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Effect of Al addition on pressureless sintering of B_4C

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Abstract

The effect of Al addition on pressureless sintering of B_4C ceramic was analyzed in the present work. Different amounts of Al, 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, crystal phases and density evolution were studied and correlated to Al additions and firing temperature. Density and grain size of sintered samples, increased significantly with Al load while less evidence is the effect of sintering temperature; 94% dense material was obtained by adding 4 wt.% Al regardless of the maximum firing temperature.
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Keywords: B_4C; Al; Pressureless sintering

1. Introduction

Boron carbide is an important non-metallic hard material with high melting point and hardness and low density as well as high resistance to chemical attack [1–3]. Due to the outstanding properties, B_4C ceramics are regarded as having 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 as wear resistant components [4–7]. However, this wide range of applications is restricted by its low strength and fracture toughness as well as poor sinterability and machinability [8]. Due to the presence of 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. 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 which represents an expensive process [1]. Since pure B_4C is very difficult to densify above 80% of theoretical density, a variety of second phases have been proposed as sintering aids [2]. Even in the presence of sintering additives, in most cases, hot pressing should be performed at high temperatures to obtain fully dense B_4C body. The addition of carbon was found to be an effective sintering additive for B_4C [2,9,10]. A small addition of boron (1–5 wt.%) to the starting boron carbide powder allowed the production of strong materials by sintering temperature around 1900–2000 °C [11]. High density boron carbide samples were prepared also by hot isostatic pressing (HIP) at lower temperature (1700 °C) [2].

In pressureless sintering process, dense components could be obtained by using a starting material of fine size in the range of <3 μm and a sintering temperature of 2250–2350 °C. To increase the volume and grain boundary diffusion and, therefore, to promote densification at lower temperatures, different additives are proposed such as Si, Al, Mg, SiC, SiC + Al, TiB_2 + C, etc. [1]. Levin et al. and Goldstein have shown that the addition of TiO_2 [12] and ZrO_2 [13] to boron carbide powders improves the density values to 95–97% by sintering temperature around 2200 °C. A promising method is the use of organic precursors, e.g. polycarbosilane with small

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amount of phenolic resin [2]. The effects of additives such as TiC, WC and BN were examined, with limited success [14,15]. Alternatively, B_4C–TiB_2 composites were investigated to improve both strength and toughness [16,17]. B_4C reacts with other oxides during sintering to form new compounds that might be detrimental with regard to the unique properties of B_4C. Nevertheless, it has been observed that the addition of small amounts of Al_2O_3 increases the sinterability of B_4C remarkably [18]. 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 [6,8,18]. 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 non-oxide ceramics with high covalency, such as silicon carbide and silicon nitride [8].

Aluminium is preferred for the development of B_4C-cermets 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 carbide–aluminium cermets have the potential for offering a combination of high hardness and toughness in a lightweight structure [19]. It has been reported 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 may be activated [20].

In the present study, the influence of Al addition as a sintering aid on the densification behaviour of pressureless sintered B_4C has been investigated.

2. Experimental procedures

The starting materials used in the present study consists 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. It was likely to have WC contamination in the powder mixture. To remove WC contamination the powder mixture 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 $50 \times 50 \times 10$ mm^3 samples in stainless steel mold. In order to increase green strength, the tiles were CIPed at 180 MPa. Each tile was cut to bars in size of $10 \times 10 \times 50$ mm^3 and then polished with SiC paper (320 grits) in order to remove the surface defects. Samples were heated in order to burn out phenolic resin. Green samples were then sintered using a microprocessor controlled graphite element furnace. Sintering was carried out in the furnace under Ar atmosphere up to the sintering temperature using a heating rate of 10 °C/min and dwell time equal to 1 h.

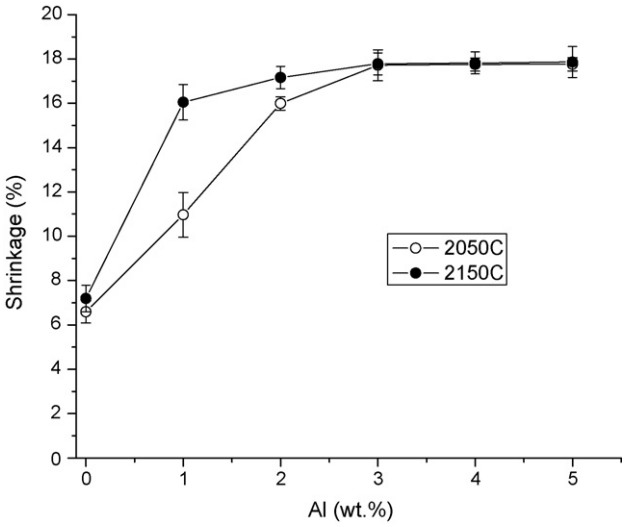

Fig. 1. Effect of Al addition on shrinkage of B_4C sintered at various temperatures.

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 electrically etched in a 0.1% KOH solution with a current density of 0.1 A/cm^2 for 60–120 s [21]. The microstructure of the specimens was observed using a scanning electron microscope (SEM) (JEOL, JSM-5500) and optical microscope (Zeiss, Axio-Imager.A1m). The bulk chemical composition of the metal containing phases was determined by energy dispersive X-ray spectroscopy (EDXS) [22]. The mean grain size of sintered samples was calculated by using the line

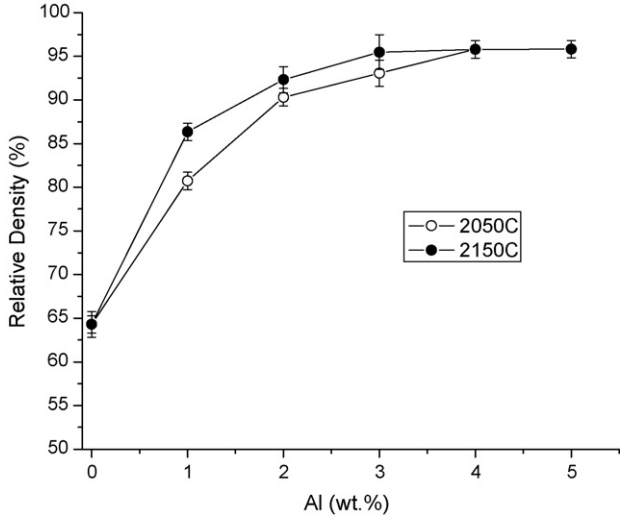

Fig. 2. Effect of Al addition on relative density of sintered B_4C samples at various temperatures.

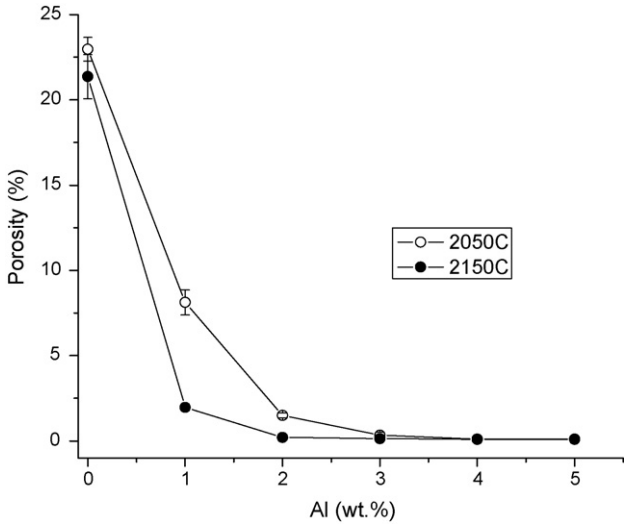

Fig. 3. Variation of porosity of B_4C samples sintered at various temperatures as a function of Al addition.

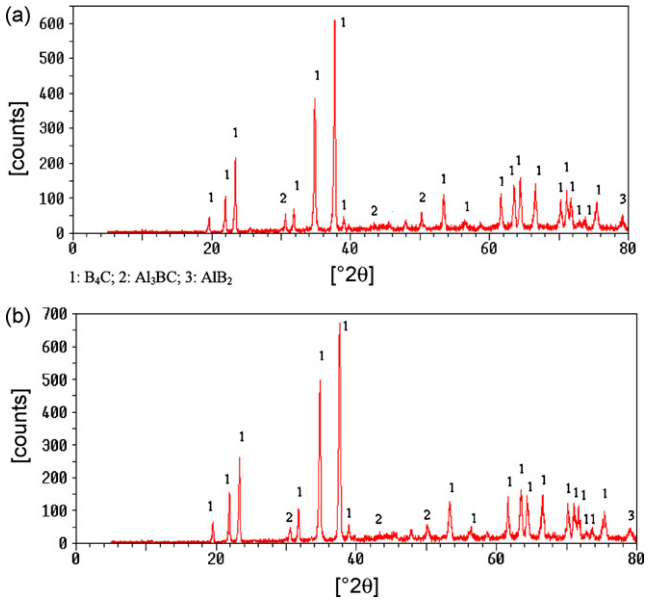

Fig. 4. XRD patterns of B_4C samples containing 5 wt.% Al sintered at. (a) 2050 °C and (b) 2150 °C.

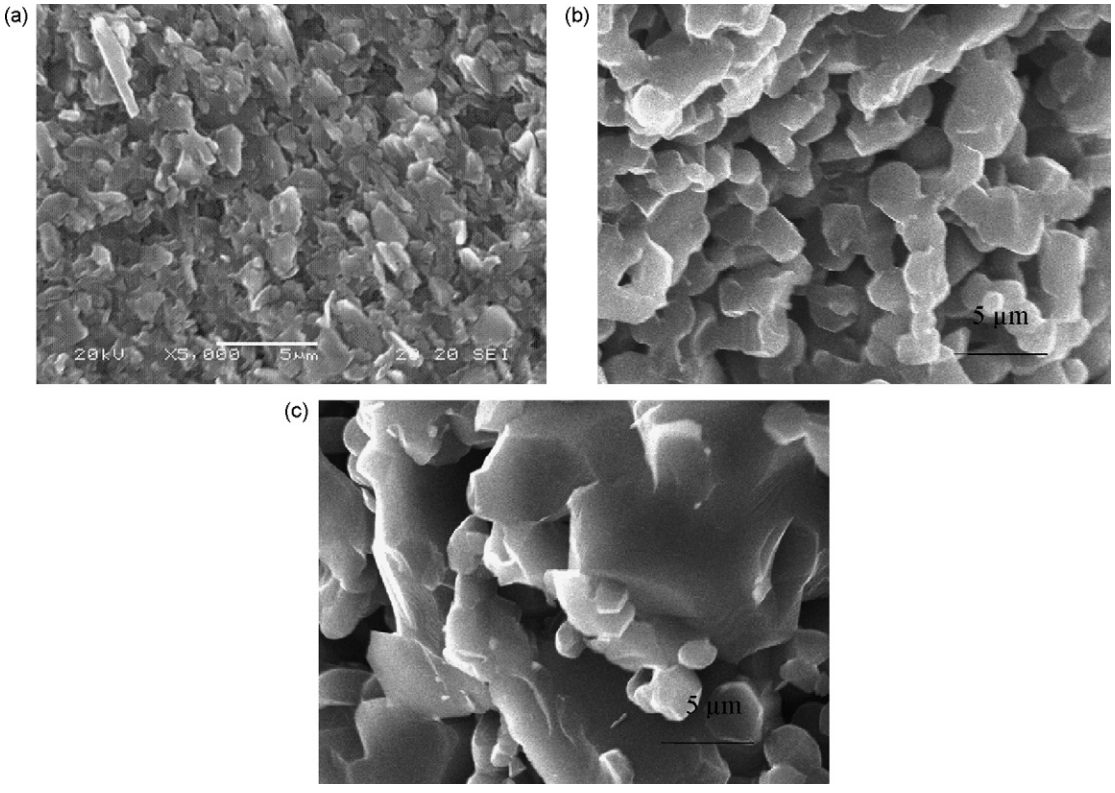

Fig. 5. SEM micrographs of B_4C samples: (a) green; (b) sintered at 2050 °C; (c) sintered at 2150 °C.

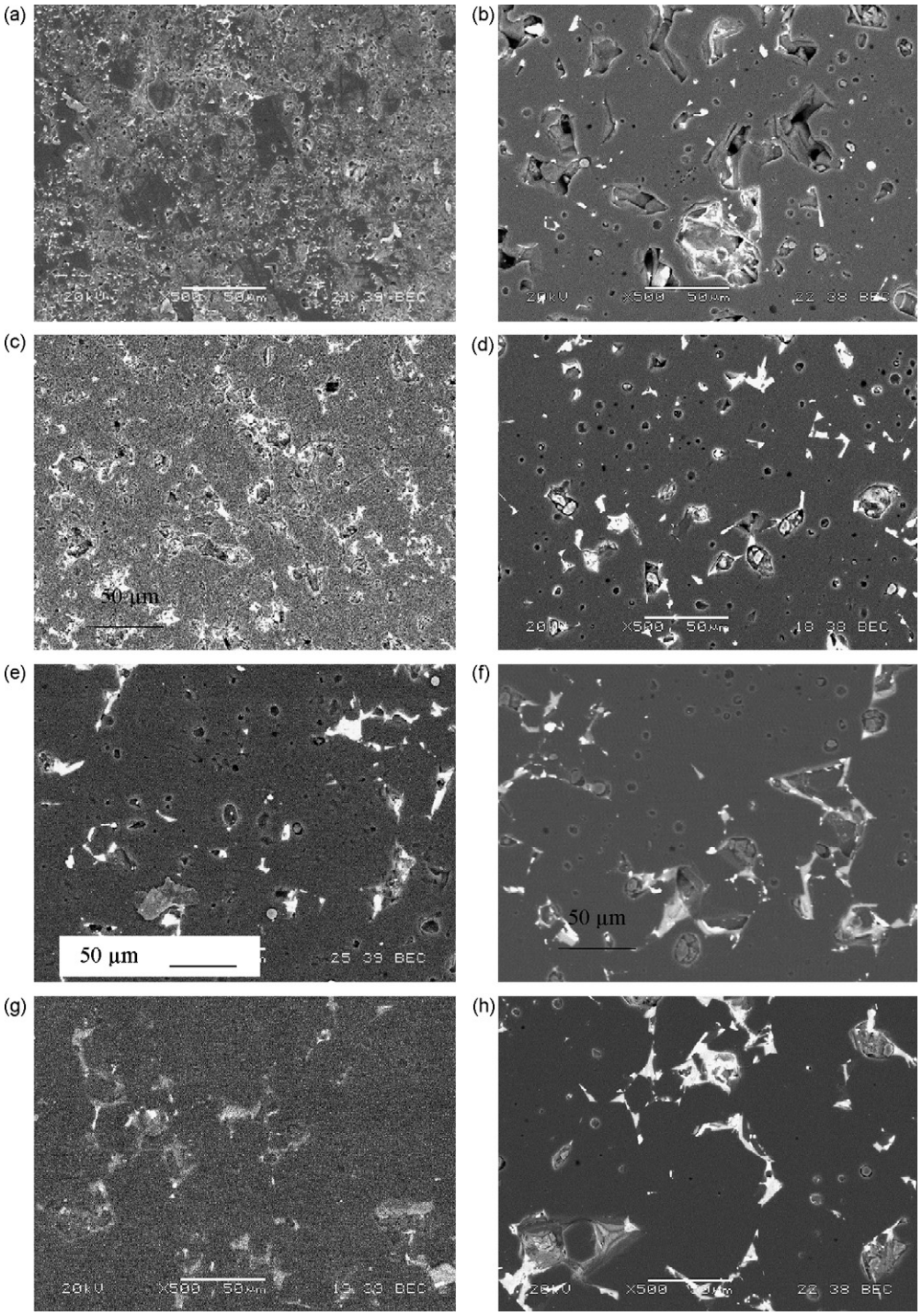

Fig. 6. SEM micrographs of sintered B_4C samples at various temperatures and containing different values of Al: (a) 2050 °C, 1 wt.%; (b) 2050 °C, 2 wt.%; (c) 2050 °C, 3 wt.%; (d) 2050 °C, 4 wt.%; (e) 2150 °C, 1 wt.%; (f) 2150 °C, 2 wt.%; (g) 2150 °C, 3 wt.%; (h) 2150 °C, 4 wt.%.

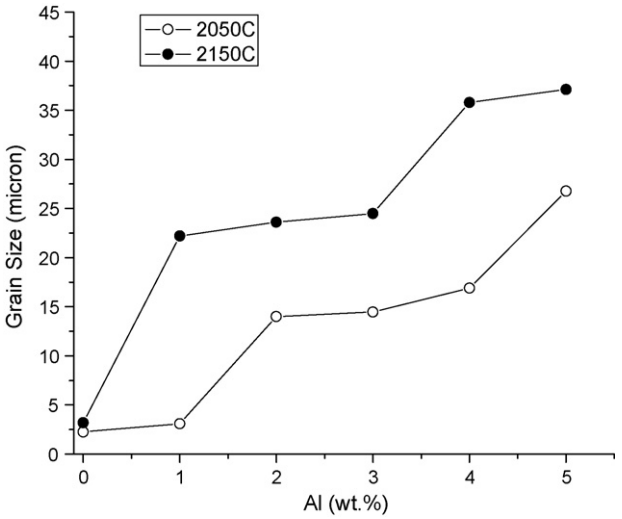

Fig. 7. Effect of Al addition on grain size of sintered B_4C at various temperatures.

intercept method in SEM micrographs [23]. Bulk density and open porosity of the samples were measured by Archimedes method. An approximate theoretical density was calculated for the various compositions of B_4C–Al system. The phases were characterized by X-ray diffraction (XRD) (Philips, model Xpert) technique by using Cu Kα.

3. Results and discussion

The effect of Al addition on shrinkage of B_4C sintered at 2050 and 2150 °C is shown in Fig. 1. Adding Al and increasing the sintering temperature increases shrinkage of the sintered B_4C samples. Therefore there is no doubt that Al addition improves the sintering behaviour of B_4C samples.

Fig. 2 shows the effect of Al addition on relative density of B_4C samples sintered at 2050 and 2150 °C. It is shown that relative density of B_4C sample sintered at 2050 °C and without additive is similar to the samples sintered at 2150 °C. Therefore it can be concluded that pure boron carbide cannot be sintered completely in the absence of pressure even at a high temperature such as 2150 °C. In this figure one can observe that Al addition results in an obvious increase of density. Since the density of Al (2.70 g/cm^3) is about the density of B_4C (2.52 g/cm^3), the recorded increase in the relative density after Al addition must be associated to intensive sintering development. It also shows that relative density increases for Al content up to 4 wt.% for both the temperatures considered in the present work (2050 and 2150 °C); more than 96% of theoretical density is obtained. For Al load above 4 wt.%, relative density of B_4C samples is almost constant.

Fig. 3 shows the effect of Al addition on porosity of sintered B_4C samples at 2050 and 2150 °C. It is observed that the porosity of the sintered B_4C at 2050 °C without Al additive is about 23% and with no decrease in porosity for the samples sintered at 2150 °C. Addition of 1 wt.% of Al determines a significant decrease of porosity. According to the density results, porosity decreases for Al additions up to about 4 wt.% leading to an open pore-free material.

Fig. 4 shows the XRD patterns of sintered B_4C at 2050 and 2150 °C containing 5 wt.% Al. Three fundamental crystallographic phases are detected in the sintered samples: B_4C, Al_3BC and AlB_2 phases. Because Al melts and reacts with B_4C to form solid ceramic phases and then porosity is decreased and shrinkage is increased. Boron carbide reacts strongly with Al and phases: 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 $AlB_{40}C_4$ are formed [3,4,24]. Liquid Al (it melts at about 660 °C) at sintering temperature has lower contact angle with solid B_4C and moves between B_4C particles. It reacts with B_4C and some of the above mentioned phases, based on the process conditions and the amount of Al addition, are formed. In this work because of the processing conditions and Al amount, the phases of AlB_2 and Al_3BC are formed.

The microstructure evolution of the samples with different sintering temperature and Al content were analyzed by SEM observations. The limited sintering pointed out previously for pure B_4C can be appreciated from the micrographs illustrated in Fig. 5. One can observe the evident porosity present in the samples heated both at 2050 and 2150 °C as well as the grain growth; changes in grain morphology (that appear slightly larger and more rounded after heating) and necks formation can be pointed out.

Fig. 6 shows the microstructure of boron carbide samples sintered at 2050 and 2150 °C containing different values of Al. The addition of even small amount of Al changes the microstructure considerably. As Al content increases, more dense 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 this figure black and dark grey are pores and B_4C, respectively. In this figure lighter area in grain boundaries are AlB_2 and Al_3BC. Obviously by increasing Al amount this area is larger and porosity is decreased.

Fig. 7 shows the grains size in sintered B_4C at 2050 and 2150 °C and containing different Al amounts by the linear intercept method of SEM micrographs. More addition of Al to B_4C, results in larger grains size. In B_4C–Al system the mechanism of sintering is liquid phase sintering and liquid phase increases the grain growth because it fills pores and then the distance between particles is smaller and diffusion is faster [25]. It is interesting to observe that in the presence of Al an increase of sintering temperature determines a larger grain size. By adding more than 3 wt.% of Al the grain growth is considerably high. This is confirmed from SEM micrographs illustrated in Fig. 8. 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. Grain growth is controlled by diffusion, and liquid phase and temperature are two important factors for diffusion.

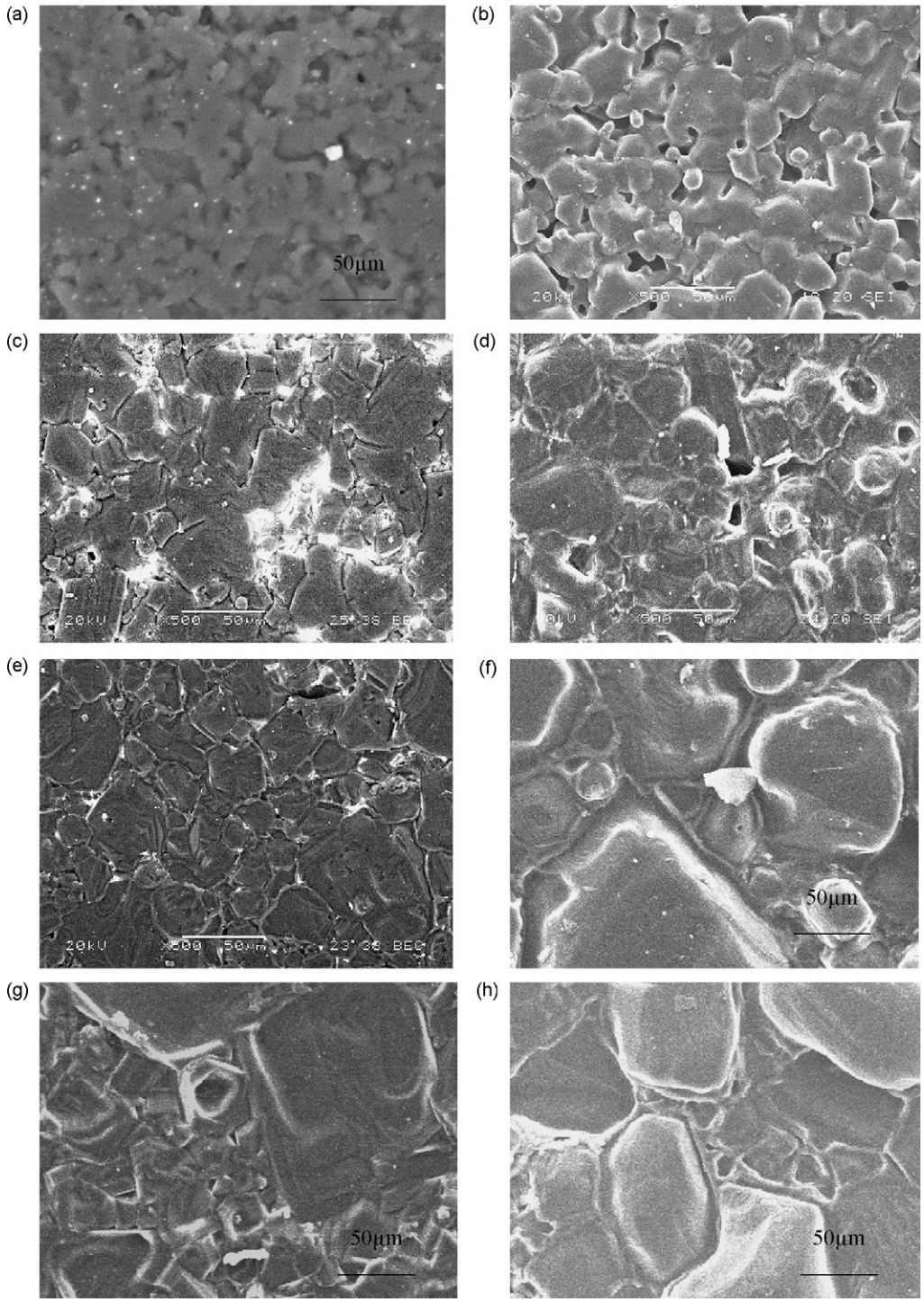

Fig. 8. SEM micrographs of sintered B_4C samples at various temperatures and containing different values of Al: (a) 2050 °C, 1 wt.%; (b) 2150 °C, 1 wt.%; (c) 2050 °C, 2 wt.%; (d) 2150 °C, 2 wt.%; (e) 2050 °C, 4 wt.%; (f) 2150 °C, 4 wt.%; (g) 2050 °C, 5 wt.%; (h) 2150 °C, 5 wt.%.

4. Conclusion

- A very dense B_4C compact is obtained by using at least amount of Al additive and by pressureless sintering method.
- B_4C and Al react and useful phases of Al_3BC and AlB_2 are formed.
- Addition of Al to B_4C samples increases the density and the grain size and decreases the porosity of sintered samples at various sintering temperatures.
- Rising the sintering temperature from 2050 to 2150 °C increases the density and the grain size and decreases the porosity of sintered samples in different amount of Al addition.

- By adding Al even 1 wt.% and sintering at 2150 °C the shrinkage of sintering will be considerably.

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