Characterization Investigations of NbB₂/NbC Particulate Reinforced Al-7 Wt.% Si Composites Synthesized via Various Milling Processes and Pressureless Sintering

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Abstract

The influence of milling type on the microstructural, physical and mechanical properties of NbB₂/NbC particulate reinforced Al - 7 wt. % Si metal matrix composites was investigated in this study. NbB₂/NbC particles were incorporated into the Al - 7 wt. % Si alloy with the amount of 2 wt. %, and NbB₂/NbC reinforced Al - 7 wt. % Si powders were prepared. They were fabricated via four different milling methods consisting of mechanical alloying in a high energy ball mill, mechanical alloying in a planetary ball mill, sequential milling in the high energy ball mill and planetary ball mill, and sequential milling in the high energy ball mill and cryogenic mill. Powder batches were mechanically alloyed (MA’d) both for 4 h in Spex 8000D Mixer/Mill (at 1200 rpm) or for 12 h in FRITSCH/Pulverisette planetary ball mill (at 400 rpm) in a hardened steel vial using hardened steel balls with 7/1 ball-to-powder weight ratio. Additionally, 4 h of MA’d powders were mixed with the non-milled powder blends and then they were MA’d for 12 h in planetary ball mill. Finally, 4 h of MA’d powders were cryomilled for 10 min in Spex 6870 Freezer/Mill and were MA’d for 1 h in Spex 8000D Mixer/Mill again to fabricate sequentially milled (mechanical alloying and cryogenic milling) powders. Microstructural characterization of the as-blended and milled powders were conducted via X-ray diffraction meter (XRD), and scanning electron microscope (SEM). Also, thermal properties of the powders were investigated by using differential scanning calorimeter (DSC). After the characterizations of the powders, they were compacted with uniaxial hydraulic press under 450 MPa to produce cylindrical samples (with 12 mm diameter). After that, compacted powders were sintered under Ar gas flowing conditions at 570°C for 2 h. Density measurements and Vickers microhardness measurements of the sintered samples were conducted. Although, microhardness value of the composite milled at planetary ball mill was 89.66 HV, microhardness values reached up to 114.53, 108.7 and 114.65 HV for the MA’d (high energy ball mill), and sequentially milled composites (high energy ball mill/planetary ball mill, and high energy ball mill/cryogenic mill), respectively. Improvement in the mechanical properties of the composites was mostly related with the microstructural evolution obtained by means of mechanical alloying and cryogenic milling.

1. Introduction

Al-Si based metal matrix composites are generally fabricated via liquid-state casting processes. However, there are some studies about the solid-state processing methods for production of Al-Si based composites [1–4]. Amongst them, MA is one of the solid-state production method that based on the welding, fracturing and rewelding of the particles due to the interaction between the powders and milling balls and/or walls of the milling media [5–7]. Various types of milling equipment are used for MA studies. They have different capacities, efficiencies and heating/cooling media [5]. Planetary ball mills (~400 rpm), SPEX™ mixer mills (~1200 rpm), attritor mills are some mill types that are usually used for MA applications. Besides, MA can be conducted at the cryogenic temperatures by using circulated liquid nitrogen in the mills. This milling method is generally used for ductile materials such as Al, Cu, etc [5]. The aim of the present study is enhancement of the physical, mechanical and microstructural properties of the NbB₂/NbC reinforced Al - 7 wt. % Si composites with milling and also determination of the effect of the different milling processes on the properties of the composites. NbB₂ and NbC powders were used as reinforcement materials due to their superior thermal, physical, chemical and mechanical properties [8,9].

2. Experimental Procedure

The powders used as starting materials were: elemental Al (supplied by Alfa Aesar™, 99.5 % purity, particle size ≤ 12 µm) and Si (supplied by Alfa Aesar™, 99.99 % purity, particle size ≤ 20 µm) powders and NbB₂/NbC composite powders that were synthesized by Balç et al.[8] at laboratory facilities. The starting materials were mixed to constitute 2 wt. % NbB₂/NbC reinforced Al – 7 wt. % Si alloys with the addition of 2 wt. % stearic acid (C₁₈H₃₇O₂, ZAG, 99.5 % purity) as a process control agent. Hereafter, this composition were named as Al7Si-2NbB₂/NbC.
Starting powders were mixed in a WAB™ T2C Turbula blender for 30 min before the milling processes to produce as-blended powders. Fabrication of the Al7Si-2NbB2/NbC composites were conducted in four different milling methods. At first process (M1), mechanical alloying (MA) of the blended powders was carried out in a Spex™ 8000D Mixer/Mill (1200 rpm) for 4 h by using a hardened steel vial (50 ml) and balls (φ 6 mm) with a ball-to-powder weight ratio of 7/1. At second process (M2), MA of the as-blended powders was carried out in a FRITSCH™ (400 rpm) for 12 h by using a hardened steel vial (500 ml) and balls (φ 6 mm) with a ball-to-powder weight ratio of 7/1. At third process (M3), as-blended powders were combined with the powders produced by M1 process (2 wt. %) and MA’d in a FRITSCH™ (400 rpm) for 12 h. Finally, at fourth process (M4), 4 h of MA’d powders (Spex™ 8000D Mixer/Mill) were cryomilled in a Spex™ 6870 Freezer/Mill using a cylindrical polycarbonate vial and stainless steel rods with liquid N2 (Linde™, refrigerated) circulated around the vial externally. Working conditions of the cryomill were: collision rate of 900 collisions/min, 15 min initial pre-cooling step followed by cycles of milling (10 min) and cooling (5 min) steps. Then, these cryomilled powders also milled for 1 h in Spex 8000D Mixer/Mill. Handling of the powder blends were done in a Plaslabs™ glove box (under Ar gas supplied by Linde™ with 99.999 % purity) to inhibit the oxidation. Phase analyses of the as-blended and milled powders were conducted via Bruker™ D8 Advanced Series powder diffractometer with CuKα (λ=1.5406 Å) radiation, 35 kV and 40 mA operating conditions. Average crystallite sizes and lattice deformations were predicted with Bruker™-AXS TOPAS 4.2 software. Thermal properties of the powders were investigated by using TA™ Instruments SDT Q600 differential scanning calorimeter (DSC). Also, particle sizes of the milled powders were measured using a Microtrac™ Nano-Flex particle size analyzer (PSA) in distilled water media. After each milling, composite powders were compacted in a MSE™ MP-0710 one-action hydraulic press under 450 MPa uniaxial pressure. Compacted samples were debinded in a Protherm™ tube furnace under Ar gas flow at 420°C for 2 h (heating and cooling rate = 2°C/min). Debinded bodies were sintered at in a Limit™ HT-1800 furnace under Ar atmosphere at 570°C for 5 h (heating and cooling rate = 10°C/min). Microstructural investigations were performed with optical microscope (OM) and JEOL™ JCM-6000Plus NeoScope scanning electron microscope (SEM) that equipped with EDS. Densities of the sintered composites were measured using the Archimedes method, and Vickers microhardness measurements of the sintered samples were conducted by using of Shimadzu™ HV100 microhardness tester under a load of 25 g for 10 s. After the 30 successful indentations, average microhardness values and standard deviations were determined. Also, wear properties of the composites were determined via sliding wear tests utilizing a Tribotechnie™ oscillating tribotester by using 100Cr6 hardfacing steel balls (φ 6 mm) under 3 N applied force, 5 mm/s sliding speed and 25,000 mm total sliding distance.

3. Results and Discussion

The microstructural characterizations of the as-blended and those of milled powders were carried out by SEM (Fig. 1). SEM micrograph of the as-blended powders shows irregular shaped initial powders (Fig. 1a). Powder morphologies transformed to flaky shaped and agglomerated particles via mechanical alloying due to the continuous welding, fracturing and rewelding mechanisms. Although, milled powders by using M1, M2 and M3 processes have plate-like morphologies, M4 powders consist of equiaxed particles. Therefore, cryogenic milling media help to the formation of equiaxed particles.

Figure 1. SEM images of the as-blended Al7Si-2NbB2/NbC powders (a) and those milled with various processes: M1 (b), M2 (c), M3 (d) and M4 (e).

After MA, only Al, Si and NbB2 phases have been identified in the XRD patterns of Al7Si-2NbB2/NbC powders. NbC phase was not detected because weight percentage of the NbC in the powders were not high enough for detection sensitivity of the XRD [8]. Additionally, there is no intermetallic phase formation and contamination from the milling media.

Figure 2. XRD patterns of the as-blended Al7Si-2NbB2/NbC powders (a) and those milled with various processes: M1 (b), M2 (c), M3 (d) and M4 (e).

Decrease in Al peak intensities and broadening of peaks represent the reductions in the average crystallite size and increases in the average lattice
strain of the MA’d powders. Calculated average crystallite size and lattice deformation values were given at Table 1. Crystallite sizes of the particles were decreased dramatically by MA. Amongst all the milled samples, M4 powders have the lowest crystallite size value. Besides, lattice strain values change significantly after milling. The highest lattice strain was reached via cryogenic milling. On the other hand, particle size measurements of all MA samples were performed and average particle sizes were listed at Table 1. Particle size of the as-blended powders were greater than the 6 μm, so they were not inside the measurement ranges of particle size. Particle sizes of the milled powders using various processes changed between 0.2 and 0.5 μm.

**Table 1.** Average crystallite sizes, lattice deformations and particle sizes of the as-blended and milled Al7Si-2NbB2/NbC powders.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average crystallite size (nm)</th>
<th>Lattice deformation (%)</th>
<th>Average particle size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-blended</td>
<td>574.1</td>
<td>0.07</td>
<td>&gt;6</td>
</tr>
<tr>
<td>M1</td>
<td>73.7</td>
<td>0.28</td>
<td>0.46</td>
</tr>
<tr>
<td>M2</td>
<td>72.8</td>
<td>0.24</td>
<td>0.20</td>
</tr>
<tr>
<td>M3</td>
<td>70.4</td>
<td>0.31</td>
<td>0.35</td>
</tr>
<tr>
<td>M4</td>
<td>40.4</td>
<td>0.51</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Representative DSC thermogram of the MA’d for 12 h with planetary ball mill powders (M2) are given at Fig. 2. Endothermic peak at the 578.29°C is very close to eutectic temperature of Al-Si binary phase diagram (577°C). Also, unmilled Al-Si powder mixtures has endothermic peak at nearly 660°C because this temperature represents the melting of Al [10]. Therefore, Si solubility into Al matrix increases via MA.

**Figure 2.** DSC thermogram of the M2 powders.

After the pressing and sintering, the presence of the porosities was observed by OM images of the as-blended and sintered composites (Fig. 3a). As seen in Fig. 3b-e, composites with low porosities were produced. Mechanical alloying processes attributed to the formation of homogeneous microstructures. These homogeneous phase distributions affect the mechanical and physical properties of the sintered composites.

**Figure 3.** OM images of the samples sintered from as-blended Al7Si-2NbB2/NbC powders (a) and from milled powders: M1 (b), M2 (c), M3 (d) and M4 (e).

SEM investigations were conducted to the representative composites sintered from both as-blended and 4 h MA’d powders (Fig. 4.). Microstructural evaluations during milling showed a uniform distribution of the phases.

**Figure 4.** Representative SEM images of the Al7Si-2NbB2/NbC composites sintered from the as-blended and M1 powders.

EDS analysis results for Al7Si-2NbB2/NbC composites are given at Table 2. Al-rich regions (region A) were surrounded by the Si-rich regions (region B) in the as-blended and sintered composites. Additionally, NbB2/NbC reinforcement particles were seen as bright points at the SEM image and region C represents the reinforcement particles. NbB2/NbC reinforcement particles were homogeneously distributed into the matrix, so mechanical and physical properties of the MA’d and sintered composites enhanced.

**Table 2.** EDS results of the as-blended and sintered Al7Si-2NbB2/NbC composites.

<table>
<thead>
<tr>
<th></th>
<th>Al (wt.%)</th>
<th>Si (wt.%)</th>
<th>Nb (wt.%)</th>
<th>B (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>99.43</td>
<td>0.57</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>2.87</td>
<td>97.13</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>0.41</td>
<td>-</td>
<td>53.17</td>
<td>46.42</td>
</tr>
</tbody>
</table>

Archimedes densities and Vickers microhardness values of the all sintered samples are given at Table 3. Samples milled with different methods and sintered had higher densities than those as-blended and sintered
one. The microhardness values increase due to the particle size refinement and dispersion strengthening. Microstructural homogeneity was observed by milling. 4 h mechanically alloyed, and sequentially milled and sintered samples have highest microhardness values (nearly 114 HV) due to their homogeneous reinforcement dispersions. Amongst the milled samples, MA’d for 12 h in planetary ball mill and sintered sample has the lowest density and inferior hardness values. Moreover, M1 and M4 samples have the similar wear volume loss value of 0.294 mm$^3$.

**Table 3. Density and microhardness results of the Al7Si-2NbB$_2$/NbC composites sintered from the as-blended and milled powders.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative density (%)</th>
<th>Hardness (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-blended</td>
<td>82.1</td>
<td>46.6±7.6</td>
</tr>
<tr>
<td>M1</td>
<td>86.3</td>
<td>114.5±11.7</td>
</tr>
<tr>
<td>M2</td>
<td>83.3</td>
<td>89.6±6.6</td>
</tr>
<tr>
<td>M3</td>
<td>87.1</td>
<td>108.7±16.1</td>
</tr>
<tr>
<td>M4</td>
<td>85.4</td>
<td>114.6±15.9</td>
</tr>
</tbody>
</table>

4. Conclusion

Based on the characterization investigations of the Al7Si-2NbB$_2$/NbC composites, general results were listed below.

- Only Al, Si and NbB$_2$ phases were detected as a result of the XRD investigations.
- Both average crystallite sizes and particle sizes reduced by MA. The lowest crystallite size value was achieved with M4 (mechanical alloying for 4 h and cryogenic milling) process. Also, M4 powders have not exhibit the lowest particle size value because of the agglomeration.
- Endothermic temperature shift to the eutectic temperature indicating that Si diffused into the Al matrix and formed Al solid solution.
- Homogeneous microstructures can be obtained with MA processes. According to the OM images, milled with M1 (mechanical alloying for 4 h) and M4 powders have more homogeneous microstructures.
- Therefore, mechanical properties of the denser M1 and M4 samples are better the other ones.

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References


