Evolution of microstructure and mechanical properties of Al-B\(_4\)C composite after recycling

Zhenjiang Guo\(^{1,2,a}\), Qiulin Li\(^{1,b}\), Wei Liu\(^2\), Guogang Shu\(^3\)

\(^1\)Graduate School at Shenzhen, Tsinghua University, Shenzhen, 518055, China
\(^2\)School of Materials Science and Engineering, Tsinghua University, Beijing, 100084, China
\(^3\)State Key Laboratory of Nuclear Power Safety Monitoring Technology and Equipment, China Nuclear Power Engineering Co. Ltd., Shenzhen of Guangdong Prov., 518172, China

E-mails: \(^{a}\)gzz15@mails.tsinghua.edu.cn, \(^{b}\)liql@sz.tsinghua.edu.cn

Abstract. A remelting method was used to recycle Al-15wt.% B\(_4\)C composite and the microstructure and mechanical properties of the composite were investigated before and after recycling. Scanning electronic microscope (SEM) showed that some of the particle clusters present in the original composite were broken down and the distribution of B\(_4\)C in the matrix was more uniform after recycling. The interface reaction was further intensified and the protection layer coated on the surface of B\(_4\)C was thicker after recycling. In addition, there were more TiB\(_2\) particles which peeled off from the surface of B\(_4\)C and distributed around B\(_4\)C. Al\(_3\)Ti phase, which was present in the original composite, disappeared after recycling, while Al\(_3\)BC phase increased markedly. Tensile test and hardness test revealed that the mechanical properties were preserved well after recycling. Therefore, it is proposed that remelting method is a feasible method for Al-B\(_4\)C composite recycling.

1. Introduction

Aluminum matrix composites (AMCs), due to their advantageous properties such as high specific strength and modulus, unique wear resistance as well as corrosion resistance, are attractive structural and functional materials for automotive, aeronautical and many other applications\[1-3]\. As far as reinforcements are concerned, boron carbide (B\(_4\)C) are an attractive reinforcement because of their low density, high hardness, excellent chemical and thermal stability\[4, 5]\. More importantly, due to their specific capability of capturing neutrons, B\(_4\)C particle-reinforced AMCs have been mainly used in nuclear spent fuel storage and transportation applications\[6, 7]\. However, in the manufacturing processes of B\(_4\)C particle-reinforced AMCs, the process scraps from rolling can reach more than 20% of the total materials produced. The need of recycling Al-B\(_4\)C composites is urgent in terms of saving energy, reducing volumes of waste and decreasing pollutants emission.

There are several methods for aluminum matrix composites recycling, including electrolysis, salt fluxing, hot pressing, and remelting \[8]\. Electrolysis has been used to recycle SiC-reinforced AMCs\[9]\. The recovery of pure aluminium is achieved and the purity is over 98%, but this method is very time-and energy-consuming. Salt fluxing has low energy consumption and the key to this technique is finding suitable salts\[10]\. This method has been used to separate SiC particles from aluminum matrix\[11]\. But the yield is low and the recovered aluminum matrix contains a small amount of Si elements. Hot pressing, similar to powder metallurgy, has been used to recycle Al\(_2\)O\(_3\)-reinforced
AMCs through pressing and hot extrusion[12]. Due to the refinement of the microstructure and the dispersion of the aluminium oxide caused by the extrusion process, mechanical properties of recycled composite are improved compared to the original composite. But this method requires high performance equipment. Remelting technique is an attractive method because of its simple process and lower energy consumption. In one previous study, the changes in the properties of SiC<sub>r</sub>-reinforced AMC after multiple remelting were studied, and the results showed that remelting times was crucial to the tensile properties of composite. As the remelting times increase, the mechanical properties decrease seriously[13]. It was also reported that with the increase of the stirring time, the fluidity of melt composite decreased and reaction products increased[14], which will have an impact on the casting and material properties. Though the remelting method has been employed to recycle aluminum matrix composites, its effect on microstructure and mechanical properties of B<sub>4</sub>C particle-reinforced AMCs has not been fully studied.

In the present work, scrap materials produced during rolling Al-B<sub>4</sub>C composite were recycled by a remelting method. Then the microstructure, including particles distribution, interfacial reaction and the reaction-induced particles, was characterized before and after recycling. In addition, mechanical properties such as tensile properties and hardness were also investigated.

2. Experimental Procedure

2.1. Recycling process
Processed scrap materials of the 1060Al-15 wt.% B<sub>4</sub>C composite in the form of rolled sheets were used in this investigation, and the thickness of the sheets was 3 mm. The rolled sheets were cut into rectangles with a sectional dimension of 30×150 mm<sup>2</sup> by water jet cutter. After the sheets were cleaned, put them into a vacuum oven and dry at 120° C for 2 hours. A stirring-casting furnace under argon protection condition was used, the temperature was kept at 730° C for a long time holding. Put the composite into the furnace to heat for 45 minutes. Then the melted composite was agitated by a mechanical stirrer with the stirring speed constant at 320 r/min and the stirring time of 10 minutes. Finally, the fusing fluids was cast into a reheating steel mold in the form of slab.

2.2. Hot rolling
Hot rolling of the slab was carried out at 450 °C. The thickness reduction for each pass of rolling was kept at a lower value of 15%. For every rolling pass, the rolled sheet was reheated at 450 °C for 20 minutes. Finally, the slab was rolled into 3 mm sheets to evaluate their microstructure and mechanical properties.

2.3. Microstructure characterization
Samples with size 3×10×10 mm<sup>3</sup> were polished by both mechanical polishing and ion beam (IB-09020CP, JEOL) polishing methods. Mechanical polishing was down to 1μm by diamond suspension. Optical microscope and a scanning electron microscope (SEM, SU8010, Hitachi, Japan) in back scattered electron (BSE) mode and equipped with Energy Dispersive Spectrometer (EDS) was applied to observe the particle distribution and interfacial microstructure along the rolling direction. X-ray diffraction (XRD, D/MAX-2500/PC, Rigaku, Japan) test was performed on samples to identify changes in reaction products.

2.4. Mechanical testing
The tensile samples and hardness samples were annealed at 400°C for 2 hours. The tensile tests were carried out according to the ASTM E8-04 standard (rectangular flat samples with a 12.5 mm width reduced section) at a test speed of 10<sup>-3</sup>s<sup>-1</sup> using a 50 mm gage extensometer, and each average value was obtained from three tensile tests. The Vickers hardness tests were carried out with a load of 300g and dwelling time of 15s on mechanical polishing samples based on the ASTM E92 standard, and each average value was obtained from 10 measurements for each sample.
3. Results And Discussion

3.1. Microstructure

Figure 1 presents the microstructure of original scrap material and recycled material observed using OM and SEM. In the original material, the distribution of B₄C in the matrix is inhomogeneous. Particle clusters, a dense solid particle complex consisting of tens to hundreds of particles, could be observed in the original materials although some particle clusters were broken down and banded distribution along the rolling direction due to the rolling deformation. After recycling, the distribution of B₄C in the matrix is more uniform and banded particle clusters is disappeared, and the amount and size of the clusters are considerably less and smaller compared with the original scrap materials. This may be attributed to the further agitation after remelting and further rolling deformation.

Figure 1. Microstructures of 1060Al-15%B₄C composite: (a, c) original material; (b, d) recycled material.

Figure 2 shows the EDS elemental mapping of B₄C particle and EDS line scan at the interface between Al matrix and B₄C particle at a high magnification. It can be seen that the Ti elements are enriched at the interface and form a protective layer around the B₄C. In the original composite, the distribution of the protection layer on the surface of B₄C is not uniform and the thickness is various at different positions, which is consistent with Li’s studies[15]. This observation is proposed to be a result of the maldistribution of the nucleation sites for the protection layer. But after recycling, the protection layer is uniformly coated on the surface of B₄C and is thicker. The protection layer was identified as TiB₂ in previous studies[16]. This protective layer not only can protect B₄C from being eroded by liquid aluminum, but also it can improve the wettability of B₄C in liquid aluminum, and strengthen the bonding between Al and B₄C when Al-B₄C composites fabricated by stir casting technique[17-19].

EDS line scan of the samples was carried out under the same parameters. The intensity of different elements is presented. At the interface, it can be seen that the intensity of Ti element increases significantly after recycling, and B elements are also gathered at the interface and form a small peak on the curve. This further proves that the protective layer consists of B and Ti elements. Comparing the two interfaces, it reveals that after the transformation of the protective layer from a fine layer to
discretely coarse layer, the TiB$_2$ grew up at some discrete interface spots and formed needle-like crystals. This needle-like crystals peel off easily when subjected to external force. As shown in Figure 1, there are more white needle-like particles around B$_4$C after melting, which means thicker protective TiB$_2$ layers peeled off from the surface of B$_4$C attributed to the rolling deformation and liquid mechanical agitation.

**Figure 2.** Microstructures of 1060Al-15%B$_4$C composite: (a, c, e, g) SEM backscattered electron image, EDS elemental mapping, EDS line scan of interface and the result of EDS line scan for the original material, respectively; (b, d, f, h) SEM backscattered electron image, EDS elemental mapping, EDS line scan of interface and the result of EDS line scan for the recycled material, respectively.
Figure 3 exhibits EDS pattern of large grey particle in Figure 1 and XRD patterns of Al-B$_4$C composites before and after recycling. The grey particle only contained Al and Ti elements, and atomic ratio of Al to Ti is approximately 3:1. The XRD patterns show that the Al$_3$Ti is present in the original composite. So it can be concluded that the grey particle in Figure 1 is Al$_3$Ti. This result shows that Ti elements is excessive in the primary production of composite materials. But it is disappeared after recycling. This can be attributed to the intensification of the interfacial reaction during the remelting process, which consumed Ti elements and lead to the decomposition of Al$_3$Ti.[16, 20]. The interfacial reaction can be expressed as follows:

$$6\text{Al}+2\text{B}_4\text{C}+3\text{Ti}=2\text{Al}_3\text{BC}+3\text{TiB}_2$$

$$\text{Al}_3\text{Ti}=3\text{Al}+\text{Ti}$$

And the reaction products from the B$_4$C particle to Al matrix are Al$_3$BC, fine TiB$_2$ and coarse TiB$_2$. The XRD patterns also show that the peak of Al$_3$BC is obviously stronger compared with the composite, which indicates that Al$_3$BC increases after recycling. But in contrast to Chen’s studies[14], we didn’t find Al$_3$BC and AlB$_2$ particles around the B$_4$C, it may be due to the shorter stirring time and excessive Ti elements.

![EDS analysis](image1)

![XRD patterns](image2)

**Figure 3.** EDS and XRD pattern analysis: (a) EDS analysis for large grey particle in Fig.1(c); (b) XRD patterns for original and recycled materials.

### 3.2. Mechanical properties

Microstructure, such as particle distribution, is tightly associated with the mechanical properties of the metal matrix composites, such as fracture strength and plastic deformation[21, 22]. Cracks are easier to generate at clusters of particles due to the elastic misfit and the plastic constraint of particles. Damage accumulation also tended to occur in clustered regions ahead of a propagating crack. Therefore, we assesses the mechanical properties of the original materials and recycled materials.

Figure 4 presents the tensile properties of Al-B$_4$C composites before and after recycling. The average yield strength, ultimate tensile strength (UTS) and elongation of the original composite is 60.5MPa, 108.1MPa and 25.2%, respectively. After recycling, the average yield strength, ultimate tensile strength (UTS) and elongation is 62MPa, 109.5MPa and 26.6%, respectively. The Vickers hardness of Al-B$_4$C composites before and after recycling is 42.1 HV and 42.8 HV, respectively. The increase of tensile properties and hardness after recycling may be attributed to the further uniform distribution of B$_4$C and TiB$_2$ which peeled off from the surface of B$_4$C and serves as strengthening phase.

Figure 5 shows the SEM micrographs of tensile fracture surfaces of composites. In the original composite, there are many dimples on the fracture surface and the dimples are large and uniform. After recycling, there are many newly formed micro dimples in the big dimples. Further observation at a high magnification of SEM reveals that some regular shape particles were found in the micro
dimples. Considering their morphology and size, these particles are assumed to be TiB$_2$ which peeled off from the surface of B$_4$C and dispersed in the matrix. It seems that these particles act as void initiation sites. The fractured B$_4$C particles can be seen clearly both in Fig. 5(a) and (b). Fig. 5(d) presents the fractured B$_4$C particle which is typical in other samples. The cross section is smooth and distributed with some steps, it is a typical brittle fracture. B$_4$C is surrounded by aluminum matrix and many dimples are around B$_4$C, it is a typical ductile fracture. It can be seen that the interface layer between the reinforcement and the matrix is stable enough, and the force from the matrix to the B$_4$C is well delivered.

Figure 4. Stress-strain curves of original and recycled materials.

Figure 5. Tensile fracture surfaces of 1060Al-15%B$_4$C composite: (a) original materials; (b-d) recycled materials.
4. Conclusions
In the current study, a remelting method was successfully employed to recycle scrap materials of 1060Al-15wt.% B4C composite. And the microstructure and mechanical properties were investigated.

It showed that after recycling, more particle clusters were broken down and B4C distributed in the matrix more homogeneously. The interface reaction was further intensified, and the protection layer coated on the surface of B4C was thicker. There were more TiB2 particles peeled off from the surface of B4C, which contributed to the good mechanical properties.

EDS and XRD showed that Al4Ti phase was present in the original composite. But disappeared after recycling due to the consumption of Ti elements at the interface. The peak of Al4BC phase was obviously stronger compared with original composite.

The average tensile properties and hardness of the recycled composite was comparable to those of the original composite suggesting that the mechanical properties of the recycled composite remained well. This work is of great use for the industrial recycling of Al-B4C metal matrix composites.

Acknowledgments
This work was founded by Joint Laboratory of Nuclear Materials and Service Safety (2013966003), China and the authors thank Dr. Liang Wang for useful discussion. The authors also thank Mr. Shangyang Feng and Mr. Xiang Zeng at Tsinghua University for experimental assistance.

References
[1] B. V. Ramnath, C. Elanchezhian, M. Jaivignesh, S. Rajesh, C. Parswajinan, A. S. A. Ghias, “Evaluation of mechanical properties of aluminium alloy-alumina-boron carbide metal matrix composites,” Materials & Design, vol. 58, pp. 332-338, Jun, 2014.
[2] K. Shirvaniemoghadam, H. Khayyam, H. Abdizadeh, M. Karbalaei Akbar, A. H. Pakseresht, E. Ghasali et al., “Boron carbide reinforced aluminium matrix composite: Physical, mechanical characterization and mathematical modelling,” Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing, vol. 658, pp. 135-149, Mar 21, 2016.
[3] A. J. Knowles, X. Jiang, M. Galano, F. Audebert, “Microstructure and mechanical properties of 6061 Al alloy based composites with SiC nanoparticles,” Journal of Alloys and Compounds, vol. 615, pp. S401-S405, Dec 5, 2014.
[4] F. Thévenot, “Boron carbide—A comprehensive review,” Journal of the European Ceramic Society, vol. 6, no. 4, pp. 205-225, 1990.
[5] V. Domnich, S. Reynaud, R. A. Haber, M. Chhowalla, “Boron Carbide: Structure, Properties, and Stability under Stress,” Journal of the American Ceramic Society, vol. 94, no. 11, pp. 3605-3628, Nov, 2011.
[6] P. Zhang, Y. L. Li, W. X. Wang, Z. P. Gao, B. D. Wang, “The design, fabrication and properties of B4C/Al neutron absorbers,” Journal of Nuclear Materials, vol. 437, no. 1-3, pp. 350-358, Jun, 2013.
[7] G. Bonnet, V. Rohr, X.-G. Chen, J.-L. Bernier, R. Chiocca, H. Issard, “Use of Alcan's Al-B4C metal matrix composites as neutron absorber material in TN International's transportation and storage casks,” Packaging, Transport, Storage & Security of Radioactive Material, vol. 20, no. 3, pp. 98-102, 2009.
[8] Y. X. Yang, R. Boom, B. Irion, D. J. V. Heerden, P. Kuiper, H. D. Wit, “Recycling of composite materials,” Chemical Engineering and Processing, vol. 51, pp. 53-68, Jan, 2012.
[9] V. Kamavaram, D. Mantha, and R. G. Reddy, “Recycling of aluminum metal matrix composite using ionic liquids: Effect of process variables on current efficiency and deposit characteristics,” Electrochimica Acta, vol. 50, no. 16-17, pp. 3286-3295, May 30, 2005.
[10] Y. Nishida, “Recycling of metal matrix composites,” Advanced Engineering Materials, vol. 3, no. 5, pp. 315-317, May, 2001.
[11] K. R. Ravi, R. M. Pillai, B. C. Pai, M. Chakraborty, “Separation of matrix alloy and
reinforcement from aluminum metal matrix composites scrap by salt flux addition,” Bulletin of Materials Science, vol. 30, no. 4, pp. 393-398, Aug, 2007.

[12] J. B. Fogagnolo, E. M. Ruiz-Nava, M. A. Simon, M. A. Martinez, “Recycling of aluminium alloy and aluminium matrix composite chips by pressing and hot extrusion,” Journal of Materials Processing Technology, vol. 143, pp. 792-795, Dec 20, 2003.

[13] A. Klasik, J. Sobczak, and K. Pietrzak, “Changes in properties of aluminium matrix composite reinforced with SiC particles after multiple remelting,” Materials Research Innovations, vol. 15, pp. S249-S252, Feb, 2011.

[14] C. J. Shi, Z. Zhang, and X. G. Chen, “Microstructure and fluidity evolution during recycling of Al-B_{4}C metal matrix composites,” Journal of Composite Materials, vol. 46, no. 6, pp. 641-652, Mar, 2012.

[15] Y. Li, Q. L. Li, W. Liu, G. G. Shu, “Effect of Ti content and stirring time on microstructure and mechanical behavior of Al-B_{4}C composites,” Journal of Alloys and Compounds, vol. 684, pp. 496-503, Nov 5, 2016.

[16] Z. Zhang, K. Fortin, A. Charette, X.-G. Chen, “Effect of titanium on microstructure and fluidity of Al-B_{4}C composites,” Journal of Materials Science, vol. 46, no. 9, pp. 3176-3185, May, 2011.

[17] D. A. Weirauch, W. J. Krafick, G. Ackart, P. D. Ownby, “The wettability of titanium diboride by molten aluminum drops,” Journal of Materials Science, vol. 40, no. 9-10, pp. 2301-2306, May, 2005.

[18] D. Kocaefe, A. Sarkar, and X. G. Chen, “Effect of Ti addition on the wettability of Al-B_{4}C metal matrix composites,” International Journal of Materials Research, vol. 103, no. 6, pp. 729-736, Jun, 2012.

[19] Q. L. Lin, P. Shen, F. Qiu, D. Zhang, Q. C. Jiang, “Wetting of polycrystalline B_{4}C by molten Al at 1173-1473 K,” Scripta Materialia, vol. 60, no. 11, pp. 960-963, Jun, 2009.

[20] J. Y. Zheng, Q. L. Li, W. Liu, G. G. Shu, “Microstructure evolution of 15wt% boron carbide/aluminum composites during liquid-stirring process,” Journal of Composite Materials, vol. 50, no. 27, pp. 3843-3852, Nov, 2016.

[21] M. K. Akbari, H. R. Baharvandi, and K. Shirvanimoghaddam, “Tensile and fracture behavior of nano/micro TiB_{2} particle reinforced casting A356 aluminum alloy composites,” Materials & Design, vol. 66, pp. 150-161, Feb 5, 2015.

[22] A. Matin, F. F. Saniee, and H. R. Abedi, “Microstructure and mechanical properties of Mg/SiC and AZ80/SiC nano-composites fabricated through stir casting method,” Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing, vol. 625, pp. 81-88, Feb 11, 2015.