 36, Issue 1, pp. (167–171), 2010.

[2] YuhuaZ., AijuL., YanshengY., RuixiaS.and YingcaiL., "Reactive and Dense Sintering of Reinforced-Toughened B_4C Matrix Composites", Materials Research Bulletin, Vol. 39, Issue 11, pp. (1615–1625), 2004.

[3] BaharvandiH. R., HadianA. M., AbdizadehA. and EhsaniN., "Investigation on Addition of ZrO_2 – 3mol% Y_2O_3Powder on Sintering Behavior and Mechanical Properties of B_4C", J. Mater. Sci. 41, pp. (5269–5272), 2006.

[4] XuC., CaiY., FlodströmK.,Li Z., EsmaeilzadehS.andZhang G., "Spark Plasma Sintering of B_4C Ceramics: the Effects of Milling Medium and TiB_2Addition", International Journal of Refractory Metals and Hard Materials, Vol. 30, Issue 1, pp.(139–144), 2012.

[5] SwarnakarA.K., Huang S.G., BiestO. V.andVleugelsJ. , "Ultrafine Al_2O_3–B_4C Composites Consolidated by Pulsed Electric Current Sintering", Journal of Alloys and Compounds, Vol. 499, Issue 2, pp.(200–205), 2010.

[6] Goldstein A., Geffen Y., and Goldenberg A., "Boron Carbide–Zirconium Boride in situ Composites by the Reactive PressurelessSintering of Boron Carbide–Zirconia Mixtures", J. Am. Ceram. Soc., Vol. 84, No. 3, pp. (642–644), 2001.

[7] Subramanian C., Roy T.K., Murthy T., SenguptaP., Kale G., KrishnaiahM.and SuriA., "Effect of Zirconia Addition on PressurelessSintering of Boron Carbide", Ceramics International 34, pp. (1543–1549), 2008.

[8] SergejevF. and AntonovM., "Comparative Study on Indentation Fracture Toughness Measurements of Cemented Carbides", Proc. Estonian Acad. Sci. Eng.,Vol. 12, No. 4, pp. (388–398), 2006.

[9] Powers J. M. and Sakaguchi R. L., "Restorative Dental Materials", 12th edition, published by Mosby Elsevier, Inc., Texas, 2006.

[10] Yuan H., Li J., ShenQ. and Zhang L., "Preparation and Thermal Conductivity Characterization of ZrB_2Porous Ceramics Fabricated by Spark Plasma Sintering", InternationalJournal of Refractory Metals and Hard Materials 36, pp. (225–231), 2013.

[11] Levin L., FrageN. and DarielM. P., "A Novel Approach for the Preparation of B_4C-Based Cermets", International Journal of Refractory Metals and Hard Materials 18, pp. (13–135), 2000.

[12] XuC., FlodströmK. and EsmaeilzadehS., "Low Temperature Densification of B_4C Ceramics with CaF_2/Y_2O_3 Additives", International Journal of Refractory Metals and Hard Materials 35, pp. (311–314), 2012.

[13] Lorenzo W. Hankla, "Mechanical Properties of Particulate-Reinforced Boron Carbide Composites", M.Sc. thesis, Department of Mechanical Engineering, College of Engineering, University of South Florida, 2008.

[14] Mashhadi M., Nassaj E. T. and Sglavo V. M., "Pressureless Sintering of Boron Carbide", Ceramics International 36, pp. (151–159), 2010.

[15] Moshtaghioun B. M., Ortiz A. L., García D. G. and Rodríguez A. D., "Toughening of Super-Hard Ultra-Fine Grained B_4C Densified by Spark-Plasma Sintering via SiC Addition", Journal of the European Ceramic Society 33, pp. (1395–1401), 2013.

[16] Peng F., "Pressureless Sintering and Oxidation Resistance of ZrB2 Based Ceramic Composites", Ph.D thesis, School of Materials Science and Engineering, Georgia Institute of Technology, 2009.
[17] Green D. J., "An Introduction to the Mechanical Properties of Ceramics", Cambridge University Press, Cambridge Solid State Science Series, 1998.
[18] Jung E. Y., Kim J. H., Jung S. H. and Choi S. C., "Synthesis of ZrB_2 Powders by Carbothermaland Borothermal Reduction", Journal of Alloys and Compounds 538, pp. (164–168), 2012.
[19] Zhu S., FahrenholtzW. G., HilmasG. E., Zhang S. C., YadlowskyE. J. and KeitzM. D., "Microwave Sintering of aZrB_2–B_4C Particulate Ceramic Composite", Composites: Part A: applied science and manufacturing 39, pp. (449–453), 2008.