Influence of Graphene Content on Sinterability and Physico-Mechanical Characteristics of Al/Graphene Composites Prepared via Powder Metallurgy

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Abstract: The main goal of the present study is to add graphene lubricant to enhance the microstructure and physicochemical properties of aluminum matrix composites. The proposed composites were prepared by mechanical alloying technique, and the graphene was added with different contents up to 0.8 wt.% as reinforcement. X-ray diffraction analysis and transmission electron microscopy were employed to inspect milled powders’ phase changes and particle features (shape and size). The obtained powders were sintered at 400, 500, and 570°C. The microstructure of fired composites was tested by scanning electron microscopy. The physical properties, hardness, compressive strength, strengthening factor, elastic-moduli, and electrical conductivity were also measured. The results displayed that the graphene particles are homogenously distributed through the Al matrix after milling. The particle size of milled powders was about 31.6 nm with an obvious degree of agglomeration. The mechanical properties of sintered composites were affected significantly by sintering temperature and graphene content as dominant factors. The highest obtained microhardness and compressive strengths were 920.8 MPa and 292.1 MPa. They achieved the composite that contains 0.8 wt.% of graphene (AG0.8). Moreover, the conductivity was decreased slightly with the increase of graphene, but it was increased with increasing sintering temperature.

Keywords: graphene; aluminum matrix composites; mechanical milling; sintering; hardness; electrical properties.

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1. Introduction

It is well established that the Al-matrix composites (AMCs) strengthened by ceramics nanopowders have impressive characteristics such as higher thermal conductivity, higher elastic modulus, higher hardness, lower density, and higher temperature stability. Thus, they could be utilized widely in numerous structural applications such as shields, space shuttles, aircraft, electronic equipment, etc. [1-3]. Many types of ceramic reinforcements have been applied to improve Al matrix composites, such as SiC [4], ZrO₂ [5], SiO₂ [6], B₄C [7], and graphene [8, 9]. Several pieces of research have been reported on Al matrix composites; for example, Arab [10] prepared Al matrix composites reinforced with different SiC contents up
to 15 vol. % using mechanical alloying and studied their mechanical properties. The researcher reached a remarkable increase in hardness, strength, and young's modulus (106 BHN (Brinell hardness number), 187 MPa, and 103 GPa, respectively). Jargalsaikhan et al. [11] extensively studied the effect of 1 wt. % carbon nanotube on Al matrix composites prepared by high energy milling. The results showed that the carbon nanotubes were homogeneously dispersed in Al powder, and the hardness increased by about 22 % compared to Al alone. Zawrah et al. [4] extensively studied the effect of 1 wt. % carbon nanotube on Al matrix composites prepared by high energy milling. The results showed that the carbon nanotubes were homogeneously dispersed in Al powder, and the hardness increased by about 22 % compared to Al alone. Their results of microstructural characterization revealed a homogenous distribution of SiC particles in the Al-Si alloy matrix. Also, the microhardness and compressive strength have been increased from 391 to 1178 and from 95 to 138 MPa, respectively, after adding 20 wt. % SiC. Moreover, the conductivity was linearly decreased with increasing SiC and reached 2.72x104 S/m. Mostafa et al. [12] reported manufacturing Al6061/Al2O3 and Al6061/BN composites by the fraction stir method. Significant improvement was observed in mechanical properties after adding Al2O3 and BN. For Al6061/Al2O3 composites, microhardness and strength exhibited an increase of about 21 and 14 % compared to the Al alloy matrix, while for Al6061/BN composites, the increase was about 46 and 38%, respectively. Recently, careful attention has been paid to graphene due to its promising properties, such as excellent mechanical properties as well as excellent electrical and thermal conductivities [1, 13-15]. So, the addition of graphene to the Al matrix significantly improves the material's mechanical properties and thermal characteristics, i.e., hardness, strength, elastic-moduli and mechanical wearing, without a huge reduction in electrical properties of composites [16]. Al-matrix composites have been prepared by numerous techniques like stir cast [17], squeeze-casting [18], fraction stir [19], and mechanical alloying [20]. Mechanical milling is an important technique to prepare AMCs with important mechanical properties due to the uniform distribution and refinement of reinforcement particles between Al matrix grains [2, 20-22]. This study uses ball milling to produce Al/graphene nanocomposite powders with different graphene percentages (0, 0.4, 0.6, 0.6, and 0.8 wt. %). The consolidation of prepared powder at 400, 500, and 570 °C is also considered. This article also examines the influence of graphene contents and firing temperature on phase composition, particle size, physical properties, microhardness, compressive strength, elastic moduli, and electrical conductivity of Al/graphene composites.

2. Materials and Methods

2.1. Materials.

The as-supplied Al powder has average particles size of 45 μm and 99.5% purity; it was provided by Sigma Aldrich, while the graphene sheet was provided by Alfa Aesar. The compositions of designed composite batches and their abbreviations are listed in Table 1.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Mass, %</th>
<th>Al</th>
<th>Graphene</th>
</tr>
</thead>
<tbody>
<tr>
<td>AG0</td>
<td>100</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>AG0.2</td>
<td>99.8</td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>AG0.4</td>
<td>99.6</td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>AG0.6</td>
<td>99.4</td>
<td></td>
<td>0.6</td>
</tr>
<tr>
<td>AG0.8</td>
<td>99.2</td>
<td></td>
<td>0.8</td>
</tr>
</tbody>
</table>
2.2. Experimental methods.

The powder mixes were ground for ten hours by ball-milling machine kind MTI-SFM-1, with 1 mass-% stearic acid as a dispersant to duck powder aggregation throughout the process. The powders were ground by alumina balls having 20 mm thickness, at 550 rpm rotating speed and a BPR ratio of 20:1. The ground powder was investigated using X-ray analysis (XRD), "Philips PW 1373" and transmission electron-microscope (TEM), JEOL JEM-1230. The crystal size (D) of the milled powders was estimated by the following Scherer formula [25]:

\[ D = \frac{0.9 \lambda}{B \cos \theta} \]  

where, \( \lambda = 1.54A^0 \), \( \beta = \) full-width at half maximum, and \( \theta = \) angle of incident.

The dislocation density (\( \delta \)) was calculated using formula 2 [26]

\[ \delta = \frac{1}{D^2} \]  

The lattice-strain (\( \varepsilon \)) was also estimated by formula 3 [12]:

\[ \varepsilon = \frac{B}{4 \tan \theta} \]  

The milled powder was cold-pressed under 20MPa to form cylindrical samples with dimensions 8 mm radius and 5 mm in length. The shaped pellets were subjected to sintering at 400\(^\circ\), 500\(^\circ\), and 570\(^\circ\)C for one hour in argon medium under a heating rate of 7\(^\circ\)/min. The relative density and apparent porosity of fired materials were tested, giving Archimedes' principle according to ASTM:B962-13. The hypothetical density of Al-graphene composite was estimated using the mixture rule, considering that the full density of Al and graphene are 2.7 and 2.267 g/cm\(^3\), respectively. After that, the relative density of fired specimens was calculated utilizing the bulk and full densities. The microhardness of the fired composite was examined according to ASTM:B933-09 with 1.961N force applied for ten seconds using a Shimadzu-HMV (Japan) microhardness tester under ambient laboratory conditions and a constant indenter dwell time of 10 s. The cold crushing strength of the fired composite was tested, giving ASTM E9.

Furthermore, the yield-strength, compression-strength, strengthening-efficiency (R), and fracture-strain were estimated using a stress-strain diagram. The ultrasonic wave velocities (longitudinal- and shear-) spread in the sintered composites were recorded by pulse-echo ultrasonic system type MBS8000-DSP at 5MHz resonance. Lame's coefficients (\( \lambda \) and \( \mu \)) were calculated giving the longitudinal- (\( V_L \)) and shear- (\( V_S \)) ultrasonic velocities according to the following equations [27]:

\[ \lambda = \rho (V_L^2 - 2V_S^2) \]  
\[ \mu = \rho V_S^2 \]  

where: \( \rho \) is the material bulk-density

The quantities s of elastic-moduli, i.e., longitudinal- (\( L \)), shear- (\( G \)), Young's- (\( E \)), bulk-moduli (\( B \)), and Poisson's-ratio (\( \nu \)) were estimated giving the next formulas [28]:

\[ L = \lambda + 2\mu \]  
\[ G = \mu \]  
\[ E = \frac{3\lambda + 2\mu}{\lambda + \mu} \]  
\[ B = \lambda + \frac{2}{3}\mu \]
$$\nu = \frac{\lambda}{2 (\lambda + \mu)}$$  \hspace{1cm} (10)

The electrical conductivity of fired specimens was examined at 25°C and 40 V utilizing the Hioki-3532-system.

3. Results and Discussion

3.1. Properties of milled powder.

XRD patterns of Al/graphene nanopowder having different percentages of graphene, e.g., 0.0, 0.2, 0.4, 0.6, and 0.8 wt.% milled for 10h, are shown in Figure 1. According to the ICDD XRD-card number 89-4037, the patterns indicate the existence of one Al phase with a cubic crystal structure. The absence of graphene phase in the XRD patterns is owing to its lower quantity, so it can not be detected. It is noticeable from the figure that with increasing the graphene content, Al peaks become broad with low intensities indicating the smaller crystallite sizes and higher lattice strain as well as higher dislocation density [1, 29, 30]. Figure 2 displays the crystallite size, lattice strain, and dislocation density of Al/graphene powder containing different graphene amounts. As indicated in the graph, the crystal size of Al decreases with the rising graphene content while the lattice strain and dislocation density are increased. This might be due to the presence of a very hard graphene sheet that improves the refining of Al-grain and activates its diffusion energy [29, 31]. The obtained crystal sizes of AG0, AG0.2, AG0.4, AG0.6 and AG0.8 are 33, 31, 26, 22 and 19 nm, respectively, whereas the dislocation-density are 9x10$^{-4}$, 1.1x10$^{-3}$, 1.6x10$^{-3}$, 2.5x10$^{-3}$ and 3.2x10$^{-3}$ %, respectively.

![Figure 1. XRD patterns of ground Al/graphene powders.](image)

![Figure 2 (a) Crystal-size and lattice-strain, (b) dislocation-density of prepared powders related to graphene percent.](image)
Figure 3. TEM images of ground Al/graphene powders.

Figure 3 shows TEM images of AG0, AG0.2, AG0.4, AG0.6, and AG0.8 powders after milling for 10 h. The graph indicates that the particles are aggregated when adding a small quantity of graphene, while improved dispersion is obtained after adding more graphene. Aluminum forms flatted and welded particles throughout milling progression, while graphene reinforcement tends to form smaller pieces. For AG0 powder, it undergoes welding with a higher agglomeration of particles because of their strong plastic deformation [21]. Subsequently, the particle size of milled powder decreased, as shown in Figure 4. It is found that graphene rarely resides within the Al matrix powder, resulting in a small particle size. This behavior may be possible because hard graphene particles may accelerate milling action since they act as milling media during the milling process [30].

![Figure 4](https://biointerfaceresearch.com/)

Figure 4. The particle size of ground Al/graphene powders in relationship with graphene percent.

3.2. Physical properties of sintered composites

The relative density and apparent porosity of Al/graphene composite fired at 400, 500, and 570°C are shown in Fig 5. The calculated theoretical density of AG0, AG0.2, AG0.4,
AG0.6, and AG0.8 composites are 2.7, 2.697, 2.695, 2.693, and 2.691 g/cm³, respectively. It is clear through the figure that the relative densities of all composites are remarkably reduced with increasing graphene content while the apparent porosity increases. The increasing sintering temperature increases the densities and reduces the apparent porosity. When the composite specimen is sintered at 400°C, a lower density value is obtained compared to the composites specimen sintered at 500 and 570°C, respectively. Higher values of densities are achieved after increasing the sintering temperature to 570 °C. Since graphene has a lower density than Al, it was added in a small amount to the composites so it could lower the density but with a small percentage [32]. The decrease of density and the increase in porosity with increasing the graphene content are due to the relatively weak bonding of Al matrix and graphene reinforcement which might restrict the interfacial interaction and diffusion. Furthermore, the amount of graphene decreases the sintering rate because the graphene particles act as a barrier during the diffusion stage of sintering [33-35]. The improvement of density with rising the sintering temperature is due to the growth of necks between particles and increasing the bonding between particles as a result of porosity reduction [36, 37].

![Figure 5](https://doi.org/10.33263/BRIAC132.192)

**Figure 5.** Relative density (a) and apparent porosity (b) of Al/graphene specimens fired at various temperatures in relationship with graphene percent.

### 3.3. Microstructure of fired composites.

Figure 6 shows SEM images of AG0.4 and AG0.8 composites sintered at 570°C in an argon atmosphere. It is observed from the micrograph that homogenous microstructure is formed with the presence of a small amount of porosity; it increases with the increase of graphene content. Moreover, it is also indicated that the graphene sheets are uniformly dispersed in the Al matrix without forming clusters. This is mainly due to optimized milling conditions, which facilitate the homogeneity of sintered composites after the sintering process. The existence of lower inter-granular pores in the dense microstructure is due to the interlocking of graphene particle sheets between the Al matrix with the formation of a compacted network. This will be reflected in the mechanical properties presented in the next section.
3.4. Mechanical properties of sintered composites.

Figure 7 shows the effect of graphene content (i.e., 0, 0.2, 0.4, 0.6, and 0.8 wt. %) on microhardness of Al-graphene composites sintered at 400, 500, and 570°C. Generally, the hardness increases with increasing both graphene content and sintering temperature. At 400°C, the hardness of AG0, AG0.2, AG0.4, AG0.6, and AG0.8 composites is 279.2, 361.2, 445.7, 642.2, and 761.4 MPa, respectively. The microhardness for composite AG0.8 sintered at 500 and 570 °C are 837.8 and 920.8 MPa, respectively.

![Graph showing microhardness of Al/graphene composites](image)

**Figure 7.** Microhardness of Al/graphene composites fired at various temperatures related to graphene percent.

The compressive stress/strain diagram of all specimens sintered at various temperatures is depicted in Figure 8. Initially, the linear increase has occurred in all lines; this is attributed to the elastic deformation of composites since the stress-strain relation follows Hooke's law. In the second stage, a slow increase in the lines occurs until the maximum stress point is reached due to the plastic deformation of composites which comes from the generation of dislocation. Finally, the stress falls rapidly, indicating the yield of materials. The figure also indicates that the addition of graphene decreases the strain of composites. On the other hand, Fig. 9 shows the compressive strength, yield strength, and fraction strain as calculated from the strain-stress curves for sintered composites. From figures 8 and 9, the increase of graphene content at the same sintering temperature increases the strengths and reduces the strain. For the AG0 sample sintered at 570 °C, the compressive strength, yield strength, and fraction strain are 187.40 MPa, 36.4 MPa, and 49.8 %, respectively. With increasing graphene content, the compressive strength and yield strength values are increased while the strain is decreased, reaching 292.1 MPa, 64.8 MPa, and 33.6 %, respectively, for the composite that contains 0.8 wt. % graphene (AG0.8).
Figure 8 Stress-strain diagrams of Al/graphene composites fired at (a) 400°C; (b) 500°C; (c) 570°C in relationship with graphene percent.

Table 2. Longitudinal- and shear-velocities of prepared specimens.

<table>
<thead>
<tr>
<th>Sintering temp., °C</th>
<th>Sample code</th>
<th>V_L (m/s)</th>
<th>V_S (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>AG0</td>
<td>4897.25</td>
<td>2602.11</td>
</tr>
<tr>
<td></td>
<td>AG0.2</td>
<td>5517.21</td>
<td>2882.15</td>
</tr>
<tr>
<td></td>
<td>AG0.4</td>
<td>6382.28</td>
<td>3295.22</td>
</tr>
<tr>
<td></td>
<td>AG0.6</td>
<td>6782.21</td>
<td>3512.29</td>
</tr>
<tr>
<td></td>
<td>AG0.8</td>
<td>7421.28</td>
<td>3781.29</td>
</tr>
<tr>
<td>500</td>
<td>AG0</td>
<td>5551.12</td>
<td>2902.61</td>
</tr>
<tr>
<td></td>
<td>AG0.2</td>
<td>6289.23</td>
<td>3260.45</td>
</tr>
<tr>
<td></td>
<td>AG0.4</td>
<td>6871.18</td>
<td>3527.88</td>
</tr>
<tr>
<td></td>
<td>AG0.6</td>
<td>7754.25</td>
<td>3941.29</td>
</tr>
<tr>
<td></td>
<td>AG0.8</td>
<td>8271.27</td>
<td>4181.25</td>
</tr>
<tr>
<td>570</td>
<td>AG0</td>
<td>6015.11</td>
<td>3122.01</td>
</tr>
<tr>
<td></td>
<td>AG0.2</td>
<td>6621.81</td>
<td>3408.92</td>
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<tr>
<td></td>
<td>AG0.4</td>
<td>7182.19</td>
<td>3671.12</td>
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<td></td>
<td>AG0.8</td>
<td>8684.33</td>
<td>4358.32</td>
</tr>
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Figure 9. Compression strength, Yield-strength, and Fracture-strain of Al/graphene composites fired at various temperatures related to graphene percent.

The results of elastic moduli for sintered composites are presented in Figure 10, while Table 2 illustrates the values of longitudinal ($V_L$) and shear ($V_S$) ultrasonic velocities. It has appeared that $V_L$ and $V_S$ values are enhanced by increasing both graphene content and sintering temperature. The results in Table 2 indicate that $V_L$ values of the composites sintered at 400, 500, and 570°C, are increased from 4897.3 to 7421.3, 5551.1 to 8271.3 and 6015.1 to 8684.5 m/s, respectively, when the graphene increased from 0.00 to 0.8 wt.%. On the other hand, $V_S$ values for the same composites are ranged from 2602.1 to 3781.3, from 2902.6 to 4181.3, and from 3122.1 to 4358.3 m/s, respectively. From Figure 11, the elastic moduli behave as the same trend of ultrasonic velocities ($V_L$ and $V_S$). The results of Young's modulus for composite AG0.8 sintered at 400, 500, and 570 °C are 85.6, 112.3 & 127.1 GPa, respectively. These results are higher than that of the AG0 composite, i.e., 42.6, 55.9 & 66.7 GPa, respectively, sintered at the same temperatures.
This noticeable improvement in mechanical properties is due to the addition of tough graphene to ductile aluminum, increasing dislocation density and grain refinement [38, 39]. In addition, the existence of hard graphene can enhance the hardness of composites giving the following equation [38]:

$$H_C = H_m F_m + H_r F_r$$

Since $H_c$, $H_m$, and $H_r$ are the microhardness of composite, Al-matrix, and reinforcing graphene, respectively, while $F_m$ and $F_r$ are the volume fractions of Al-matrix and graphene reinforcement, respectively. Increasing the hard reinforcement particles in the matrix leads to increasing the generation of dislocations that act as a barrier to plastic deformation, thereby increasing the mechanical properties of composites [40–42]. Furthermore, the presence of the hard phase decreases the fracture strain. Narasaraju et al. [43] and Dora Siva Prasad et al. [44] reported that hard ceramic particles in the composite matrix increase strength and decrease the fracture strain. On the other hand, the improvement of mechanical properties with increasing sintering temperature, i.e., 570°C, is due to increasing the density as well as the plasticity and decreasing the porosity [45, 46].

### 3.2.4. Electrical properties of sintered specimens.

Figure 11 shows the electrical conductivity of all composites sintered at different temperatures. It is indicated that the conductivity of sintered composites decreases with the increase of graphene weight percentages and increases remarkably with increasing sintering temperatures. The conductivity of AG0 composite sintered at 400, 500, and 570 °C are $3.41 \times 10^7$, $14.13 \times 10^7$, and $4.58 \times 10^7$ S/m, respectively, while the conductivity of AG0.8 is $3.99 \times 10^6$, $7.25 \times 10^6$ and $1.03 \times 10^7$ S/m, respectively. This decrease in conductivity is attributed to the lower conductivity of graphene reinforcement compared to the Al matrix. Also, high dislocation density near the interface and elastic discontinuity at the interface leads to increased electron scattering sites [39, 47]. The increasing conductivity of sintered composites with
increasing sintering temperature might be due to the reduction of porosity and improving density [48, 49].

Figure 11. Electrical-conductivity of Al/graphene composites fired at various temperatures in relationship with graphene percent.

4. Conclusions

In the present work, Al-matrix composites reinforced with graphene sheets (0, 0.2, 0.4, 0.6, and 0.8 wt.%) were successfully fabricated after milling for 10h and sintering at 400, 500, and 570°C for 1h in an inert argon atmosphere. According to the obtained microstructure, the graphene sheet was distributed homogeneously in the Al matrix with the formation of interlocked microstructure. The physical and mechanical properties of sintered composites were enhanced with increasing graphene content and sintering temperature. The composite that contained 0.8 wt. % graphene (AG0.8) and sintered at 570°C showed the highest mechanical properties. Its microhardness, compressive strength, and elastic modulus were 920.8 MPa, 292.1 MPa, and 189.3 GPa. Moreover, the conductivity of sintered composites was also reduced with rising graphene amount and improved with rising firing temperature.

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Conflicts of Interest

The authors declare no conflict of interest.

References


