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INTERFACE SCIENCE

Pre-treatment process of B_4C particles to improve incorporation into molten AA2014 alloy

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Abstract The properties of particle-reinforced aluminum alloy composites depend on the microstructure and evolved uniformity distribution of particles in the matrix, wettability of particles by the melt and chemical reactions between particles and matrix. The wettability of B_4C particles by the molten aluminum alloys is generally poor below 1100 °C making their incorporation difficult. In this study, in order to improve incorporation of the B_4C particles by AA2014 alloy melt a novel pre-treatment process was presented and B_4C-2014 Al composites containing B_4C particles up to 12 vol.% were manufactured by using stir casting. SEM observations have shown that uniformity distribution of B_4C in the matrix was satisfactory and there was no reaction at the particle-matrix interface due to low processing temperature. However clustering of B_4C particles was observed in relatively high particle-containing composites, which is commonly associated with the casting route.

Introduction

Metal Matrix Composites (MMCs) have received increasing attention as engineering materials in the recent decades. The introduction of a ceramic reinforcement into a metal matrix produces a composite material with an attractive combination of physical and mechanical properties that cannot be obtained by monolithic alloys [1].

Casting of MMCs is an attractive processing method for these advanced materials since it is relatively cheap, and it offers various options for materials and processing conditions.

A critical step in the processing of cast, particle-reinforced, MMCs is the incorporation of the ceramic particles into the molten matrix alloy. Therefore, in a foundry MMC fabrication method, wettability of the reinforcement particles by the matrix alloy is one aspect of the process that must be optimised. In general, wettability of the reinforcement ceramic particles by a liquid metal is very poor. Good wetting between the solid ceramic phase and the liquid metal matrix is essential condition for the generation of a satisfactory bond between these two during and after the casting [2].

The mechanical properties of MMCs are controlled to a large extent by the structure and properties of this reinforcement-metal interface [3–6]. It is believed that a strong interface permits transfer and distribution of load from the matrix to the reinforcement, resulting in an increased elastic modulus and strength.

In recent years aluminum and aluminum alloy composites reinforced with ceramic particles have been widely investigated. The most of the studies on particle-reinforced composite have been devoted to SiC and Al_2O_3 reinforced composites because of the above-mentioned reasons and research into B_4C reinforced composites is relatively limited. High stiffness, hardness and small density difference between B_4C, aluminum, and aluminum alloys make B_4C an attractive reinforcement [7]. Its high cost compared to SiC and poor wetting by molten aluminum alloys below 1100 °C limits its choice as reinforcement [8, 9].

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The interface chemistry of the B_4C-Al couple has been addressed in several studies [10–14]. Boron carbide and aluminum react at temperatures greater than 700 °C producing AlB_2 and aluminum borocarbide, Al_3BC, which has only recently been identified [11, 15]. Other more complicated phases develop at temperatures greater than 900 °C; however, such temperatures can easily be avoided in processing since the melting point of aluminum is 660 °C. The decomposition mechanisms of boron carbide in liquid aluminum between 700 °C and 900 °C have been summarised by Viala et al. [11]. The formation of these phases degrades the particles and results in composites with poor mechanical properties [10, 11, 16]. These phases may form during prolong working at high temperatures as well as during processing if the production temperature is high. It is therefore important to develop low temperature production methods for B_4C-aluminum alloy composites [17].

Different methods have been studied for wettability enhancement, including addition surface active elements such as magnesium and lithium into the matrix [18, 19], coating or oxidising the ceramic particles [20, 21], pre-treatment of particles [22, 23], cleaning the particle surface by ultrasonic techniques and various etching techniques [17, 24, 25]. Pre-treating and pre-heating prior to the addition of particles assists in removing surface impurities, desorbtion of gases and altering the surface composition [26].

The basic means used to improve wetting [6, 26] are (a) increasing the surface energies of solid, (b) decreasing the surface tension of the liquid matrix alloy, and (c) decreasing the solid–liquid interfacial energy at the particles-matrix interface [27].

The purpose of the present work, therefore, was to: (a) investigate and optimise the pre-treatment process of B_4C particles in order to improve incorporation with liquid AA2014 alloy; (b) present an optimal fabrication process for AA2014/B_4C_p composites by a vortex method; (c) produce the B_4C particle-reinforced metal matrix composite by using the new pre-treatment process for B_4C particles.

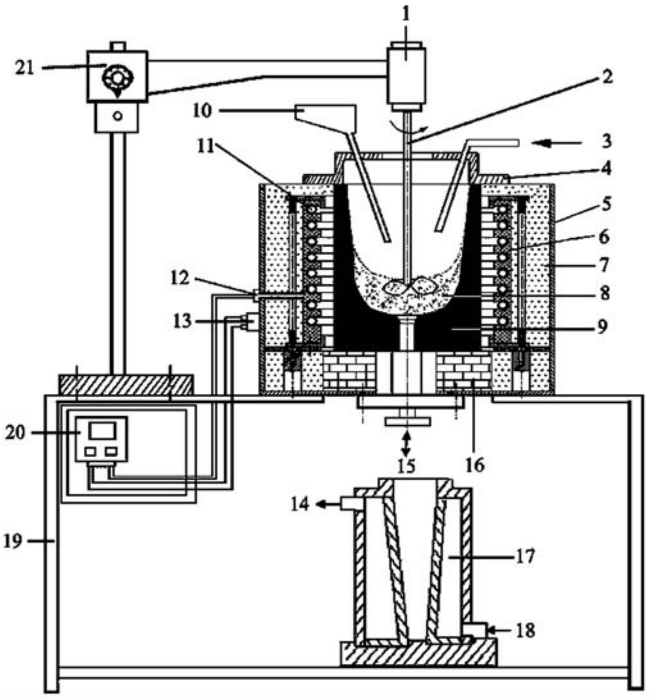
Experimental procedure

In this study, AA2014 alloy was used as the matrix material and B_4C particles as the reinforcement. The AA2014 alloy was supplied by Seydişehir Aluminium Co. in Konya and the B_4C particles were manufactured by Wacker Ceramics Kempten GmbH (Kempten, Germany). The chemical composition (in wt.%) of the AA2014 alloy was as follows: 0.955% Si, 0.269% Fe, 5.570% Cu, 0.656% Mn, 0.742% Mg, 0.006% Zn, 0.019% Ti, 0.002% Cr, with the balance being Al. The average particle size was about 85 µm which varies between 45 µm and 125 µm.

The details of the various pre-treatments and their effects on the status of the B_4C particles in the AA2014 alloy were summarised in Table 1; some of the processes were similar to the techniques introduced in literature [18, 19–24, 28]. In the first group of experiments, pre-treatment of B_4C particles with some alcohols and acids such as C_2H_5OH, HCl, H_2SO_4 and HF was applied for cleaning particle surfaces. In the second group of experiments, pre-treatment of B_4C particles was done by using some alcohols and acids, and then additionally (1–2) wt.% magnesium was added to molten AA2014 alloy. Since boron carbide is slowly attacked in hyrdrofluoric/sulfuric acid or hyrdrofluoric/nitric acid mixtures [29, 30], pre-treatment of B_4C particles was performed by using acid mixture (HF/H_2SO_4), which contributes to the wetting and dispersion improvements of B_4C particles. After the etching process in HF/H_2SO_4 mixture for 3 min, the resulting mixture of acid-B_4C particles was diluted with ethanol and then particles were ultrasonically cleaned in ethanol. Later, the cleaned particles were air dried for 6 h at room temperature and then heated for 24 h at 150 °C. The heated

Table 1 Pre-treatment applied to B_4C paticles and resulting status in AA2014 alloy

Pre-treatment		
No	Process	Status in AA2014 alloy
1	As-received	Particles floating, not incorporated
2	Calcination at 400–800 °C for different times	Particles floating, not incorporated
3	Cleaning in some alcohols and acids + calcination at 400 °C for 3 h	Particles floating, not incorporated
4	Cleaning in some alcohols and acids + calcination at 400 °C for 3 h and addition of (1–2)wt.% Mg to molten AA2014 alloy	Particles floating, not incorporated
5	Chemical Pre-treatment Holding in acid mixture (50 vol.% HF + 50 vol.% H_2SO_4) for 3 min, mixture was diluted with ethanol then ultrasonic cleaning in ethanol and air drying at room temperature for 6 h and then oven drying at 150 °C for 24 h and finally calcination at 400 °C for 3 h	Particles incorporated into melt and uniformly dispersed in melt



1. Stirrer motor, 2. Stirrer shaft and impeller, 3. Argon gas entry, 4. Furnace cover, 5. Body, 6. Ceramic blanket, 7. Glass fibres for heat insulation, 8. Molten metal+particles mixture, 9. Graphite crucible, 10. Reinforcing addition unite, 11. Electrical resistance, 12. Thermocouple, 13. Main power entry, 14. Cooling water outlet, 15. Stopper, 16. Fire brick, 17. Water cooled mold, 18. Cooling water inlet, 19. Experiment table, 20. Temperature controller, 21. Speed controller

Fig. 1 Schematic diagram of experimental set-up for fabrication of B_4C-2014 Al composites

particles were milled and then calcinated for 3 h at 400 °C (Table 1).

Schematic diagram of the experimental set-up was shown in Fig. 1. Thus pre-treated B_4C particles were incorporated and dispersed into molten AA2014 alloy using vortex method under the argon atmosphere in order to prevent oxidation and not to alter the interface properties between the particles and the melt [25]. The alloy was melted in a resistance heated furnace and heated up to 700 °C, which was well above the liquidus temperature of 638 °C, and the dross was skimmed from the surface of the melt before stirring. Temperature control of the melt was done with a precision of ±1 °C. The molten alloy was stirred at a fixed speed of 450 rev min^{-1} at which vortex was formed during the addition of particles using a pre-heated three bladed impeller made of stainless steel. The impeller was driven by an a.c. motor with changeable speed. Stirring was continued for 3 min before the addition of pre-treated and pre-heated B_4C particles. Particles were added using a vibratory feeder at a rate of approximately 10 g per minute. After adding the particles, impeller was driven for 5 min at a lower speed of 350 rev min^{-1}. The slurry was cast into a water cooled cylindirical steel mould at 680 °C by bottom pouring and cooled to room temperature. The steps of the processing of composites were shown in Fig. 2. The cast ingots had a conical shape with a changing diameter, between 40 mm and 70 mm and length of 185 mm. The B_4C particle-reinforced AA2014 aluminium alloy matrix composites containing 3, 6, 9, and 12 vol.% B_4C were produced by using pre-treated B_4C particles. In order to investigate the particle distribution within the ingot, each ingot was sectioned at five different locations as shown in Fig. 3.

Specimens for metallographic observation were prepared by grinding through 800 grit papers followed by polishing with 6 and 0.25 µm diamond paste. Some of the samples were etched with Keller's reagent (1 mL hydrofluoric acid, 1.5 mL hydrochloric acid, 2.5 mL nitric acid and 95 mL distilled water) prior to microscopic examination [31]. Optical microscopy and scanning electron microscopy were used to study the metallographic structures. The amounts of incorporated B_4C particles were obtained by a point counting method [32]. Yield rate was obtained by comparing the amount of added and measured B_4C particles. Drying and calcination of B_4C particles in air was carried out using a 3 kW electrical resistance furnace. An ultrasonic device (CQ-250) were used to clean the B_4C particles. The morphology of the B_4C particles before and after pre-treatment and microstructural characteristics of the resulting composites were investigated by a SEM (JEOL JSM 3600). The qualitative composition of the as-received and pre-treated B_4C particles was determined from X-ray diffraction (XRD) spectra obtained using an XRD spectrometer with Cu K_α radiation.

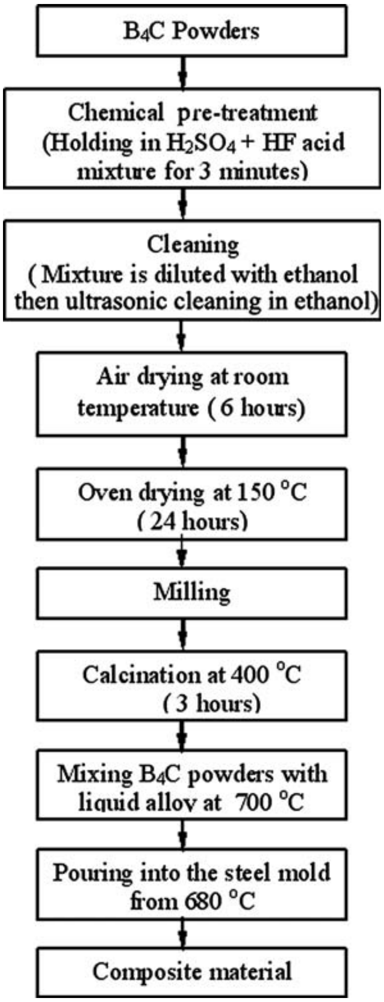


Fig. 2 Processing route of the composites

Results and discussion

The addition of magnesium (Mg) is known to improve wettability of SiC particles [33]. In order to study the effect of Mg addition, experiments were carried out by increasing Mg content of the matrix alloy up to 2.0 wt. %. But microscopic observation on casted samples showed no B_4C particles within the matrix alloy. It was found that the most of the added particles were accumulated at the surface of the ingot. However, pre-treatment with some alcohols and acids such as C_2H_5OH, HCl, H_2SO_4 and HF was also not successful. Experimental results show that cleaning of B_4C particles in an acid mixture (HF/H_2SO_4) contributes to the wetting and dispersion improvements of B_4C particles; therefore, the acid mixture concentration must be 50 vol.% HF + 50 vol.% H_2SO_4 and B_4C particles must be exposed to acid mixture for 3 min. The effects of pre-treatments given in Table 1 suggest that the steps for an optimum pre-treatment process of B_4C particles are (1) cleaning of B_4C particles surface in an acid mixture of the HF/H_2SO_4, (2) dilution of this acid-B_4C particles mixture with ethanol, (3) cleaning B_4C particles in the diluted mixture with ethanol ultrasonically, (3) drying the cleaned B_4C particles for 6 h at room temperature, (5) heating the dried B_4C particles for 24 h at 150 °C, (6) milling the heated particles, and lastly (7) calcinating the milled particles at 400 °C for 3 h. Thus, pre-treated B_4C particles were successfully incorporated and dispersed in the molten AA2014 alloy using vortex method. Moreover, the B_4C particles do not cluster together before addition to the melt.

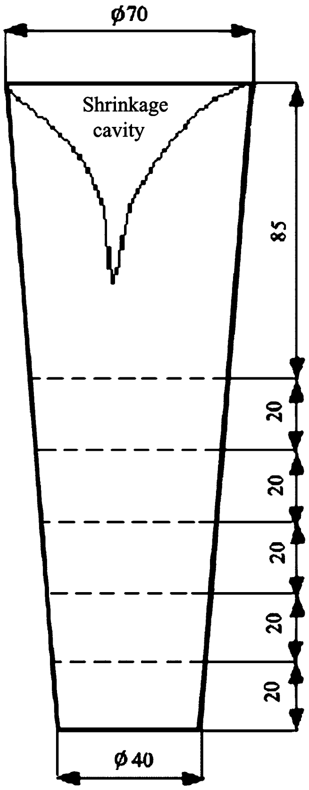


Fig. 3 Schematic diagram showing the locations of metallographic specimens

Li et al. [28] has stated that the SiC particles thus pre-treated can be easily incorporated and dispersed in the semisolid ZA27 alloy slurry. Furthermore, there are many pre-treatment processes which have been developed to improve wettability. These include [25] (a) pre-treatment of silicon carbide by dehydrated sodium tetraborate for infiltration by molten aluminium [34], (b) pre-treatment of carbon by tetraisopropytitanate for infiltration by molten aluminium and magnesium [35], (c) pre-treatment of B_4C by one of the various alcohol or other organic solvent for infiltration by molten aluminium at elavated temperature [36].

SEM micrographs of the as-received and the pre-treated B_4C particles were given in Fig. 4. As seen in Fig. 4a, the

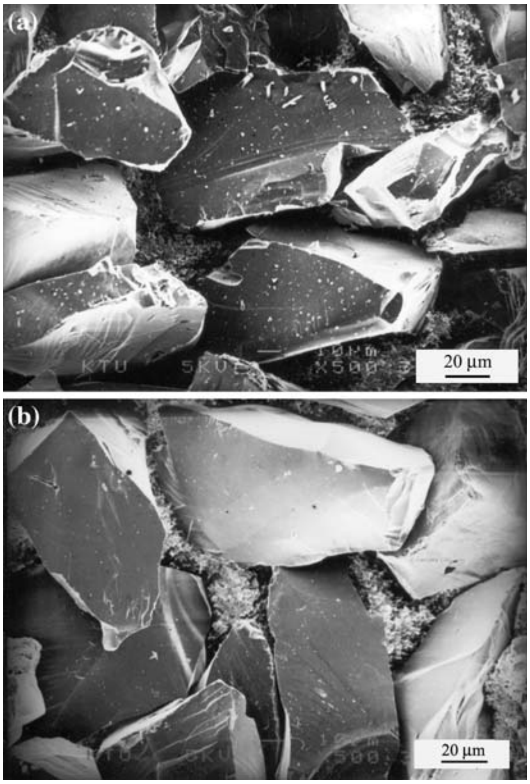


Fig. 4 Surface morphology of as-received (**a**) and pre-treated (**b**) B_4C particles

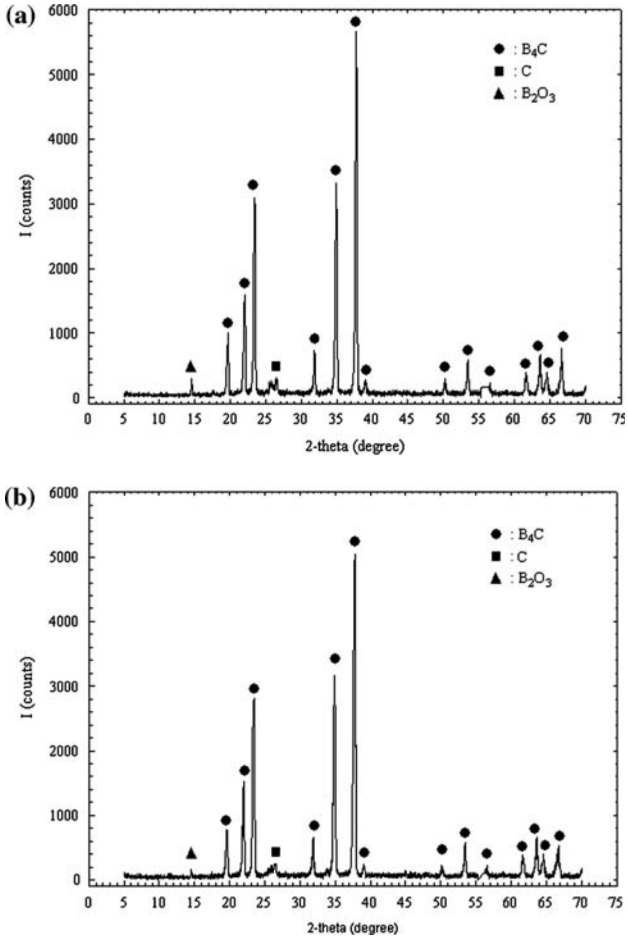


Fig. 5 The XRD data of B_4C samples. (**a**) as-received (**b**) pre-treated

surface of the received particles were coated by ultrafine powders and the surface of the pre-treated B_4C particles were relatively powder free and smoother than the as-received ones (Fig. 4b). The ultrafine powders are easily combined with B_4C particles through polar mediums (such as O_2, N_2, and vapour) due to unsaturated boron ions [37, 38] that probably exist on the B_4C surface. The powders and boron ions perhaps facilitate physical and chemical adsorption of gas on the surfaces of the B_4C particles, and the gases are difficult to remove, thereby hindering wetting of the B_4C particles [28]. A clean surface provides a better opportunity for melt-particle interaction and thus enhances wetting [17, 25, 39]. Two obvious changes on the surfaces of the B_4C particles after pre-treatment were the reduced amount of ultrafine powder and the decrease of oxide (B_2O_3) content.

The compositions of the B_4C particles before and after pre-treatment were analysed by XRD (Fig. 5). In the figures, the XRD peaks of the B_4C particles before and after pre-treatment were almost identical. There exist characteristic B_4C, C and B_2O_3 diffraction peaks in the spectra. The JCPDS card numbers of B_4C, C and B_2O_3 diffraction peaks were 35-0798, 26-1077 and 06-0297, respectively. However, the intensity of diffraction peaks of as-received B_4C particles were relatively higher than that of the zpre-treated B_4C particles. Therefore, it can be concluded that the pre-treatment process was activating the B_4C surfaces by removing surface impurities, ultrafine particles and desorption of gases and altering the surface composition [26], which improves wetting.

A series of AA2014 alloy matrix composites containing B_4C particles up to 12 vol. % were fabricated using vortex method. Examples of their microstructures are shown in Fig. 6. It can be seen that most B_4C particles were dispersed throughout the matrix (Fig. 6a–b), but there exist macro or micro gas blows, shrinkage porosity near B_4C particles, clustering of B_4C particles at high particle-containing composites, and void trapped between B_4C particles (Fig. 6b). Irrespective of attempts to optimise the fabrication parameters, these defects are very difficult to overcome except using vacuum stirring techniques such as the Duralcan process [17]. As seen in Fig. 6b, small-scale clustering of the reinforcing phase occured. The clustering phenomenon was observed in different types of particle-containing composites by other investigators using the casting route [40].

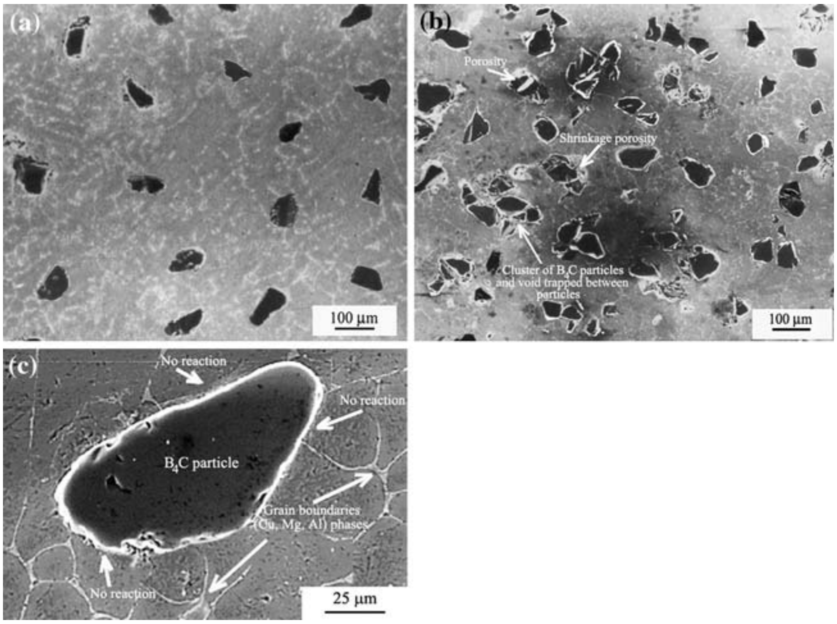


Fig. 6 Microstructure of AA 2014/B_4C composites containing various volume fractions of B_4C particles. (**a**) 3 vol.%; (**b**) 12 vol.%; (**c**) a B_4C particle in the matrix

Figure 6c shows one specific B_4C particle in a AA2014 matrix in detail. There is no evidence of other phases either at the particle-matrix interface or in the matrix suggesting that no reaction occurs between B_4C and Al during manufacturing.

SEM examinations of samples taken from different locations within the ingot showed that the B_4C particles added up to 9 vol.% were uniformly distributed in the composites. However, above this level, the particle ratio decreased slightly (~1.5 vol.%) towards the top of the ingot which was attributed to increasing viscosity of the slurry with increasing particle content. But, particles may also be pushed up towards the ingot surface by a directional solidification since our ingot was conical. Some particle-porosity clustering was also observed in the samples containing relatively high porosity towards the top of the ingot. The porosity content increased from 1.9 vol.% to 3.1 vol.% with increasing particle content from 0 vol.% to 12 vol.% respectively.

The comparison of added and incorporated particle ratios (the yield rate) showed that the amount of incorporated particles decreased with increasing particle ratio. Thus the yield rate decreased from 95% to 65% for the particle content of 3 vol.% to 12 vol.% respectively.

Conclusions

1. This study showed that using the new pre-treatment process consisting of the operations of etching with an acid mixture, cleaning, drying, milling and calcination, facilitates the incorporation and dispersion of the B_4C particles within the AA2014 alloy melt at 700 °C. Thus it can be concluded that this pre-treatment improves wetting of B_4C particles at relatively low temperatures. This was attributed to activating the B_4C surfaces by removing ultrafine particles, desorption of gases and altering the surface composition.
2. Increasing the volume percentage of B_4C particles in the matrix alloy decreases the B_4C particle incorporation into the matrix. This was explained in terms of increasing viscosity of the slurry with the increasing of volume fraction of B_4C.
3. Some particle clustering and particle-porosity clustering were observed at relatively high particle containing composites which was inherent to casting route. Nevertheless, these composites can be used as metallurgically sound ingots by exposing secondary processings such as extrusion and rolling.
4. SEM observations indicated that there was no interface reactions between B_4C particles and matrix during production.

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