Wear resistant aluminum alloy - B₄C composites fabricated by rheo-casting and rolling process

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Abstract
To reveal the formation and wear mechanisms of rheo-formed aluminum alloy - B₄C composites, A356 alloy + 10 mass% B₄C composite material was fabricated by semi-solid stirring rheo-casting and rolling process. The presence of Al₃BC was confirmed by XRD analysis and hinted that chemical bonding formed at interfaces between aluminum matrix and B₄C particles. Tensile test results demonstrated that addition of B₄C facilitated improving the tensile strength by refining matrix and providing particle strengthening. Failure tests revealed that the failure type of the composite transferred from interfacial debonding to particle cracking with increasing wear load. The wear rate of the composite was approximately 48% lower than that of aluminum alloy under 60 N load. The friction coefficient of the composite under 60 N load also significantly decreased due to formation of B₂O₃ and H₃BO₃ as solid lubricants.

1. Introduction
Carbide based engineering ceramics such as boron carbide (B₄C) and silicon carbide (SiC) are known for their unique combination of mechanical and thermal properties [1, 2]. For example, B₄C is considered an ideal material yet with low density for aerospace application due to its hardness, high temperature applicability, and high wear resistance. Unlike silicon carbide, B₄C exhibits strong neutron absorption ability which in turn yielded its applicability as neutron absorption material for fast breeder reactor and boiling water reactors [3]. However, conversion of properties of such covalently bonded ceramic into industrial applications lies in the near net shaping of it as a composite or a dense sintered microstructure [4, 5]. Despite many favorable characteristics of B₄C as reinforcement particles in metal matrix, low fracture toughness, higher sintering temperature and poor antioxidant capacity undermine its application [6]. Particulate-reinforced metal matrix composites exhibit favorable mechanical properties due to their combined advantages of both the metal matrix and the reinforcing particles [7, 8]. Aluminum alloys have excellent electrical, thermal conductivity and high ductility [9]. Thus, aluminum boron carbide composite materials have gained a greater attention due to its exhibition of combined properties of engineering ceramic and metal, which appropriately meet the requirements of modern industry including light weight, high strength, high hardness and high wear resistance [10–12].

At present, there were many methods to fabricate Al - B₄C composite, including infiltration [13], stirring casting [14], electric spark sintering [15], composite rolling [16] etc. Ruifeng Liu et al fabricated Al - B₄C composite by as-rolling, but decreased microhardness owing to the coarse grains and residual stress release was observed [17]. R Manikandan et al studied mechanical and tribological behaviours of AA7075 alloy hybrid composites reinforced by natural ceramic and B₄C [18]. A maximum increase in hardness, tensile strength and wear resistance was up to 30%, 56% and 56% respectively, and then a slight decrease in impact was found in...
increasing ceramic particles. Dimples, transgranular cleavage facets, cracks and micro ploughing, micro cuttings are revealed from the fractured specimens of tensile, impact and wear respectively. AA6061 alloy - B4C composite was fabricated by Ravi et al using stir-casting method at 850 °C. The tensile strength of the composite gained 23.9% increase compared with the alloy [19]. Wear characteristics of aged AA7075 composites reinforced with B4C and MoS2 particles were revealed by Hemendra Patle et al [20]. The heat-treated (T6) composites exhibited superior wear resistance in comparison to that of the base alloy and untreated composites. Alizadeh et al prepared Al - B4C composite by hot extrusion and pointed out that the mechanical performance increased with the B4C volume fraction while plasticity decreased [21]. Chen et al prepared the Al6061 — 35 mass%B4C composite by powder metallurgy method, and the composite’s hardness reached 157.3 HV after hot rolling [22]. The size of B4C particles in their study reduced significantly due to fracture and deformation during compression. H R Lashgari examined the influence of T6 heat treatment on the microstructure, tensile properties and dry sliding wear behavior of A356—10% B4C cast composites. The results showed T6 treatment could contribute to the strong bonding between B4C and matrix alloy and also could change eutectic silicon morphology from acicular to near spherical [23]. Although many efforts have been made to enhance the mechanical performance of B4C composites, the fabrication methods still need to improve to establish solid bonding between B4C particles and aluminum matrix. Compared with traditional processing methods, semi-solid slurring and rheological forming method can effective homogenize the microstructure by reducing dendrites [24]. Grains could be fully refined and spheroidized during the process while agglomeration is also reduced. The processing method was proved successful to fabricate Al - B4C composite in our previous study [25]. Based on this method, two types of B4C particles with different size were used to fabricate A356 alloy — 10 mass% B4C composite materials in the present study. Via dry sliding wear tests, their microstructure and wear properties are investigated, and the wear mechanism is revealed.

2. Experimental procedure

The particle size distribution of the B4C particles used in this study was 5–20 μm (99 mass%, Forsman, Beijing, China). A356 alloy was used as the metal matrix in this study. The liquidus temperature of A356 alloy was 888K (615 °C). The alloy was prepared by pure aluminum (99.7 mass%, Shandong Pingyin Xinsheng Aluminum Co., Ltd, Shandong, China), pure magnesium (99.95 mass%, Yinguang Magnesium Industry Group Co., Ltd, Shanxi, China), Al-9mass%Si master alloy (Zouping Huixin Metallurgical Materials Co., Ltd, Shandong, China). Chemical composition of the alloy (table 1) was analyzed by Inductively Coupled Plasma - Optical Emission Spectrometry (Agilent 5100, Santa Clara, the USA). B4C particles were pretreated by acid washing and then the surface of B4C was modified. Firstly, B4C particles were rinsed by HCl solution (4 vol%) followed with stirring for 4h at 400 r min⁻¹. Then B4C was filtered and rinsed with deionized water. After drying in a vacuum drying oven, the particles were oxidized to modify the surface. The particles were treated in a thermal analyzer (STA449, NETZSCH Analyzing & Testing, Selb, Germany). The heating temperature was from 20 °C to 650 °C and raised by 10 °C min⁻¹.

The alloy was melted in a resistance furnace under protective atmosphere, and the alloy was heated to 993K (720 °C). Hexachloroethane was used for degassing and deslagging. The stirring speed varied from 350 to 500 rpm, and B4C particles were added into the melt at a ratio of 10 mass% during stirring process. The stirring time changed between 10 and 20 min, and the stirring temperature varied from 853K (580 °C) to 943 K (670 °C). Subsequently, the prepared A356 — 10 mass% B4C slurry was cast via a vibration slurring system [25]. The material was heated at 450 °C for 1.5h in advance to rolling process, and the total rolling reduction was 70%. 10 mm thick slabs were rolled into 3 mm thick sheets by 8 passes at speed of 0.2–0.3 m s⁻¹ (table 2). Samples on the polished surface were etched in 0.5 vol% HF at room temperatures for 5 s. The microstructures were imaged by Olympus metallographic microscope (Olympus; BX51, OLYMPUS, Osaka, Japan), and were analyzed by scanning electron microscopy (SEM; Carl Zeiss, Jena, Germany) equipped with an energy-dispersive (EDS) energy spectrum analyzer. X-ray diffraction (XRD) measurements were employed for the phase analysis, equipped with a diffractometer (Siemens D5000, Germany) with Cu Kα 1 radiation (wavelength k = 0.15406 nm) and a secondary monochromator. The step size was 0.02 mm, and the time at each step was 3 s.

The dry sliding wear tests were performed using a wear and friction tester (MMW-1A, Spai Tech, Jinan, China). Pin-on-disk dry sliding wear tests were done under atmospheric conditions (1 atm., room temperature)

| Table 1. Chemical composition of the A356 alloy. |
|-----------------------------------------------|
| Element | Si | Mg | Fe | Zn | Cu | Mn | Al |
| Content (mass%) | 6.50–7.50 | 0.20–0.40 | ≤0.20 | ≤0.10 | ≤0.20 | ≤0.10 | balance |
for the sliding speeds of 1.0 m s\(^{-1}\). The counterpart’s top is spherical with a diameter of 5.00 mm made from bearing steel with an average hardness of HBN 700. The applied load was 20 N, 40 N, 60 N and 80 N, and the total sliding distance was 2400 m. The sample sheets (68 mm \(\times\) 30 mm \(\times\) 2 mm in size) were mechanical polished, ultrasonically cleaned and vacuum dried in prior to wear tests. A restraint fixture was used to fix the sample to ensure no removal or deformation during the test. The wear rate \((WR)\) is computed using the formula \[ WR = \frac{\Delta m}{m_0}, \] where \(\Delta m\) is the mass difference of before and after test, and \(m_0\) is the mass before test. An electronic tensile testing machine (CMT5305; MST, China) was used to analyze the fracture morphology, and the tensile speed was set as 3 mm min\(^{-1}\). Furthermore, the chemical composition of the species present on the wear scars’ surface was identified using x-ray induced photoelectron spectroscopy (XPS, Kratos Analytical Ltd, Manchester, UK). The spot size was 300 \(\mu\)m \(\times\) 300 \(\mu\)m and the pass energy was 40 eV at the measured regions. \(1s\) core energy levels from XPS survey spectra were analyzed. Statistics were performed using the SigmaStat package (Systat software, Erkrath, Germany). Standard analysis comparing more than two treatments was done by using the one-way ANOVA with Holm-Sidak versus control group Post Hoc testing. Statistical values are indicated at the relevant experiments.

3. Results and discussions

3.1. Microstructure and interface

Typical SEM micrographs and EDS analysis of B\(_4\)C are shown in figure 1. The O content on the surface of B\(_4\)C particles increased from 0.03 at\% to 2.07 at\% after acid washing, which hinted B\(_2\)O\(_3\) generated and adhered to the surface of B\(_4\)C particles. B\(_2\)O\(_3\) could enhance wettability through a liquid-liquid reaction when contacted with aluminum liquid by forming B\(_2\)O\(_3\)·Al\(_2\)O\(_3\) [26]. Therefore, stronger interfacial bonding interface between B\(_4\)C and alloy matrix was obtained after acid washing. The microstructure of A356 alloy – 10 mass\%B\(_4\)C composite sheet fabricated by rheo-casting and rolling was shown in figure 2. The distribution of B\(_4\)C particles in matrix was more compact and homogeneous after rolling than the cast material due to the reduction of agglomeration. Compression stress induced by rolling process led to bidirectional extension, because of which the B\(_4\)C particles were dispersed by the melt laminar. The average size of the 5 \(\mu\)m particle was reduced to ca. 4.0 \(\mu\)m during rolling process, while average size of the 20 \(\mu\)m particle was reduced to ca. 9.0 \(\mu\)m due to fracture and deformation during rolling process [22]. As the rolling reduction increased, the proportion of fine lamella increases. As a result, the distance between B\(_4\)C rich layers and B\(_4\)C poor layers narrowed and the distribution of B\(_4\)C particles also homogenized.

The SEM image with EDS analysis and the XRD phase analysis of the 5 \(\mu\)m particle reinforced composite before and after rolling is demonstrated in figure 3. The composite was mainly composed of \(\alpha\)-Al, Mg\(_2\)Si, Al\(_{12}\)Mg\(_{17}\), Al\(_3\)BC and B\(_4\)C. During the surface treatment before rheo-casting, the surface of B\(_4\)C particles was oxidized and formed B\(_2\)O\(_3\) (figures 3(B), (C)) [27]. Due to the higher temperature in rheo-casting process, B\(_2\)O\(_3\) on the surface of B\(_4\)C particles was liquefied (the melting point under standard atmospheric pressure is 460 °C) and reacted with aluminum melt rapidly. The reaction produced thin layers of Al\(_2\)O\(_3\) surrounding the B\(_4\)C particles, which prevented the inner content from further reacting with aluminum melt. According to this

| Pass No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|----------|---|---|---|---|---|---|---|---|
| Thickness (mm) | 9 | 8.1 | 7.2 | 5.8 | 5.1 | 4.1 | 3.7 | 3 |
| Reduction (%) | 10 | 10 | 11.1 | 10.8 | 12 | 10.9 | 9.8 | 18.9 |

Figure 1. SEM micrographs and EDS analyses of the B\(_4\)C particles before acid washing (A) and after acid washing (B).
mechanism, a part of B₄C particles could release free B and C atoms at high temperature, which could then react with Al atoms to form Al₃BC. Furthermore, the dispersed B₄C particles provides heterogeneous nucleation conditions for the formation of Al₃BC phases, which also accelerated the growth of Al₃BC phases [27]. The presence of Al₃BC hints that chemical bonding was formed on the interface between B₄C particles and metal matrix, which was effective in pinning grain boundaries and blocking the motion of dislocations. Due to this firm chemical bonding, applied load was allowed to transfer from aluminium matrix to the B₄C particles via the interface. Thus the composite was effectively reinforced by B₄C particles with higher hardness.

Figure 4 draws the fracture morphology of A356 alloy - B₄C composite after tensile test and the according composition analysis. Both complete and broken particles were found on the fractured surface. 5 μm B₄C particles stood lower stress due to their smaller size, so only few flaked particles were observed in 5 μm B₄C reinforced composite. Therefore, the failure of A356 alloy — 5 μm B₄C composite was mainly due to debonding between B₄C particles and the metal matrix. For A356 alloy - 20 μm B₄C composite, more flaked particles were observed (figure 4(b)) hinting that larger particles stood higher shear stress in the tensile deformation process. Furthermore, residual stress might exist surrounding B₄C particles and inducing cracks when higher load performed. The failure type of A356 alloy - B₄C composite material gradually changed from interfacial debonding to strengthening phase fracture with increasing particle size. From the SEM images of the longitudinal section of tensile fracture (figure 5), it can be concluded that the fracture grew and propagated along grain boundaries leading to intergranular fracture. Addition of B₄C facilitated improving the tensile strength by refining matrix and providing particle strengthening. The refined grains could effectively hinder the nucleation and propagation of cleavage cracks. Therefore, the composite could withstand higher load and larger deformation.
3.2. Wear morphology

As shown in figures 6 and 7, the wear scar widened with increasing wear load. Under lower load condition, oxidation wear was the dominant wear form. When the wear load increased, the oxidized surface cracked and the inner material contacted the grinding head directly. As a result, adhesive wear happened and the wear rate consequently increased. While higher wear load was performed, higher temperature brought by friction and more transformation from oxidation wear to adhesive wear was observed. With developing wear process, B₄C particles shattered from the composite material surface and were involved in the wear system as abrasive particles, which formed furrows on the soft aluminum matrix surface. When adhesive wear happened, sharp increase in wear and tear led to destructive wear.

To the 5 μm B₄C particles reinforced composite, the worn surface of the composites presented furrow wear characteristic. With increasing wear load, spalling areas appeared and grew. To the 20 μm B₄C particles reinforced composite, spalling is the main wear mechanism, while abrasive wear also existed. During the wear process, the B₄C particles stood the shearing force transferred by the matrix, and the bigger size of the particles made them more prone to crack or flake. With more flaked particles between the friction surfaces, the composite behaved mainly the abrasive wear. Due to the higher hardness of the B₄C particles than the metal matrix, furrow morphology was formed with the abrasive wear process. It can be concluded that spalling and abrasive wear is the main wear mechanism of the composite, accompanied by oxidation wear.

3.3. Wear properties and mechanism

Wear rate and friction coefficient under different load of the 20 μm particle reinforced composite material were shown in figure 8. The wear rate of the composite was approximately 48% lower than that of the A356 alloy.
Figure 6. Wear scars’ SEM morphologies of 5μm particle reinforced composite after dry sliding wear tests under different load: (A) 20 N; (B) 40 N; (C) 60 N; (D) 80 N.

Figure 7. Wear scars’ SEM morphologies of 20μm particle reinforced composite after dry sliding wear tests under different load: (A) 20 N; (B) 40 N; (C) 60 N; (D) 80 N.

Figure 8. Comparison of wear rate and friction coefficient between the composite and A356 alloy with increasing load. The experiments were carried out in five-duplicates and mean value ± standard deviation is presented.
under 60 N load (from 2.92% in A356 alloy to 1.53% in the composite). Similar to other particulate reinforced metal matrix composites, B₄C particles could stand mostly the wear load as hard phases and avoid shear stress concentration [28, 29]. It can be observed that the wear rate of the composite always increases with the increasing load. When the load increased, the real contact area between the friction pairs also increased, which led to more severe wear. Besides, due to the lower hardness of the metal matrix than the B₄C particles, B₄C particles gradually emerged from the worn metal matrix during the wear process. Therefore, the particles were getting more prone to crack and flake, and the flaked particles entered the gaps between the friction surfaces leading to abrasive wear. While the real contact area between the friction pairs increased, more flaked particles entered the gaps between the friction surfaces.

The chemical composition of the species present on the wear scars’ surface was identified using XPS. B 1s core energy spectra peaked at 193.7 eV, indicating the presence of B₂O₃ and H₃BO₃ as the result of oxidation wear (figure 9). The exposed surfaces of B₄C particles were oxidized to B₂O₃ under friction heat, which further reacted with H₂O in the air to H₃BO₃. Both B₂O₃ and H₃BO₃ could provide superior lubrication and decrease the friction coefficient [30]. Al₂O₃ always existed on the alloy surface under atmospheric condition, and its amount would be increased by the surface oxidation during wear tests [31]. Oxides fell off from the test materials with increasing test time, which led to a mixture of oxidation wear with abrasive wear. When abrasive wear happened, the fallen oxides accelerated the wear while decreased the friction coefficient. Therefore, the effect of performing higher wear load is revealed not only to increase the wear rate, but also to decrease the friction coefficient between the friction surfaces especially when higher load was performed.

Homogeneous distribution of B₄C particles in aluminium matrix was attributed to the strong shear force generated in rheo-casting process with vibration slurring system [32]. Rheo-casting and the following stirring process effectively refined and spheroidized the microstructure which also increased the composite’s wear resistance [33]. Compared with A356 alloy processed by traditional methods, the rheo-rolled B₄C reinforced composite presents superior wear resistance. More favorable wear resistance of the composite than A356 alloy allows its application in more severe wear conditions. Future improvement of the composite will include optimization of rheo-casting technical parameters and surface modification of B₄C particles to obtain more homogenous distribution and better wear resistant performance.

4. Conclusions

This article reported the formation and wear mechanisms of rheo-formed aluminum alloy – 10 mass% B₄C composites. The average size of the 5 μm particle was reduced to ca. 4.0 μm during rolling process, while average size of the 20 μm particle was reduced to ca. 9.0 μm due to fracture and deformation during rolling process. Addition of B₄C facilitated improving the tensile strength by refining matrix and providing particle strengthening. Spalling and abrasive wear is the main wear mechanism of the composite, and the wear rate of the composite was approximately 48% lower than that of the alloy under 60 N load. Collectively, rheo-casting and
the following stirring process effectively refined and spheroidized the microstructure, which led to a significant increase in wear resistance.

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