



# Solid-state reaction in mechanically milled and spark plasma sintered Al–B<sub>4</sub>C composite materials

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## ABSTRACT

Air-atomised pure aluminium powder with additions of 12.5 at%, 37.5 at% and 62.5 at% of B<sub>4</sub>C was mechanically alloyed (MAed) by using a vibrational ball mill, and MAed powders were consolidated into bulk materials by a spark plasma sintering (SPS) process. Solid-state reactions of the MAed powders during heat treatments were examined by X-ray diffraction (XRD), and mechanical properties of the MAed powder obtained under various heat treatment conditions and those of the SPS materials were evaluated by hardness tests. The solid-state reactions occurred among pure aluminium, B<sub>4</sub>C and stearic acid, added as a process control agent (PCA), after heating at 673 K to 873 K for 24 h to form AlB<sub>10</sub>, Al<sub>3</sub>BC and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The products obtained by solid-state reactions have affected the Vickers microhardness of the heat-treated MAed powders. The near full density was obtained for the SPS materials under the conditions of an applied pressure of 49 MPa at 873 K for 1 h. The Al–12.5B<sub>4</sub>C SPS material from 16 h MAed powder exhibited the highest hardness value of 210 HV in the as-fabricated state.

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## 1. Introduction

Particle-reinforced aluminium matrix composites with lightweight are of a considerable interest as a class of materials capable of advanced structural and functional applications [1]. In order to produce composite powders and/or to synthesise a variety of stable and metastable nanocrystalline powders prior to particle-reinforced bulk composite materials, mechanical alloying (MA) is one of effective techniques that eliminate reinforcement segregation typically occurring in the ingot metallurgy process [2,3]. In addition, the MA processing technique can also be used to obtain nanoparticles in aluminium alloys in the presence of a process control agent (PCA) which enables a balance between fracture and welding to be established enabling refinement of the powder particle size [4]. Furthermore, the PCA can also react with the aluminium during milling or subsequent heat treatments leading to the formation of second phases such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and/or Al<sub>4</sub>C<sub>3</sub> [5].

The technique of mechano-chemical synthesis (i.e. reaction milling (RM) [6]) has attracted considerable interest as one of the promising routes for the synthesis of composite materials. Chemical reaction can be induced by either during the MA process or subsequently heat treatments of the MAed powders. In this process, metal powders in the presence of reactive solids or gases are milled to synthesise thermally stable compounds, such as metal

oxides, nitrides and carbides, depending upon a combination of metal powders and reactive elements. Those stable compounds are generally formed as *in situ* reaction.

The Spark plasma sintering (SPS) method is a novel technique that a pulsed DC current is used concurrently with a uniaxial pressure to in principal sinter the MAed powders. The major advantage of the SPS process is that it allows fabrication of bulk materials from the MAed powders using relatively short sintering times at nominally low temperatures compared to that of hot press and hot isostatic press processes. Therefore, coarsening of both fine grains and nano-sized particles in the MAed powders can be avoided. In addition, another advantage of SPS is that the plasma generated between particles to facilitate the sintering process also aids in the elimination of surface impurities, leading to enhanced sintering and consolidation [7]. It is well known that the aluminium powders are hardly sinterable materials because of the oxide layer on its surface. This layer should be broken up in order to achieve high packing density. It can be thus possible to obtain bulk materials of the MAed aluminium powders using SPS [5].

Boron carbide is an important non-metallic hard material with high hardness and low density. Due to such the superior properties, B<sub>4</sub>C recognises a great potential for structural and functional applications. In particular, B<sub>4</sub>C can be used for neutron absorber. From this point of view, aluminium alloy containing B<sub>4</sub>C has been paid attention to use as a basket material of the cask because of its lightweight, excellent thermal conductivity and superior neutron absorbing abilities. A typical method for producing this type of composite materials is based on ingot metallurgy process that involves melting and casting techniques. Recently, a new type of

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the cask has been developed for high performance and reliable transportable storage using powder metallurgy process. However, solid-state reactions between aluminium and  $B_4C$  are still unknown at high temperatures for relatively long time exposures.

The aim of the present work was thus to investigate effects of MA times and heat treatment temperatures on solid-state reactions and mechanical properties of MAed powders and SPS materials fabricated from MAed powders.

## 2. Experimental procedures

The starting material was air-atomised 99.9% pure aluminium and 99.5% pure  $B_4C$  powders with an average diameter of 100  $\mu m$  and 45  $\mu m$ , respectively. Stainless steel balls of 7 mm diameter together with 10 g of the Al- $B_4C$  ( $Al_{100-x}(B_4C)_x$  where  $x = 12.5, 37.5$  or  $62.5$  (at%)) powder mixture and stearic acid ( $CH_3(CH_2)_{16}COOH$ ), added as a PCA, were sealed in a hardened steel vial using a glove box filled with argon. The ball to powder mass ratio was approximately 7:1. The MA process was performed at room temperature using an SPEX8000 mixer mill. The MA processing time was varied from 2 h to 32 h. The MAed powders were heat treated at temperatures ranging from 573 K to 873 K for 24 h under air atmosphere. X-ray diffraction (XRD) analysis was performed on both the MAed powders and SPS materials using a  $CuK\alpha$  radiation source and operating at 40 kV and 60 mA. The average Vickers microhardness of the MAed powders was determined from 15 particles per sample with a microhardness tester using an applied load of 98 mN. The MAed powders were consolidated into bulk materials by an SPS apparatus. Seven grams of the MAed powder was placed in a graphite die of 20 mm in diameter and heated under vacuum with an applied pressure of 49 MPa at 873 K for 1 h. The Vickers hardness of the SPS materials was measured with a hardness tester using an applied load of 9.8 N.

## 3. Results and discussion

Fig. 1 presents the changes in the Vickers microhardness of the Al- $B_4C$  composite powders produced by MA as a function of different MA times, where pure Al powder is included for reference. The hardness of the pure Al powder before MA was approximately 44 HV. The hardness of all of the different compositions in the Al- $B_4C$  powders increased dramatically to over 145 HV after 4 h of MA, but a slight increase was observed to a value of 160 HV for the Al-12.5 $B_4C$  powders and a moderate increase was obtained to a value of 270 HV and 375 HV for the Al-37.5 $B_4C$  and Al-62.5 $B_4C$  powders after 32 h of MA, respectively. It can be thought that these hardness results are attributable to not only large strain introduced by MA, but also uniform dispersion of fine scale  $B_4C$  particles. The hardness of the pure Al powder, however, displayed a reduction of a value of 120 HV after 8 h of MA. It is interesting to note that the pure Al powder exhibits a broad hardness plateau at 105 HV after 16 h of MA, suggesting saturation of strain introduced by MA.

Fig. 2 shows the changes in the Vickers microhardness of the MA powders after 4 h of MA and subsequent heating at temperatures ranging from 573 K to 873 K for 24 h. The Vickers microhardness

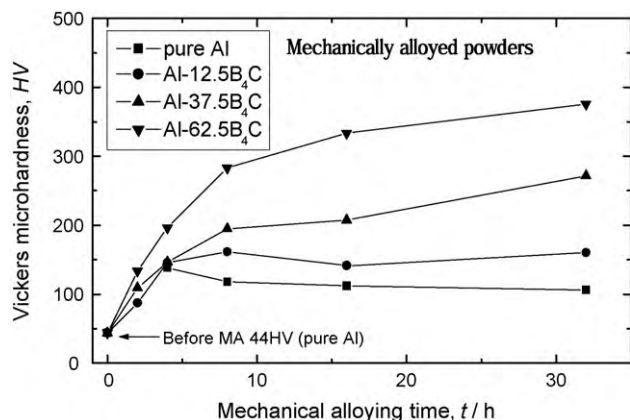


Fig. 1. Changes in the Vickers microhardness of the Al- $B_4C$  composite powders together with pure Al powder as a function of mechanical alloying time.

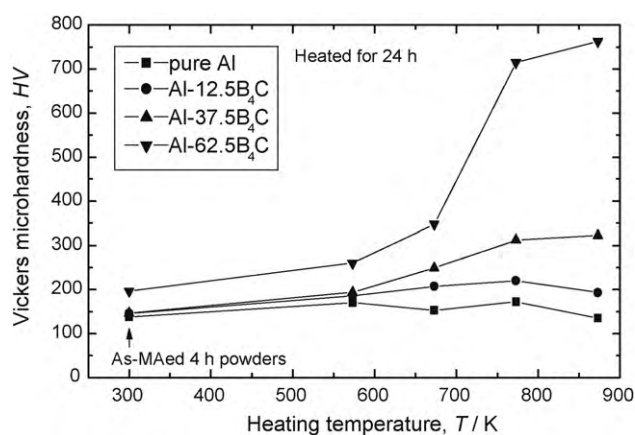


Fig. 2. Changes in the Vickers microhardness of the Al- $B_4C$  composite powders after 4 h of MA as a function of heat treatment temperature. All samples were heat treated for 24 h.

of the Al-12.5 $B_4C$  and Al-37.5 $B_4C$  powders increased gradually between the heat treatment temperatures at 573 K and 773 K. However, the Vickers microhardness of those powders decreased when the heating temperature was raised to 873 K. In contrast, the Vickers microhardness of the Al-62.5 $B_4C$  powder increased sharply with increasing the heat treatment temperatures up to 873 K. The hardness was to reach a value of 750 HV. When increasing the MA time to 32 h, the hardness level for all of the compositions was increased. No significant decrease in the Vickers microhardness was observed for all of the compositions of MAed powders after 32 h of MA as a result of heat treatment at 873 K for 24 h, assuming that stable intermetallic compounds may be formed as products of solid-state reactions during heating. The hardness level of the Al-62.5 $B_4C$  powder was significantly greater than that of other compositions.

XRD patterns obtained for the (a) Al-12.5 $B_4C$  and (b) Al-62.5 $B_4C$  powders after 4 h of MA and subsequent heating at temperatures ranging from 573 K to 873 K for 24 h are presented in Fig. 3. No solid-state reaction between aluminium and  $B_4C$  with the presence of PCA in all of the different compositions during MA was detected. Intensity of the diffraction peaks corresponding to  $B_4C$  gradually weakened with increasing the MA time, whereas it was stronger with increasing the amounts of  $B_4C$ . In the Al-12.5 $B_4C$  powder (Fig. 3(a)), partial reactions occurred to form  $AlB_{10}$  phase after heating at 573 K. The intensity of the diffraction peaks from  $AlB_{10}$  increased after heating at 773 K and 873 K, suggesting the promotion of solid-state reaction with rising heating temperatures. Further solid-state reaction was observed to form both  $Al_3BC$  and  $\gamma-Al_2O_3$  together with remaining  $AlB_{10}$  after heating at 773 K and 873 K. When the MA time increased to 32 h for the Al-12.5 $B_4C$  powder, no solid-state reaction occurred after heating up to 673 K. However, partial reactions occurred to form  $AlB_{10}$  and  $Al_3BC$  together with unknown phases after heating at 773 K. It should be noted that after increasing the MA time, the suppression of a solid-state reaction during heating was apparently observed for the Al-12.5 $B_4C$  powder. When the amount of  $B_4C$  increased to 62.5% in 4 h of MA (Fig. 3(b)),  $B_4C$  was not completely decomposed after heating at 873 K, suggesting that both the heating time and/or the MA time might be not enough to generate and promote solid-state reactions. When increasing the MA time to 32 h for the Al-62.5 $B_4C$  powder, solid-state reaction occurred after heating up to 773 K, and the formation of only  $AlB_{10}$  and  $Al_3BC$  without aluminium matrix occurred after heating at 873 K. These results suggest that lower heating temperatures promote solid-state reaction in the MA powders when the MA processing time increases as well as increasing the amount of  $B_4C$ . The reason is that a large

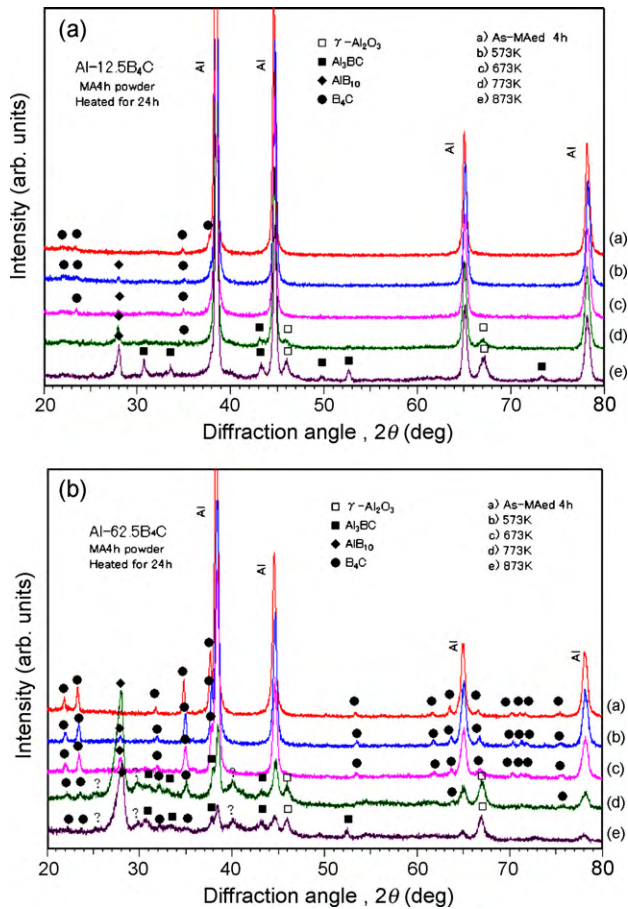


Fig. 3. XRD patterns of the 4 h MAed (a) Al-12.5B<sub>4</sub>C and (b) Al-62.5B<sub>4</sub>C powders before and after heating at various temperatures for 24 h.

amount of strain is induced to the MAed powders as increasing the MA time. A degree of thermodynamically instability of the MAed powders thus becomes larger. As a result, solid-state reactions can be promoted at lower heating temperatures. In addition, surface areas for solid-state reactions simply increase with increasing the amount of B<sub>4</sub>C particles. It should be noted that these results are also corresponding to the hardness of the heat-treated MAed powders. Thermodynamic calculations are needed for a further detailed explanation regarding the solid-state reactions.

Fig. 4 compares the Vickers microhardness of the MAed powders and Vickers hardness of the corresponding bulk materials produced by the SPS process for the Al-12.5B<sub>4</sub>C material. The hardness values of the SPS materials produced from all of the different times of the MAed powders except for 32 h of the MAed powder were higher than that of the MAed powders. These results imply that the SPS process was generally beneficial for the consolidation of the MAed Al-12.5B<sub>4</sub> powders, and the selected conditions for the SPS process in the present research were optimal for the MAed powders used. However, in the case of the higher amounts of B<sub>4</sub>C, such as 37.5% and 62.5% added to the aluminium powder, the hardness values of the bulk materials fabricated by SPS were lower than that of the MAed powders. These results indicate that a further detailed study of the sintering conditions, such as sintering temperatures and holding time including sintering pressure, needs to be done.

An XRD pattern of the SPS materials produced from 4 h of the MAed powders in the different compositions is presented in Fig. 5. In the case of the bulk Al-12.5B<sub>4</sub>C material, B<sub>4</sub>C was fully decomposed to form both  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Al<sub>3</sub>BC after sintering at 873 K for 3.6 ks. However, in the case of the bulk Al-37.5B<sub>4</sub>C and Al-62.5B<sub>4</sub>C

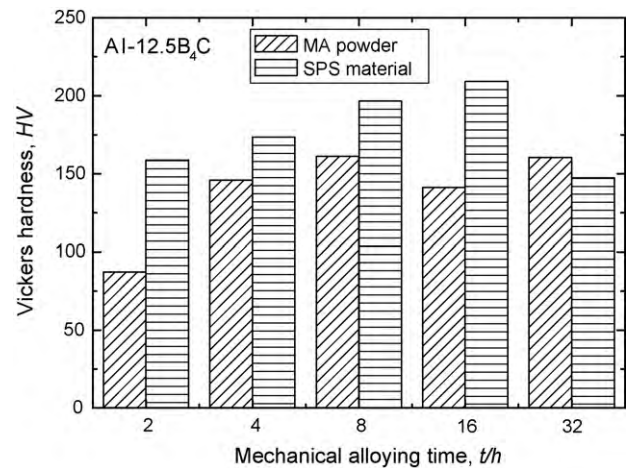


Fig. 4. Comparison of the Vickers hardness between the MAed powders and SPS materials for the Al-12.5B<sub>4</sub>C material.

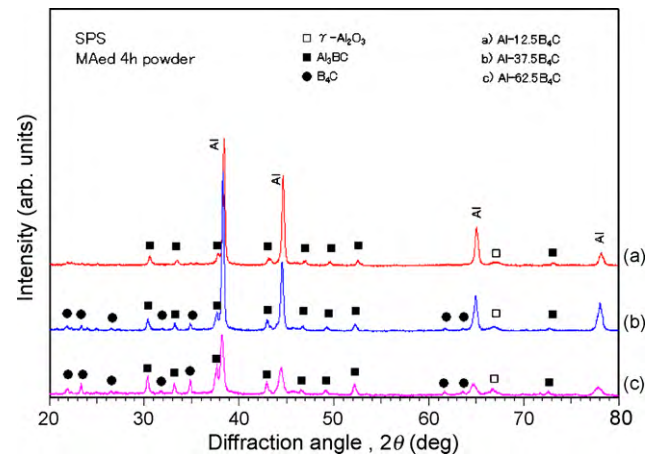


Fig. 5. XRD pattern of the SPS materials fabricated from 4 h of MAed powders.

materials, B<sub>4</sub>C was partially decomposed to form  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Al<sub>3</sub>BC after consolidation at 873 K for 1 h. When the MA time increased to 32 h, constituent phases to form by the solid-state reaction were the same. It is interesting to note that, comparing to the phases formed by the solid-state reaction in the heat-treated MAed powders, AlB<sub>10</sub> was not detected for the bulk SPS materials. Although a detailed mechanism of the formed phases is still unknown, these results suggest that the reaction process in the MAed powders and the bulk SPS materials can be different routes.

#### 4. Summary

The bulk Al-B<sub>4</sub>C composite materials were produced from the MAed powders by SPS. Solid-state reactions of the MAed powders before and after heating were examined by XRD, and mechanical properties of the MAed powders and SPS materials were evaluated by hardness measurements. The following conclusions are obtained:

The solid-state reactions in the Al-B<sub>4</sub>C powders occurred between the MAed powders and stearic acid after heating temperatures ranging from 673 K to 873 K for 24 h. The products of the solid-state reaction were a mixture of AlB<sub>10</sub>, Al<sub>3</sub>BC and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, depending upon amounts of B<sub>4</sub>C, the MA time and heating temperatures. The MA time and heating temperatures for the MAed powders affect the products by the solid-state reactions. The lower heat treatment temperatures promoted the solid-state reaction in

MA powders when the MA time increases as well as increasing the amount of  $B_4C$ . The products obtained by the solid-state reactions have affected the Vickers microhardness of both the as-MAed powders and the heat-treated powders. The near full density was attained for the SPS materials consolidated from the various MAed Al– $B_4C$  powders under an applied pressure of 49 MPa at 873 K for 1 h. The Al–12.5 $B_4C$  SPS material from 16 h MAed powder exhibited the highest hardness value of 210 HV at room temperature.

## References

- [1] S.C. Tjong, Z.Y. Ma, *Materials Science and Engineering: R* 29 (2000) 49–113.
- [2] L. Lu, M.O. Lai, *Mechanical Alloying*, Kluwer Academic Publishers, USA, 1998.
- [3] B.S. Murty, S. Ranganathan, *International Material Reviews* 43 (1998) 101–141.
- [4] C. Suryanarayana, *Progress in Materials Science* 46 (2001) 1–184.
- [5] M. Kubota, *Journal of Alloys and Compounds* 434–435 (2007) 294–297.
- [6] P.G. McCormick, *Material Transactions, JIM* 36 (1995) 161–169.
- [7] R. Orrù, R. Licheri, A.M. Locci, A. Cincotti, G. Cao, *Materials Science and Engineering: R* 63 (2009) 127–287.