Synthesis and structural characterization of Al–B₄C nano-composite powders by mechanical alloying

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This paper consists of two parts. In the first part, attrition milling of commercially available (0.7 µm) boron carbide (B₄C) particles was optimized to prepare B₄C nano-particles. In the second part of the study, mechanical alloying was successfully employed to synthesize metal matrix composite powders with a nanocrystalline Al 6061 alloy as the matrix and B₄C as the reinforcement. Different amounts of B₄C particles (5 wt.% and 10 wt.%) having various sizes of 90 nm (produced in the first part of study), 0.7 µm and 1.2 µm were mixed with different sized (21 µm and 71 µm) Al 6061 powder particles and they were milled for different times. The results showed that the nano-sized B₄C particles may be fabricated when they were milled for 110 h. The size of powder particles in the milled powder mixture was affected by the initial size and content of B₄C particles and Al powders. The SEM and TEM micrographs demonstrated a uniform distribution of B₄C particles in aluminum powders after 8 h milling of an Al + B₄C powder mixture. XRD results confirmed that the crystal size of aluminum reached to 57 nm after 16 h milling of powder mixture and addition of B₄C resulted in a finer grain size of Al in the Al + B₄C mixture during the early stages of milling.

1. Introduction

In direct comparison with the corresponding monolithic alloys, aluminum metal matrix composites (Al MMCs) offer a combination of (a) higher stiffness-to-density ratio, (b) better elevated temperature properties and (c) improved wear resistance. These composites are applicable particularly to the structural, wear, aerospace and transportation industries. The size of the reinforcement particles in particulate aluminum MMCs can vary from around 10 nm up to 500 µm or larger. Composites with a fine and uniform dispersion of particles in the range of 10 nm to 1 µm are referred to as “nano-composites”. The mechanical properties of nano-metric dispersion strengthened MMCs are far superior to those of micron-sized composites with a similar volume fraction of particulates. However, a homogeneous distribution of the reinforcing particles is essential for achieving the improved properties in the composites. Powder metallurgy (P/M) techniques are known to contribute to the good distribution of the reinforcement particles, without the segregation phenomena typical of the casting processes [1]. The distribution of the reinforcement particles depends on the processing route involved, as well as the size of the matrix particles in relation to that of the reinforcement particles. A decrease in the reinforcement particle size can bring about an increase in both the mechanical strength and ductility of the composite at the expense of increased clustering. Therefore, a proper selection of particle size may enhance the homogeneity in particle distribution.

Ceramic nano-particles (<100 nm in size) have received great attention owing to their property advantages over conventional coarse grained counterparts. Currently, a number of techniques are available for the preparation of nano-sized ceramics. Examples of these techniques are reactive sputtering, chemical vapor condensation and high-energy milling. Attrition milling is a suitable method for producing the nano-particles because of its simplicity and applicability to all classes of materials. The kinetics and breakage mechanisms of particles in this technique have been studied by a number of researchers [2,3] and it has been used for the synthesis of a variety of nano-particles such as Al₂O₃ [4], Fe₃S [5], TiO₂ [6], B₄C [7] and Fe₃O₄ [8].

Mechanical alloying (MA) is a high-energy milling process, which produces composite metal powders with a fine microstructure. MA is a simple and useful technique offering a decrease in the ceramic particle size during mixing together with a better homogeneity of the reinforcement into the matrix alloy. The principles, several important process parameters and applications of this technique have been reviewed in some related papers [9–11]. The ability of the MA technique for producing composite powders with a uniform distribution of nano-particles within the matrix alloy resulted in synthesizing a verity of nano-composite systems such
as Mg/carbon nanotube (CNT) [12], Mg/Co3O4 [13], Cu/Fe3C [14], Co/Al2O3 [15], Zn/Al2O3 [16] and Ni/AlN [17].

Aluminum alloys have reasonable strength and ductility with attendant workability. Therefore, these alloys have been widely used for synthesizing of nano-composites with different nano-sized ceramic particulates such as Al2O3 [18,19], CNT [20] and MoAl2 [21] by MA. The 6XX series of Al–Mg–Si alloys (i.e. 6061) due to its excellent mechanical properties, good weldability and corrosion resistance is a good choice for being used as the matrix alloy. Boron carbide (B4C) ranks third in hardness only after diamond and cubic boron nitride and has a density as low as 2.51 g/cm³. These unique characteristics along with other attractive properties, such as high impact and wear resistance, high melting point, good resistance to chemical agents and high capacity for neutron absorption [22], make B4C a good reinforcement for Al matrix composites. However, due to the poor wettability of B4C with the molten Al alloys, fabrication of dense Al–B4C composites through liquid phase approaches is difficult. It has been reported that Al requires a temperature as high as 1100 °C to wet the B4C surface completely and processing at such high temperatures leads to the formation of a series of components by chemical reactions between these two phases [23,24]. Schoenung and co-workers have optimized the cryo milling technique for the processing of composite powders consisting of particulate B4C reinforcement in different aluminum matrices [25,26]. It has been reported that the Al–B4C composites prepared by consolidation of the cryomilled powder particles exhibited better wear resistance [27] and improved mechanical properties [28] when compared to the un-reinforced alloys. The effect of interfacial debonding on the mechanical properties of Al–B4C composites consolidated by different thermomechanical techniques was reported in another study [29]. However, in the abovementioned studies, cryomilling was used to prepare the Al–B4C composite powders by using micrometer-sized B4C particles. Therefore, the optimization of conventional milling for preparation of nano-composite powders and characterization of such powders seems to be lacking.

The present work aims to investigate the effect of milling time on the size distribution, morphology and structure of B4C powders. Another aim is to observe the effect of initial size and content of B4C and Al powders on the size distribution of the milled powders as well as the grain size of the matrix alloy when a mixture of these two powders was milled for different periods of time.

2. Experimental

2.1. Materials

Al6061 powder produced by nitrogen gas atomization was used as the matrix alloy. Its chemical composition (in wt.%) was 1.12Mg, 0.64Si, 0.04Cr, 0.33Cu, 0.48Fe and Al (balance). The matrix powder was sieved and two different sieve fractions of 21 μm and 71 μm were used. Commercially available B4C particles of average sizes of 0.7 μm and 12 μm together with nano-sized particles with the average size of 90 nm produced by milling of the as-received (0.7 μm) particles were used as the reinforcing materials.

2.2. Milling

The milling was performed under a high purity argon gas in an attrition mill (Union Process, model 1-S) using a hardened stainless steel vial and hardened steel balls with 6 mm in diameter. The ball to powder weight ratio and rotational speed were 20:1 and 320 rpm, respectively. The as-received B4C particles as well as different mixtures of Al + B4C particles (various B4C particle sizes and contents mixed with different sized Al6061 alloy powder particles) were milled for different lengths of time.

2.3. Powder characterization

The size distribution of as-received and milled powders was quantified by a laser particle size analyzer (Cilas-1064) and their morphology was characterized by scanning electron microscopy (CamScan MV2300) and transmission electron microscopy (Leo 912-AB). The grain size of milled Al powders was quantified by XRD analysis (Philips PW-1730) using William–Hall method [30]. Powder samples were designated by AlxCx (x%) in which x, y and z indicate aluminum particle size (μm), B4C particle size (nm) and B4C percent (wt.%), respectively. The Al particle size, B4C particle size and B4C weight percents corresponding to the used sample codes are presented in Table 1.

3. Results and discussion

3.1. Milling of B4C particles

Fig. 1 shows the SEM micrographs of the as-received and 110 h attrition milled B4C particles. The as-received (0.7 μm) B4C particles exhibit a wide size distribution of irregular shaped particles (Fig. 1(a)), but a narrow size distribution of nearly equiaxed particles was achieved with the progress of milling up to 110 h (Fig. 1(b)). At this stage, it can be seen that most of the particles are agglomerated. Fig. 2 shows the TEM micrograph of B4C particles after 110 h milling and confirms the generation of nano-metric sized particles.

The variation of the median size (D50) of B4C particles as a function of milling time, quantified by laser particle size analyzer is shown in Fig. 3. It can be seen that at the initial stages of milling (i.e. for the first 32 h of milling) a sharp decrease in the particle size has occurred but the rate of decrease in the particle size gradually decreases. These results are consistent with those reported by other investigators regarding milling of boron carbide [7] and are attributable to the breakage and aggregation events that take place simultaneously during milling. Fig. 3 confirms that while the breakage process is the dominant mechanism at the early stages of milling, the agglomeration process dominates with further milling.

Fig. 4 shows the XRD patterns of the as-received and 110 h milled B4C particles revealing the characteristic rhombohedral structure of boron carbide for the as-received material. After milling for 110 h, the crystalline phases were preserved but the intensity of the characteristic X-ray diffraction peaks decreased and some of the peaks were broadened. This can be attributed to the decreased size of B4C particles by increasing the milling time. The results of crystal size measurement by William–Hall method [30] revealed that the average crystalline size of B4C was 57 nm after 110 h milling.

3.2. Milling of Al + B4C powder mixtures

3.2.1. Evolution of morphology and size of powders

Fig. 5 shows the SEM micrographs of an Al + B4C powders mixture Al71C90 (10%) after different milling times. It can be seen that the as-received aluminum powders are rather spherical (Fig. 5(a)) but after milling the mixture for 2 h, plate-like particles are formed (Fig. 5(b)). As shown in Fig. 5(c), after 4 h milling the flattened aluminum particles are cold welded to each other. Finally, in the milling time of 16 h, a balance between cold welding and fracturing has
occurred and equiaxed particles are formed as shown in Fig. 5(d). In Al + B₄C systems, B₄C particles adhere to aluminum powder during the early stages of milling. These Al powders with B₄C particles sticking onto them are cold welded with other surfaces. As a result, the B₄C particles are entrapped in the Al matrix. These B₄C clusters, which are formed within the Al matrix during mechanical milling, provide easier propagation of the cracks in Al matrix under cyclic loading during milling. Also the cold working induced during MA process, intensifies the initiation and propagation of cracks within powder particles. These cracks would propagate through the matrix alloy and finally fracture the aluminum particles. These fresh fractured surfaces with B₄C particles on them, would weld with other surfaces. With the repeated fracturing and cold welding processes that take place during the energetic ball milling, B₄C particles are eventually distributed uniformly within the Al matrix.

In order to quantify the effects of size and content of Al and B₄C particles on the size and size distribution of the milled Al + B₄C powder mixtures, a series of milling experiments was conducted and the results are shown in Fig. 6(a–f). It can be seen that during the first 4 h of milling, the average particle size increases indicating formation of a large amount of laminates due to cold welding of particles. At this stage, particle deformation and cold welding are predominant mechanisms. For longer milling times, the decreased $D_{50}$ indicates that fragmentation has been the predominant mechanism. Finally, after 12 h milling, the slope of $D_{50}$ versus milling time curves is decreased which is attributable to attainment of equilibrium between fracturing and welding. Similar results have been reported by Abdoli et al. [31] for an Al–AlN system.

As shown in Fig. 6(a–d), addition of B₄C particles to the Al powders resulted in decreased size of powder mixture at least for the first 8 h of milling confirming the acceleration of the milling process by addition of nano- and micro-scaled B₄C particles. These results which are in agreement with those previously reported
suggest that at the presence of the hard ceramic particles, the steady state milling condition for powders, i.e. formation of fine equiaxed particles, takes place after a shorter milling time and can be attributed to the following facts:

(1) The as-received B₄C particles are finer than both the as-received Al powder particles. Therefore, the increased B₄C content in the mixture, results in decreased particle size during milling. It must be noted that the as-received B₄C particles are initially agglomerated as shown in Fig. 1(a), so that this effect is not significant for the Al–B₄C mixtures before milling. However, after milling for at least 4 h, these agglomerated particles are broken to finer ones and affect the size of the powder mixture.

(2) As will be discussed later, the fine B₄C particles embedding into the Al powders during milling lead to their fracture toughness reduction enhancing their fracture.

In fact, the presence of B₄C particles within an individual Al powder resembles the microstructure of a typical particulate reinforced metal matrix composite (MMC)[32]. It is consistently reported that particulate reinforced MMCs exhibit reduced fracture toughness compared with that of the matrix material [32,33]. For example, Hasson and Crowe [34] reported a 60% fracture toughness reduction after incorporating SiC particles in 6061 Al. The possible reasons for the lower fracture toughness of MMCs, as summarized by Davidson [35] include (i) altered slip characteristics, (ii) increased strain to failure at crack tip due to the presence of hard particles, (iii) increased yield point and (iv) debonding at the interface between matrix and particles. Also when compared to MA of soft powders, the presence of hard particles results in increased local deformation of the matrix in the vicinity of the reinforcement particles enhancing the work hardening rate of the matrix. This increased work hardening rate of the alloy may be regarded as another reason for the decreased fracture toughness
of the material. Therefore, it is reasonable to consider that the presence of B₄C particles lowers the fracture toughness of the Al powders during milling leading to an increased fracturing tendency.

The abovementioned mechanisms are intensified when a higher content of B₄C particles is added to Al powders leading to decreased size of the powder mixture shown in Fig. 6(a–d). Fig. 6(e) shows the decreased size of powder mixture with decreased B₄C particle size when 5 wt.% of B₄C particles were milled with 21 μm aluminum powders. However, as shown in Fig. 6(f), the adverse results were obtained when the coarser (71 μm) aluminum powder particles were milled with 5 wt.% of B₄C particles. These results are attributed to the embedding of fine B₄C particles in the coarser aluminum powder particles. In fact the fine B₄C particles can penetrate more easily into the coarser aluminum powders leading to decreased volume fraction of free B₄C particles within the powder mixture resulting in increased overall particle size distribution. Note that the embedding of the nano-scaled particles within ductile particles, should significantly contribute in their work hardening enhancing their fracture. On the other hand, it has been recently reported [36,37] that the presence of nano-sized particles enhances the ductility of composites. This may explain the identical size of powder mixtures after 8 h milling, when different contents of nano-sized B₄C particles were milled with coarse Al powders as shown in Fig. 6(c). It seems that the increased ductility of the composites by increased content of nano-scaled B₄C particles has compensated the decreased fracture toughness resulting in identical fracture process.

### 3.2.2. Embedding of B₄C particles within Al powders

In order to demonstrate the uniform distribution of B₄C in Al matrix, a cross-section sample of Al₁₇₁C₉₀ (10%) milled for 8 h was prepared and examined by SEM. Fig. 7(a) is an image at low magnification, indicating formation of plate like aluminum particles. Fig. 7(b) is an image at higher magnification of the same sample revealing the presence of B₄C particles (little white spots) distributed uniformly within the Al matrix. Fig. 7(c) shows the X-ray mapping of this sample confirming the uniform B₄C particles within the Al matrix.

Fig. 8(a) shows a typical low-magnification TEM image of 8 h milled Al₁₇₁C₉₀ (10%) sample indicating the penetration of nano-sized B₄C particles into the Al powder and formation of nano-composite powder. Fig. 8(b) is a TEM image of the same sample at a higher magnification. It can be seen that a good interface between the B₄C reinforcement and the Al matrix is formed, and no high temperature phases, such as AlB₂₄C₄, Al₂BC, Al₄C₃ and AlB₂ can be detected from TEM characterization. In addition, there are no voids or cracks between the matrix and the B₄C particles. These results are of great importance to the performance of the composites. The mechanism of embedding of hard ceramic particles (Si₃N₄) in a soft matrix (Al) has been discussed by Fogagnolo et al. [38,39] and this phenomenon has been reported in many systems such as Al–SiC [40] and Al–ZrB₂ [1].

As was mentioned before, during mechanical milling, repeated fracturing and cold welding events as well as continuous exposure of fresh metallic surfaces occur. This process can yield a strong metallurgical bonding between the matrix and the reinforcement.
This metallurgical bond, which is usually expected to have high cohesion, results in a better mechanical performance. In contrast to MA, the conventional powder metallurgy methods used for processing of MMCs may not result in good interfacial characteristics. For example, Zhang et al. [29] observed extensive debonding during mechanical testing of a bulk Al–B₄C composite fabricated with conventional PM method attributable to a weak bonding between the reinforcement and matrix.

### 3.2.3. Grain refinement of the alloy

Fig. 9 shows the XRD plots taken from Al₇₁ powder particles milled for different times. The full width at half maximum (FWHM) for the different planes was calculated using such plots. Fig. 10 displays the variation of the FWHM for the different planes versus the milling time. It can be seen that by increasing milling time the Al peaks were broadened. Line broadening of the milled powders represents a decrease in the crystallite size and accumulation of lattice strain. The grain size of Al powders was calculated from Fig. 9 by means of the William–Hall method [30] utilizing the following equation:

\[ \beta_s \cos \theta = \frac{K \lambda}{d} + 2 \varepsilon \sin \theta \]  

(1)

where \( \beta_s \) is the peak broadening in radians, \( 2 \theta \) is the position of peak maximum, \( K \) is the Scherrer constant (0.9) [41], \( \lambda \) is the X-ray wavelength (Cu Kα1 = 0.15406 nm), \( d \) is the so-called crystallite dimension and \( \varepsilon \) is an approximate upper limit of the lattice distortion. The instrumental broadening \( \beta_i \) was removed by applying the following equation according to Gaussian–Gaussian relationship by using an annealed aluminum powder:

\[ \beta_e^2 = \beta_c^2 - \beta_i^2 \]  

(2)

where \( \beta_e \) is the FWHM of the measured XRD peak. The results showed that the grain size of monolithic aluminum particles decreased from 160 nm to 57 nm after 16 h milling. In order to investigate the effects of boron carbide addition on the line broadening...
and grain size of the milled powders, the same procedure was performed on Al$_{71}$C$_{70}$ (5%), Al$_{71}$C$_{90}$ (5%) and Al$_{71}$C$_{90}$ (10%) powder mixtures.

These results confirmed that addition of B$_4$C particles to Al powder broadened the FWHM (at least for the first 12 h milling) and this effect was intensified for increased B$_4$C content. The variation of the calculated grain size of these powders as a function of milling time is shown in Fig. 11. It can be seen that the calculated crystallite size decreases rapidly at the early stage of milling and levels off at prolonged milling times. Furthermore, addition of B$_4$C resulted in finer grain size in the first 12 h of milling and this effect was intensified for increased B$_4$C content and/or decreased B$_4$C size. The unchanged grain size after 12 h milling has been attributed to a balance between the grain refinement introduced by severe impact deformation of milling and its thermal recovery due to the material itself. In a related study Chung et al. [17] found that a small addition of AlN particles with an initial size of 2 μm into Ni enhanced the grain refinement process for Ni after 8 h of mechanical milling and led to the reduced Ni grain size from 132 nm to 65 nm and 37 nm for 0.5 wt.% and 2 wt.% AlN addition, respectively. The enhancement in grain refinement during MA process can be interpreted on the basis of a mechanism evolving the generation of dislocations by the cyclic loading and also by the thermal expansion coefficient mismatch between matrix and reinforcement. The interaction of these dislocations with nano-scaled particles generates sub-boundaries which in turn results in the decomposition of the initial large grains into smaller ones. The decreased size of the Al grain size when milled at the presence of hard and non-deformable small sized B$_4$C particles can be in part attributed to the hindering of the dislocation movement by Orowan bowing mechanism, leading to an increase in the dislocation density thereby accelerating the grain refining progress. This may explain the decreased aluminum grain size by increasing B$_4$C nano-particles from 5 wt.% to 10 wt.% as shown in Fig. 11. Furthermore, when nanoscaled B$_4$C particles are used, the mean free path between the particles decreases. This means more interaction between dislocations and particles and thus faster increase in grain size.
in dislocation density. Therefore, the grain refining process in the nano-composite powder should be accelerated as shown in Fig. 11. It must be noted that the different results obtained by XRD and TEM techniques for the average grain size of the milled Al powder (as shown in Figs. 11 and 8, respectively) can be attributed to the common errors associated with XRD techniques as well as the limited number of grains that can be pictured in a typical TEM image.

4. Conclusions

Nano-sized boron carbide particles can be produced from commercially available boron carbide particles after 110 h attrition ball milling. The increased content of B₄C particles during co-milling of boron carbide and aluminum powders resulted in decreased size of powder mixture. The increased size of B₄C particles in Al (21 μm) + B₄C mixture resulted in increased size of powder mixture. However, by milling the coarser (71 μm) aluminum powder particles with B₄C particles, the adverse results were obtained due to embedding the ceramic particles into the aluminum particles. This effect was confirmed by SEM, TEM and X-ray studies revealing a uniform distribution of the B₄C particles embedded in the aluminum matrix. The lack of voids, cracks or brittle distractive compounds at the interface indicated strong metallurgical bonding between the matrix and the reinforcement. The average grain size of aluminum particles decreased from 160 nm to 57 nm after 16 h milling. Addition of B₄C resulted in finer grain size in the first 12 h of milling and this effect was intensified for increased B₄C content and/or decreased B₄C size.

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