Effect of grapheneno-nano-platelets on the mechanical properties of Mg/3wt%Al alloy-nanocomposite

Pravir Kumar1*, MilliSuchita Kujur1,2, Ashis Mallick1, Khin Sandar Tun2 and Manoj Gupta2

1Indian Institute of Technology (ISM), Department of Mechanical Engineering, Dhanbad – 826004, India
2National University of Singapore, Department of Mechanical Engineering, Singapore 117576, Singapore
*Correspondence: pravirkumar30@gmail.com

Abstract. The bulk Mg/3%Al/0.1%GNP alloy-nano composite was fabricated using powder metallurgy route assisted with microwave sintering and followed by hot extrusion. The microstructural and Raman spectroscopy studies were performed to characterize the graphene nano-platelet(GNP).EDX tests confirmed the presence and the homogeneous distribution of Al and graphene nano-platelets in the magnesium alloy-nanocomposite. The addition of 3 wt% Al and 0.1 wt% GNP to the Mg changed Vicker hardness, ultimate tensile strength and failure strain by +46.15%, +17.6% and -5% respectively. The fabricated composite offers higher resistance to the local deformation than monolithic Mg and Mg/3%Al alloy, revealed by the load/unload-indentation depth curve.

1. Introduction
Magnesium based metal matrix composites are getting relevant attention in material science community due to their weight saving capabilities owing to its density of 1.74 g/cm3[1-3].Magnesium is also the sixth most abundant element on the earth and finds widespread applications in aerospace and automotive industry due to its excellent properties like high specific strength, high damping capacity, high electromagnetic shielding and good machinability. However, magnesium displays low ductility and corrosion resistance compared to aluminium and that limits its application to some extent [4-6].To overcome these limitations, alloying and composite technology have been tried in last few decades. Magnesium based composites have been developed in recent years by incorporating nano size reinforcements like ceramic oxides, carbides and carbon nanotubes which led to simultaneous improvement in strength and ductility [7-8]. Few studies also report that aluminium can be used as alloying element to increase the strength and ductility of magnesium [9-10]. The use of nanoparticles is also in frontline of current research interest for the improvement of mechanical properties of metal matrix composite [11].
The two dimensional carbonaceous material graphene displays various superior properties like high elastic modulus, high mechanical strength, high thermal and electrical conductivity. Graphene exhibits Young’s modulus of 1 TPa and intrinsic fracture strength of 125 GPa [12-13]. Many of the likeable properties of single layer graphene are inherited by multilayer graphene or graphene nano-platelet (GNP). Alongside, it is also less expensive, easier to produce and handle than single layer platelet [14]. Few studies in recent years, have reported improvements in mechanical properties of magnesium and Mg/Al alloys when they are reinforced with GNP. However, the study of GNP reinforcement metal matrix nanocomposite is in initial stage. The main challenge with the GNP is its homogeneous dispersion in the metal matrix. The large surface area of GNP leads clustering which reduces the performance of MMCs. For the better dispersion of GNP in metal matrix, some advanced techniques like ultrasonic assisted casting, stir casting, friction stir casting and powder metallurgy have been used in recent years.

Accordingly, the basic aim of the study was to synthesize bulk Mg/3wt%Al alloy reinforced with 0.1wt% of graphene nano-platelets and study the effect of GNP addition on the properties of composite. The powder metallurgy process assisted with innovative hybrid microwave sintering technique followed by hot extrusion was used for synthesis of the nanocomposite.

2. Experimental procedure

2.1. Material
Magnesium powder (98.5% purity) of particle size 60-300 μm, received from Merck (Germany) was used as base material and the aluminium powder (99.9 % purity) of particle size 7-15 μm, received from Alfa Aesar (Haverhill, MA, USA) was used as alloying element. Graphene nano-platelets (6-10 nm thickness and 15 μm width) received from Tokyo Chemical Industry Co., Ltd., (Japan) was used as reinforcement.

2.2. Primary processing
Monolithic magnesium, magnesium alloy (Mg/3wt%Al) and alloy-nanocomposite (Mg/3wt%Al/0.1wt%GNP) samples were synthesized using the powder metallurgy method. The required amount of powders were weighed and blended in a mechanical alloying machine [Model: RETSCH PM-400] for 1 hour at 200 rpm. The blended powders were cold compacted subsequently at a pressure of 510 MPa to form billet of sizes 35 mm in diameter and 40 mm in height. Monolithic magnesium was cold compacted using same conditions without blending. The compacted billets were then sintered immediately for 13 minutes to reach a temperature of 643 °C near melting point of magnesium. An innovative hybrid microwave sintering technique [15] was used for the sintering using a 900 W, 2.45 GHz SHARP microwave oven.

2.3. Secondary processing
The sintered compacts of pure magnesium, alloy, and alloy-nanocomposite were soaked at a temperature of 400 °C at constant temperature furnace for 1 hour followed by hot extrusion at 350 °C using a 150 ton hydraulic press. An extrusion ratio of 20.25:1 was used to obtain rods of 8 mm diameter.

2.4. Density Measurements
Experimental densities of extruded rods were determined using Archimedes’ principle. Three randomly selected samples from different cross sections of the extruded rod were removed and polished. The polished samples were weighed accurately in air and when immersed in distilled water using a Mettler-Toledo (MS205DU), Switzerland weighing machine with an accuracy of ±0.0001 g. Theoretical densities of the samples were calculated using rule of mixture considering theoretical densities for Mg, Al and GNPs as 1.74 g/cm³, 2.7 g/cm³ and 2.25 g/cm³ respectively.

2.5. Microstructural Characterization
To investigate grain morphology, porosity and distribution of the reinforcement in the extruded polished sample, micrographs were captured using Olympus metallurgical optical microscope (Japan).
EDAX of the extruded samples, Field emission scanning electron microscopy (FESEM) images of GNP and the composite were taken by using FESEM, model Supra 55 Carl Zeiss (Germany).

2.6. Hardness
Microhardness of the extruded samples were obtained using Micro-Nano Indenter MTR3/50-50/NI machine supplied by MICROTEST S. A, Spain. Hardness test was performed according to ASTM standard E384. Indentations were made on mirror polished surfaces of the samples by Vickers’ pyramidal indenter (with a phase angle of 136°). With the loading rate of 5 N/min, maximum load of 5N was applied on the sample followed by a dwell period of 30 seconds, then left for unloading. The machine is fully automated and commands were preset through software (Tribotester). Tests were repeated 5 times for each sample under same parameters.

2.7. Tensile testing
Tensile specimens of 5 mm diameter and 25 mm gauge lengths were prepared from extruded rods of the samples. Tests were performed based on ASTM E8M-05 in BISS 25 KN universal testing machine with crosshead speed of 0.01 mm/s. Three samples for each composition were used for the test.

Figure 1. (a) FESEM image of graphene nano-platelet, (b) Raman spectra of graphene nano-platelet.

Figure 2. Microstructural study of etched sample (a) pure Mg, (b) Mg/3%Al/0.1GNP composite.
3. Results and discussions
FESEM image and Raman spectroscopy of as received graphene nano-platelets are shown in figure 1. Figure 1(a) shows wrinkled layer of graphene and stacks of overlapped multilayer graphene nano-platelets. Figure 1(b) shows Raman spectra of graphene nano-platelets obtained from Raman spectroscopy (an efficient technique for characterizing graphene). The spectra display D band at 1358 cm\(^{-1}\), G band at 1584 cm\(^{-1}\) and 2D band at 2712 cm\(^{-1}\). The intensity ratio \(I_{2D}/I_G\) in the spectra indicates the multilayer feature of the graphene nanoplatelets. Figure 2 shows micrographs of etched samples captured from optical microscope. Figure 2 (a) reveals grain morphology of pure magnesium sample and figure 2 (b) represents grain morphology of Mg/3%Al/0.1%GNP composite sample. Particle boundaries are visible in both the micrographs. The micro-pores are almost negligible in the samples. Figure 3 shows FESEM image of the composite and EDS (Energy-dispersive X-ray spectroscopy) of the selected area. The peaks obtained from the EDS result confirm the presence of included elements in the Mg/3%Al/0.1%GNP composite.

![Figure 3](image)

**Figure 3.** (a) FESEM image of Mg/3%Al/0.1%GNP composite, (b) EDS of selected area under rectangle.

![Figure 4](image)

**Figure 4.** Energy dispersed X-ray area mapping of (a) Electron image of Mg/3%Al/0.1%GNP composite, (b) Magnesium, (c) Aluminium, (d) Carbon.
Figure 4 represents energy dispersive X-ray area mapping of Mg/3%Al/0.1%GNP which signify that metal matrix composite is enriched in Mg phase and Al and carbon are homogeneously distributed. Table 1 presents comparisons between theoretical and experimental densities of the samples indicating percentage porosity is almost zero and synthesized samples are nearly dense. Figure 5 presents engineering stress-strain graph for the samples.

![Figure 5. Room temperature tensile stress-strain curves.](image)

**Table 1.** Density measurement of pure Mg, alloy Mg/3%Al and composite Mg/3%Al/0.1%GNP.

| Material          | Element (wt %) | Theoretical density (g/cm$^3$) | Experimental density (g/cm$^3$) | Porosity (%) |
|-------------------|----------------|-------------------------------|--------------------------------|---------------|
|                   | Al             | GNP                           |                                |               |
| Mg                | 0              | 0                             | 1.7400                         | 1.7402        | ~0            |
| Mg/3% Al          | 3              | 0                             | 1.7587                         | 1.7577        | ~0            |
| Mg/3%Al/0.1% GNP  | 3              | 0.1                           | 1.7601                         | 1.7607        | ~0            |

**Table 2.** Results of tensile response and hardness measurements.

| Material          | 0.2 %YS (MPa) | UTS (MPa) | Failure strain (%) | Vicker hardness (HV) |
|-------------------|---------------|-----------|--------------------|----------------------|
| Mg                | 106           | 202.76    | 10.65              | 39                   |
| Mg/3% Al          | 133           | 227.43    | 11.28              | 51                   |
| Mg/3% Al/0.1% GNP | 141           | 238.44    | 10.12              | 57                   |

Table 2 presents experimental results of the tensile and hardness test of the samples. Hardness increased by ~ 46% in case of the nanocomposite when compared to monolithic magnesium. The
presence of relatively stronger reinforcement particles (GNP+Al), distributed in the nanocomposite increases the hardness [16]. High sintering temperature also assist in making strong interfacial bonding between GNP and Mg matrix resulting increment in hardness. The ultimate tensile strength and yield strength of the nanocomposite was found to be improved by 17.5% and 33% respectively but the failure strain was decreased by 5% with respect to the monolithic magnesium. Strengthening of the Mg alloy matrix is associated with the basic mechanisms comprising load transfer from matrix to GNP [17-18], mismatch in coefficient of thermal expansion [19-20] and Orowan looping [21-22].

For the equiaxed nano-platelets, an increase in the yield stress due to load transfer \( \Delta \sigma_{LT} \) can be expressed as [23]

\[
\Delta \sigma_{LT} = \sigma_e - \sigma_m = 0.5f \sigma_m
\]  

(1)

Where, \( \sigma_e \) is yield strength of the nanocomposite, \( \sigma_m \) is yield strength of matrix and \( f \) is volume fraction of reinforcement. Effective load transfer from matrix to reinforcement is dependent on the interfacial bonding between the reinforcement and Mg alloy matrix [24] and volume fraction of graphene nano-platelets. The yield strength of a composite according to Modified shear-lag model [23] can be expressed as

\[
\sigma_c = \sigma_m \left( 1 + \frac{(L + t)A}{4L} \right) f + \sigma_m (1 - f)
\]  

(2)

Where, \( L \) is size of the nano-platelet parallel to the load direction, \( t \) is the thickness of the nano-platelet and \( A = L/t \) is the nano-platelet aspect ratio.

The coefficient of thermal expansion for Mg and Al are \( 25 \times 10^{-6} \text{K}^{-1} \) and \( 23.6 \times 10^{-6} \text{K}^{-1} \) respectively [25]. On the other hand coefficient of thermal expansion for GNP is \( 10^{-6} \text{K}^{-1} \). Moreover, elastic modulus of GNP, magnesium and aluminium are 0.7-1.2 TPa, 40-45 GPa and 69.6 GPa [26] respectively. Therefore mismatches in the coefficient of thermal expansions and elastic modulus of magnesium alloy nanocomposite may lead generation prismatic punching of dislocation at the interface [27, 28]. A higher dislocation density in the composite yields a higher level of internal stress which resist fracture of composite while compression.

Orowan strengthening mechanism also plays an important role in increasing strength of the nanocomposite. Millerand Humphreys [29] showed this mechanism is effective when size of reinforcement particles is less than 1 μm. Due to inserted GNP nano-platelets, residual loops are formed around each nano-platelet after dislocation lines bow and bypass. These loops result high strain hardening rate and help to strengthen the nanocomposite [24, 30]. Additionally, dispersion of GNPs is also important so that maximum number of particle can participate in increasing the strength [31]. The increase in yield strength by Orowan looping strengthening mechanism can be expressed by the equation [32]

\[
\Delta \sigma_{Orowan} = M \frac{0.4Gb}{\pi \lambda} \ln \left( \frac{\bar{d}}{b} \right) \sqrt{1 - \nu_{Matrix}}
\]  

(3)

Where \( M \) is strengthening coefficient, \( \lambda \) is the inter-nano-palatelet distance given by \( \lambda = \bar{d} \left( \sqrt{\pi/4f} - 1 \right) \), \( \nu_{Matrix} \) is Poisson’s ratio of magnesium alloy matrix, G is shear modulus of Mg alloy matrix, \( b \) is Burgers vector, \( \bar{d} \) is average diameter of the nano-platelets.

Figure 6 shows the loading/unloading-indentation depth cycles for all the three samples obtained from the indentation test. The indentation force Vs indentation depth curve shows local deformation behaviour of the samples. DSI (Depth Sensing Indentation), included with the machine have given lowest value of maximum indentation for the composite Mg/3%Al/0.1%GNP which is in consonance with the fact that highest resistance was offered by the composite to the local deformation due to the presence of GNPs in the composite.
4. Conclusions
Bulk Mg/3%Al/0.1%GNP composite, Mg/3%Al alloy and pure Mg samples were successfully synthesized through powder metallurgy route assisted with microwave sintering and followed by hot extrusion. The samples were nearly dense. Higher resistance to local deformation was offered by the nanocomposite than Mg/3%Al alloy and pure Mg, resulting in higher hardness value for the fabricated nanocomposite. Besides higher yield strength and ultimate tensile strength were exhibited by the fabricated nanocomposite. Also the failure strain of nanocomposite is in the range of magnesium. Therefore, the prepared nanocomposite has potential to be used in weight critical applications, like for making of casings for electronic components (mobile, laptop and digital camera) and sport components (frame and wheel of bike, golf club and archery bow).

References
[1] Evans A, Marchi C S and Mortensen A 2003 Metal matrix composites in industry: an introduction and a survey Kluwer Academic Publishers (Boston)
[2] Goh C S, Wei J, Lee L C and Gupta M 2007 Acta Mater. 555115-21
[3] Mallick M, Tun K S and Gupta M 2012 Mater. Sci. Eng. A 551 222-30
[4] Edward B and Warda I I 1989 Light Metals Age p 34
[5] Luo A, Renaud J, Nakatsugawa I and Plourde J 1995 JOM 47(7)28-31
[6] Clow B B 1996 Advanced Materials and Processes 15033-34
[7] Hassan S F and Gupta M 2006 J Mater Sci 41 2229-36
[8] Goh C S, Wei J, Lee L C and Gupta M 2006 Nanotechnology 17 7-12
[9] Wong W L E and Gupta M 2006 Adv Eng Mater 8 735-40
[10] Dargusch MS, Pettersen K, Nogita K, Nave M D and Dunlop GL 2006 Materials transactions 47(4)pp 977-82
[11] Balandin A A, Ghosh S, Bao W, Calizo I, Teweldebrhan D, Miao F and Lao C N 2008 NanoLetters 8 902
[12] Bolotin K I, Sikes K J, Jiang Z, Klima M, Fudenberg G, Hone J, Kim P and Stormer H L 2008 Solid State Communications 146(9)pp 351-5
[13] Lee C, Wei X, Kysar J W and Hone J 2008 science 321 (5887) pp 385-8
[14] Novoselov K S, Fal V I, Colombo L, Gellert P R, Schwab M G and Kim K 2012 Nature 490pp192-200
[15] Gupta M and Wong W L E 2005 Scripta Materialia 52 (6)479-83
[16] Rashad M, Pan F, Asif M, Hussain S and Saleem M 2014 Mater. Characterization 95 140-47
[17] Dai L H, Ling Z and Bai Y L 2001 Compos. Sci. Technol. 61 1057-63
[18] Cox H L 1952 Br. J. Appl. Phys. 3 72
[19] Arsenault R J and Shi N 1986 Mater. Sci. Eng. 81 175-87
[20] Miller W S and Humphreys F J 1991 Scrip. Metall. Mater. 25 33-38
[21] Zhang Z and Chen D L 2006 Scripta Materialia 54(7) 1321-26
[22] Vogt R, Zhang Z, Li Y, Bonds M, Browning N D, Lavernia E J and Schoenung J M 2009 Scripta Materialia 61 1052-55.
[23] Aikin Jr RM and Christodoulou L 1991 Scripta Metall Mater 25 9-14
[24] Wong WLE and Gupta M 2006 Compos Sci Technol 67 1541-52
[25] Rashad M, Pan F, Tang A and Asif M 2014 Progress in Natural Science: Mater. International 24 101-8
[26] Clyne TW and Withers PJ 1993 An Introduction to Metal Matrix Composite Cambridge University Press (Cambridge) pp 120-21
[27] Arsenault RJ and Shi N 1986 Mater. Sci. Eng. 81 175
[28] Dieter GE 1976 Mechanical Metallurgy, 2nd ed. McGraw-Hill (New York) pp 49-70
[29] Miller WS and Humphreys FJ 1991 Scripta Metal 25 33-8
[30] Szaraz Z, Trojanova Z, Cabbibo M and Evangelista E 2007 Mater Sci Eng A 462 225-9
[31] German RM 1994 Metal Powder Industries Federation, Princeton (New Jersey)