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Effect of passivation and precipitation hardening on processing and mechanical properties of B_4C–Al composites

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Abstract

Boron carbide–aluminium composites were produced by infiltrating aluminium alloys into porous boron carbide preforms at different temperatures under an argon gas atmosphere.

Aim of this study was controlling the reaction between starting constituents by the use of various heat treatments. In order to reduce consumption of the starting constituents (B_4C and Al) due to formation of reaction products, a thermal passivation process was employed to the as-received B_4C powders, which facilitates easier and faster infiltration of liquid Al into the porous compacts at temperatures as low as 900 °C.

The Al constituent of the composites was then subjected to a precipitation hardening heat treatment to further improve their bending and compressive strength. This heat treatment was observed to result in a remarkable increase in both the bending and compressive strengths of the composites.

Keywords: B. Composite; Infiltration; Passivation; Precipitation hardening; Compressive strength

1. Introduction

B_4C–Al composites have a potential to be used as armour materials in body protection, helicopters, military aircrafts and vehicles where lightweight is of utmost importance. For such kind of applications mechanical properties such as hardness, bending strength, compressive strength, elastic modulus and fracture toughness need to be balanced carefully along with low density and a homogeneous microstructure almost free of pores.

B_4C imparts high hardness, elastic modulus and compressive strength to the composite. Al, which is one of the lightest metals and that also has a low melting point, is commonly used to increase the fracture toughness of the composite to an acceptable level and to render fabrication of these composites in a cost-effective manner through employment of novel processing routes such as pressureless melt infiltration. The pressureless infiltration method has many advantages over hot pressing which is widely used, for example, in the production of monolithic B_4C. In hot pressing, forming shapes other than flat plates is inherently more difficult. Processing costs are also much higher compared to other methods such as pressureless melt infiltration.

Producing B_4C–Al composites having the desired properties described above requires a strict control of the character and quantity of each component present in the initial powder compact as well as in the final product. A powder compact rich in B_4C is crucial to keep the hardness, strength and elastic modulus of the composite at sufficiently high values. This can be achieved by adjusting the packing density of the powder mixture to result in compacts having green densities of around 70% or higher.

It is known that B_4C strongly reacts with Al, starting from temperatures at about 500 °C [1–3], resulting in a variety of binary and ternary compounds. However, at a temperature range between 900 °C and 1125 °C main reaction products formed are Al_3BC and AlB_2. At higher temperatures Al_3BC may be replaced by Al_4C_3 and compounds richer in boron. Since unless precautions are taken, the reaction rates between

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as-received B_4C powders and liquid Al (alloys) are generally too fast to ensure the formation of reaction products in a controlled manner, the fast reaction kinetics between the starting constituents may result in (i) depletion of the metallic phase before complete infiltration of the porous compact is achieved, (ii) a composite with a composition completely different from the initial one and (iii) the formation of a reaction layer which may act as a barrier against further infiltration of liquid Al, resulting in an adverse impact on the overall composite properties [1].

Successful attempts to accelerate Al infiltration by application of pressure or modification of the surface of B_4C powders were reported in literature. Lee and Kang [4] coated B_4C powders with $Ti(OH)_4$ and converted the coated layer to TiB_2 via sol–gel processing in order to enhance wettability of B_4C powders with Al melt. Kouzeli et al. [5] applied an argon gas pressure of 8 MPa to ensure infiltration. Jung and Kang [6] mixed B_4C powders with Ti-based compound powders to shorten processing time and to lower processing temperature by enhancing wettability of Al.

In this study, in order to lower reactivity between Al and B_4C, a thermal passivation treatment was employed to as-received B_4C powders prior to compaction. The theory of passivation is based on the studies of Pyzik and Aksay [1]. They found that when B_4C is heated up to a temperature between 1250 and 1800 °C the reactive surface boron designated as B_3', is converted into a less reactive form, designated as B_3. The reduced reactivity between B_4C and Al results in a decrease in the amount of reaction products and thus an increase in the amount of starting materials remaining in the final composite. Thermal passivation treatment renders it possible to accelerate infiltration without any additional processing steps such as coating or the application of an external pressure.

The aim of this work, therefore, was to show quantitatively, that application of a passivation heat treatment to the starting B_4C powders followed by a classical precipitation hardening heat treatment to Al present in the composites after infiltration is an effective combination to control the reaction rate between B_4C and Al, and the mechanical properties of the produced composites, without significantly altering the chemical composition of the starting powder mixture.

2. Materials and methods

B_4C–Al composites were produced by melt-infiltrating Al alloys (4.4% Cu, 1.5% Mg, 0.6% Mn, 0.5% Si) [7] into porous B_4C preforms under a flowing argon gas atmosphere. Passivation and infiltration steps were employed in graphite crucibles. The preforms were prepared by first uniaxially (100 MPa) and then cold isostatically (300 MPa) pressing the fine (<10 μm), coarse (22–59 μm) and the mixture of starting B_4C powders (Alfa Aesar, Germany). Infiltration temperatures chosen were between 900 and 1300 °C. Heating and cooling rates were set to 10 °C/min.

A thermal passivation process was employed to the as-received B_4C powders prior to compaction. The passivation process included heat-treating the starting B_4C powders at 1400 °C for 2 or 4 h [8]. After compaction, Al alloy blocks (AA2024) were infiltrated into porous compacts under an argon gas atmosphere. Mechanical properties of the Al alloy are given in Table 1 [9].

Table 1
Mechanical properties of the 2024 Al alloys before and after precipitation hardening heat treatment [9].

	σ_{yield} (MPa)	$\sigma_{tensile}$ (MPa)	Hardness (H_B)
AA 2024	76	185	47
2024 (precipitation hardened)	325	470	120

Composites prepared by melt-infiltration were then subjected to a precipitation hardening heat treatment in order to investigate its effects on the mechanical properties of the overall composite. The classical precipitation hardening heat treatment cycle applied to AA 2024 was 2 h of solutionizing at 500 °C followed by 24 h of aging at 120 °C [7].

X-ray diffraction (Rigaku Rint 2200, Tokyo, Japan) was performed using monochromatic CuK_α radiation ($\lambda = 1.5406$ Å). Microstructural characterization of the composites was performed with a scanning electron microscope (Zeiss Supra 50 VP) attached with an energy dispersive X-ray spectrometer (EDX).

Compression tests were carried out using a fully computer controlled Instron 5581 model mechanical testing machine at a strain rate of $10^{-3}\,s^{-1}$. Specimen size was adjusted to 5 mm × 5 mm × 9 mm with a surface finish with 1200 grid SiC grinding paper. Compressive load was applied on the 5 mm × 5 mm cross section of each sample. Mean compressive strength values were obtained by taking the average of 5 specimens' test results.

Bending tests were performed with a 4-point bending attachment in a universal testing machine (Instron, Series IX, Automated Materials Testing System 1.38). 3 mm × 4 mm × 40 mm sized specimens were bent at a cross-head speed of 0.5 mm/min until fracture occurred according to the ASTM Standard C 1161-94. Specimen surface that was to be subjected to tensile stress during the bending test was polished down to 3 μm diamond solution. Mean bending strength values were obtained by taking the average of 5 specimens' test results.

3. Results and discussion

3.1. Effect of starting B_4C particle size and distribution on microstructure of the composites

B_4C powder size is an important parameter in terms of preform green density. In order to improve the packing density,

Table 2
Green densities of the preforms prepared with different sized B_4C powders.

	Fine B_4C	Coarse B_4C	Bimodal B_4C
Green density (% X-ray density)	55	63	69

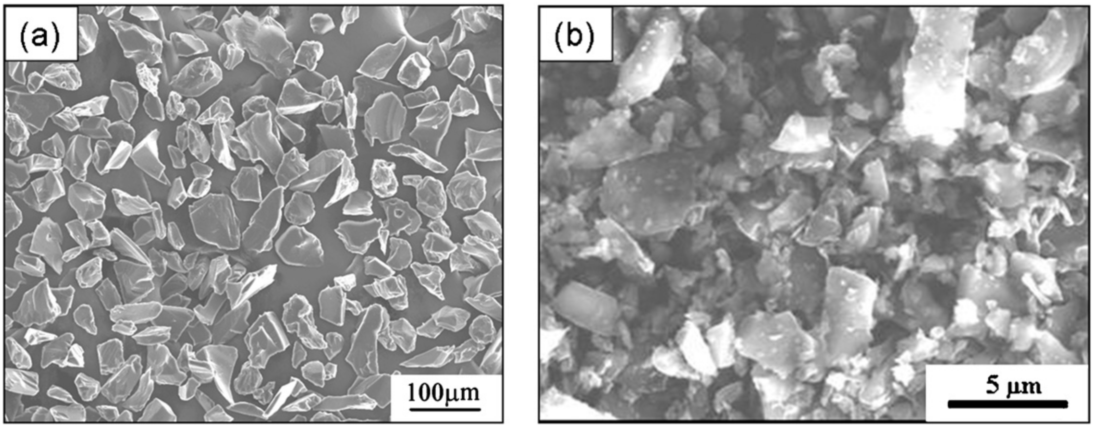

Fig. 1. SEM images of (a) coarse and (b) fine B_4C powders.

bimodally distributed B_4C powders were used. According to the Furnas Model [10], when two different sized powders having a size ratio of about 1:7 are considered, the highest packing density is achieved by mixing 25 wt% of fine powders with 75 wt% of coarse powders. In fact, the green density of the compacts was observed to increase from 55 (fine B_4C) or 63% (coarse B_4C) to 69% when the fine and coarse B_4C powders were mixed (Table 2). SEM images of coarse and fine B_4C powders showed that both of them are chunky in shape (Fig. 1). The relatively higher green density of compacts fabricated from coarse B_4C powders with respect to those obtained from fine B_4C powders may be mainly attributed to the difference in their particle size distribution (Fig. 2). Coarse powders have a wider size distribution which is an advantage in terms of higher density packing.

The size and distribution of the starting B_4C powders had a considerable effect on the mechanical and microstructural properties of the final product. Fig. 3 shows the SEM microstructures of the three composites produced from different B_4C particle size and distributions. The black points in Fig. 3a represent fine B_4C particles whereas the light grey areas show the matrix metal. The white regions show the metal matrix relatively rich in heavy alloying elements such as Cu. The dark grey regions consist of reaction products (mainly Al_3BC) that formed during infiltration. Coarse B_4C particles are clearly seen in Fig. 3b and c. Slightly darker areas in light grey background represent reaction products in Al matrix. It is obviously seen that composites produced from fine starting B_4C powders include larger amounts of reaction products when compared to those that were produced from the coarse ones.

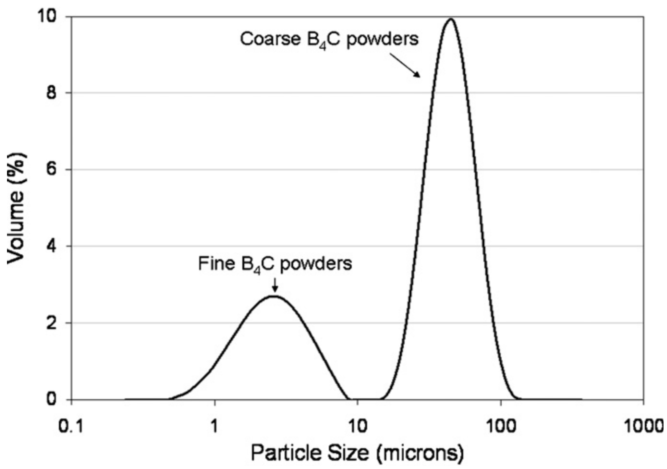

Fig. 2. Powder size distribution of coarse and fine B_4C powders.

Bulk densities of the composites produced by melt-infiltration in the temperature range 900–1300 °C were determined to be above 99% of the X-ray density. The SEM micrographs confirm the high bulk density of the products as almost no pores are visible (Fig. 3).

3.2. Effect of passivation on reaction between starting constituents

Changing the surface character of B_4C powders, namely applying a passivation heat treatment, affected the microstructure, infiltration characteristics and mechanical properties of the composites positively.

Fig. 4 shows the XRD profiles of the composites produced from passivated and as-received B_4C powders. Intensities of Al and B_4C peaks in the XRD spectrum of the composites produced from passivated B_4C powders are observed to be higher than that of those produced from as-received B_4C powders. This shows that passivation causes more Al, and thus B_4C, to remain unreacted in the system.

The use of passivated starting powder was found to accelerate the infiltration process. This may possibly indicate that the passivation process helps improving the wettability of B_4C by Al leading to an improvement in the infiltration rate of the liquid metal through the channels in the porous pellet. It is also likely that even when wettability is not improved, the infiltration process may be accelerated, by means of a speedy flow through the pore channels of powder corners. This resulted in infiltration of Al alloys into the porous B_4C compacts at

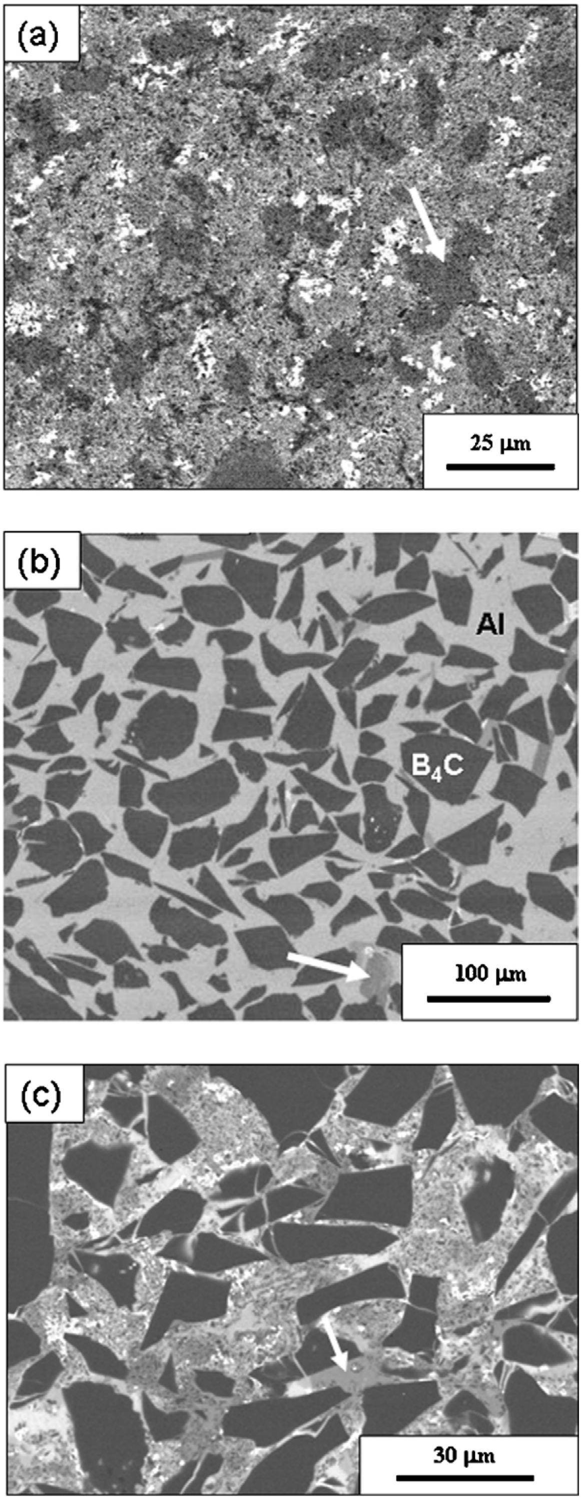

Fig. 3. SEM micrographs of the composites produced from (a) fine (<10 µm) and (b) coarse (22–59 µm) and (c) bimodal size B_4C powders. Arrows show reaction products.

temperatures as low as 900 °C provided that the holding time is extended from 10 min to 60 min.

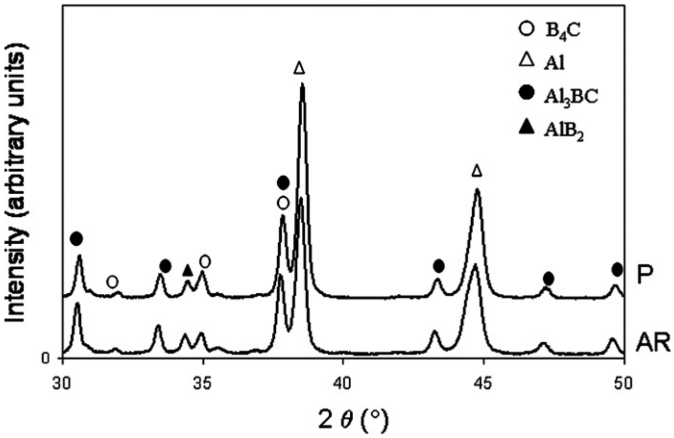

Fig. 4. XRD profiles of the B_4C–Al composites produced from passivated and as-received B_4C powders. P: passivated, AR: as-received.

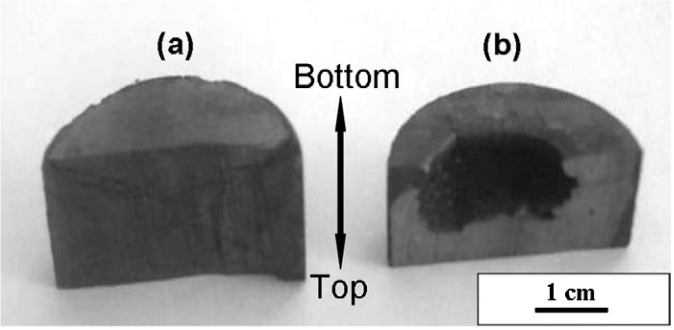

Fig. 5. The cross sectional views of the composites produced from (a) passivated and (b) as-received fine B_4C powders both infiltrated at 1100 °C for 10 min.

Fig. 5 shows the cross sectional views of the two composites produced from fine B_4C powders infiltrated at 1100 °C (10 min holding). It is clearly seen that Al was fully infiltrated into the porous B_4C compact with 8 mm height reaching the bottom of the pellet produced from passivated B_4C powders (Fig. 5a) whereas there exists an uninfiltrated zone in the pellet produced from as-received B_4C powders (Fig. 5b). This confirms the hypothesis that the thermal passivation heat treatment increases the infiltration rate and that in the absence of it the reaction rate between B_4C and Al is observed to be faster than the infiltration rate of the liquid metal through the pore channels. This may result in uninfiltrated regions, especially in locations far away from the metal source, due to the local depletion of the metal phase.

3.3. Effect of precipitation hardening heat treatment on mechanical properties

3.3.1. Bending strength

The effect of a precipitation hardening heat treatment on the bending strength of the composites was also investigated. The obtained results indicate that a remarkable increase is observed in the bending strengths. Table 3 shows effect of precipitation hardening on bending strengths of the composites produced from passivated B_4C powders. A strength increase of 79 and

Table 3
Bending strengths of the heat treated and as-infiltrated composites.

	<10 μm B_4C	22–59 μm B_4C
Bending strength after infiltration (MPa)	370 ± 25	543 ± 22
Bending strength after heat treatment (MPa)	662 ± 90	678 ± 69
[12]	600–700	
[11]	440–480	

25% in the composites produced from <10 μm and 22–59 μm B_4C powders, respectively, was achieved.

When the obtained results are compared with the data in literature, it is seen that much higher strength values are provided than that in the work of Pyzik and Nilsson [11] in which no post-infiltration heat treatment was applied to the composites. Furthermore, strength values are similar to those of Pyzik et al. [12] in which a post-infiltration heat treatment was applied to the composites. Pyzik et al. [12] carried out a heat treatment process at temperatures between 625 and 1200 °C in order to allow further formation of ceramic reaction products, and thus to increase bending strength of the composite. On the other hand, in this study, utilization of the precipitation hardening heat treatment resulted in a considerable increase in bending strengths with an insignificant loss of the Al phase due to the lower heat treatment temperature (500 °C) which is expected to be accompanied by an improved ductility and toughness.

3.3.2. *Compressive strength*

Starting powder size, passivation and precipitation hardening heat treatments were found to significantly affect the compressive behaviour of the composites. Composites produced from B_4C powders passivated for 2 and 4 h did not show any clear tendency in terms of strength (Table 4). However, it is clear that that composites subjected to a precipitation-hardening heat treatment after the infiltration step have higher compressive strength values when compared to their respective as-infiltrated counterparts. This strength increase might also be attributed to formation of Al_3BC phase during solutionizing treatment which is a stage of the precipitation hardening heat treatment. However, Viala et al. [3] reported that XRD line of Al_3BC was too weak to ensure the presence of this phase in the composites heated up to 1173 °C for 160 h. This finding implies that formation of Al_3BC during aging at 500 °C for 24 h is not very probable.

Although higher preform density (in bimodal case) resulted in higher amount of B_4C in the final product, compressive strength of the composites produced from fine B_4C powders was found to be nearly equal to those produced from bimodal powder. This may be attributed to the ease of crack propagation in the coarse B_4C particles of the bimodal composites (Fig. 6a). Fig. 6a also reveals the strong interfacial bonding between B_4C

Table 4
Compressive strengths of the produced composites in as-infiltrated and heat treated states.

	Precipitation hardened (MPa)		As-infiltrated (MPa)	
	2 h passivation	4 h passivation	2 h passivation	4 h passivation
Bimodal	1296.7 ± 49.8	1360.6 ± 9.1	1003.6 ± 81.1	950 ± 47
Fine	1320 ± 16.0	1222 ± 35.3	1056.8 ± 24.7	1044.9 ± 23.6
Coarse	914 ± 53.2	1068.3 ± 10.6	639 ± 37	645.4 ± 7.5

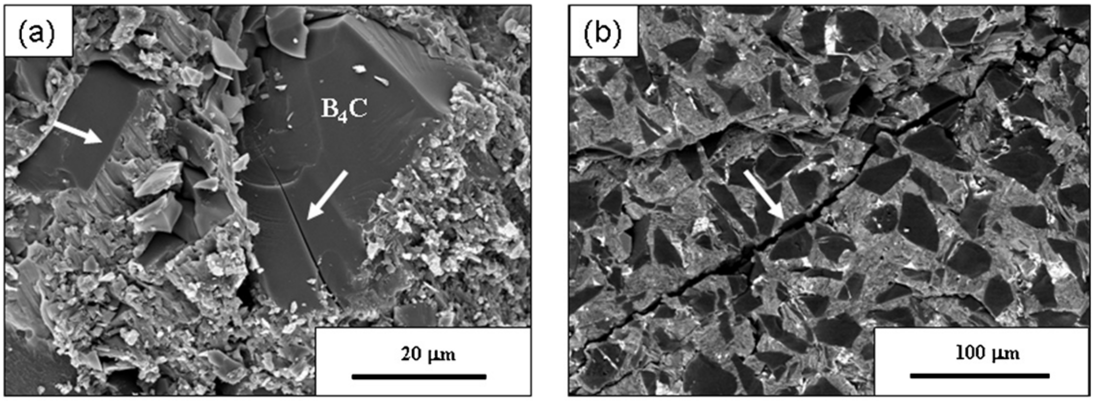

Fig. 6. Fracture surface of the composites produced from bimodal sized passivated B_4C powders: (a) strong interfacial bonding between B_4C and reaction products and (b) linear crack propagation.

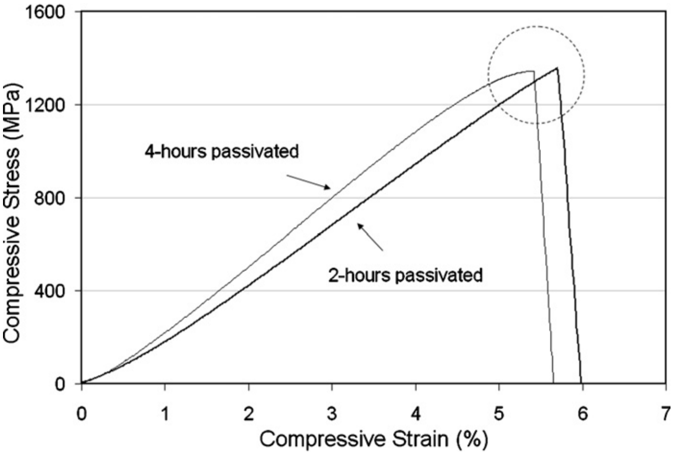

Fig. 7. Compressive behaviour of the two bimodal composites produced from 2 and 4 h passivated B_4C powders by infiltrating Al at 1200 °C for 10 min.

particles, reaction products and Al matrix (shown by the arrow). Fig. 4 (b) shows crack propagation in the composites produced. Crack propagates rather in a linear manner cracking coarse B_4C particles which also reveals the strong interfacial bonding between the phases.

Fig. 7 shows the compressive stress- strain diagram of the two composites produced from 2 and 4 h passivated B_4C powders. Although Table 4 displays no clear supremacy of either of the holding times in terms of compressive strength, stress-strain graphs were found to be clearly different. Data obtained imply that longer passivation durations decreased the tendency of reaction between B_4C and Al, leaving more unreacted ductile Al in the matrix. Hence the composite shows a small portion of plastic deformation at high strains. On the other hand, composites produced from B_4C powders passivated for 2 h shows a completely brittle behaviour possibly due to higher amount of reaction between starting constituents resulting in a less fraction of Al remaining in the final composite.

Table 5
The effect of B_4C powder size distribution on the amounts of phases in the composites after infiltration. This table is corresponding to Fig. 8b.

	Phase content (wt.%)		
Starting B_4C powder	B_4C	Al	Al_3BC
Coarse	48	35	17
Bimodal	49	20	31

Fig. 8a compares the compressive stress–strain diagram of as-infiltrated and precipitation hardened composites. While the former composite shows a certain degree of plastic deformation the latter one shows an almost brittle behaviour. This is mainly to be attributed to the controlled conversion of the ductile Al phase to the more brittle reaction product of Al_3BC (Fig. 1). The decrease in the plasticity of the latter composite is accompanied by an increase in the compressive strength, as expected.

In Fig. 8b the compressive behaviour of a composite produced from coarse B_4C powder (in the as-infiltrated condition) is compared with that one of a composite produced from a B_4C powder mixture having a bimodal particle size distribution (subjected to a precipitation hardening heat treatment). The reduced compressive strength, relatively high ductility and significant plasticity of the former one is to be attributed to its lower green density (Table 2), higher susceptibility to crack propagation due to the large B_4C particles, lower amount of total ceramic phase due to the reduced reactivity (surface area of B_4C powder is decreasing with increasing B_4C powder particle size) between the starting constituents (Table 5). Fig. 9b clearly shows how compressive behaviour could be controlled in a wide range without altering composition or infiltration conditions. The fractographs of these composites (Fig. 9) and the data presented in Table 5 provide further evidence to the higher ductility and plasticity of the former composite. The data in Table 5 were obtained by using the ratio of slopes method [13].

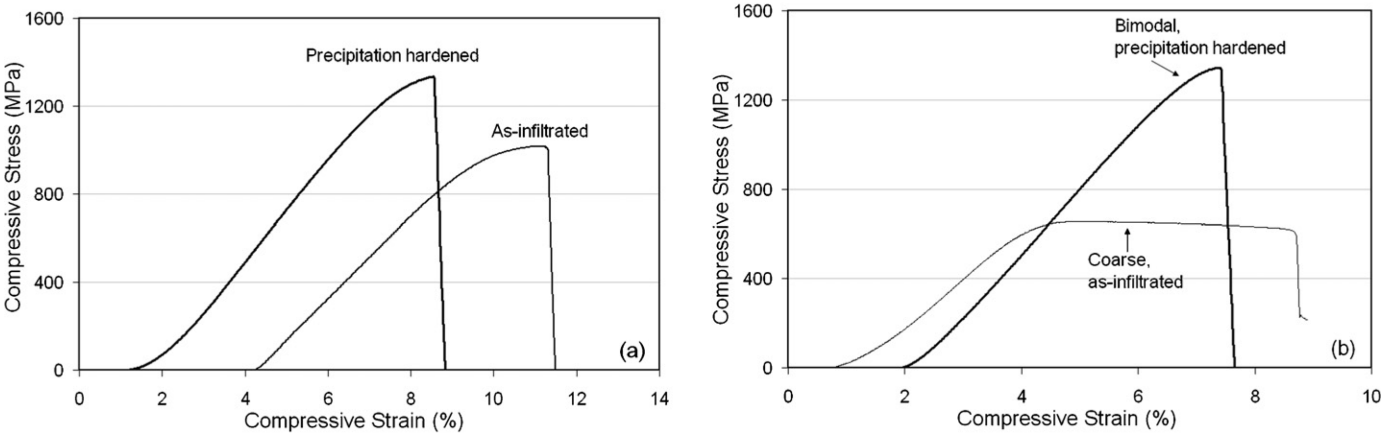

Fig. 8. Compressive stress–strain graphs showing (a) the effect of precipitation hardening and (b) combined effect of B_4C powder size distribution and precipitation hardening heat treatment (graphs were shifted to right to ease distinguishing).

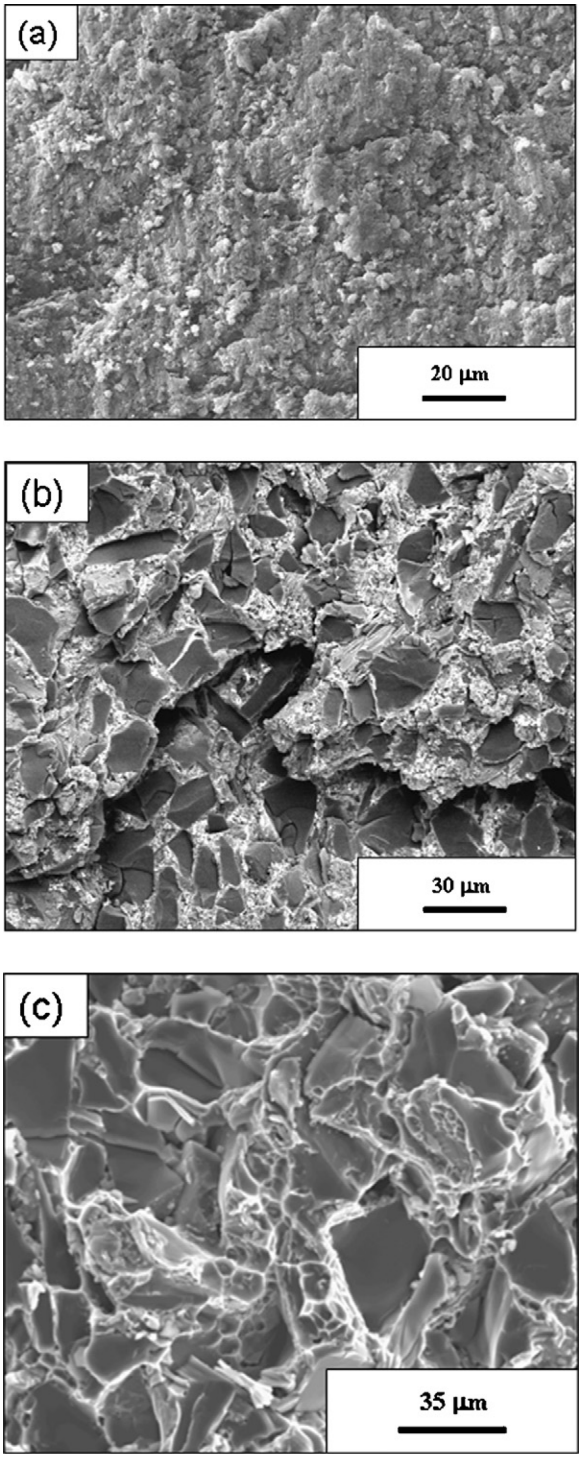

Fig. 9. Fracture surfaces of the composites produced from (a) fine, (b) bimodal, and (c) coarse B_4C powders.

4. Conclusions

Boron carbide–aluminium composites were produced by infiltrating AA2024 aluminium alloys into porous boron carbide preforms at different temperatures in the range of 900–1300 °C under an argon gas atmosphere. Passivation of B_4C powders rendered it possible to produce B_4C–Al composites even at 900 °C. The reaction rate between B_4C and Al was found to depend on the infiltration temperature, holding time, particle size and surface chemistry of B_4C powders. A considerable effect of precipitation hardening heat treatment on bending strength and compressive behaviour was observed without necessarily increasing the brittleness of the composite by the consumption of the ductile phase thanks to the low heat treatment temperature (precipitation hardening of the Al phase).

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