Low energy solution ball milling of graphene nanoplatelets (GNPs) reinforced aluminium nanocomposites and its mechanical properties

Z Baig 1, O Mamat 1, M Mustapha 1, S Ali 1, and M Yasir 1

1Mechanical Engineering Department, Universiti Teknologi PETRONAS, 32610, Bandar Seri Iskandar, Perak, Malaysia

Email: meteng81@gmail.com, drothman_mamat@utp.edu.my

Abstract. Graphene Nanoplatelets (GNPs) possess outstanding properties which can be utilized to reinforce Al metal for various applications of automotive and aerospace sectors. The major hurdle for real-time applications is the GNPs dispersion in Al matrix which is a challenging task. To address this issue, a combination of processing like solvent dispersion via tip sonication and low energy ball milling at 200 and 300rpm were employed to investigate the GNPs dispersion at various fractions and their effects on final nanocomposite properties. Microstructural analysis of nanocomposite powder was carried out to investigate dispersion analysis. A decrease in relative density with increase in GNPs content showed by all samples. Hardness and wear characterization of the nanocomposite samples were performed. It was found that 0.3wt%GNPs/Al samples has shown maximum increase in hardness (35.61%) and reduce wear rate of (76.68%) than pure Al at 300rpm milling. Finally, GNPs have shown their reinforcing effect by increasing hardness and wear rate by provide effective lubrication.

1. Introduction

Aluminium matrix composites (AMCs) have found interesting applications in the automotive and aerospace sectors where high structural loadings and contact motions are involved [1]. Aluminium matrix composites (AMCs) possess high specific strength, low density, high thermal conductivity and improved tribological properties. Noteworthy, still the AMCs properties are not up to the mark as theoretically calculated due to limitations associated with reinforcements such as their micron size. Therefore, size and type of the reinforcement basically dictate the final properties of the composites. From last few years, aluminium nanocomposite (AMNCs) has attracted a lot of attention due to the superior properties exhibited by them [2]. Graphene, a 21st century wonder material is considered as the ideal reinforcing agent to improve overall properties of the AMNCs to fulfill the increasing demands raised by the potential applications consumers. Graphene possesses high mechanical properties like high elastic module, high tensile and fracture strength due to its 2D planar sheet morphology and tightly bonded covalently attached carbon in a honeycomb structure and more favourable to load transfer [3]. Importantly, graphene has high surface area and aspect ratio which cause high attractive forces to attract sheets due to van der Waal forces and form aggregates. Due to these reasons, graphene dispersion in metal matrices is a most challenging task. It is well established that uniform dispersion of the graphene in Al matrix ultimately lead to final nanocomposite superior properties and highlighted in many research works [4]. In recent years,
various approaches were adopted to cater the problem graphene agglomeration via novel or modified processing coupling graphene surface modification covalent or non-covalent functionalization [5]. In terms of processing, powder metallurgy (P/M) processing of the graphene/Al nanocomposite under dry conditions emerged as the most successful technique to ease of fabrication, the potential for uniform dispersion and less chemical reactions [6]. The high energy ball milling processing effectively employed to obtain well-dispersed graphene in Al powders but at the expense of graphene structure deterioration due to harsh conditions involved. As a result, defects formed in graphene structure lead to unwanted reactions with metals and drastically effects final properties. Similarly, there are also some other techniques available employed by researchers to control dispersion issue but mostly are time-consuming and have their own limitations such as molecular level mixing and in situ graphene formation on the metal particles [7]. In recent years, a solvent dispersion of the graphene has been adopted combine with other processing techniques [8]. Now solvent dispersion of graphene is considered as the pre-requisite technique for graphene dispersion. Solvent dispersion of the graphene can be achieved by bath or tip sonication which effectively produces quality solvent dispersion because high energy ultrasonic waves effectively break the notorious irresistible attraction of van der Waals forces to restrict agglomerates formation [9]. In this research, an investigation of the graphene dispersion in Al powders and their effect on properties was performed by using combine processing of graphene solvent dispersion by tip sonication and low energy solution ball milling to avoid possible graphene structure impairment. The low energy solution ball milling of the GNPs/Al nanocomposite powders were processed at two rotational speed (200 and 300 rpm) in order to analyse their effect on dispersion and final nanocomposite properties.

2. Materials
Argon gas atomized and spherical shaped pure Aluminium (Al) powder having >99% purity and particle size up to 10-15μm also confirmed by laser diffraction (Mastersizer 2000) as shown in Figure 1a. Al powder was purchased from CNPC Powder group Co. Ltd., China. High quality Graphene nanoplatelets (GNPs) was supplied by U-Gent technology, Malaysia contains average thickness of GNPs was 5-10nm equals to 15 to 20 graphene sheets per stack of GNPs. The size equals to 6μm-26μm with carbon > 99.5 wt % as depicted in Figure 1b showing stacks of graphene layers. GNPs showed density of 2.17 g/cm3 and Al powder have 2.700 g/cm3 as per measured with helium pycnometer.

![Figure 1. SEM micrographs of (a) as-received Al powder and (b) Graphene nanoplatelets (GNPs).](image)

3. Methodology
A facile low energy blending also known as tumbling ball milling was used to incorporate GNPs into the Al powder using solution blending. Firstly, dispersion of GNPs was achieved in Ethanol solvent using tip sonicator purchased from Qsonica (Model Q500), USA. The GNPs solvent dispersion was attained using optimized sonication parameter equals to sonication time of 30 min and at 60%
amplitude [10]. Different GNPs dispersion solutions were prepared using various GNPs factions such as 0.1, 0.3, 0.5 and 1 wt. %. Secondly, after GNPs solvent dispersion, each solution underwent for solution ball milling for 10 min at 250 RPM to achieve GNPs exfoliation. The 1.0-liter Roalox Alumina-Fortified grinding jar with ZrO$_2$ balls (10mm) using US Stoneware ball milling machine was used. Thirdly, 50g of Al powder was added into each ground GNPs solution jars with a ball-to-powder ratio of 10:1 and further milling was conducted for 2 hours at 200 and 300 RPM respectively. After every 30 min stays for 5 min was given to avoid heating. After dispersion processing completion, GNPs/Al solutions were vacuum filtered and dried in vacuum oven at 90°C for 10 hours to obtain dry GNPs/Al nanocomposite powder for powder dispersion analysis and consolidation. Pure Al and nanocomposite powders were compacted via uniaxial cold compaction at 500Mpa for 1 min hold time. The obtained compact have dimension equals to 30 mm diameters and 4-5mm thickness. The consolidation of the compact samples was done in box furnace under the N$_2$ atmosphere at 620°C sintering temperature for 2 hours as dwell time. After completion of process, samples were furnace cooled and taken out for testing.

4. Characterization techniques
Sintered density of the pure Al and nanocomposite sintered samples were measure by using Archimedes’ Principle. Relative sintered densities (%) were calculated by dividing sintered density (g/cm$^3$) to theoretical density of the pure Al and nanocomposite powders. Theoretical density of nanocomposite powders can be find by using rule of mixture as per formula (1) given below [11]:

\[
\frac{1}{\rho_c} = \frac{W_m}{\rho_m} + \frac{W_f}{\rho_f}
\]  

Where, $\rho_c$ = composite theoretical density, $\rho_m$ = density of Al (2.7g/cm$^3$), $\rho_f$ = density of GNPs (2.17 g/cm$^3$), $W_m$ and $W_f$ are the weight fractions of the Al matrix and GNPs powders used respectively. Micro hardness of the polished sintered samples were measured using Vickers hardness testing at 200gf for 15 minutes holding time. At least five values were calculated and averaged value was recorded. Dispersion analysis and graphene presence in the Al nanocomposite powders were performed via microstructural analysis using scanning electron microscope (SEM) (Phenom- Pro X) equipped with an energy-dispersive X-ray spectrometer (EDS). Wear testing on the polished samples were performed via a pin on disc under dry condition by using Taber Linear Abraser 5750. The process detail and parameters were used same as previously used in our experiment can be found elsewhere [5].

5. Results and discussions
5.1. Dispersion analysis
Figure 2 and 3 represents the SEM images of the as-received Al and GNPs/Al nanocomposite ball milled powders processed at two rotational speed (200 and 300rpm). As can be seen that as-received Al powders have spherical shape morphology (Figure 2a). However, interesting results were showed by the nanocomposite powders at both rotational speeds. Figure 2 shows the various content of the GNPs dispersion in ball milled Al powders. It can be seen that at 200rpm GNPs dispersed only up to 0.1wt% content due to less involvement of the impact forces required for uniform dispersion. While other fractions of the GNPs present as agglomeration in the Al powders as shown in Figure with 1 wt. % GNPs content. It should also be noted that due to low energy rpm, Al powder morphology has remained same i.e. spherical which depicts no effect of balls impact during the milling process. This may be the reason for low content dispersion of GNPs in Al powders. Similarly, Figure 3 presents dispersion state of the different GNPs content in Al powder after solution ball milling at 300rpm. At this rotational speed, GNPs were uniformly dispersed up to 0.3wt% as compared to other GNPs content as seen in Figure 3. Such behaviour can be related to the increase in
rotational speed which readily disperses the GNPs into the Al powder up to 0.3wt% and others content showed agglomerations availability in the Al powders. This can also be confirmed by the change of the morphology of the Al powders under 300rpm i.e. transform to flake shape reveals deformed morphology. The morphological transformation is more pronounced up to 0.3wt% GNPs and after that flaky shape of powders were not observed due to the GNPs lubrication effect provide the cushion for powder deformation and contribute to the reagglomeration of the GNPs. Overall, it can be found that major dispersion was provided by the solvent dispersion and further dispersion assistance was more provided by ball milling at 300rpm than 200rpm due to increase in impact forces by balls. Further, at a high content, GNPs re agglomeration was severely formed and clearly seen in the micrographs.

**Figure 2.** SEM images of the (a) Pure Al and GNPs/Al powder ball milled at 200 rpm at various GNPs fractions (0.1, 0.3, 0.5, and 1 wt. %). The magnified images are also shown along with EDX results showing graphene presence and its agglomerations.

**Figure 3.** SEM images of the (a) Pure Al and GNPs/Al powder ball milled at 300 rpm at various GNPs fractions (0.1, 0.3, 0.5, and 1 wt. %). The magnified images are also shown along with EDX results showing graphene presence and its agglomerations.

5.2. **Density and hardness analysis**

Figure 4a illustrates the relative density (%) of the pure Al and sintered GNPs/Al samples at 200 and 300 rpm. As can be seen that at low content both types of GNPs/Al samples density increases as compared to pure Al than abruptly decreases due to the addition of high content of low-density GNPs.
This kind of behaviour also reported by Rashad et al [9]. It can also be related to the formation of agglomeration after GNPs reagglomeration at high content because with increase in content graphene sheets tend to close to each other and attracted to each other thus form agglomerates [12]. Figure 4b represents the hardness behaviour of the GNPs/Al samples processed at two rotational speeds. GNPs/Al samples processed at 200rpm showed the increase in hardness to 45Hv at 0.1wt% GNPs content than pure Al hardness (36Hv) whereas beyond this GNPs content hardness decreases. Similarly, at 300 rpm, GNPs/Al samples exhibit an increase in hardness of 48.82Hv at 0.3wt% GNPs content as compared to pure Al (36Hv) equals to 35.61% increase. The increase in hardness showed by both nanocomposite samples can be attributed to the uniform dispersion of GNPs whereas a decrease in hardness can be ascribed to the agglomeration effect which is in accordance with SEM results (Figure 2 and 3). In addition, GNPs/Al samples processed at 300rpm has shown the highest hardness of about 35.61% and 200 rpm exhibit 25% increase than pure Al. The improvement in the hardness of nanocomposite samples validates the reinforcing effect of GNPs addition to the Al matrix which effectively restricts the dislocations motion and caused grain pinning. Similarly, GNPs/Al samples ball milled at 300rpm has shown the highest increase due to the higher impact of the balls to disperse GNPs at higher content and also due to the morphological change i.e. spherical to flaky shape lead to the higher surface area and results in better sinterability.

Figure 4. (a) Trends of relative sintered density (%) of Al and GNPs/Al Nanocomposite. (b) Micro hardness response of the pure Al and different fractions of GNPs/Al nanocomposite.

5.3. Wear analysis
Figure 5a and b demonstrate the wear behaviour of the GNPs/Al nanocomposite samples processed via solution low energy ball milling at 200 and 300rpm. Figure 5a reveals the wear loss of GNPs/Al samples at both rotational speeds. It can be seen that samples also exhibit the same as shown by hardness behaviour because hardness and wear have proportional relationship as reported earlier [13]. Therefore, GNPs/Al processed at 200rpm showed lowest wear loss and ultimately wear rate (Figure 5b) at 0.1wt% GNPs fraction than pure Al and after this fraction wear rate increases. Similarly, at 300rpm, GNPs/Al displayed lowest wear loss and wear rate at 0.3wt% GNPs fraction. It should be noted that wear behaviour of all nanocomposite reduced than pure Al. It can be seen that GNPs/Al samples processed at 300 rpm have lowest wear loss and wear rate equals to 76.68% and at 200rpm GNPs/Al showed 80.92% reduction in wear rate than pure Al. The decrease in wear rate of the nanocomposite samples can be endorsed to GNPs lubrication effect and uniform dispersion in Al matrix whereas higher wear rate represents the effect of GNPs agglomeration. During the sliding motion of the mating surfaces, GNPs readily comes up on the surface of nanocomposite after removal of oxide layer and form intact lubricant layer protect the surface from wear. Thus, uniform dispersion of the GNPs in Al matrix ensured improved wear response as can be seen in both composites but at low GNPs content.
Figure 5. (a) Trends of wear loss (g) of Al and GNPs/Al Nanocomposite. (b) Wear rate response of the pure Al and different fractions of GNPs/Al nanocomposite.

6. Conclusions
In this research, graphene nanoplatelets (GNPs) at various fractions were dispersed in the Al powders via tip sonication solvent dispersion and low energy ball milling performed at two rotational speed (200 and 300 rpm). Consolidation was done by cold compaction and pressureless sintering. Analyzing the SEM results of nanocomposite powders processed at 200 and 300 rpm showed that GNPs were uniformly dispersed at low content i.e. 0.1wt% and 0.3 wt.% respectively. It has been shown that agglomerations still exist at higher content. Relative density (%) of all the composite decreases with increase in GNPs content. GNPs/Al samples processed at 200rpm exhibit 25% at 0.1wt% and at 300rpm display increase of 36% in hardness than pure Al. Similarly, wear rate also followed the same trend at both rotational speeds due to the GNPs lubrication effect and uniform dispersion at low content. Further improvement in the dispersion at higher content will be planned via GNPs surface modification in the Al powder along with compaction and sintering behaviour of the developed Al nanocomposite.

7. References
[1] A. D. Moghadam, E. Omrani, P. L. Menezes, and P. K. Rohatgi, "Mechanical and tribological properties of self-lubricating metal matrix nanocomposites reinforced by carbon nanotubes (CNTs) and graphene–A review," Composites Part B: Engineering, 77, pp. 402-420, 2015.
[2] Z. Hu, G. Tong, D. Lin, C. Chen, H. Guo, J. Xu, et al., "Graphene-reinforced metal matrix nanocomposites–a review," Materials Science and Technology, pp. 1-24, 2016.
[3] N. A. Koratkar, Graphene in Composite Materials: Synthesis, Characterization and Applications: DEStech Publications, Inc, 2013.
[4] Z. Baig, O. Mamat, and M. Mustapha, "Recent Progress on the Dispersion and the Strengthening Effect of Carbon Nanotubes and Graphene Reinforced Metal Nanocomposites: A Review," Critical Reviews in Solid State and Materials Sciences, 41, pp. 1-46, 2016.
[5] Z. Baig, O. Mamat, M. Mustapha, and M. Sarfraz, "Influence of surfactant type on the dispersion state and properties of graphene nanoplatelets reinforced Aluminium matrix nanocomposites," Fullerene, Nanotubes and Carbon Nanostructures, 25, pp. 545-557, 2017.
[6] A. Das and S. P. Harimkar, "Effect of Graphene Nanoplate and Silicon Carbide Nanoparticle Reinforcement on Mechanical and Tribological Properties of Spark Plasma Sintered Magnesium Matrix Composites," Journal of Materials Science & Technology, 30, pp. 1059-1070, 2014.
[7] C. Zhao, "Enhanced strength in reduced graphene oxide/nickel composites prepared by molecular-level mixing for structural applications," Applied Physics A, 118, pp. 409-416, 2015.
[8] Z. Baig, O. Mamat, M. Mustapha, A. Mumtaz, M. Sarfraz, and S. Haider, "An Efficient Approach to Address Issues of Graphene Nanoplatelets (GNPs) Incorporation in Aluminium Powders and Their Compaction Behaviour," *Metals*, 8, p. 90, 2018.
[9] D. W. Johnson, B. P. Dobson, and K. S. Coleman, "A manufacturing perspective on graphene dispersions," *Current Opinion in Colloid & Interface Science*, 20, pp. 367-382, 2015.
[10] Z. Baig, O. Mamat, M. Mustapha, A. Mumtaz, K. S. Munir, and M. Sarfraz, "Investigation of tip sonication effects on structural quality of graphene nanoplatelets (GNPs) for superior solvent dispersion," *Ultrasonics Sonochemistry*, 45, pp. 133-149, 2018.
[11] R. M. German and S. J. Park, *Handbook of mathematical relations in particulate materials processing: ceramics, powder metals, cermets, carbides, hard materials, and minerals* 3: John Wiley & Sons, 2009.
[12] K. S. Munir, Y. Li, D. Liang, M. Qian, W. Xu, and C. Wen, "Effect of dispersion method on the deterioration, interfacial interactions and re-agglomeration of carbon nanotubes in titanium metal matrix composites," *Materials & Design*, 88, pp. 138-148, 2015.
[13] H. Prashantha Kumar and M. Anthony Xavior, "Effect of graphene addition and tribological performance of Al 6061/graphene flake composite," *Tribology-Materials, Surfaces & Interfaces*, pp. 1-10, 2017.