

GRAPHENE REINFORCED MAGNESIUM MATRIX COMPOSITES BY HOT PRESSED SINTERING

X. M. DU*, K. F. ZHEN, F. G. LIU

*School of Materials Science and Engineering, Shenyang Ligong University,
Shenyang 110159, China*

Magnesium matrix composites reinforced with graphene are fabricated by the combination of ball-milling and hot pressed sintering methods. The effects of the graphene with various wt.% (0-1.25) on the microstructures and mechanical properties such as micro hardness and density of the composites were examined. Microstructure of composites have been investigated by scanning electron microscope and energy dispersive spectroscopy (EDS) for better observation of dispersion of reinforcement. It is indicated that graphene are mainly embedded and dispersed inside the Mg powder, and a small amount of graphene distributed at the grain boundaries. The increase in wt% (up to 1.25 wt.%) of graphene improves the mechanical properties of the composites. The improved mechanical properties is ascribed to the effect of uniform distribution of graphene in the grain interiors and at the grain boundaries.

(Received June 1, 2018; Accepted September 12, 2018)

Keywords: Magnesium alloys, Composites, Graphene, Strengthening

1. Introduction

Magnesium and its alloys have widespread applications in the field of aerospace and automotive industry due to their low mass density, excellent damping capacity, castability, and machinability. However low strength and ductility magnesium and its alloys limits their extensive applications [1]. Therefore, there is a need to improve their strength and ductility by developing composite materials [2]. Many researchers have tried to use different types of reinforcement particles (SiC, TiC, BC₄ etc.) to enhance the strength and ductility of Mg alloys [3-7]. But the large volume fraction of reinforcement particles, significantly affects the lightweight properties of magnesium alloys. The density of the composite B₄C/Mg was measured to be 2.147 g/cm³, which is much weightier than magnesium alloys[5]. It is not beneficial to improve the specific strength of magnesium matrix composites.

Graphene (graphite thin sheets with a thickness of less than 100 nm) exhibit extraordinary mechanical, electrical, and thermal properties [8,9]. Additionally, graphene is extremely light; the density of graphene was estimated to be as low as 1.06 g/cm³[10]. These exceptional properties make it a perfect reinforcement for metal matrix composites.

A number of graphene-based polymer composites [11,12] and aluminum composites [13-16] were reported. Graphene has shown great promise to enhance the properties of polymer and aluminum matrices. The tensile strength of Polyvinyl alcohol (PVA) filled with 0.7 wt.% graphene nanosheets increased 76% [17]. The tensile strength of Al composite reinforced with only 0.3 wt-% GNSs increased 62% over the unreinforced Al matrix [18]. Despite the potential to improve the mechanical properties mentioned above, GNPs are difficult to disperse well in metals because of their large surface area which will lead to irreversible clusters and deteriorate the mechanical performance consequently.

Recently the research work of graphene-based magnesium composites has been reported [19-21], but it still has not received much attention compared to graphene-based aluminum composites. The possible problems are the great difficulties in homogeneous dispersion of graphene in the metal matrix and the likely interfacial chemical reactions between graphene and

*Corresponding author: du511@163.com

the metal matrix. The majority of researches have concentrated on magnesium matrix composites with a uniform distribution of reinforcement, which leads to improved stiffness and strength. Chen et al. [22] have fabricated the Mg composites reinforced with graphene nanoplatelets by combination of liquid state ultrasonic processing and solid state stirring and obtained dramatically enhanced properties. Rashad et al. [21,23,24] fabricated magnesium reinforced metal matrix composites using graphene nanoplatelets (GNPs) via powder metallurgy processing. The Young's modulus, yield strength, and failure strain of extruded nanocomposite of magnesium composite reinforced with only 0.3 wt-% GNSs increased 131%, 49.5% and 74.2% respectively, over the unreinforced pure magnesium matrix [23].

In this work, the graphene-reinforced magnesium matrix composites were synthesized by ball milling and hot-press sintering. The distribution and morphology of graphene in composite matrix were analyzed. The mechanical properties of Mg composites reinforced with graphene were tested and the relevant strengthening mechanisms of graphene discussed based on the primary experimental evidences.

2. Experimental details

2.1 Materials

Graphene sheets used in our experiments were prepared by modified hummers method as reported previously [25]. The experimental material is natural graphite with particle size of about 45 μ m. Graphene oxide was reduced at 95 °C for 24 hours by using hydrazine hydrate. The preparation method was similar to that of Ref.[25].The matrix, pure Mg powder of 60 μ m particle size was supplied by Henan Jianglang Magnesium Material Co., Ltd. China.

2.2 Composites preparation

The ball milling was conducted on a planetary machine under the high purity (99.999%) Ar atmosphere for preventing the Mg oxidation. The milling was paused for 5 minutes after every 40 minutes to prevent heating. The stainless steel vial was sealed with an elastomeric O ring. The stainless steel balls to powder weight ratio was 7:1, and the rotation rate of the vial was 40 rpm under a total milling time of 72 h.

A variety of ball-milled powders were fabricated by varying the mass fraction of graphene sheets (i.e. 0.25, 0.75, and 1.25 wt.%). The ball-milled powder was containerized in a heat-resisting steel die (50 mm in diameter, 200 mm in height, and 10 mm in thickness), then compacted. The compacted composite billets were sintered at 610°C for 1.5 hours under a pressure of 25 MPa by hot-press sintering.

2.3 Characterization of microstructure and mechanical properties

The optical microscopy (OM) (Axiovert200MAT, Carl Zeiss, German), scanning electron microscopy (SEM) (S-3400, Hitachi, Japan) equipped with energy-dispersive spectrometer (EDS) were used to study the microstructure and surface morphology of the composites. The specimens for OM and SEM analysis were sectioned by wire-electrode cutting and ground on SiC abrasive paper with water lubricant in a sequence from 1000 to 2000mesh. Next, the specimens were gently mirror-polished on the cloth with an alumina suspension to avoid the excessive pressure.

Density was measured by the Archimedes method. Theoretical densities of composites were calculated using rules of mixtures. Hardness measurements of composites samples were carried out on a Vickers hardness testing machine (Shanghai Shuangxu, Inc., HVS-50, China), using a load of 9.8 N, and the mean values of at least five measurements conducted on different areas of each sample was considered.

3. Results and discussion

Microstructure and mechanical characterization of ball-milled and sintered graphene reinforced magnesium matrix composites included metallographic examinations with SEM, EDS,

optical microscope, micro hardness and density measurements.

Fig. 1 shows the representative morphology of graphene and pure magnesium powder. As shown in Fig. 1(a), graphene have a two-dimensional high aspect ratio sheet geometry, and the wrinkles and folds is also showed on the exfoliated graphene sheet. The graphene consisted of platelets with the morphology of irregular shaped flakes with mean diameters less than 0.5-10 μm and agglomerated powders with opaque structure. The thickness of the graphene sheets is several nanometers (3-20 nm), corresponding to approximately 10-50 sheets of graphene. The particle shape of magnesium is irregular lamellar. The mean size of the particles appears to be $\sim 60\mu\text{m}$ with some smaller particles of 10-20 μm and some larger particles of about 80 μm (Fig.1 (b)).

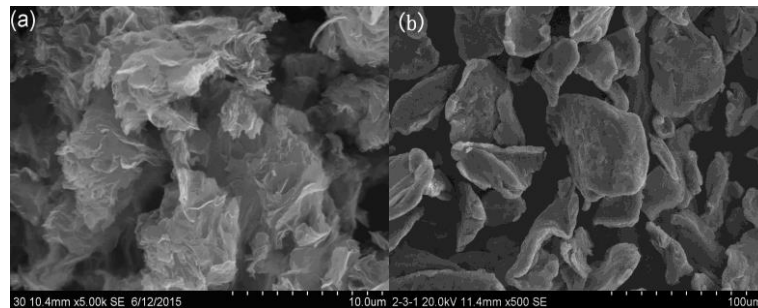


Fig. 1. SEM micrograph of powders used, (a) graphene, (b) pure magnesium powder.

Morphologies of ball-milled graphene/Mg composite powders with 1.25 wt.% graphene under 24 h and 72 h of milling time are shown in Fig. 2. Exfoliated graphene sheets with sizes below 10 μm are observed on the surface of the Mg powder under 24 h of milling time, where graphene sheets are marked by an arrow in Fig. 2(a). Fig. 2(b) displays magnified images of rectangles in Fig. 2(a). As shown in Fig. 2(b), graphene sheets are agglomerate, wrinkled and kinked, indicating the dispersion of graphene in Mg matrix is poor. Fig. 2(c) exhibits the powder morphology after ball milling of 72 h. Graphene sheets are not observed on the powder surface even in the magnified images of Fig. 2(d). This can be attributed to a prolonged ball milling time, which make graphene agglomeration get broken into sheets with high energy balling. Hence, the graphene sheets are supposed to be embedded and dispersed inside the Mg powder.

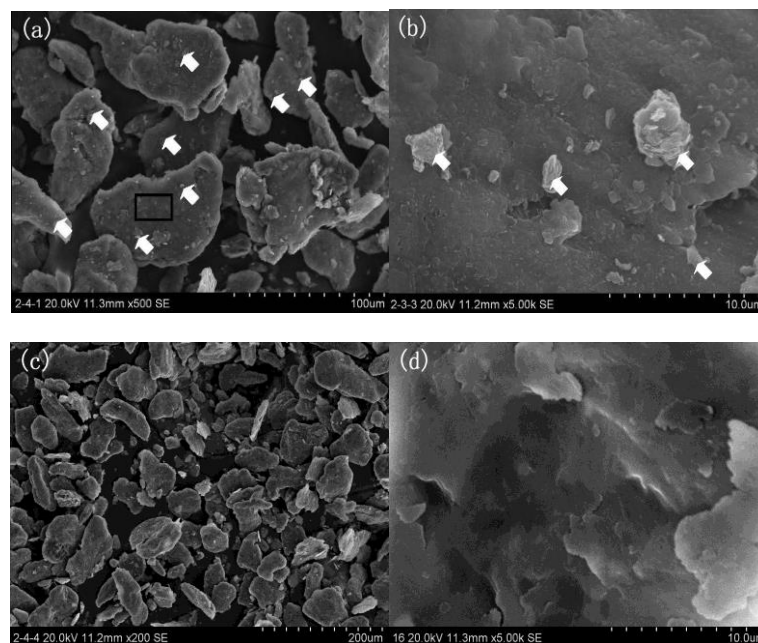


Fig.2. SEM images of (a) 24 h and (c) 72 h of milling time in the as-milled condition for 1.25 wt.% graphene/Mg composite powder, (b) and (d) display the magnified images of (a) and (c), respectively.

The optical photographs of cross-sections of the hot-pressed graphene/Mg composites with different graphene contents are shown in Fig. 3. It can be found that there is a small amount of graphene to distribute on the grain boundaries of magnesium matrix, and the distribution of graphene on the grain boundaries is inhomogeneous. The size of the grains in the graphene-rich region is smaller than that of graphene-lean region. It is indicated that the presence of graphene can obstruct the growth of Mg grains, leading to the refined grains in the graphene-rich region.

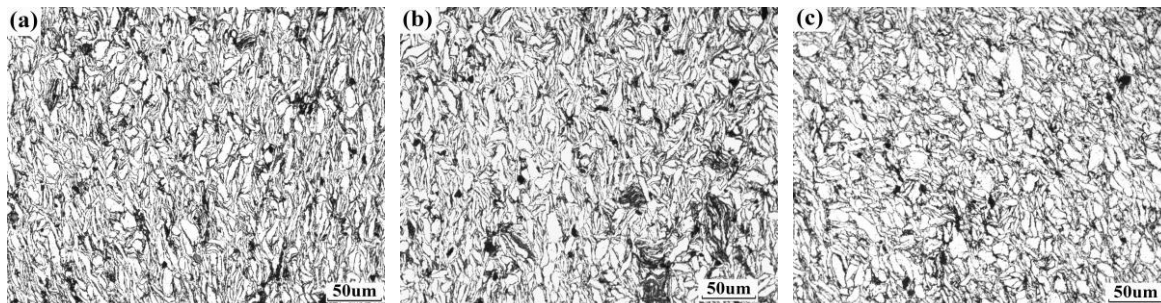


Fig.3. Optical micrograph of hotpressed sintering graphene/Mg composites with different graphene content for ball-milling time of 72 h, (a) 0.25 wt.%, (b) 0.75 wt.%, (c) 1.25 wt.%.

EDS analysis of the 1.25 wt.% graphene reinforced Mg matrix composites is presented in Fig. 4. As shown in Fig. 4(b), it is clear that the peaks for magnesium, oxygen and carbon are obtained. The EDS analysis confirms that graphene is present within the composites. Therefore, these SEM and EDS analysis are evidence of successful incorporation graphene in Mg matrix composites. The EDS mapping of Mg, C and O is presented in Fig. 4(c), (d) and (e), respectively. The EDS analysis of C shows the continuous shape of the particle, which proves that graphene exist in the composite. Besides, Fig. 4(d) exhibits the minor content of O on the surface, as a result of the tiny oxidation of Mg during the standard metallography preparation.

The hardness of the graphene reinforced composites was evaluated using Vickers hardness tester. Fig. 5 shows the effect of wt.% graphene on hardness of the samples. From the figure, it can be seen that the micro hardness increases with the increased graphene content. The maximum of hardness is obtained at the graphene content of 1.25 wt.%. The hardness of pure magnesium sample, was 59.3 ± 3.0 HV, while the hardness of 1.25 wt.% graphene reinforced magnesium matrix composites was 89.9 ± 4.5 HV, showing 51% increments over the unreinforced magnesium under the same experimental conditions. This superior hardness is ascribed to the effect of two possible important strengthening mechanisms: i) the graphene embedded and dispersed inside the Mg grains can block the movement of dislocation within the grains passing through the matrix, and make it difficult to reach the grain boundaries at the low stress levels; ii) the nano-structured graphene distributed at the grain boundaries can inhibit grain growth in magnesium matrix through grain boundary pinning and therefore lead to a finer grains of magnesium. Finer grains cause higher hardness values.

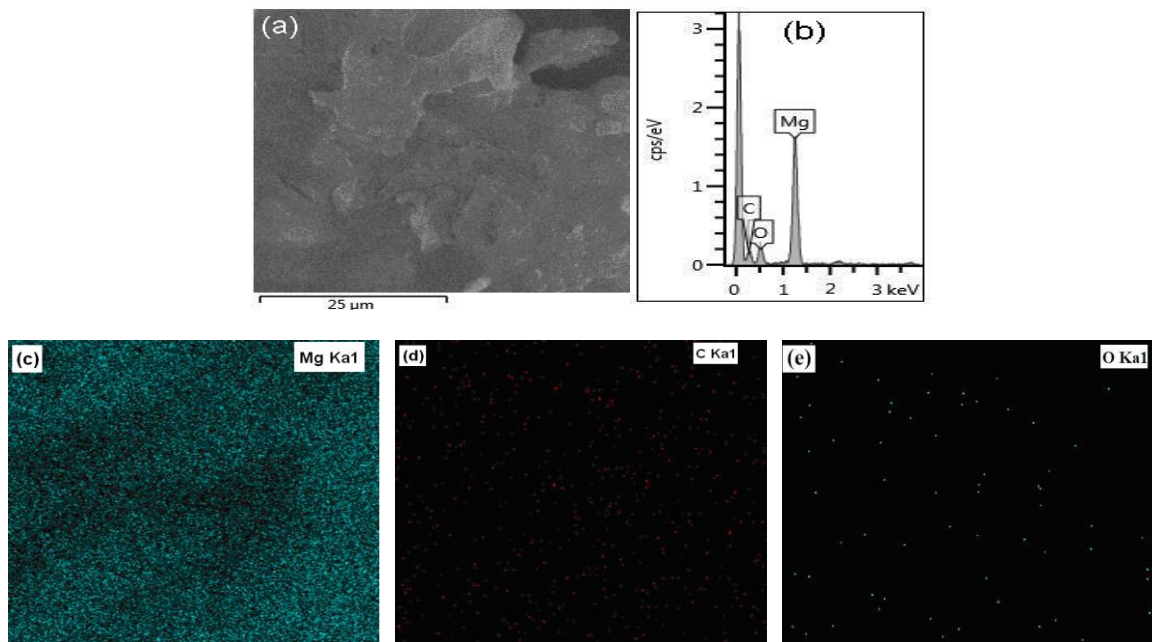


Fig. 4. Characterization of composites. (a) SEM images of composite surface with 1.25 wt.% graphene; (b) the EDS of the selected area in (a); (c-e) SEM mapping of composite: (c) magnesium; (d) graphene; (e) oxygen.

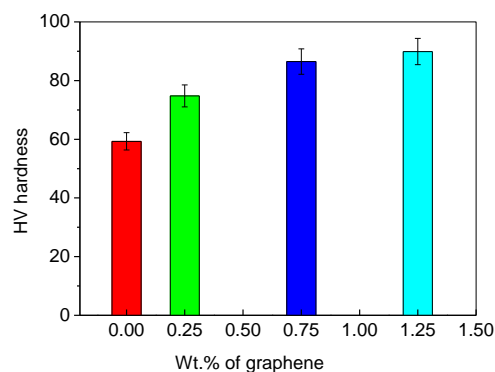


Fig. 5. The effect of wt.% of graphene on micro hardness.

The theoretical density, ρ_{th} of graphene/Mg composites, was calculated by the rule of mixtures, using the theoretical density 1.74 g/cm^3 for pure magnesium powder and approximately 2.25 g/cm^3 for graphene, as follows.

$$\rho_{th} = \frac{100}{\frac{W_{al}}{\rho_{al}} + \frac{W_g}{\rho_g}}$$

where ρ_{al} and ρ_g is specific weight of the base magnesium powder and graphene, respectively; W_{al} and W_g is weight percentage of the magnesium powder and graphene, respectively.

Based on above equation, the theoretical densities of the composites were expected to be increased compared with the density of pure magnesium powder. The effect of graphene on the density of the sintered composites as a function of wt.% graphene shown in Fig. 6. As can be seen from the figure, theoretical and measured densities increase by increasing wt.% of graphene. The deviation between experimental values and theoretical values is due to the presence of a few pores in the samples.

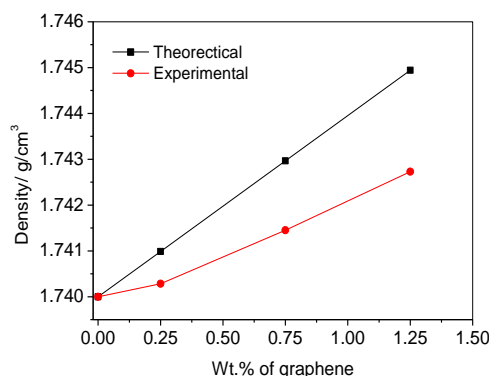


Fig. 6. The effect of wt.% of graphene on density.

4. Conclusions

In this paper, the graphene reinforced magnesium matrix composites were fabricated by ball-milling mixing of pure magnesium powder and graphene, followed by hot pressed sintering methods. The contents of graphene was varied from 0.25 to 1.25 wt.% in magnesium matrix. The microstructures of as-milled and as-sintered composites were analysed, the density and microhardness were also tested for as-sintered composites. Experimental results revealed that the graphene are mainly embedded and dispersed inside the Mg powder when the ball-milling time is prolonged to 72 hours. Besides, a small amount of graphene distributed at the grain boundaries has an important effect on refining grains of magnesium matrix. The hardness of composites increases with the increased graphene content. The strengthening is ascribed to the effect of uniform distribution of graphene in the grain interiors and at the grain boundaries.

Acknowledgements

This work is supported by the Natural Science Foundation of Liaoning (No. 2015602642), Shenyang science and technology project (No. 18-013-0-33) in Liaoning Province, China.

References

- [1] T. W. Clyne, P. J. Withers, An Introduction to Metal Matrix Composites. London: Cambridge University Press; 1993.
- [2] Z. Hu, G. Tong, D. Lin, C. Chen, H. Guo, J. Xu, L. Zhou, Materials Science and Technology **32**(9), 1 (2016).
- [3] K. K. Deng, X. J. Wang, Y. W. Wu, X. S. Hu, K. Wu, W. M. Gan, Materials Science and Engineering A **543**(1), 158 (2012).
- [4] J. G. Li, F. F. Wang, W. Wen, Y. J. Zhang, M. L. Wang, H. W. Wang, Materials & Design **37**, 533 (2012).
- [5] Y. T. Yao, L. Q. Chen, Journal of Materials Science & Technology **30**(7), 661 (2014).
- [6] I. A. Ibrahim, F. A. Mohamed, E. J. Lavernia, Journal of Materials Science **26**(5), 1137 (1991).
- [7] Q. Dong, L. Q. Chen, M. J. Zhao, J. Bi, Materials Letter **58**(6), 920 (2004).
- [8] A. K. Geim, K. S. Novoselov, Nature Materials **6**(2), 183 (2007).
- [9] V. Singh, D. Joungh, L. Zhai, S. Das, S. I. Khondaker, S. Seal, Progress in Materials Science **56** (8), 1178 (2011).
- [10] M. A. Rafiee, J. Rafiee, Z. Wang, H. Song, Z. Z. Yu, N. Koratkar, ACS Nano **3**(12), 3884 (2009).
- [11] J. R. Potts, D. R. Dreyer, C. W. Bielawski, R. S. Ruoff, Polymer **52**(1), 5 (2011).

- [12] W. H. Kai, Y. Hirota, L. Hua, *Journal of Applied Polymer Science* **107**(3), 1395(2008).
- [13] S. F. Bartolucci, J. M. Paras, A. Rafiee, J. Rafiee, S. Lee, D. Kapoor, N. Koratkar, *Materials Science and Engineering A* **528** (27), 7933 (2011).
- [14] Z. Li, G. Fan, Z. Tan, Q. Guo, D. Xiong, Y. Su, Z. Li, D. Zhang, *Nanotechnology* **25**(32), 325601 (2014).
- [15] J. L. Li, Y. C. Xiong, X. D. Wang, S. J. Yan, C. Yang, W. W. He, J. Z. Chen, S. Q. Wang, X. Y. Zhang, S. L. Dai, *Materials Science and Engineering A* **626**, 400 (2015).
- [16] N. A. Syed, K. Lailesh, *Materials Science & Engineering A* **667**, 16 (2016).
- [17] J. J. Liang, Y. Huang, L. Zhang, Y. S. Chen, *Advanced Functional Materials* **19**(14), 2297 (2009).
- [18] J. Wang, Z. Li, G. Fan, H. Pan, Z. Chen, D. Zhang, *Scripta Materialia* **66**(8), 594 (2012).
- [19] S. L. Xiang, M. Gupta, X. J. Wang, L. D. Wang, X. S. Hu, K. Wu, *Composites: Part A* **100**, 183 (2017).
- [20] Q. H. Yuan, G. H. Zhou, L. Liao, Y. Liu, L. Luo, *Carbon* **127**, 177(2018).
- [21] Q. H. Yuan, Z. Q. Qiu, G. H. Zhou, X. S. Zeng, L. Luo, X. X. Rao, Y. Ding, Y. Liu, *Materials Characterization* **138**, 215 (2018).
- [22] L. Y. Chen, H. Konishi, A. Fehrenbacher, M. Chao, J. Q. Xu, H. Choi, H. F. Xu, F. E. Pfefferkorn, X. C. Li, *Scripta Materialia* **67**, 29 (2012).
- [23] M. Rashad, F. Pan, H. Hu, M. Asif, S. Hussain, J. She, *Materials Science & Engineering A* **151**, 159 (2015).
- [24] M. Rashad, F. Pan, A. T. Tang, M. Asif, *Journal of Industrial & Engineering Chemistry* **23**, 243 (2014).
- [25] W. S. Hummers, R. Offeman, *J. Am. Chem. Soc.* **80**, 1339 (1958).