PROCESSING AND CHARACTERIZATION OF Mg-3 % Al / GRAPHENE NANOCOMPOSITE

KUMAR Pravir[1], KUJUR Milli Suchita[1,2], MALLICK Ashis[1], TUN Khin Sandar[2], GUPTA Manoj[2]

[1]*Indian Institute of Technology (ISM), Department of Mechanical Engineering, Dhanbad - 826004, India*
[2]*National University of Singapore, Department of Mechanical Engineering, Singapore 117576, Singapore*

Abstract

In this work, Mg-3 % Al alloy was reinforced by graphene nano-plates using powder metallurgy technique including microwave sintering and hot extrusion. Graphene nano-plates were synthesised using modified Hummer's method. Raman test and FESEM analyses were carried out to confirm the formation of graphene nano-plates. The powders of Mg and 3 wt.% Al were mixed with graphene nano-plates. The microstructural characterization of the bulk composite revealed a reasonably uniform distribution of the graphene nano-plates in the matrix. The EDX result showed the presence of aluminium in the composite, while XRD result revealed that the aluminium powder completely dissolves and makes a solid solution of Mg and Al. An attempt is made to correlate the microstructural characteristics with the mechanical response of the monolithic and composite samples.

Keywords: Magnesium, graphene nanoplates, microstructure, mechanical properties

1. INTRODUCTION

Magnesium alloy and its composites are the lightest metal based structural materials with strong potential in wide spectrum of industrial applications including automobile, aerospace and electronics industries [1]. Magnesium is one of the most abundant element having a density about 1.74 gm/cm^3. Magnesium is ~ 35 % and ~75 % lighter than aluminium and steel, respectively [2]. Mg based materials including alloys and composites exhibit excellent mechanical properties such as high specific strength, good machinability, thermal conductivity, damping capacity and superior capacity to resist the electromagnetic radiation [3-4]. The magnesium based materials are widely used as weight saving material that essentially reduce the fuel consumption by developing lightweight vehicles. Mg based materials normally exhibit strong texture and the plastic deformation is largely dominated by the limited number of active slip systems, such as basal slip and tension/compression twins. Due to limited slip systems available in the hexagonal closed-packed structure, magnesium suffers from poor corrosion resistance, low strength and limited ductility that often restricts its usages in many engineering applications [5]. To overcome these limitations, an urgent need to develop the Mg based materials using alloying and composite technology is required. Over the last few decades continuous efforts have been made for developing the Mg based materials. Most of the developments are either by alloying the materials or reinforcing the material by ceramic particles. In recent years, few studies have reported enhanced ductility and strength by the addition of Al as an alloying element [6-7]. The use of nanoparticles as reinforcement for improving the mechanical properties is also in the forefront of current research interest [8]. There are many techniques, such as conventional casting, spray deposition, disintegrated melt deposition (DMD), powder metallurgy technique and additive manufacturing process that are used for synthesizing the alloys and composites of Mg based materials. Out of these, the powder metallurgy technique is simple and efficient for the synthesis of bulk nano-composite sample. In this method, the alloying element and reinforced particles can be homogeneously mixed with the base material. The open literature search demonstrates that limited studies are available on the synthesis and mechanical characterization of Mg nanocomposite containing graphene nano-plates. The aim of the present study is to synthesize and investigate the mechanical properties of magnesium metal matrix composite reinforced with 0.1 wt.% graphene nano-plate. The choice of graphene nano-plates is due to its numerous extraordinary properties such as high aspect ratio (length to thickness), high modules of elasticity, high strength, and high thermal and electrical conductivity. The synthesis of bulk sample of monolithic Mg and its composite was carried out by powder metallurgy technique incorporating energy efficient microwave assisted rapid sintering and hot extrusion. The microstructural characteristics were investigated using XRD, FESEM and an optical microscope. The micro hardness and scratch tests were performed to investigate the mechanical responses.

2. EXPERIMENTAL

2.1. Materials

The graphite powder (98.9 % purity) of 250 μm particle size and potassium permanganate supplied by Loba Chemical Pvt. Ltd, Mumbai, and Sodium Nitrate (99 % purity), sulphuric acid (98% purity), hydrogen peroxide and hydrazine hydrate obtained from Merck, Mumbai, India were used to synthesis graphene nano-plates which was used as reinforcement in the composite. The powder of Mg (98.5 % purity) of 60-300 μm particle size received from Merck (Germany) was used as matrix material and the aluminium powder (99.9 % purity) of 7-15 μm particle size supplied by Alfa Aesar (Haverhill, MA, USA) was used as alloying element.

2.2. Synthesis

The Graphene nano-plates were synthesized from graphite powder using modified Hummer's method [9] followed by reduction of graphene oxide using hydrazine hydrate [10]. The powder of graphene (GA) nano-plate was mixed with the commercial powders of Mg and Al at weight ratio of Mg:Al:GA is 96.9:3:0.1. The mixing of the powders was performed in RETSCH PM-400 mechanical alloying machine for 1 hr. The mixture of three powders was consolidated by cold compaction at a pressure of 9.7 MPa using a 100-tonne press followed by microwave sintering and hot extrusion. The extrusion was carried out at a die temperature of 350 °C. The compacted billets were extruded at an extrusion ratio of 1:25 from cylindrical billet to cylindrical extruded rod. Prior to extrusion, the sintered billet was soaked at 400 °C for 1 hr. The samples for microstructural study and mechanical test were prepared from the 8 mm diameter extruded rods in accordance to ASTM standard.

2.3. Density measurement

The mass density of the extruded samples of pure Mg and its composite was estimated using the Archimedes principle. The polished samples of the extruded rod were weighed in air and when immersed in distilled water. Mettler-Toledo (MS 205DU), Switzerland weighing machine with an accuracy of ± 0.0001 g was used to measure the weights of the samples. The theoretical mass densities of the samples were calculated using rule of mixture. The results of theoretical and experimental density measurement and the corresponding porosity are shown in **Table 1.**

Table 1 Comparisons of density (g/cm^3) and porosity of pure Mg and its alloy and composite

Material	Theoretical	Experimental	Porosity (%)
Mg	1.74	1.740021	~ 0
Mg / 3 % Al	1.75876	1.7577	0.06
Mg / 3 % Al / 0.1 % GA	1.7591	1.7665	~ 0

2.4. Microstructural analysis

The microstructural studies of pure Mg and its composite were carried out on the extruded sample. The presence of graphene nano-plate in Mg matrix was investigated using Olympus metallographic optical microscope (Model: Zeiss Axio Immezer) with image analyser software. The solid solution of Mg and Al in the extruded samples was verified by X-ray diffraction (XRD) line analysis. The FESEM analysis and Raman test were carried out to confirm the formation of graphene nano-plates, synthesised from the graphite powder. The samples for microstructural analysis were prepared by the standard procedure of metallographic polishing until the sample surface gets mirror finish.

2.5. Micro-hardness and scratch test

The micro-hardness tests for pure Mg and its composite were performed with a micro-hardness testing machine (Model: Economet VH-1MD) supplied by Chennai Metco Pvt Ltd, India. The test samples were machined from the extruded rods and then mirror polished. The polished surfaces were ultrasonically cleaned and dried before performing the hardness and scratch tests. The measurements were made on samples with a 100 g load applied by the indenter for 20 s. The tests were repeated in five different regions to get the average value of Vickers hardness. To study the sliding contact behaviour, micro-scratch test was carried out using MTR3/50-50/NI instrument supplied by MICROTEST S.A, Spain. The initial force, 9.8 N, was applied to the polished samples in order to get an initial penetration before scratch start.

3. RESULTS AND DISCUSSION

The graphene nano-plates synthesised following modified Hummer's was analysed by Raman spectroscopy and presented in **Figure 1.** The test machine was operated with a 532 nm excitation wavelength and 2 mW laser power. The spectrum exhibits three major peaks namely D band, G band and 2D band, appeared at about 1348 cm^{-1}, 1583 cm^{-1} and 2718 cm^{-1}, respectively. The presence of broad 2D band with FWHM of ~ 73 cm^{-1} indicates the formation of graphene. The stacking order of the graphene sheets can be identified by the quantitative analysis of 2D band. The ratio of intensity of 2D band to G band is about, I_{2D} / I_G = 0.41, indicates the formation of multilayer graphene [11]. **Figure 2** represents the typical FESEM image of graphene nano-plates which shows ultrathin wrinkled platelets of the graphene sheets that are very transparent to the electron beam.

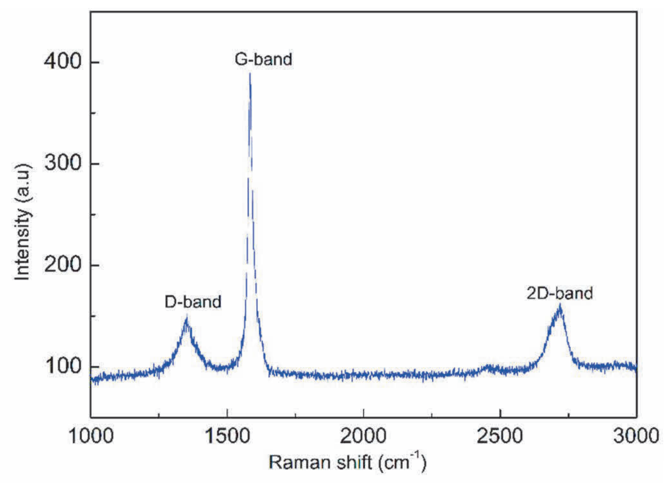

Figure 1 Raman spectra of graphene nano-plate

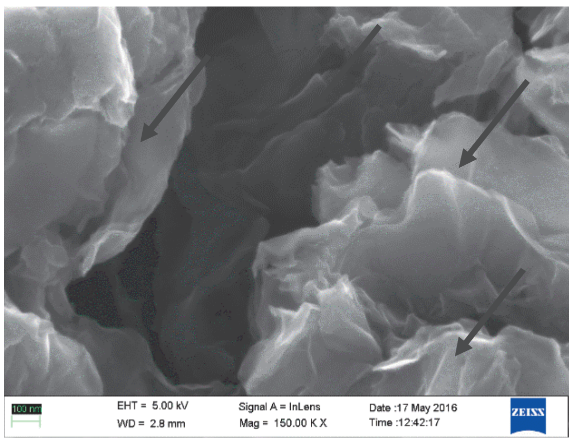

Figure 2 FESEM image of multilayer graphene

The X-ray diffraction analyses of the powder and extruded sample of the composite are depicted in **Figure 3**. The peak of Al (1 1 1) was detected in the powder sample while, no matching peak of Al was observed in the extruded sample. This result revealed that Mg and Al powder makes a solid solution primarily during microwave sintering and extrusion steps. The absence of graphene peak in powder and extruded sample may be attributed to the low volume fraction (0.1 wt.%) of graphene in the Mg matrix. The increase of Mg (1 0 0) peak in the extruded sample indicates that the pyramidal plane possibly rotates in [1 0 0] direction to coincide with the extrusion direction. The microstructural study of the polished extruded sample of nanocomposite is presented in **Figure 4**.

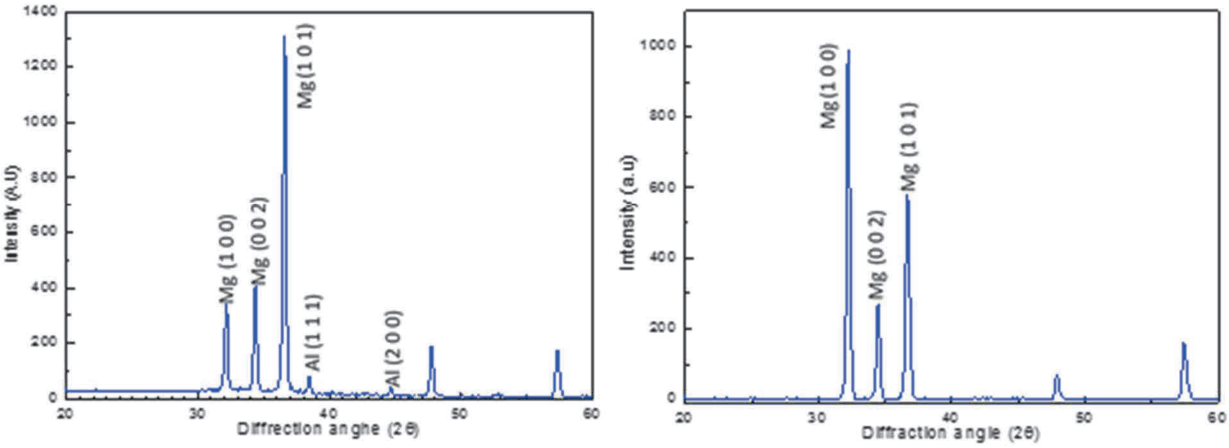

Figure 3 X-ray diffraction spectra of (a) powder sample and (b) extruded sample of the composite

It can be seen that the distribution of the graphene nano-plates is more or less uniform. In some places, few clusters of graphene nano-plates are also observed. **Figure 5** shows the FESEM image of indentation morphology on composite obtained using maximum 5N load. Findings indicate that no obvious micro-cracks and micro-protrusions were visible in or near the indentation.

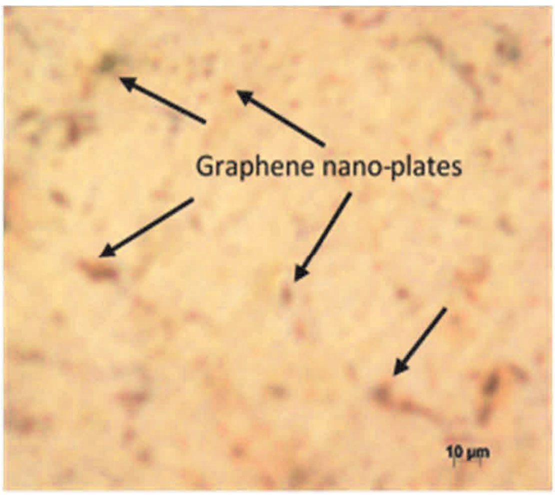

Figure 4 Optical micrograph of the polished sample of the composite

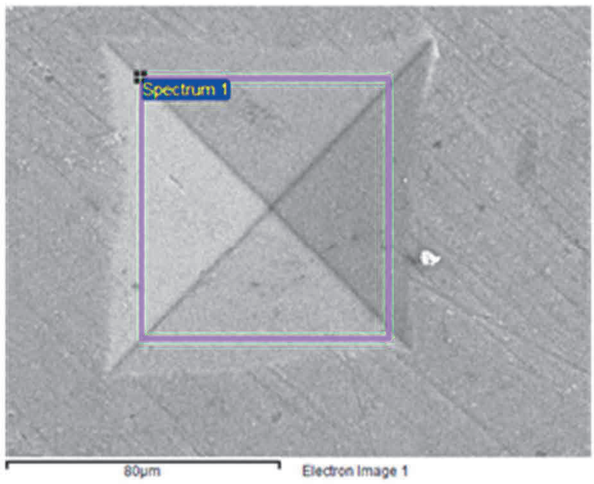

Figure 5 FESEM image of indentation morphology of the composite sample

The corresponding EDX analysis of the assigned area (within rectangular box in **Figure 5**) was presented in **Figure 6**. The results further reveal the presence of Al and graphene in the Mg matrix. The analysis shows that the atomic ratio from Mg to O is approximately 14:1. This result suggests that the formation of MgO oxide in the extruded sample is very limited. To describe the mechanical properties of the composite, the micro hardness values and the scratch forces are presented in **Table 2**. The results are compared with the monolithic Mg and Mg / 3 wt.% Al alloy. The additions of Al powder and graphene nano-plates resulted in a steady improvement in the hardness of pure Mg. The hardness value of ~ 41 Hv was estimated in pure Mg sample. While, the hardness values of ~49 Hv (20 % increase) and ~57 Hv (~39% increase), a bit higher than pure Mg, were observed in Mg / 3 wt.% Al alloy and Mg / 3 wt.% Al / 0.1 wt.% GA nano-composite respectively. The increase of hardness in the alloy may essentially be attributed to the effect of solid solution of Mg and Al. Further, the significant enhancement in hardness may be attributed due to the constraint to localized deformation in the presence of graphene nano-plates, homogeneously distributed in the Mg matrix. The scratch forces at constant penetration load 9.8 N were measured following ASTM G171-03 standard using MTR3/50-50/NI instrument. The average scratch forces in pure Mg ~ 3.5 N, Mg /3 wt.% Al alloy ~ 5.37 and Mg / 3 wt.% Al / 0.1 wt.% GA nano-composite ~ 3.2 N were obtained. The average widths of scratch track in pure Mg sample ~186 μm, in Mg /3 wt.% Al alloy ~ 150 μm, and in Mg / 3 wt.% Al / 0.1 wt.% GA nano-composite ~100 μm were estimated. This result suggests that the additions of 3 wt.% Al as an alloying element and 0.1 wt.% GA as reinforcement improved the mechanical strength in Mg. It is worth to be noted that the scratch force depends on the initial penetration depth and the corresponding volume of material to be removed by the stylus and the coefficient of friction between the stylus and the sample. Lower scratch force in the composite sample may be attributed due to the presence of graphene nano-plate which act as a lubricant.

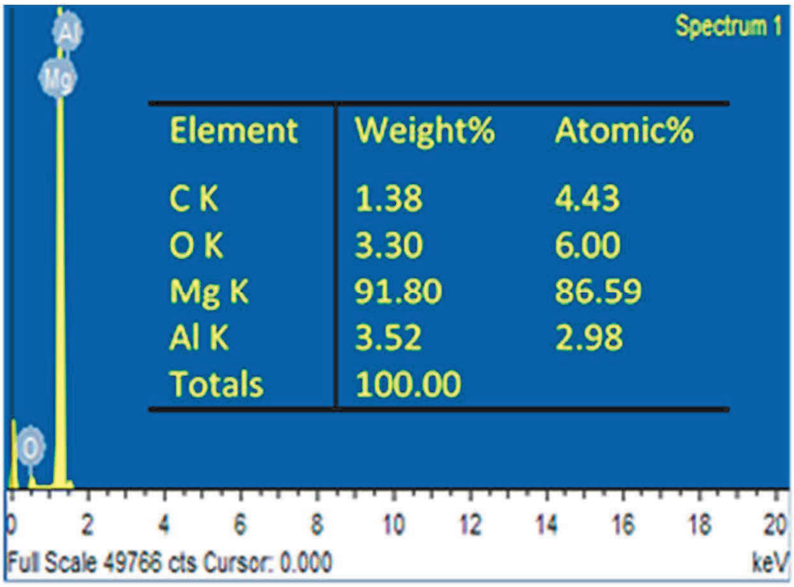

Figure 6 EDX result of the indented portion

Table 2 Results of micro hardness and the scratch behaviour of pure Mg sample and its alloy and composite

Sample	Indentation force 100 g for 20 sec		Initial penetration force 9.8 N	
	Ave. indentation diameter (μm)	Microhardness (HV)	Scratch force (N)	Scratch width (μm)
Mg	66.7 ± 2	42 ± 3	3.506	186.43
Mg /3 wt.% Al	61.6 ± 3	49 ± 5	5.372	150.38
Mg / 3 wt.% Al / 0.1 wt.% GA	57.1 ± 2.5	57 ± 5	3.217	100.10

The scratch images for all the samples are presented in **Figure 7**. It can be seen that in each samples, more or less repeated build-up of material are ascertained in the both sides of scratch track. The scratch tracks are identified by chevron markings.

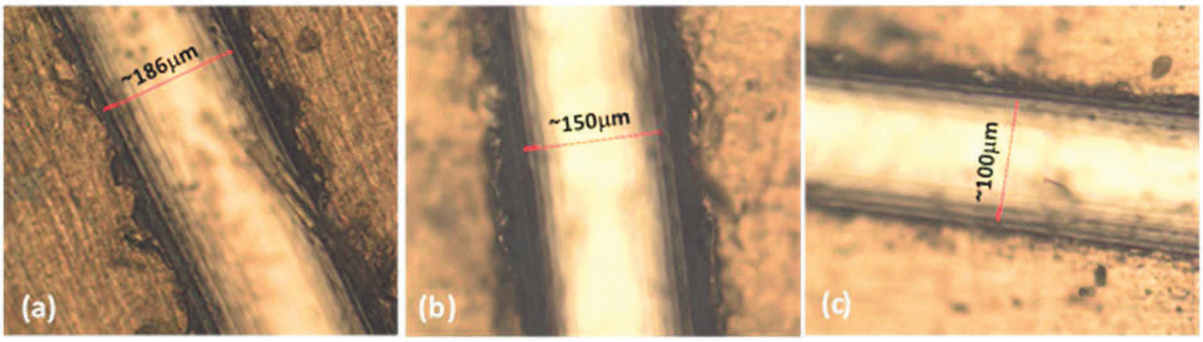

Figure 7 Scratch tracks: (a) pure Mg, (b) Mg / 3 wt.% Al alloy, (c) Mg / 3 wt.% Al / 0.1 wt.% GA composite

4. CONCLUSIONS

In conclusion, the bulk samples of pure Mg, Mg / 3 wt.% Al alloy and Mg / 3 wt.% Al / 0.1 wt.% GA nano-composite were successfully synthesised using powder metallurgy technique incorporating cold compaction of powders, energy efficient microwave sintering and hot extrusion. The Raman and FESEM studies of the filler materials confirm the formation of multilayer graphene nano-plates. Uniform distribution of graphene nano-plates confirms the suitability of the processing steps and parameters. The hardness properties were found to be significantly improved in the composite. The minimum scratch width and scratch force for a given indentation load was observed in the composite sample. This result indicates that the graphene nano-plates improve the wear properties of the composite sample. These observations are expected to have important consequences in the processing and application of these technologically useful alloy-composite.

REFERENCES

[1] KAINER, K. U. *Magnesium alloys and their applications.* Wiley-VCH Verlag GmbH, 2000.

[2] NGUYEN, Q. B., GUPTA, M., SRIVATSAN, T. S. On the role of nano-alumina particulate reinforcements in enhancing the oxidation resistance of magnesium alloy AZ31B. *Mater. Sci. Eng. A*, 2009, vol. 500, pp. 233-237.

[3] MEENASHISUNDARAM, G. K., GUPTA, M. Emerging environment friendly magnesium-based composite technology for present and future generation. *The journal of the Minerals, Metals & Materials Society*, 2016, vol. 68, pp. 1890-1901.

[4] FARRARO, K. F., KIM, K. E., WOO, S. L., FLOWERS, J. R., McCULLOUGH, M. B. Revolutionizing orthopaedic biomaterials: The potential of biodegradable and bioresorbable magnesium-based materials for functional tissue engineering. *Journal Biomech*., 2014, vol. 47, pp. 1979-1986.

[5] MORDIKE, B. L., EBERT, T. Magnesium: Properties - applications - potential. *Mater. Sci. Eng. A*, 2001, vol. 302, pp. 37-45.

[6] MALLICK, A., VEDANTAM S., LU, L. Grain size dependent tensile behavior of Mg-3%Al alloy at elevated temperatures. *Mater. Sci. Eng. A*, 2009, vol. 515, pp. 14-18.

[7] HIRSCH, J., Al-SAMMAN, T. Superior light metals by texture engineering: Optimized aluminum and magnesium alloys for automotive applications. *Acta Materialia*, 2013, vol. 61, pp. 818-843.

[8] MALLICK, A., TUN, K. S., VEDANTAM, S., GUPTA, M. Mechanical Characteristics of Pure Mg and Mg/Y_2O_3 Nanocomposite in 25 - 250°C Temperature Range. *J. of Mat. Sci.,* 2010, vol. 45, pp. 3058-3066.

[9] XU, L. Q., YANG, W. J., NEOH, K. G., KANG, E. T., FU, G. D. Dopamine- induced reduction and functionalization of graphene oxide nanosheet. *Macromolecules*, 2010, vol. 43, pp. 8336-8339.

[10] STANKOVICH, S., DIKIN, D. A., PINER, R. D., KOHLHAAS, K. A., KLEINHAMMES, A., JIA, Y., WU, Y., NGUYEN, S. T., RUOFF, R. S. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon*, 2007, vol. 45, pp. 1558-1565.

[11] SHAN, C., TANG, H., WONG, T., HE, L., LEE, S. T. Facile synthesis of a large quantity of graphene by chemical vapor deposition: an advanced catalyst carrier. *Advanced Materials*, 2012, vol. 24, pp. 2491-2495.