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Pressureless sintering of boron carbide

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Abstract

The effect of small Al addition on pressureless-sintering and mechanical properties of B_4C ceramic was analyzed. Different amounts of aluminium powder, from 0% to 5 wt%, were added to the base material and pressureless-sintering was conducted at 2050 and 2150 °C under argon atmosphere. Microstructure, crystalline phases, density evolution, fracture strength, elastic modulus, hardness and fracture toughness were analyzed and correlated to Al additions and firing temperature. Density and grain size of sintered samples increased significantly with Al load while the effect of sintering temperature was less evident; 94% dense material was obtained by adding 4 wt% Al. Bending strength, hardness and fracture toughness of sintered B_4C samples were shown to increase for Al content up to 4 wt% while further additions resulted in a decrease of the mechanical resistance. Conversely, elastic modulus showed an increase with Al load especially between 1 and 3 wt%.

Keywords: C. Mechanical properties; B_4C; Al; Pressureless sintering

1. Introduction

Boron carbide is an important non-metallic hard material with high melting point, hardness and low density as well as high chemical resistance [1,2]. Due to the outstanding properties, B_4C ceramics have great potential for many structural applications at room temperature. Boron carbide can be used as neutron absorber, armor, abrasive media for lapping and grinding, polishing media for hard materials and wear resistant components [2,3]. However, its disadvantages are the limited strength and fracture toughness as well as poor sinterability and machinability. Due to the very strong covalent bonds, the high resistance to grain boundary sliding and absence of plasticity, densification of stoichiometric boron carbide (B_4C) is extremely difficult [4]. Simple shapes of dense boron carbide are industrially prepared by hot pressing under vacuum or inert atmosphere fine (<3 μm) pure powder at high temperature (2100–2200 °C) and pressures of 30–40 MPa for 15–45 min holding time, i.e. by a very expensive process [1]. Since pure B_4C hardly densifies above 80% theoretical density, a variety of second phases have been proposed as sintering aids [5].

In pressureless sintering, dense components can be obtained by using fine grained starting powder (<3 μm) and sintering temperature of 2250–2350 °C. To increase the volume and grain boundary diffusion and, therefore, to promote densification at lower temperatures, different additives such as C, B, TiB_2, Si, Al, Mg, SiC, SiC + Al, TiB_2 + C, TiO_2, ZrO_2, TiC, WC, BN, etc. have been proposed [6–15]. A promising method is the use of organic precursors, e.g. polycarbosilane with small amount of phenolic resin [2]. Other additives such as Fe, Ti, B, Mg, Co, Ni and Cu have also been used, with various degrees of improvement in sintering behaviour and mechanical properties [1]. Aluminium and Al-containing compounds such as AlF_3 and Al_2O_3 were also found to be effective for the densification of B_4C [16].

Liquid phase sintering is expected to be an alternative method for fabricating dense B_4C ceramics with improved mechanical properties, analogously to the densification of covalent non-oxide ceramics such as silicon carbide and silicon nitride [4].

Aluminium is preferred for the development of B_4C–Al systems because it is a stable metal with a low specific gravity. It is also ductile, non-toxic, relatively inexpensive, easy to obtain, and available in corrosion-resistant forms. Boron

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carbide–aluminium systems have the potential for offering a combination of high hardness and toughness in a lightweight structure [17]. It has been reported elsewhere that volume diffusion is enhanced in the boron-rich area of the homogeneity range of boron carbide (B_4C–$B_{10.5}C$ in B–C diagram phase) due to the generation of point defects. Since aluminium can also substitute carbon, a similar mechanism can be activated [18]. Therefore researchers have focused on aluminium because of its light weight, ready availability and reactivity with boron carbide under reasonable processing conditions [19–24].

Nevertheless, none successful attempts in producing products which may be easily manufactured has been reported so far. In the present study, the effect of small Al addition on the microstructure and mechanical properties of B_4C ceramics is investigated.

2. Experimental procedure

The starting materials used in the present study consist of high-purity B_4C (B:C ratio of 3.8–3.9) and high-purity and fine Al and high-purity phenolic resin powders. The average grain size and the specific surface area of B_4C powder were measured to be 1.3 μm and 6.6 m^2/g, respectively. Different amounts of Al, from 1% to 5 wt% were considered as sintering aid. The powders were milled and mixed in a planetary mill with tungsten carbide lining in methanol for 1 h using high-purity tungsten carbide balls. Due to possible WC contamination in the powder mixture this was leached in sulphuric acid. Phenolic resin (5 wt%) powder was added to each batch as binder. The mixtures were dried at 70 °C and then sieved through a 60 mesh sieve to form granules. The powder mixtures were uniaxially cold pressed under 80 MPa into 50 mm × 50 mm × 10 mm samples in stainless steel mold. In order to increase green strength, the tiles were CIPed at 180 MPa. Each tile was cut into bars 10 mm × 10 mm × 50 mm and which were polished with SiC paper (320 grits) in order to remove macroscopic surface defects. Samples were then heated for 1 h at 900–1000 °C in order to burn out phenolic resin. Green samples were then sintered using a microprocessor controlled graphite element furnace. Sintering was carried out under Ar atmosphere up to 2050 and 2150 °C using a heating rate of 10 °C/min and dwell time equal to 1 h.

The sintered bodies were surface ground and polished with diamond paste down to 1 μm grain size for successive microstructure examinations. The polished surfaces were then electrochemically etched in a 0.1% KOH solution with a current density of 0.1 A/cm^2 for 60–120 s [25].

The microstructure of the specimens was observed using scanning electron microscope (SEM) (JEOL, JSM-5500) and optical microscope (Zeiss, Axio-Imager.A1m). Bulk chemical composition of the metal containing phases was determined by energy dispersive X-ray spectroscopy (EDXS). Mean grain size of sintered samples was calculated by using the line intercept method in SEM micrographs [26]. Bulk density and open porosity of the samples were measured by the Archimede's method. The crystalline phases were characterized by X-ray diffraction (XRD) (Philips, model Xpert) technique by using Cu Kα radiation.

In order to measure the mechanical properties, samples 3 mm × 4 mm × 45 mm were cut and polished with diamond

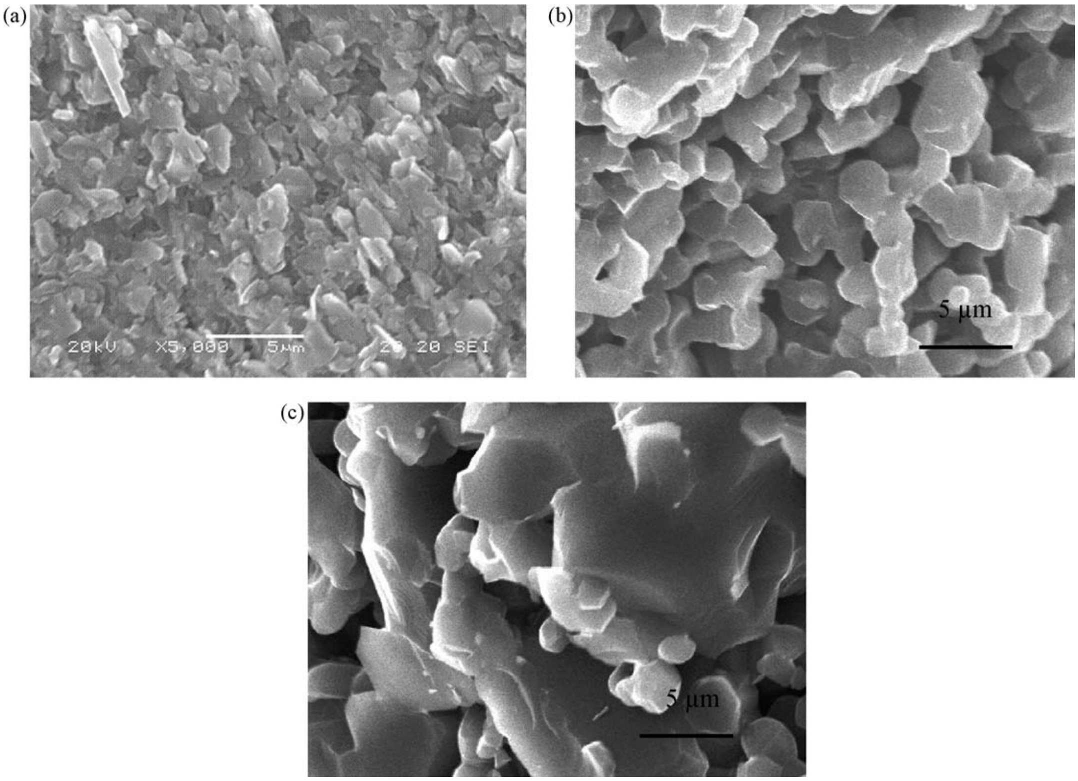

Fig. 1. SEM micrographs of B_4C samples: (a) green; (b) sintered at 2050 °C and (c) sintered at 2150 °C.

paste down to 1 μm surface finish. A Vickers diamond pyramidal indenter was used to measure hardness and fracture toughness [27,28]. Every sample was indented with a load of 30–100 N for 15 s. The values were calculated from the average of 10 indentations. Bending strength and elastic modulus were measured by four-point bending test method using a universal testing machine (MTS-810) with a crosshead speed of 1 mm/min [27,28]. Inner and outer spans equal to 20 mm and 40 mm, respectively, were used.

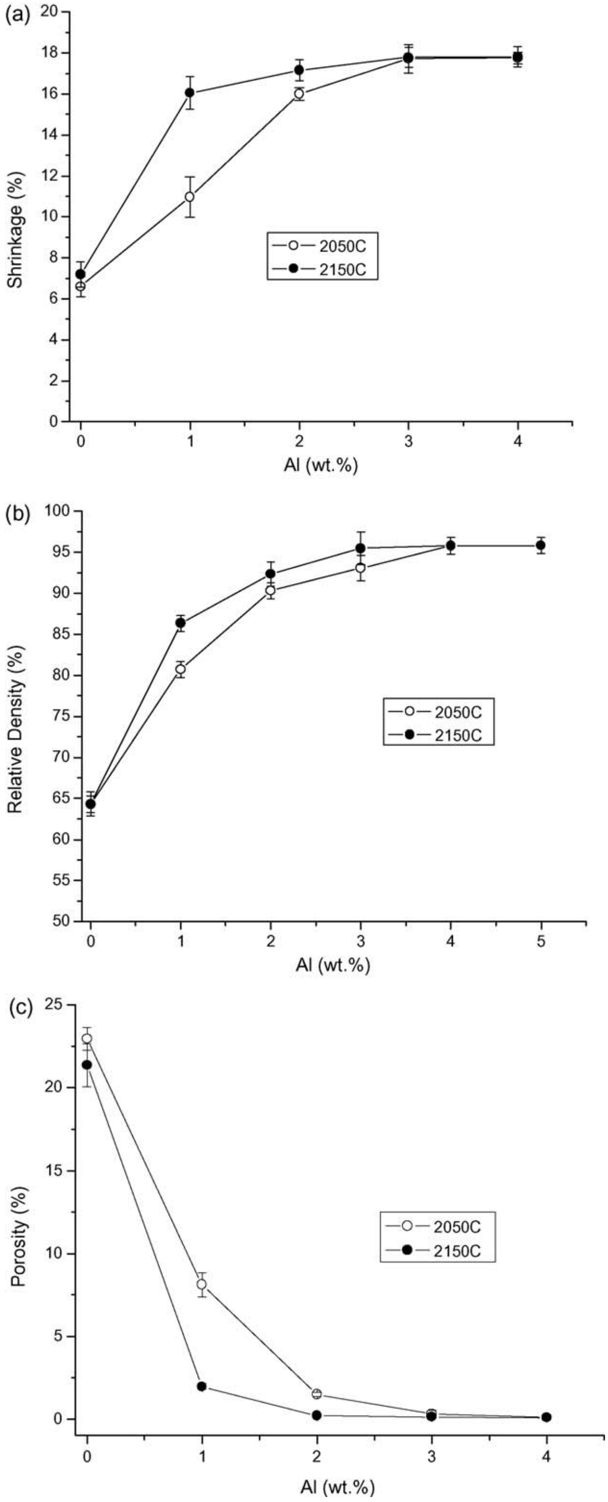

Fig. 2. Effect of Al addition on: (a) shrinkage, (b) relative density and (c) porosity of B_4C sintered at various temperatures.

3. Results and discussion

From X-ray diffraction patterns of B_4C samples without any additive sintered at 2050 and 2150 °C, only presence of B_4C was ascertained.

SEM micrographs of the microstructure of green and sintered B_4C samples are reported in Fig. 1. It is shown that boron carbide cannot be sintered without pressure and additives even at very high temperature (2150 °C), maintaining relatively high porosity. After sintering at 2050 °C (Fig. 1b) necks are formed and grains and porosities become coarser. According to Fig. 1c by increasing the sintering temperature up to 2150 °C more necks are formed though the porosity remains quite high (about 22%). One can also observe that by increasing the sintering temperature up to 2150 °C, porosity remains almost constant while considerably grain growth occurs. This can be accounted for the B_4C strong covalent bonds, and limited self-diffusion than result in low sinterability [29].

The effect of Al addition on shrinkage, density and porosity of B_4C sintered at 2050 and 2150 °C is shown in Fig. 2. Adding Al and increasing the sintering temperature increases shrinkage and density and decreases porosity.

Fig. 3 shows the XRD patterns of B_4C containing 5 wt% Al sintered at 2050 and 2150 °C. Three main phases are detected in the sintered samples: B_4C, Al_3BC and AlB_2. Aluminium melts and reacts with B_4C to form solid ceramic phases this resulting in porosity reduction and shrinkage associated to liquid phase sintering mechanisms. The reaction between boron carbide and aluminium generates other several crystalline phases such as AlB_2, Al_3BC, AlB_{12}, $AlB_{12}C_2$, $AlB_{24}C_4$, Al_4C_3, $Al_4B_{1–3}C_4$, $Al_3B_{48}C_2$, $AlB_{48}C_2$ and $AlB40C_4$ [20]. Liquid Al (melting temperature is about 660 °C) at sintering temperature has lower

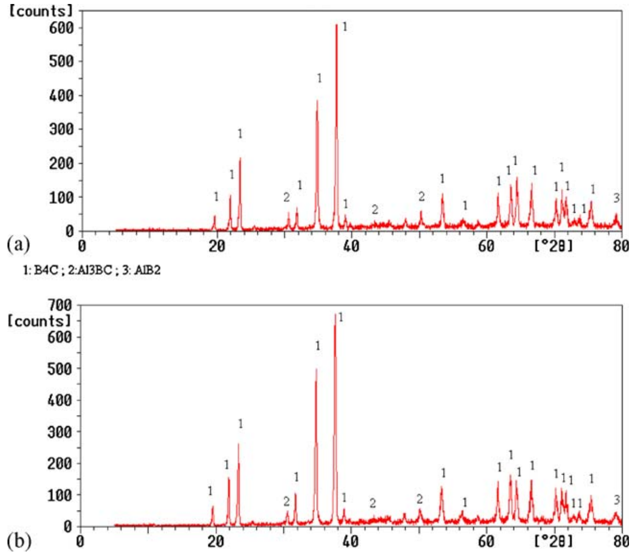

Fig. 3. XRD patterns of B_4C samples containing 5 wt% Al sintered at: (a) 2050 °C and (b) 2150 °C.

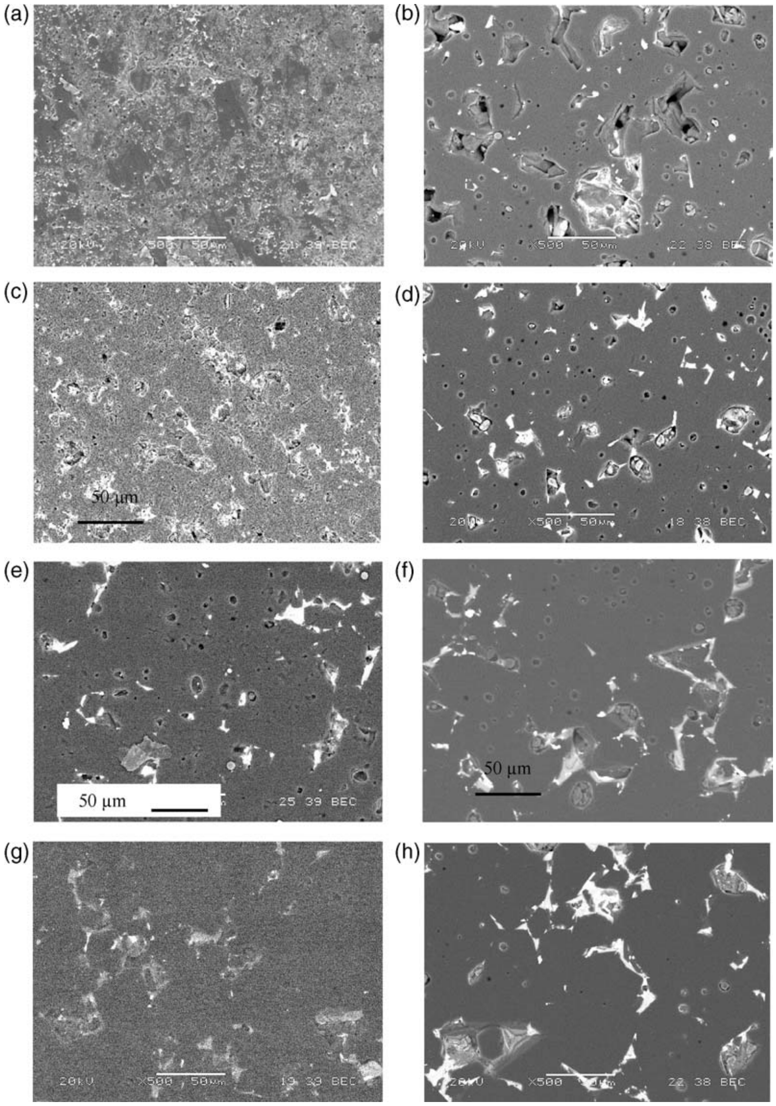

Fig. 4. SEM micrographs of sintered B_4C samples at various temperatures and containing different Al amounts: (a) 2050 °C, 1 wt%; (b) 2050 °C, 2 wt%; (c) 2050 °C, 3 wt%; (d) 2050 °C, 4 wt%; (e) 2150 °C, 1 wt%; (f) 2150 °C, 2 wt%; (g) 2150 °C, 3 wt% and (h) 2150 °C, 4 wt%.

contact angle with solid B_4C and moves between B_4C particles [30]. It reacts with B_4C and some of the above mentioned phases, depending on the process conditions and the amount of Al addition, are formed. In this work, because of the processing conditions and Al amount, AlB_2 and Al_3BC phases are formed.

Fig. 4 shows the microstructure of boron carbide samples containing different amounts of Al sintered at 2050 and 2150 °C. The addition of even small amount of Al changes the microstructure considerably. As Al content increases, denser materials are obtained with limited influence of the sintering temperature this being in agreement with density and porosity measurements previously shown. More in detail, one can point out that as Al load increases, interconnected pores are transformed into isolated and coarser pores, this accounting for the zero open porosity measured previously. In Fig. 4 black and dark grey regions correspond to pores and B_4C, respectively. Lighter areas within grain boundaries are AlB_2 and Al_3BC. It is clear that by increasing Al amount such regions become larger and porosity is decreased.

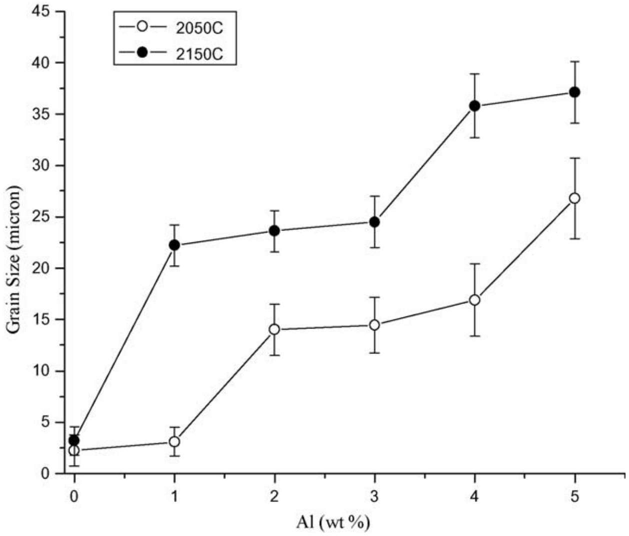

Fig. 5. Effect of Al addition on grain size of sintered B_4C at various temperatures.

Fig. 5 shows the grains size in B_4C containing different Al amounts sintered at 2050 and 2150 °C. The addition of Al to B_4C results in larger grains size. As pointed out before, in B_4C–Al system the sintering mechanism is liquid phase sintering. Liquid phase increases grain growth because diffusion is faster [31,32]. It is interesting to observe that an increase in sintering temperature determines a larger grain size. By adding more than 3 wt% of Al the grain growth is considerably higher. This is confirmed by SEM micrographs reported in Fig. 6. It is shown that by increasing Al amount at constant sintering temperature and by increasing sintering temperature at constant Al amount, B_4C grains are coarser.

Fracture strength and open porosity of sintered boron carbide as a function of Al amount are shown in Fig. 7. One can observe that boron carbide sintered at 2050 °C without additive possesses the minimum fracture strength (about 90 MPa) and

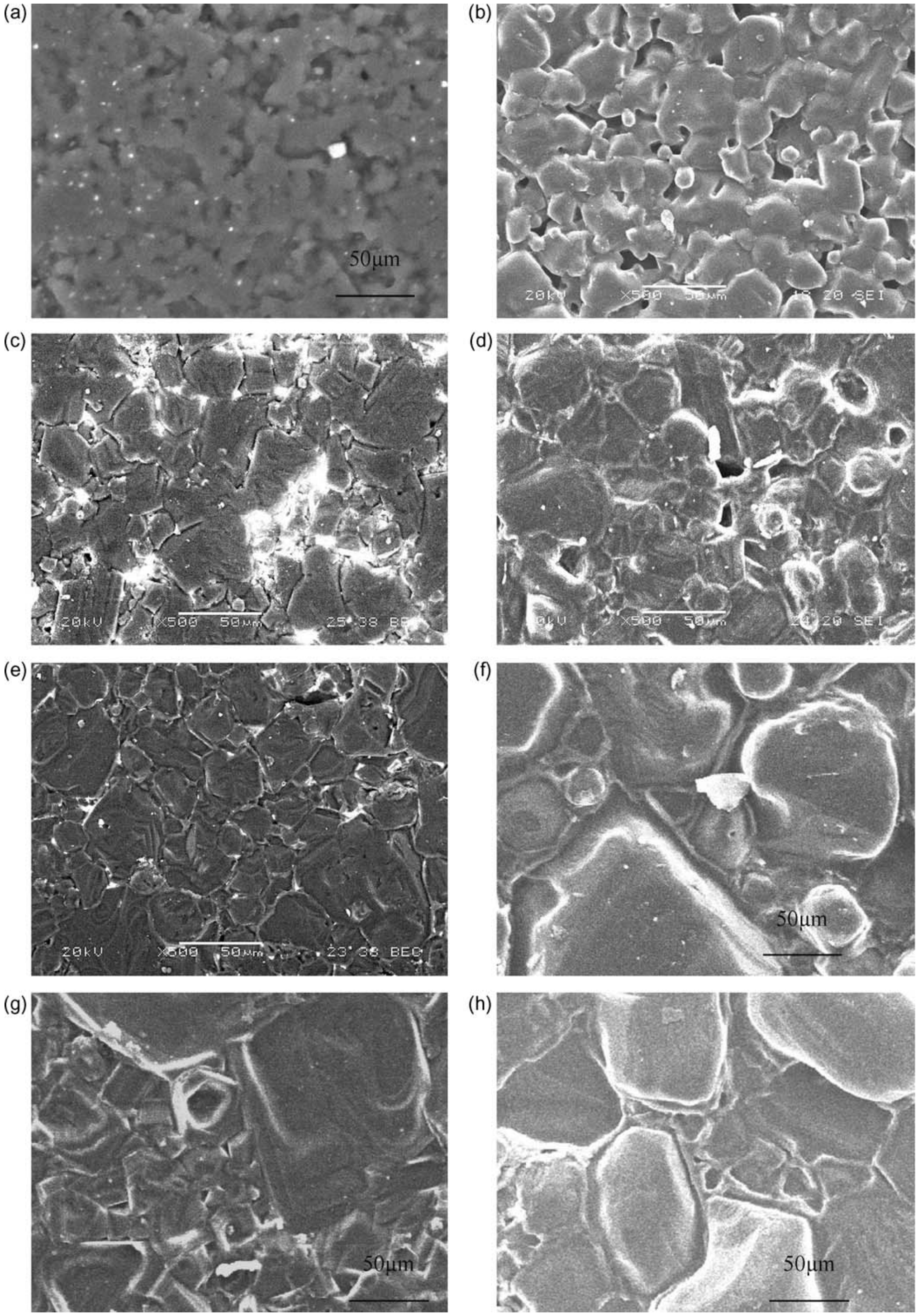

Fig. 6. SEM micrographs of sintered B_4C samples at various temperatures and containing different Al amounts: (a) 2050 °C, 1 wt%; (b) 2150 °C, 1 wt%; (c) 2050 °C, 2 wt%; (d) 2150 °C, 2 wt%; (e) 2050 °C, 4 wt%; (f) 2150 °C, 4 wt%; (g) 2050 °C, 5 wt% and (h) 2150 °C, 5 wt%.

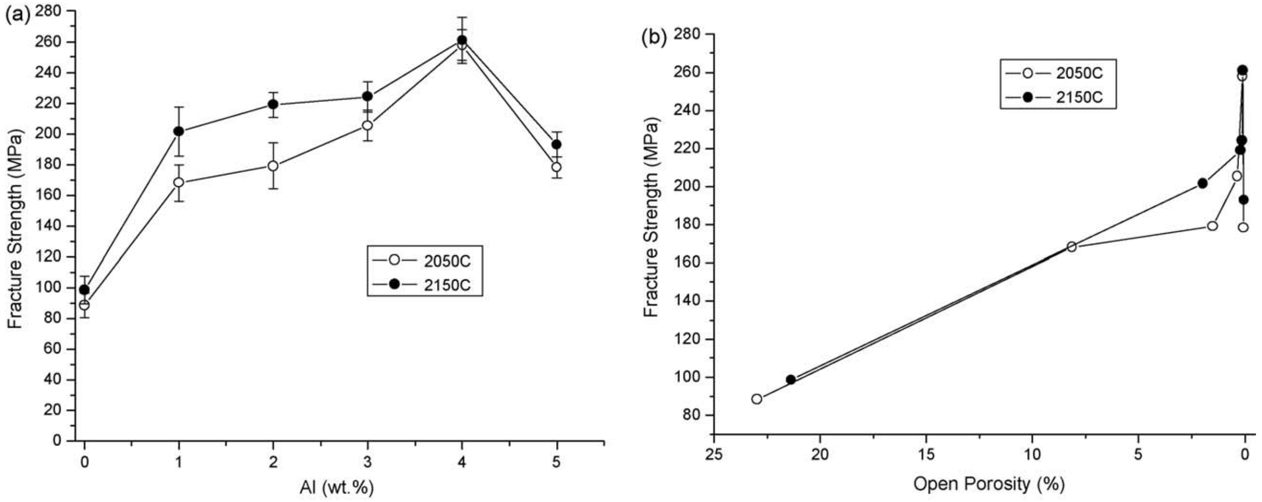

Fig. 7. Fracture strength of sintered B_4C samples at various temperatures as a function of: (a) Al addition and (b) open porosity.

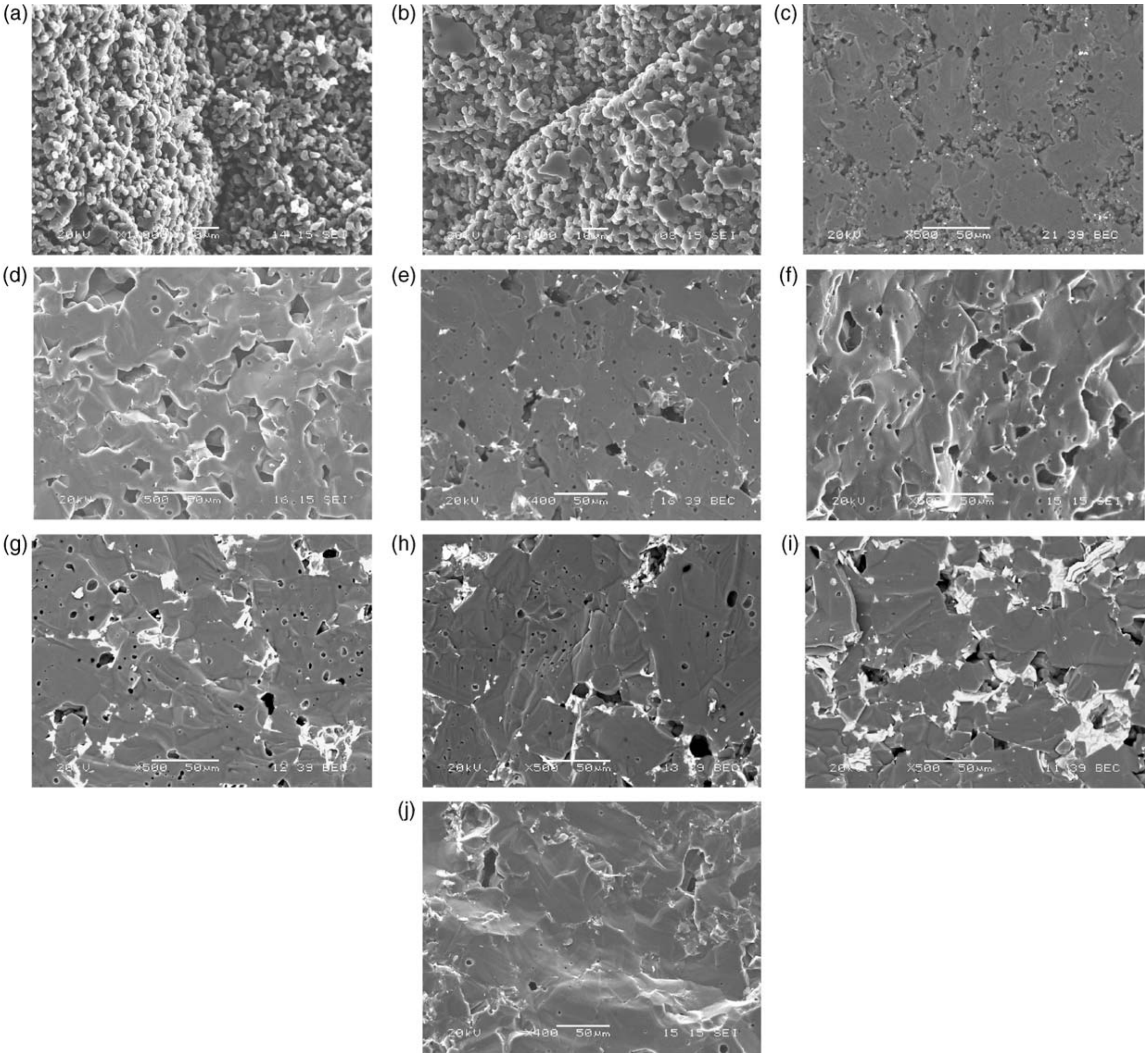

Fig. 8. SEM micrographs of fracture surfaces of sintered B_4C samples at various temperatures and containing different Al contents: (a) 2050 °C, 0 wt%; (b) 2150 °C, 0 wt%; (c) 2050 °C, 1 wt%; (d) 2150 °C, 1 wt%; (e) 2050 °C, 2 wt%; (f) 2150 °C, 2 wt%; (g) 2050 °C, 3 wt%; (h) 2050 °C, 4 wt%; (i) 2050 °C, 5 wt% and (j) 2150 °C, 5 wt%.

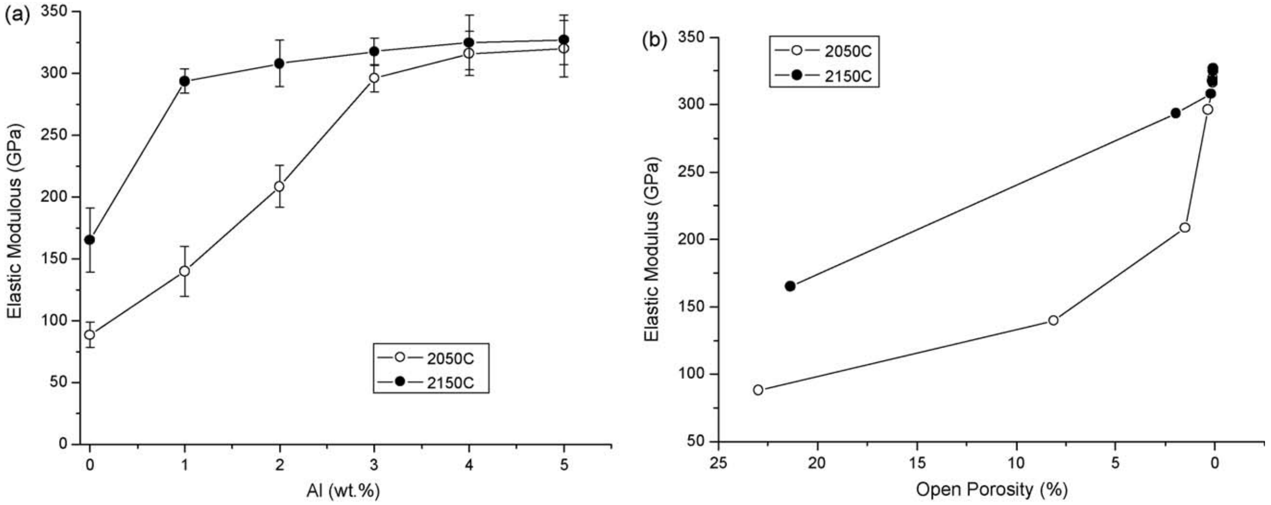

Fig. 9. Elastic modulus of sintered B_4C at various temperatures as a function of: (a) Al amount and (b) residual open porosity.

increasing the sintering temperature up to 2150 °C changes the failure stress limitedly (around 100 MPa). Al addition up to 4 wt% determines a larger increase in fracture strength up to 270 MPa; further Al addition does not affect the strength value. As expected Fig. 8 points out that strength increases while porosity decreases, this being associated to the important effect of Al on sintering behaviour [2].

Fig. 8 shows SEM micrographs of fracture surfaces of B_4C samples containing different values of Al sintered at 2050 and 2150 °C. Samples without additive show intergranular fracture that can be associated to weak grain boundaries. After Al addition, fracture mode changes to transgranular and this is probably due to the formation of grain boundary phases produced by liquid phase sintering reactions.

The trend of the elastic modulus as a function of Al additions and residual open porosity is shown in Fig. 9. Al content up to 3 wt% results in a clear increase of the elastic modulus, this remaining quite constant for larger Al loads. In addition the effect of porosity on elastic modulus roughly follows the prediction defined by MacKanzie equation [33,34]:

$$E = E_0(1 - 1.9P + 0.9P^2) \qquad (1)$$

where P is the porosity of the material.

Fig. 10 shows the effect of Al addition on hardness of sintered B_4C. It is clear that Al addition increases the hardness and this is associated to the decrease of porosity and grain size with Al load [34,35]. At the highest sintering temperature (2150 °C), additions of Al in excess to 4 wt% result in hardness decreases because coarser grain size is developed and the effect of softer aluminium addition becomes important.

Fig. 11 shows the effect of Al addition on fracture toughness. An increase of the amount of Al up to 3 wt% results in higher fracture toughness. Aluminium inclusions can increase fracture toughness of sintered B_4C by two mechanisms [36]: (i) toughening due to crack bridging and plastic deformation of

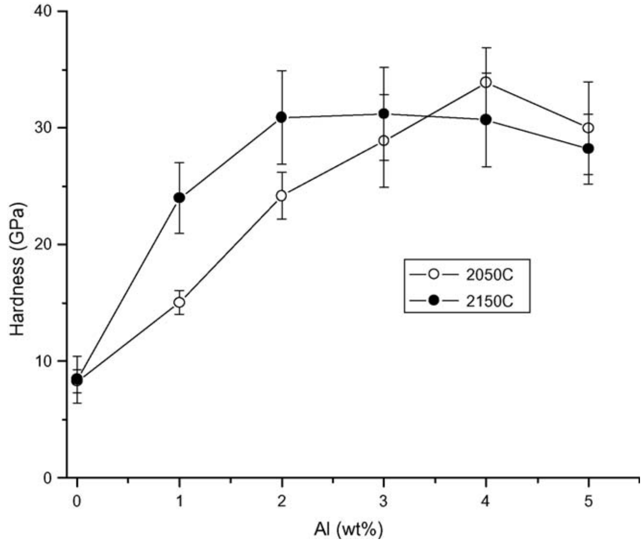

Fig. 10. Effect of Al addition on hardness of sintered B_4C at various temperatures.

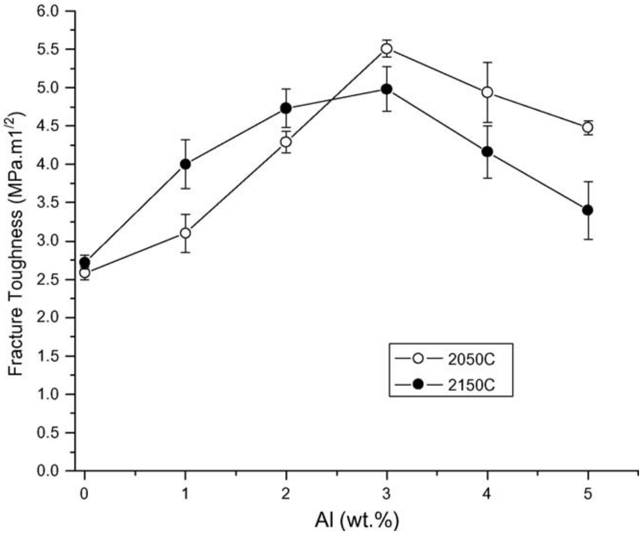

Fig. 11. Effect of Al addition on fracture toughness of sintered B_4C at various temperatures.

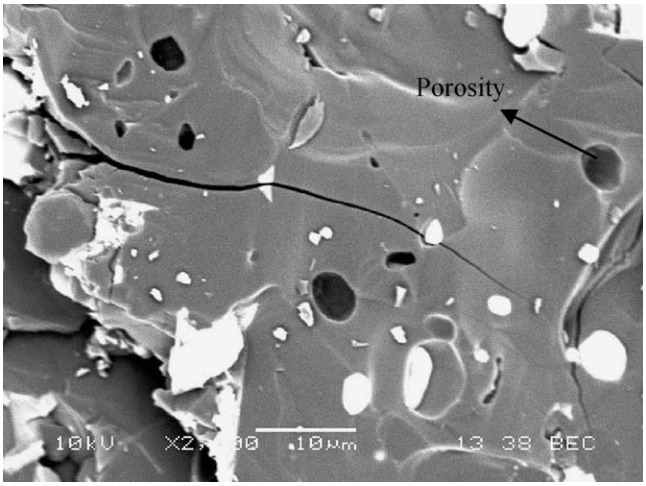

Fig. 12. SEM micrograph of fracture surface of B_4C sintered containing 4 wt% Al sintered at 2050 °C.

aluminium particles; (ii) toughening due to thermal residual stress. In the present situation the reason for toughness increase seems to be the interaction of cracks with tougher Al phase or crack deflection by microcracks around Al compounds phases (Fig. 12). Due to thermal expansion mismatch between Al and B_4C, microcracking can be supposed around Al phase. Furthermore, less porosity is observed in the samples sintered with Al as sintering aid. One can observe that Al additions in excess to 3 wt% and higher sintering temperature lead to lower fracture toughness values. Similarly to hardness trend, this can be accounted for an increase of the grain size. Since increasing grain size decreases the grain boundary, the effect of grain boundary in toughening of sintered B_4C containing Al additive, decreases. Increasing the grain size decreases the bridging length and in conclusion, toughness decreases.

4. Conclusions

- Dense B_4C compacts can be obtained by pressureless sintering at 2050–2150 °C by using Al as sintering aid.
- The addition of Al to B_4C samples increases the shrinkage upon sintering, density and grain size and decreases the porosity of sintered samples.
- Bending strength, hardness and fracture toughness of pressureless sintered B_4C were shown to increase with Al content up to 4 wt% while further additions resulted in a decrease of the mechanical resistance mainly associated to grain growth. Conversely, elastic modulus showed an increase with Al load especially between 1 and 3 wt%.

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