SYNTHESIS AND CHARACTERIZATION INVESTIGATIONS OF Al-7 WT.%Si COMPOSITES HYBRIDIZED WITH LABORATORY-SYNTHESIZED NbB-NbB_2-Nb_3B_4 PARTICLES VIA MECHANICAL ALLOYING AND PRESSURELESS SINTERING

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Abstract

In this study, Al-7 wt.% Si powders and composites hybridized with niobium boride powders were prepared by a combined method of mechanical alloying (MA) and pressureless sintering. Niobium boride powders containing NbB-NbB_2-Nb_3B_4 phases were mechano-chemically synthesized (for 5 h) from Nb_2O_5-B_2O_3-Mg blends and purified with HCl leaching treatment in our laboratory facilities.Laboratory-synthesized NbB-NbB_2-Nb_3B_4powders were incorporated into the Al - 7 wt.% Si matrix powders with the amount of 2 wt.% via mechanical alloying for different durations (1, 4 and 8 h) in a Spex™ Mixer/Mill using hardened steel vial/balls with a ball-to-powder weight ratio of 7/1. Mechanically alloyed Al-7 wt.% Si-2 wt.% NbB-NbB_2-Nb_3B_4 powders were compacted using a uniaxial hydraulic press with a pressure of 400 MPa and green bodies were sintered at 570 °C for 2 h under Ar gas flowing conditions. Characterization investigations of the hybrid powders and composites were performed using X-ray diffractometer (XRD), optical microscope (OM), scanning electron microscope (SEM), particle size analyzer (PSA) and differential scanning calorimeter (DSC). Sintered samples were also characterized in terms of density, Vickers microhardness and wear volume loss. MA has positive contribution on the density and microhardness values of the sintered samples. Amongst allthe samples, a full densification was not achieved and hence the highest relative density value of 96 % and the highest microhardness value of 94 ± 9 N/mm^2 were obtained by the utilized powder metallurgy techniques.

Keywords: Aluminum matrix composites, niobium boride powders, mechanochemical synthesis, mechanical alloying, pressureless sintering

1. INTRODUCTION

Aluminum and its alloys are widely used at aerospace, automotive and many other industrial applications due to their lightweight and high specific strength [1, 2]. Silicon is the most important and main alloying element of aluminum alloys [3]. Al-Si based particulate reinforced composites are utilized in several application areas with their advanced properties such as low density, high strength, high elastic modulus, high wear and corrosion resistances [1-4]. Metal matrix composites are mostly produced with liquid-state methods (stir casting, squeeze casting, etc.) and solid-state techniques especially powder metallurgy [1].

As a solid-state technique, mechanical alloying (MA) which isdriven by high-energy ball milling is a novel andfacile method to produce non-equilibrium alloys and advanced materials [5, 6]. In this method, two or more componentsare blended and then welded due to the collisions of the balls in a high-impact vial environment. Welded structures are repeatedly fractured and crushed to form new alloys which are difficult to be produced by conventional methods [6].

There are many different reinforcement materials (boride, carbide, oxide-based) utilized in the metal matrix composites [1, 5]. Amongst them, niobium borides have high melting temperature (nearly 3000 °C), high

strength, high chemical stability at high temperatures, high thermal and electrical conductivity [7-8] and they are suitable to be used in high-temperature applications. Niobium borides include different types of stable and unstable phases such as NbB, Nb_3B_4, NbB_2, Nb_3B_2 and Nb_5B_6[8]. In this study, a mixture of stable niobium boride powders (NbB-NbB_2-Nb_3B_4) which were mechano-chemically synthesized and purified in our laboratory facilities were used as reinforcement materials in the Al-Si matrix composites due to improve their physical, microstructural and mechanical properties.

2. EXPERIMENTAL PROCEDURE

Elemental Al powders (Alfa Aesar™, 99.5% purity, 12 µm) and Si powders (Alfa Aesar™, 99.99% purity, <20 µm) were used as the starting materials in the experiments. Niobium boride powders containing NbB-NbB_2-Nb_3B_4 phases obtained in our laboratories were added as reinforcement materials in the Al-Si matrix. They were mechano-chemically synthesized (for 5 h) from the Nb_2O_5-B_2O_3-Mg powder blends in a high-energy ball mill using hardened steelvial/balls with a 10/1 ball-to-powder weight ratio (BPR) and purified by leaching with 4 M HCl [8]. Al powders, 7 wt.% Si powders and 2 wt.% of laboratory-synthesized NbB-NbB_2-Nb_3B_4powderswereblended and mechanically alloyed (MA'd) for 1, 4 and 8 h in a Spex™8000D Mixer/Mill (1200 rpm) using hardened steelvial/balls with a 7/1 BPR. Also, 2 wt.% of stearic acid ($CH_3(CH_2)_{16}COOH$) was added as a process control agent (PCA) to prevent agglomeration and excessive cold welding during the mechanical alloying (MA) process.Milling atmosphere was selected as Ar gas (Linde™, 99.999% purity)and sample handling was done in a Plaslabs™ glove-box. MA'd powders are hereafter referred to as Al-7 wt.% Si-2 wt.% NbB-NbB_2-Nb_3B_4 powders. Microstructural and phase characterizations of the powders and sintered samples were carried out using a Leica™ ICC50 HD optical microscope (OM), a Jeol™-6000 Neoscope scanning electron microscope (SEM) and a Bruker™ X-ray diffractometer (XRD) (Cu K_α radiation). Average crystallite sizes and lattice strains of the MA'd powders were determined utilizing Bruker-AXS™ TOPAS V3.0 software. Particle size analyses(PSA) of the powders were conducted with a NanoFlex™ particle sizer. Due to disperse the Al particles in liquid media, zeta potentials of the particles were changed from ~ pH = 5 to pH = 9. Besides, thermal analysis was performed using a TA™Instruments SDT Q600 differential scanning calorimeter (DSC) to determine the sintering temperature. MA'd powders were compacted in a 10 ton capacity MSE™ uni-action hydraulic press with a pressure of 400 MPainto cylindrical green compacts with a diameter of about 12 mm. PCA was removed from the compacted green bodies by debinding at 420 °C for 1 h with a heating and cooling rate of 2°C/min under Ar flow. Samples were sintered at 570 °C for 2 h under Ar gas in a Linn™ HT-1800 high temperature controlled atmosphere furnace with a heating and cooling rate of 5 °C/min. After the preparation of the hybrid composite samples, densities of the samples were determined by using Archimedes method. Hardness measurements were carried out in a Shimadzu™ Vickers microhardness tester under a load of 100 g for 10 s, and average results were calculated after 25 successful indentations. Sliding wear testswere carried out using a Tribotech™ Oscillating Tribotester under 3 N loading conditions with a sliding speed of 10 mm/s and a stroke length of 5 mm for a total sliding distance of 25000 mm, using a 100Cr6 steel ball (ø 6 mm diameter).

3. RESULTS AND DISCUSSION

Figure 1 illustrates the XRD patterns of the as-blended and MA'd(for 1, 4 and 8 h) Al-7 wt. % Si-2 wt. % NbB-NbB_2-Nb_3B_4powders. There are only diffraction peaks of Al, Si and NbB phases both for the as-blended and MA'd powders. Since NbB is the major phase in the laboratory-synthesized niobium borides and the amount of reinforcement is only 2 wt.% of the overall powder blend, NbB_2 and Nb_3B_4 phases cannot be observed in the XRD patterns. Any secondary phase or intermetallic phase was not detected, indicating that any reaction between Al, Si and Nb boride particles or Fe impurity worn from the milling vials/balls was not take place even after MA for 8 h. Peak intensities were decreased and broadened with increasing MA time. It corresponds to a decrease in the crystallite sizes of the particles. Increasing plastic deformation during milling leads to the further lattice strain and deformation. Crystallite sizes and lattice strains of Al were calculated by the TOPAS

software coupled with the diffractometer. Although, as-blended powders have 0.17 % lattice deformation, MA'd powders (for 1, 4 and 8 h) have 0.250, 0.407 and 0.454 % lattice deformation values, respectively. On the other hand, crystallite size values of the as-blended and 1, 4 and 8 h of MA'd powders are 481.9, 72.9, 47.6, 42.5 nm, respectively.

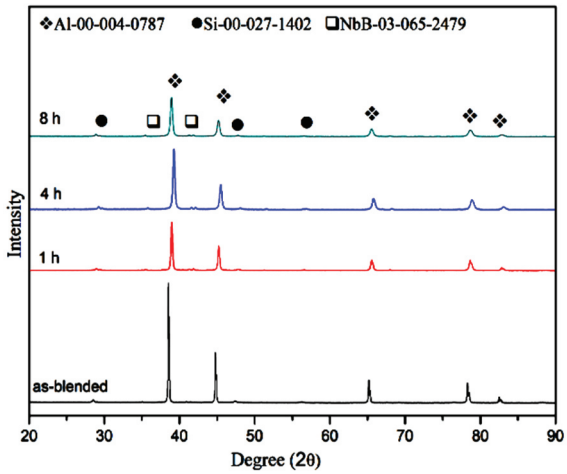

Figure 1 XRD patterns of the as-blended and MA'd Al-7 wt.% Si-2 wt.% NbB-NbB_2-Nb_3B_4 powders at various durations (1, 4 and 8 h)

Figure 2 shows the SEM images of the as-blended and 4 h of MA'd powders. The effect of MA on the powders can be obviously observed from the particle surfaces. As-blended powders are like a mixture in which different sized Al, Si and Nb boride particles distributed throughout the microstructure (**Figure 2(a)**). MA for 1 h results in flaky shaped particles due to their continuous fracturing mechanism during milling (**Figure 2(b)**).After MA for 4 and 8 h (**Figures 2(c)** and **(d)**), particles are getting more incorporated structures by colliding and welding of them with each other and with milling vial/balls. Due to the ductile character of Al, Si and Nb boride particles can be easily embedded into the Al matrix. Even though the average crystallite sizes of Al after 1, 4 and 8 h of MA are smaller than that of as-blended one, they have great tendency to be agglomerated by the effect of increase in their surface areas.

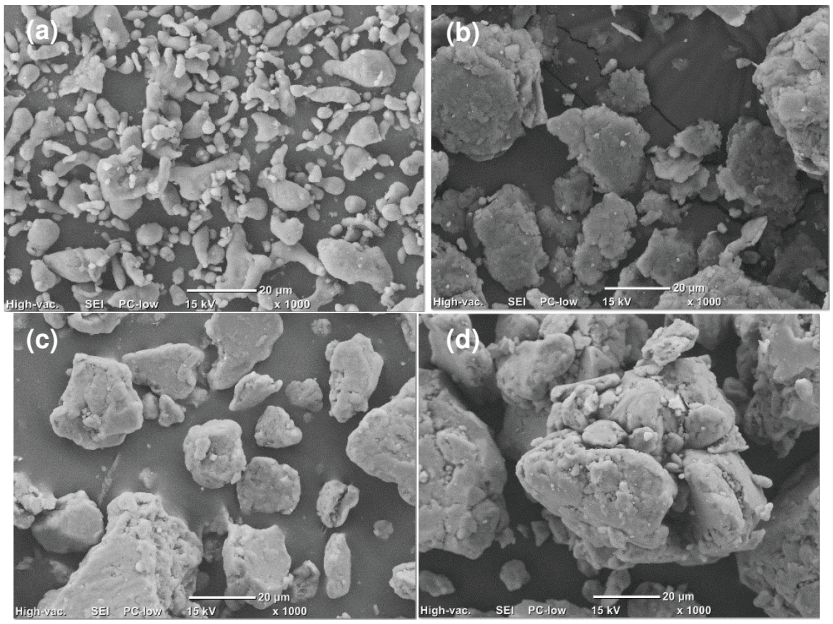

Figure 2 SEM images of the as-blended and MA'd Al-7 wt.% Si-2 wt.% NbB-NbB_2-Nb_3B_4 powders: (a) as-blended, (b) MA'd for 1 h, (c) MA'd for 4 h and (d) MA'd for 8 h

Table 1 displays the PSA results of the as-blended and MA'd powders after dispersion of them in liquid media by changing zeta potentials. As MA time increases, the average particle size of the powders decreases up to 156 nm. Also, their particle size distributions are seen in **Figure 3**. MA enables a homogeneous particle size distribution with a maximum peak point value.

Table 1 Average particle sizes of the as-blended and MA'd Al-7 wt.% Si-2 wt.% NbB-NbB_2-Nb_3B_4 powders

Sample	**Average particle size** (μm)
as-blended	> 6.00
MA'd for 4 h	0.413
MA'd for 8 h	0.156

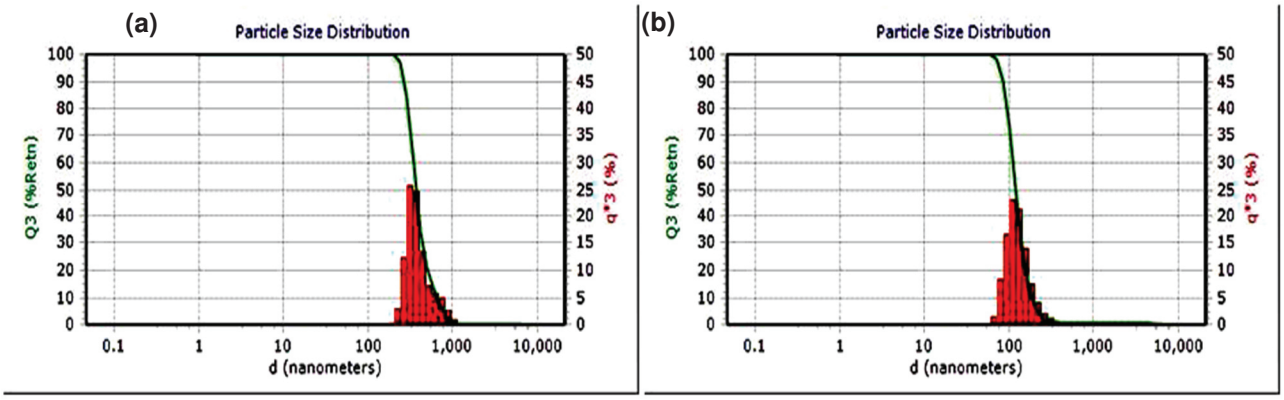

Figure 3 Particle size distributions of the MA'd Al-7 wt.% Si-2 wt.% NbB-NbB_2-Nb_3B_4 powders: (a) MA'd for 4 hand (b) MA'd for 8 h

In order to determine the sintering temperature of the MA'd samples, DSC analysis was conducted and it was exemplified for the 4 h of MA'd powders. Although the melting point of Al is 660°C, its melting temperature decreases in the case of Si addition by its diffusion through the eutectic temperature (577 °C), in consideration of the Al-Si phase diagram [3]. The DSC scan in **Figure 4** shows that there is a sharp endotherm peaking at about 578 °C, indicating that Si particles settle into the Al lattices by its dissolution. Sintering must be carried out at a lower temperature than this endothermic temperature for the solid-state sintering. Thus, the sintering temperature was determined as 570 °C.

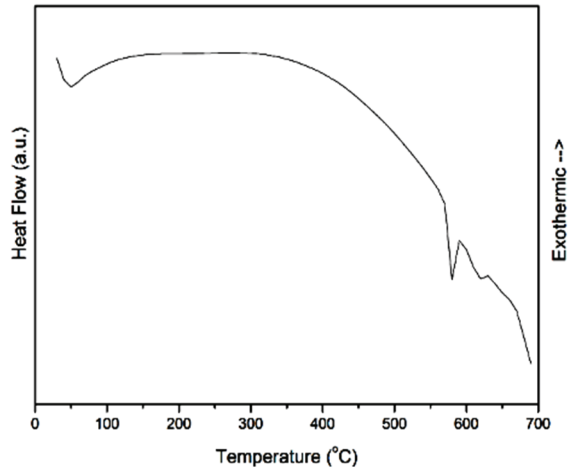

Figure 4 DSC scan of the Al-7 wt.% Si-2 wt.% NbB-NbB_2-Nb_3B_4 powders MA'd for 4 h

Figures 5(a) through **(d)** display the OM images of the sintered Al-7 wt.% Si-2 wt.% NbB-NbB_2-Nb_3B_4 composites originated from as-blended and MA'd powders. There is not a homogeneous distribution of the particles in the microstructure of the as-blended and sintered samples (**Figure 5(a)**). There are still some clusters of Si and boride particles after 1 h of MA (**Figure 5(b)**). Although the average crystallite sizes and the microstructures of the 1, 4 and 8 h of MA'd powders are similar with each other, the OM images of the sintered bodies exhibit some differences.It can be said that homogeneous distribution is obtained in the microstructure of 4 and 8 h of MA'd and sintered samples (**Figures 5(c)** and **(d)**). Besides, there are Al and Si-rich regions in their microstructures. SEM image of the 4 h of MA'd and sintered Al-7 wt.% Si-2 wt.% NbB-NbB_2-Nb_3B_4 composite is also given in **Figure 6**. Al and Si-rich regions can be clearly seen and confirmed with the SEM image.

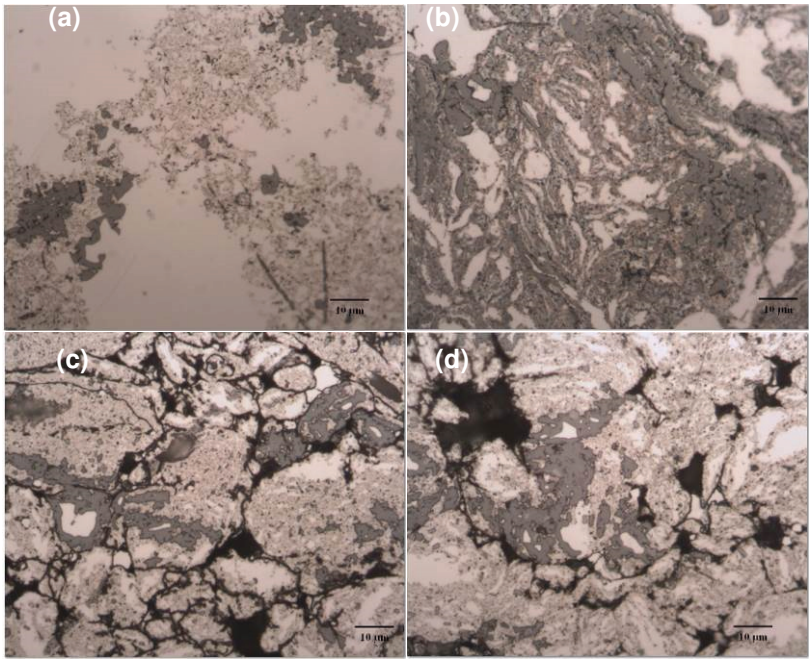

Figure 5 OM images of the as-blended/MA'dand sintered Al-7 wt.% Si-2 wt.% NbB-NbB_2-Nb_3B_4composites: (a) as-blended, (b)MA'dfor 1 h, (c) MA'd for 4 h and (d) MA'dfor 8 h

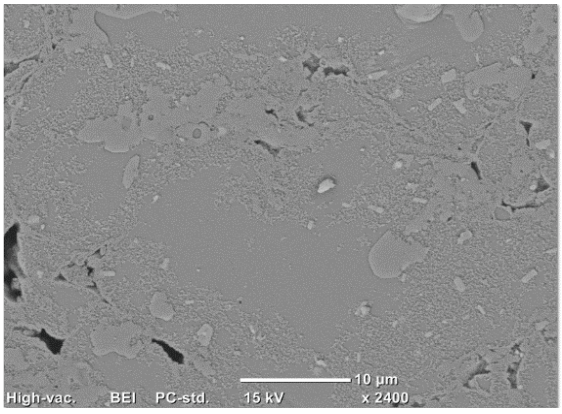

Figure 6 SEM image of the 4 h of MA'd and sintered Al-7 wt.% Si-2 wt.% NbB-NbB_2-Nb_3B_4 composite

Table 2 shows the density and hardness values of the as-blended/MA'd and sintered Al-7 wt.% Si-2 wt.% NbB-NbB_2-Nb_3B_4composites. As can be seen from **Table 2**, all Archimedes density values are not very close to the theoretical density which it means that there is no full densification in the samples. However, MA has a positive contribution on the density values of the samples. The microstructural changes in the 1 h of MA'd

powders and their sintered samples are in good accordance with the increase in its relative density value as compared with the as-blended and sintered sample (from 84.8 to 96.6 %). 4 and 8 h of MA'd and sintered samples have close relative density values in the order of 95 %, as expected from their similar average crystallite sizes and microstructures. Dense samples namely MA'd and sintered bulks have higher microhardness values than that of as-blended and sintered sample. The increase in the microhardness values is above the twice of its reference value (from 43 ± 6 to 94 ± 9). The highest microhardness value was obtained for the 8 h of MA'd and sintered sample as 94 ± 9 whereas the highest relative density values was determined for the 1 h of MA'd and sintered sample. **Figures 7(a)-(c)** are the OM and SEM images of the worn surfaces taken from the 4 h of MA'd and sintered Al-7 wt.% Si-2 wt.% NbB-NbB_2-Nb_3B_4 composite. The wear volume loss value of the selected sample is about 0.289 mm^3.

Table 2 Density and microhardness values of the as-blended/MA'd and sintered Al-7 wt.% Si-2 wt.% NbB-NbB_2-Nb_3B_4composites

MA duration	Theoretical density (g/cm^3)	Archimedes density (g/cm^3)	Relative density (%)	Vickers microhardness
as-blended	2.694	2.295	84.89	43 ± 6
1 h		2.611	96.57	90 ± 11
4 h		2.574	95.23	90 ± 8
8 h		2.582	95.52	94 ± 9

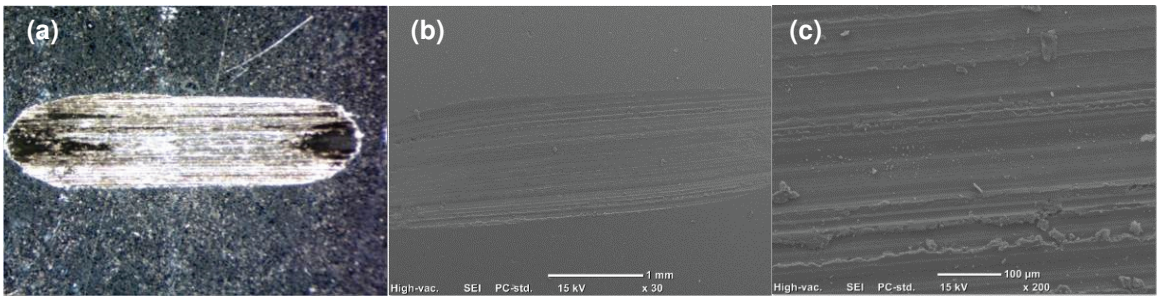

Figure 7(a) OM,(b) SEM and (c) SEM images of the worn surfaces taken from the 4 h of MA'd and sintered Al-7 wt.% Si-2 wt.% NbB-NbB_2-Nb_3B_4 composite

4. CONCLUSIONS

Physical, microstructural and some mechanical properties of the laboratory-synthesized NbB-NbB_2-Nb_3B_4 reinforced hypo-eutectic Al-Si matrix hybrid composites were improved by mechanical alloying and pressureless sintering. Amongst all the MA'd samples, the highest relative density value of 96 % and highest microhardness value of 94.013±9.165 were obtained.

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