DEVELOPMENT AND CHARACTERIZATION OF LaB_6 REINFORCED Al-5 WT.% Si HYBRID POWDERS AND COMPOSITES PREPARED BY MECHANICAL ALLOYING AND PRESSURELESS SINTERING

ERDOĞAN Ezgi Burcu, MERTDİNÇ Sıddıka, TEKOĞLU Emre,
AĞAOĞULLARI Duygu, ÖVEÇOĞLU M. Lütfi

Istanbul Technical University, Chemical and Metallurgical Engineering Faculty,
Metallurgical and Materials Engineering Department, Particulate Materials Laboratories (PML),
Maslak, Istanbul, Turkey

Abstract

This study reports the effect of LaB_6 particles on the Al-5 wt.% Si matrix powders and composites in regard of physical, microstructural and mechanical properties. Two different types of LaB_6 particles such as laboratory-synthesized (LaB_6(S)) and commercial (LaB_6(C)) were used as reinforcement materials. (LaB_6(S)) were prepared by mechanochemical synthesis (for 5 h) and leaching (4 M HCl) of La_2O_3-B_2O_3-Mg powder blends. In order to obtain hybrid powders, Al-5 wt.% Si-2 wt.% LaB_6(S) and Al-5 wt.% Si-2 wt.% LaB_6(C) blends were mechanically alloyed (MA'd) for 1, 4 and 8 h in a high-energy ball mill. A hydraulic press with a uniaxial pressure of 450 MPa was used for the compaction of the as-blended/MA'd powders. Green compacts were sintered at 570 °C for 2 h under Ar gas. X-ray diffractometry (XRD) and scanning electron microscopy (SEM) techniques were utilized for the phase and microstructural characterization of the as-blended/MA'd powders and sintered composites. Particle size analysis (PSA) and differential scanning calorimetry (DSC) technique were also conducted on the powder products. Sintered samples were characterized by density and Vickers microhardness measurements and sliding wear tests. With applying MA, physical and mechanical improvements in composite properties were observed. Al-5 wt.% Si-2 wt.% LaB_6(C) MA'd for 8 h had the highest density value of 98.11%. Al-5 wt.% Si-2 wt.% LaB_6(S) MA'd for 4 h had the highest microhardness value of 115.25±10.12 MPa. Al-5 wt.% Si-2 wt.% LaB_6(C) MA'd for 4 h has lower wear volume loss value (0.441) than that of Al-5 wt.% Si-2 wt.% LaB_6(S).

Keywords: Aluminum composites, mechanochemical synthesis, mechanical alloying, pressureless sintering

1. INTRODUCTION

Aluminum (Al) is a crucial component for the manufacturing of metal matrix composites (MMCs). Al MMCs find applications in the aerospace and automobile industries as a low cost, lightweight material with excellent mechanical and tribological properties. Many researchers have tried to reinforce aluminium metals and their alloys with carbon, metallic or most commonly ceramic particles to improve their properties. Al MMCs mostly combine the low density of aluminum with the benefits of ceramics, such as strength, stiffness (by increasing the modulus of elasticity), wear resistance and high-temperature stability. Therefore, a good combination of ceramic reinforcements with ductile aluminum matrix has given outstanding characteristics that make Al-MMCs an ideal candidate for high-tech applications [1-5].

Casting method and powder metallurgy (P/M) are popular techniques to produce conventional MMCs. Powder metallurgy can produce metal matrix composites in the whole range of matrix reinforcement compositions without the segregation phenomena which is a typical problem of the casting processes. One of the main challenges inherent to this technique is to obtain a homogeneous distribution of the reinforcement in the metal matrix. The first requirement for a composite material to show its superior performance is the homogeneous distribution of the reinforcing phase. The agglomeration of the reinforcement particles deteriorates the mechanical properties of the composite [6-7]. Thus, mechanical alloying (MA) is the process involving repeated

cold-welding, fracturing and rewelding of powder particles to obtain a homogenous distribution of reinforcement particles during high-energy ball milling [8-10]. This technique first developed by Benjamin [11]to produce nickel superalloys hardened by oxide dispersion [12]. Uniaxial cold pressing or die compaction is commonly applied to powder particles to promote the densification prior to consolidation of the cold-pressed powders by sintering [13].

In the present study, Al-Si matrix composites reinforced with laboratory-synthesized and commercial LaB_6 particles were fabricated via mechanical alloying, cold pressing and pressureless sintering methods. The effects of MA duration on the microstructure and properties of the Al-Si matrix composites were investigated.

2. EXPERIMENTAL PROCEDURE

Elemental aluminum (Al, Alfa Aesar™, 99.5% purity, 12 µm) and silicon (Si, Alfa Aesar™, 99.99 purity, <20 µm) powders were used as the matrix of the hybrid systems. Two different types of LaB_6 powders (2 wt.%) which are laboratory-synthesized and commercial were added into the Al-5 wt.%Si matrix as reinforcement materials. Laboratory-synthesized LaB_6 powders were obtained from stoichiometric La_2O_3, B_2O_3 and Mg containing blends via mechanochemical synthesis for 5 h and leaching with 4 MHCl and they were hereafter referred to as LaB_6(S) [14-15]. Commercial LaB_6 powders (Alfa Aesar™, 99.5% purity,≤ 44 µm) were hereafter referred to as LaB_6(C). Also, 2 wt.%stearic acid powders ($C_{18}H_{36}O_2$, ZAG, 99.5% purity)were used as process control agents (PCA) to minimize cold welding and inhibit agglomeration of the powder particles. Powder batches of 8 g with the compositions of Al-5 wt.% Si-2 wt.% LaB_6(S) and Al-5 wt.% Si-2 wt.% LaB_6(C) (hereafter referred to as Al5Si2LaB_6(S) and Al5Si2LaB_6(C) samples, respectively) were mechanically alloyed (MA'd) for 1, 4 and 8 h in a Spex™8000 DMixer/Mill (1200 rpm rotation speed) with a ball-to-powder weight ratio (BPR) of 7:1 in a hardened steel vial (50 ml) with hardened steel balls (ø 6 mm). As-blended powders were loaded and MA'd powders were unloaded under Ar gas (Linde™, 99.999% purity) atmosphere in a Plaslabs™ glove box since flammable Al powders quickly oxidize in contact with air.Mechanochemical synthesis experiments were carried out using the same conditions with those of MA, excepting the total amount of powder blend (6 g) and the BPR (10:1) [14-15]. Additionally, non-milled powders (0 h) which is referred to as-blended powders will be compared with the MA'd ones.

As-blended and MA'd powders were placed in the press dies inside the same glove box and the die rods were squeezed with hand from both directions to minimize oxidation when the die set is taken outside of the glove box. As-blended and MA'd powders in each die set were compacted in a 10 ton capacity MSE™ MP-0710 uniaction hydraulic press to obtain cylinders with a diameter of 12.7 mm under apressure of 450 MPa. The green compacts were debinded at 420°C for 1 h in a MTI tube furnace with a heating and cooling rate of 2°C/min. The debinded bodies were sintered at 570 °C for 2 h in a Linn™ HT-1800 high temperature controlled-atmosphere furnace with a heating and cooling rate of 5 °C/min. Debinding and sintering process were conducted under Ar gas flowing conditions in order to prevent probable oxidation of the compacts.

X-ray diffraction (XRD) investigations of the as-blended and MA'd powders and sintered composites were carried out using a Bruker™ D8 Advanced Series powder diffractometer with CuK_αradiation in the 2θ range of 20-90° incremented at a step size of 0.01° at a rate of 5 °C/min. The average crystallite sizes and lattice strains of the Al phase in the as-blended and MA'dpowders were determined using a Bruker™-AXS TOPAS V3.0 software.4 h of MA'd powders were heated in a TA™ Instruments SDT Q600 differential scanning calorimeter (DSC) up to 700 °C under Ar gas at a heating rate of 10 °C/min and spontaneous cooling. Microstructures of the as-blended and MA'd powders and the sintered samples were examined by using a JEOL™-6000 Neoscope scanning electron microscope (SEM) operated at 15 kV. Densities of the sintered composites were measured in ethanol using the Archimedes method and the results were reported as the arithmetic means of three different measurements taken from the same samples.

Vickers microhardness measurements of the sintered samples were conducted using a Shimadzu™ HMV Microhardness Tester under a load of 100 g (9.807 N) for 10 s. Microhardness test result for each sample includes the arithmetic mean of 25 successive indentations and standard deviation. Sintered samples were subjected to sliding wear tests at room temperature in a laboratory atmosphere in a Tribotech™ Oscillating Tribotester using a 100Cr6 steel ball (ø 6 mm) under an applied force of 3 N, with a sliding speed of 10 mm/s and a stroke length of 5 mm for a total sliding distance of 25.000 mm. Wear tracks were examined by a Veeco™ Dektak 6 M Stylus profiler and test results are given as the arithmetic mean of three different measurements for each sample. Wear tracks were imaged by using the above-mentioned SEM.

3. RESULTS AND DISCUSSION

After mechanochemical synthesis and leaching process, laboratory-synthesized LaB_6 powders (LaB_6(S)) were obtained with high purity(>99.9 %) and with an average particle size of 62 nm [14-15]. **Figure 1(a)** through **(h)** illustrates the XRD patterns of the as-blended and MA'd (for 1, 4 and 8 h) Al5Si2LaB_6(C) and Al5Si2LaB_6(S) powders. According to **Figure 1a - h**, as-blended and MA'd powders contain Al (ICDD Card No: 04-0787, Bravais lattice: face-centered cubic, a = 0.405 nm), Si (ICDD Card No: 27-1402, Bravais lattice: face-centered cubic, a = 0.543 nm) and LaB_6 (ICDD Card No: 34-0427, Bravais lattice: primitive cubic, a = 0.416 nm) phases. Any peaks belonging to a secondary or intermetallic phasecould not be detectedeven after MA for 8 h, implying that Al, Si andLaB_6 particles did not react with each other during MA. There is a gradual decrease in the intensities of the Al peaks and broadening in the shape of the peaks with increasing MA duration (**Figure 1a - d** and **Figure 1e - h**).

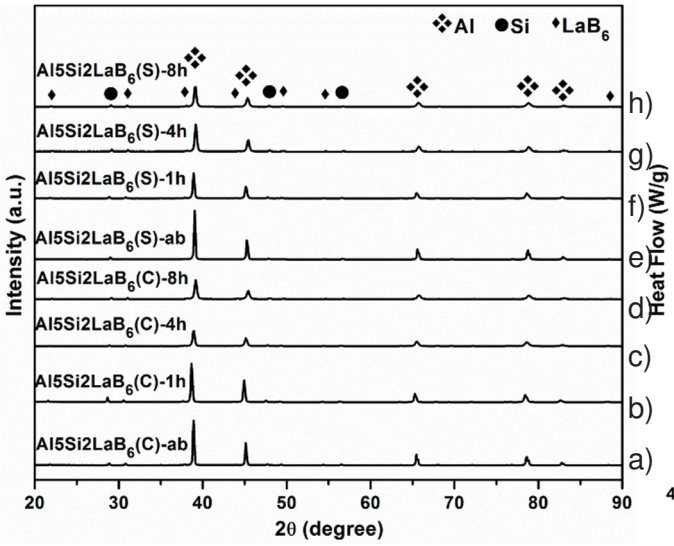

Figure 1 XRD patterns of the as-blended and MA'd powders

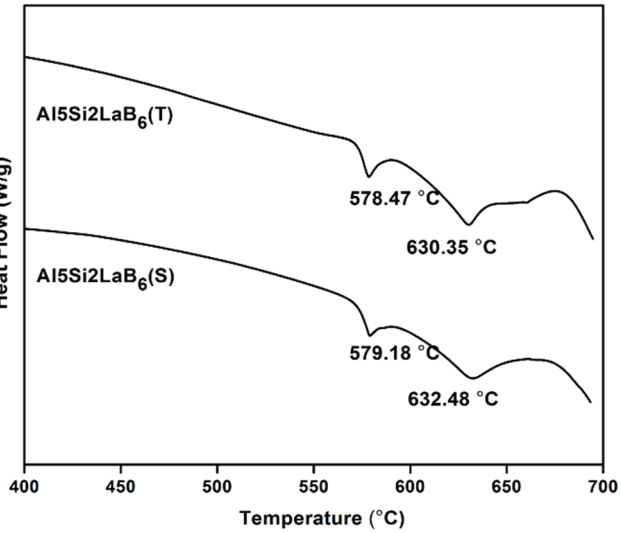

Figure 2 DSC analysis of the 4 h of MA'd hybrid powders

Depending on the Al-Si phase diagram, eutectic temperature is 577 °C [16]. However, Al-5 wt.% Si hypoeutectic composition shows two different endothermic peaks during DSC heating process (**Figure 2**). Hypoeutectic compositions have endotherms at about 579 °C. Due to the Si dissolution and MA, they behave like a eutectic composition. Although the melting temperature of Al is 660 °C, the addition of Si shifts this temperature to about 630 °C. It can be also said that two different types of LaB_6 particles had no effect on the thermal behavior of the 4 h of MA'd powders since they are stable at this temperature range.

The average crystallite sizes and lattice strains of the Al phase in the as-blended and MA'd powders are given in **Table 1**. The decrease in the average crystallite sizes of the Al particles result in higher lattice strain valueswith increasing MA duration and hence continuous deformation. After MA for 8 h, the average crystallite

sizes of the Al particles decreased in the order of 85 % for bothAl5Si2LaB$_6$(S) and Al5Si2LaB$_6$(C) powders. Also, the lattice strains of the 8 h of MA'd powders are about 6-8.5 times higher than those of as-blended ones.

Table 1 The average crystallite sizes and lattice strains of the Al phase in the as-blended and MA'd powders

Sample	MA duration (h)	Average crystallite size (nm)	Lattice strain (%)
Al5Si2LaB$_6$(S)	0	474	0.05
Al5Si2LaB$_6$(S)	1	172	0.13
Al5Si2LaB$_6$(S)	4	84	0.26
Al5Si2LaB$_6$(S)	8	73	0.31
Al5Si2LaB$_6$(C)	0	436	0.04
Al5Si2LaB$_6$(C)	1	179	0.11
Al5Si2LaB$_6$(C)	4	109	0.24
Al5Si2LaB$_6$(C)	8	64	0.34

Figures 3(a) through **(h)** show the SEM images of the as-blended/MA'd powders both for laboratory-synthesized and commercial LaB$_6$reinforcements.SEM images illustrate that powder particles formed flakes starting with MA. Then equiaxed-shaped agglomerated particles occurred by the repeated fracturing and cold-welding mechanism with increasing MA duration. Besides, the effect of laboratory-synthesized and commercial LaB$_6$ reinforcements could be observed within these images.

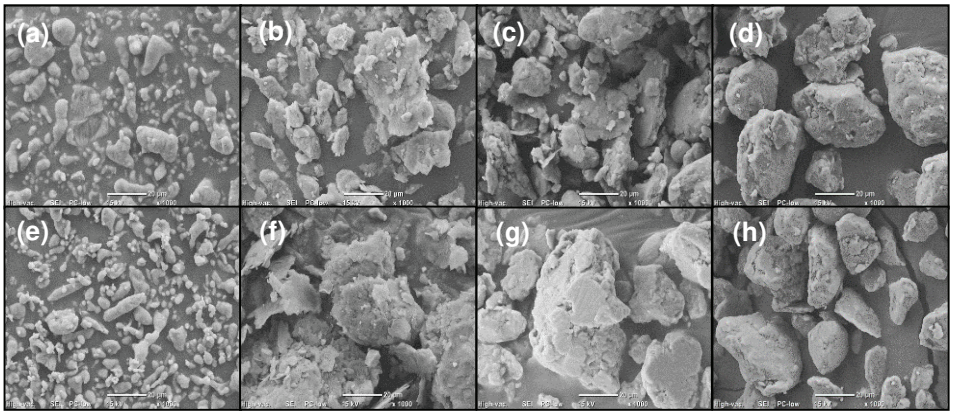

Figure 3 SEM images of the as-blended and MA'd powders: (a) as-blended Al5Si2LaB$_6$(S), (b) Al5Si2LaB$_6$(S) - 1 h, (c) Al5Si2LaB$_6$(S) - 4 h, (d)Al5Si2LaB$_6$(S) - 8 h,(e) as-blended Al5Si2LaB$_6$(C), (f) Al5Si2LaB$_6$(C) - 1 h, (g)Al5Si2LaB$_6$(C) - 4 h and (h) Al5Si2LaB$_6$(C) - 8 h

The sintered samples have the Al, Si and LaB$_6$ phases which were already present in the as-blended/MA'd powders. Due to the elimination of internal stresses during sintering, the XRD peaks of these phases (not given) were obtained more intense than those of the as-blended/MA'd powders. There is no reaction between Al, Si and LaB$_6$ phases after sintering at 570 °C for 2 h.Relative density and Vickers microhardness measurements of the sintered Al5Si2LaB$_6$(C) and Al5Si2LaB$_6$(S) samples MA'd for different durations are also given in **Table 2**.Relative density values of the Al5Si2LaB$_6$(S) samples changed from 93.6 to 97.9 % whereas those of Al5Si2LaB$_6$(C) samples changed from 97.6 to 98.1 %. There is not a good correlation between the relative density values and MA time since the highest values were obtained for different MA durations in the Al5Si2LaB$_6$(C) and Al5Si2LaB$_6$(S)samples. Moreover, Vickers microhardness of the hybrid composites varied between 40 and 115 for the Al5Si2LaB$_6$(S) samples, and 57 ± 16 and 106 ± 11 for the Al5Si2LaB$_6$(C) samples. MA increased the microhardness values of the composites up to a limited duration. Both forAl5Si2LaB$_6$(S) and

Al5Si2LaB$_6$(C) samples, microhardness measurements reach the highest values after 4 h of MA and sintering.SEM images taken from the polished surfaces of the 4 h of MA'd and sintered hybrid composites are given in **Figure 4**. There are Al and Si-rich regions in their microstructures. Besides, they have similar microstructures in accordance with their close relative density and microhardness values. It can be said that the laboratory-synthesized and commercial LaB_6 reinforced Al5Si composites exhibit similar quality and characteristics.

Table 2 Density and microhardness values of the as-blended/MA'd and sintered hybrid composites

Sample	MA duration (h)	$\rho_{relative}$ (%)	$HV_{0.1}$
Al5Si2LaB$_6$(S)	0	93.6	40 ± 8
Al5Si2LaB$_6$(S)	1	97.9	91 ± 9.6
Al5Si2LaB$_6$(S)	4	96.7	115 ± 10
Al5Si2LaB$_6$(S)	8	96.0	103 ± 9
Al5Si2LaB$_6$(C)	0	97.6	57 ± 16
Al5Si2LaB$_6$(C)	1	96.3	59 ± 6
Al5Si2LaB$_6$(C)	4	96.9	106 ± 11
Al5Si2LaB$_6$(C)	8	98.1	91 ± 12

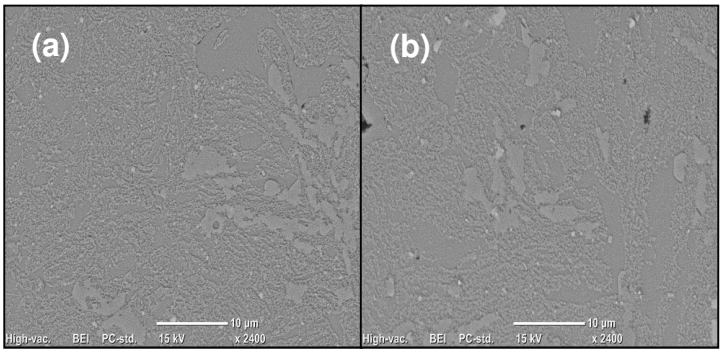

Figure 4 SEM images taken from the polished surfaces of the 4 h of MA'd and sintered hybrid composites: (a) Al5Si2LaB$_6$(S) and (b) Al5Si2LaB$_6$(T)

Figures 5 (a) and **(b)** show the SEM images of the wear tracks of the MA'd(for 4 h) and sintered hybrid composites. Besides, wear volume losses of the Al5Si2LaB$_6$(S) and Al5Si2LaB$_6$(T) sintered hybrid composites are found as 0.651 and 0.441mm^3, respectively. Although Al5Si2LaB$_6$(S) sample has higher microhardness value, Al5Si2LaB$_6$(C) sample has lower wear volume loss and narrower wear track.

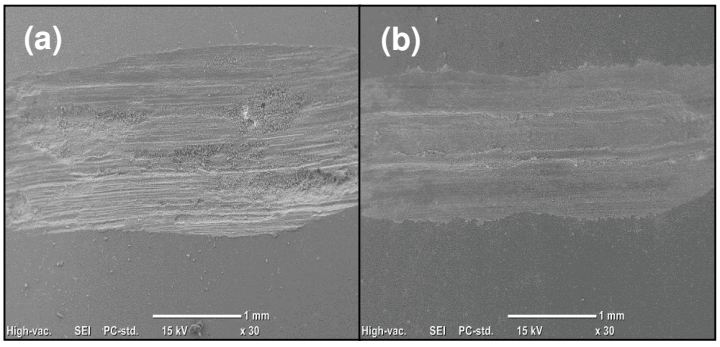

Figure 5 SEM images of the wear tracks of the MA'd(for 4 h) and sintered hybrid composites: (a) Al5Si2LaB$_6$(S) and (b) Al5Si2LaB$_6$(T)

4. CONCLUSIONS

Laboratory-synthesized and commercial LaB_6 reinforced Al-5 wt.%Si matrix composites were successfully developed via a combined method of mechanical alloying, cold pressing and pressureless sintering using different milling durations. Based on the results of this study, the following conclusions can be drawn:

1) XRD investigations of the mechanically alloyed Al5Si2LaB_6(S) and Al5Si2LaB_6(C) powders revealed no intermetallic compounds even after mechanical alloying for 8 h. XRD investigations of the MA'd powders did not show the emergence of Fe contamination released by the hardened steel milling vial and balls.
2) Mechanical alloying resulted in a sharp decrease in the average crystallite sizes of Al particles, and a homogeneous distribution and incorporation of the Si particles and LaB_6 reinforcements in the matrix.
3) It seemed that there were no correlation between MA duration and densities of the sintered hybrid composites. However, when MA prolonged to 4 h, the highest microhardness values were obtained.

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