# Properties of AI-AIB<sub>2</sub> Materials Processed by Mechanical Alloying and Spark Plasma Sintering

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#### Abstract

Powder mixtures of air-atomized pure aluminium and AlB<sub>2</sub> were mechanically alloyed (MA) using a vibrational ball mill to produce  $AI_{100-x}(AlB_2)_x$ , where X = 15, 30, 50. Mechanically alloyed powders were consolidated by spark plasma sintering (SPS). Mechanochemical reactions of the MA powders after various heat treatments were studied. The mechanical properties of the SPS materials were evaluated by hardness and compression testing. The  $AI_{50}(AlB_2)_{50}$  powder exhibited a Vickers hardness greater than 400 after milling for 64 h. Formation of  $AI_3BC$  and  $\gamma$ - $AI_2O_3$  occurred in MA powders after heating at 773 K for 24 h. No significant softening of the MA powders was observed after heating at 773 K for 24 h. Full densification of the SPS materials from MA powders of  $AI_{85}(AlB_2)_{15}$  was achieved using an applied pressure of 49 MPa at 873 K for 1 h. The room temperature compressive proof stress of SPS-consolidated  $AI_{85}(AlB_2)_{15}$  was 520 MPa and 620 MPa after 4 h and 8 h of MA, respectively.

#### 1. Introduction

Mechanical alloying (MA) and subsequent hot extrusion of aluminium-based composite materials has been shown to produce desirable mechanical properties at room and elevated temperatures [1]. The microstructures that are formed during the MA process contain nano-sized particles, uniformly dispersed in a work hardened, fine grained Al matrix [1]. Various particulate-strengthened aluminium composites have been experimentally developed for applications in structural components by applying the MA process [1-3]. Furthermore, the technique of mechanochemical synthesis (i.e. reaction milling (RM) [4]) has attracted considerable interest due to the unique material structures [5] and properties that can be developed. In this process, thermodynamically unstable ceramics powders are decomposed by solid-state reactions with the matrix after heat treatment of MA powders. Consequently, *in situ* formation of stable dispersoids may be achieved.

Spark plasma sintering (SPS) is a novel technique developed for sintering advanced ceramics and composite materials. The advantage of the SPS process is that it allows fabrication of bulk materials from powders using relatively short sintering times at low temperatures. Therefore, coarsening of fine grains and nano-sized dispersed particles in MA powders can be avoided.

In the present work, pure aluminium powder was mechanically alloyed with AlB<sub>2</sub> powder, with the aim of obtaining materials of high specific strength. Additionally, characteristics of the MA powders, such as mechanical properties and solid-state reaction, were clarified.

### 2. Experimental Procedures

Mixtures of 99.9% pure Al powders and 99% pure AIB<sub>2</sub> with average diameters of 100  $\mu m$  and 74  $\,\mu m.$ respectively, were mechanically The composition and alloved. designation of the experimental materials are listed in Table 1. Stainless steel balls of 7 mm in diameter together with 10 g of the AI-AIB<sub>2</sub> (AI<sub>100-x</sub>(AIB<sub>2</sub>)<sub>x</sub> where X=15, 30 or 50) powder mixture and stearic acid as a process control agent were sealed in a hardened steel vial using a glove box filled with argon. The ball to powder

Materials (at%)	Materials (mass%)	Designation	
AI-15AIB <sub>2</sub>	AI-9.58AIB <sub>2</sub>	Al <sub>85</sub> (AIB <sub>2</sub> ) <sub>15</sub>	
AI-30AIB <sub>2</sub>	AI-20.47AIB <sub>2</sub>	AI <sub>70</sub> (AIB <sub>2</sub> ) <sub>30</sub>	
AI-50AIB <sub>2</sub>	AI-37.52AIB <sub>2</sub>	AI <sub>50</sub> (AIB <sub>2</sub> ) <sub>50</sub>	
Pure Al		Pure Al	

Table 1: Test materials and designations.

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 4 h to 64 h.

The MA powders were heat treated at temperatures from 573 K to 873 K for 24 h. XRD analysis was performed on both the MA powders and SPS materials using a CuK $\alpha$  radiation source and operating at 40 mA and 60 kV. The average Vickers hardness of the MA powders was determined from 15 particles per sample with a microhardness tester using an applied load of 98 mN.

The MA powders were consolidated by SPS. 7 g of MA powder was placed into 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 using an applied load of 9.8 N. The density of the SPS materials was determined using Archimedes' principle.

#### 3. Results and Discussion

Figure 1 presents the change in Vickers microhardness of the Al-AlB<sub>2</sub> powders as a function of different MA processing times, where pure Al powder is included for reference. The hardness of pure Al powder before MA was approximately HV44. The hardness of the  $AI_{75}(AIB_2)_{15}$  powder increased dramatically to over HV100 after 4 h of MA, and a steady increase was observed up to a value of HV175 after 64 h of MA. The  $AI_{50}(AIB_2)_{50}$  powder exhibited a hardness greater than



Figure 1: Change in Vickers microhardness of Al-AlB<sub>2</sub> and pure Al powders with mechanical alloying

HV400 after 64 h of MA. Significant broadening and reduction in the X-ray diffraction peaks of the  $\alpha$ -Al (311) profile occurred as the MA time was increased, suggesting the formation of fine crystalline grains and/or a high density of defects in the matrix [6].



Figure 2: Change in Vickers microhardness of powders after (a) 4 h and (b) 32 h of MA as a function of heat treatment temperature. All samples heated for 24h.

Figure 2 shows the change in the Vickers microhardness of the MA powders after (a) 4 h and (b) 32 h of MA and heating at temperatures from 573 K to 873 K for 24 h. The Vickers microhardness of the powder after 4 h of MA increased gradually between the heat treatment temperatures of 573 K and 673 K, and sharply increased at 773 K. However, the Vickers microhardness decreased after heat treatment at 873 K. In contrast, no significant decrease in the Vickers microhardness was observed after 32 h of MA after heating at 873 K for 24 h. Similar trends in the hardness as a function of heat treatment temperature were served for all of the compositions.



Figure 3: XRD patterns of MA powders before and after heating at various temperatures for 24 h: (a)  $AI_{85}(AIB_2)_{15}$  4 h MA, (b)  $AI_{50}(AIB_2)_{50}$  4 h MA, (c)  $AI_{85}(AIB_2)_{15}$  32 h MA and (d)  $AI_{50}(AIB_2)_{50}$  32 h MA.

X-ray diffraction patterns of the MA powders after (a), (b) 4 h and (c), (d) 32 h of MA and heating at temperatures from 573 K to 873 K for 24 h are presented in Figure 3. Diffraction peaks for both AI and AIB<sub>2</sub> [7] were observed in the as-MA AI<sub>85</sub>(AIB<sub>2</sub>)<sub>15</sub> (Figure No solid-state reaction occurred after heating up to 673 K. However, partial 3(a)). decomposition of AIB<sub>2</sub> was observed, and the formation of AI<sub>3</sub>BC [8] was observed after heating at 773 K. In addition, new diffraction peaks were observed near  $2\theta$  = 46 and 67° which were identified as  $\gamma$  -Al<sub>2</sub>O<sub>3</sub> [9]. The intensity of the Al<sub>3</sub>BC peaks increased after heating at 873 K, suggesting the promotion of a solid-state reaction during heating. Incomplete decomposition of AIB<sub>2</sub> occurred after heating at 873 K. In the case of higher  $AIB_2$  contents, such as  $AI_{50}(AIB_2)_{50}$  (Figure 3(b)), the formation of  $AI_3BC$  occurred after heating at 873 K. These results imply that decomposition of AIB<sub>2</sub> occurred at higher heating temperatures as the amount of AlB<sub>2</sub> was increased. The formation of Al<sub>3</sub>BC and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is thought to cause an increase in the hardness. Even though the MA processing time for AI<sub>85</sub>(AIB<sub>2</sub>)<sub>15</sub> and AI<sub>50</sub>(AIB<sub>2</sub>)<sub>50</sub> was increased to 32 h, no solid-state reaction was observed after heated up to 573 K (Figure 3(c), (d)). However, after heating at 673 K, partial decomposition of AIB<sub>2</sub> and formation of AI<sub>3</sub>BC was observed. These results suggest that solid-state reaction in MA powders is promoted by lower heat treatment temperatures as the MA processing time increases. Thus, complete decomposition of AlB<sub>2</sub> was not achieved even with increased amounts of AlB<sub>2</sub> and MA processing time.

Materials (at%	MA time (h)	SPS (HV)	Density (a/ cm <sup>3</sup> )	Theoretical density (a/ cm <sup>3</sup> )	Relative density (%
pure Al	0	39	2.6891		99.6
	4	139	2,7488		101.8
	8	158	2,7599	2.699	102.3
	32	143	2,7249		101
	64	180	2.7834		103.1
Al- 15AlB2	4	178	2,7569	0.7440	100.5
	8	187	2.7898		101.7
	32	176	2 6944	2.7443	98.2
	64	147	2.505		91.3
	4	202	2.8216		100.9
	8	189	2,7194	0 7059	97.3
	32			2.7958	
	64				
AI- 50AIB2	4	109	2,4366		84.7
	8	100	2 3773	2.9764	82.6
	32			2.0704	
	64				

Table 2: Hardness and density of SPS materials.

Figure 4 compares the Vickers hardness of the MA powders and bulk materials produced by the SPS process from  $AI_{85}(AIB_2)_{15}$ . The hardness values of the SPS materials



Figure 4: Comparison of hardness between MA powders and SPS materials of  $AI_{85}(AIB_2)_{15}$ .

the MA powders and bulk materials produced The hardness values of the SPS materials produced from 4 h, 8 h and 32 h MA powders were higher than that of the MA powders, but lower than that of the 64 h MA powder. These results indicate that the SPS process was beneficial for the consolidation of the bulk materials, and the selected conditions for the SPS process in the current research were optimal for the MA powders used.

The relationship between the hardness and density obtained from measurements of the SPS materials together with theoretical values of density is presented in Table 2. The SPS materials produced from 4 h and 8 h MA powders showed a relative density greater than 100%. It is presumed that the SPS materials contain intermetallic compounds formed by solid-state reactions during the SPS process and/or due to contamination by Fe originating from the container and balls during MA. However, the relative density of the SPS materials decreased when increasing the amounts of AIB<sub>2</sub> and MA time. These results suggest a need for finding the optimal SPS sintering conditions.

Figure 5 shows the X-ray diffraction patterns of the  $AI_{85}(AIB_2)_{15}$  SPS materials. The products of solid-state reactions, such as  $AI_3BC$  and  $\gamma$ - $AI_2O_3$ , were formed during the SPS process and complete decomposition of the added  $AIB_2$  did not occur. This result is similar to that of the heat heated MA powders as shown in Figure3.



Figure 5: XRD patterns of the SPS materials of  $AI_{85}$  ( $AIB_2$ )<sub>15</sub> sintered from MA powders after different MA times.

The value of the 0.2% compressive proof stress for the SPS materials (also from pure Al powder) are shown in Table 3. The compressive proof stress of the Al-AlB<sub>2</sub>-based SPS materials was approximately 1.4 times higher than that of the pure Al SPS material. Furthermore, the values were higher than that of conventional high strength 7075-T6 alloy. The Al<sub>85</sub>(AlB<sub>2</sub>)<sub>15</sub>-based SPS material using 8 h MA powder showed the highest compressive proof stress of 620 MPa.

The following relationship (Equation 1) between the tensile proof stress and hardness of mechanically alloyed AI alloys at room temperature has been proposed [10]:

$$\sigma_{\rm ty} = HV \times 2.90 \tag{1}$$

where HV is the Vickers hardness and  $\sigma_{ty}$  is the tensile proof stress (MPa). From the present research, Equation 2 was derived from the values of Vickers hardness and 0.2% compressive proof stress of the SPS materials as shown in Table 2 and 3.

$$\sigma_{\rm cy} = HV \times 2.98 \tag{2}$$

where  $\sigma_{cy}$  is the 0.2% compressive proof stress (MPa). The coefficients in these two equations are approximately equal. Thus, it can be implied that the tensile proof stress of

Material	0.2% compressive stress (MPa)	ΗV	$\sigma_{v}/HV$
AI-15AIB₂ MA4h SPS	520	178	2.97
AI-15AIB₂ MA8h SPS	620	187	3.18
7075-T6	505		
Pure Al MA0h SPS	173	39	4.4
Pure Al MA8h SPS	440	158	2.78

Table 3: 0.2% compressive proof stress at room temperature for SPS materials together with 7075-T6 alloy and pure AI SPS materials.

Average 2.98

The formation of Al<sub>3</sub>BC occurred by solid-state reaction between AlB<sub>2</sub> and stearic acid in the heat heated MA powders. Incomplete decomposition of AlB<sub>2</sub> was observed even after heating the MA powders at 873 K for 24 h. The formation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> occurred after heating the MA powders at 773 K for 24 h. A higher heat treatment temperature was needed to promote solid-state reaction for powders with a higher AlB<sub>2</sub> content. In contrast, for a given composition, solid-state reaction occurred at relatively lower heating temperatures when the MA time was increased. Full densification was obtained in the SPS materials using the 4 h or 8 h MA powders of Al<sub>85</sub>(AlB<sub>2</sub>)<sub>15</sub> under an applied pressure of 49 MPa at 873 K for 1 h. However, optimal SPS sintering conditions still need to be determined for materials containing higher amounts of AlB<sub>2</sub> and/or MA powders produced using longer MA times. The SPS materials based on 4 h and 8 h MA Al<sub>85</sub>(AlB<sub>2</sub>)<sub>15</sub> exhibited room temperature compressive proof stresses of 520 and 620 MPa, respectively.

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