

SYNTHESIS AND CHARACTERIZATION OF GRAPHENE NANOSHEETS/MAGNESIUM COMPOSITES PROCESSED THROUGH POWDER METALLURGY

SINTEZA IN KARAKTERIZACIJA MAGNEZIJEVIH KOMPOZITOV, OJAČANIH Z GRAFENSKIMI NANOPLASTMI, IZDELANIH Z METALURGIJO PRAHOV

Xiaoming Du, Kaifeng Zheng, Fengguo Liu

Shenyang Ligong University, School of Materials Science and Engineering, Shenyang 110159, China
du511@163.com*Prejem rokopisa – received: 2017-04-12; sprejem za objavo – accepted for publication: 2017-06-28*

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Magnesium-matrix composites reinforced with graphene nanosheets (Mg-Gr) were fabricated using a combination of powder metallurgy and hot rolling. The effects of the graphene-nanosheet content on the microstructures and density of the composites were investigated. It was found that the graphene nanosheets were gradually dispersed in the magnesium matrix with an increasing ball-milling time and a uniform dispersion was achieved after 72 h for the composite with a graphene content of 1.0 % of mass fraction. In addition, no obvious agglomeration of graphene was observed in the as-sintered and as-rolled composites with the graphene contents of up to 1.0 % of mass fraction. A coordinated deformation of multilayer graphene nanosheets occurs with a deformation of the surface grains during the rolling, which may cause a significant reduction in the number of layers of the graphene nanosheets. When increasing the graphene content, the density of the Mg-Gr composites shows an increase.

Keywords: magnesium-matrix composites, graphene nanosheets, powder metallurgy

Kompoziti s kovinsko osnovo, ki so bili ojačani z grafitnimi nanoplastmi (Mg-Gr), so izdelani s kombinacijo postopkov metalurgije prahov in metodami vročega valjanja. Raziskani so bili vpliv vsebnosti grafitnih nanosov na mikrostrukturo in gostoto kompozitov. Ugotovljeno je bilo, da se grafenske nanoplasti postopoma razpršijo v magnezijevo matriko, s povečanjem časa krogljčnega mletja. Pri kompozitu z 1,0 % utežnih odstotkov vsebnosti grafena so dobili enakomerno disperzijo po 72 h mletja. Pri obeh, sintranih in valjanih kompozitih niso opazili nobene očitne aglomeracije grafena do vsebnosti 1,0 % utežnih odstotkov grafena. Med valjanjem je istočasno z deformacijo površinskih zrnopotekala usklajena deformacija grafenskih nanoplasti, kar lahko povzroči znatno zmanjšanje števila grafenskih nanoplasti. Z zviševanjem vsebnosti grafena se je povečevala gostota Mg-Gr kompozitov.

Ključne besede: kovinski kompoziti, ojačani z grafenom; grafitne nanoplasti, metalurgija prahov

1 INTRODUCTION

Owing to a low density, high specific strength, good machinability and easy recycling, magnesium and its alloys have widespread applications in the fields of the automobile, aerospace and electronics industries. However, the usage of magnesium is limited due to its low strength and ductility, as compared to steel and aluminium. Many attempts have been made to improve the mechanical properties of magnesium by developing magnesium-base metal-matrix composites, such as Y_2O_3/Mg , Al_2O_3/Mg , $SiCp/Mg$ and Ti/Mg , during the past decades.^{1–5} Recently, the researchers focused on the lighter reinforcements, such as graphene and carbon nanotube (CNT), to enhance the mechanical properties of Mg alloys.^{6–7}

Graphene, a single atomic layer of sp^2 hybridized carbon, has extraordinary electrical, thermal, and physical properties. The nanometric nature and high specific surface area allow a great interaction of the reinforcement phase with the matrix even in small concentrations.

The modulus of elasticity and intrinsic fracture strength of monolayer graphene are 1 TPa and 125 GPa, respectively.^{8–10} Compared to one-dimensional carbon nanotubes, two-dimensional graphene is much easier to be controlled and dispersed in a metal matrix. Furthermore, graphene can be prepared in large quantities using chemical exfoliation of graphite.¹¹ Therefore, graphene is considered as an ideal reinforcement for metal-matrix composites.

In the past few years, research results for nanoscale graphene-reinforced polymer¹² and ceramic¹³ matrix composites were reported. The tensile strength of polyvinyl alcohol (PVA) filled with 0.7 % mass fraction of graphene nanosheets increased by 76 %.¹² The bending strength and breaking strength of an Al_2O_3 ceramic matrix filled with 0.78 % of volume fraction of graphene nanosheets increased by 30.75 % and 27.20 %, respectively.¹³ However, the Mg composites reinforced with graphene nanosheets are relatively limited. The existing results in the literature indicate that graphene has incomparable advantages in solving the dispersion and wettability

lity conundrums, compared with carbon nanotubes. There is an obvious reinforcement effect and graphene has potential applications as the ideal reinforcement in graphene-reinforced magnesium-matrix composites.^{14–16}

In this study, graphene-nanosheet-reinforced magnesium-matrix composites (Mg-Gr) were fabricated using high-energy ball milling, hot-press sintering and hot rolling. The effects of the ball-milling time on the morphologies and structures of the graphene nanosheets in the composites were studied. Meanwhile, the effects of the graphene nanosheets on the microstructure and density of the composites were also investigated.

2 EXPERIMENTAL PART

The graphene nanosheets used in our experiments were prepared with a modified Hummers method as reported previously.¹⁷ The experimental material was natural graphite with a particle size of about 45 μm . Natural graphite was reduced at 95 °C for 24 h using hydrazine hydrate. Graphene nanosheets with a thickness of several atomic layers were obtained. The preparation method was similar to that from reference¹⁷. A magnesium powder with a 99.5 % purity was bought from Hebi Jianglang Metals Co., Ltd., China, with the average particle size of 20 μm and it was used as the matrix material. The densities of magnesium powder and graphene nanosheets were 1.74 g/cm^3 and 2.25 g/cm^3 , respectively.

Pure magnesium powders were initially mixed with (0.5, 1.0, 1.5, 2.0) % of mass fractions of the as-prepared graphene nanosheets in a conventional rotating ball-milling machine using a stainless jar and balls. Ball milling was carried out in an argon atmosphere at a rotating speed of 90 min^{-1} for 6–72 h with a ball-to-powder weight ratio of 3:1. No process-control agent was used. The milling was paused for 5 min after every 40 min to prevent heating. The above Mg-Gr powders were loaded into a graphite die with a diameter of 50 mm. A

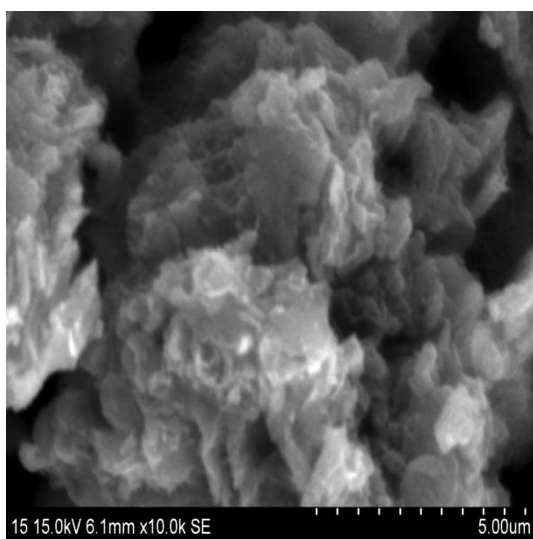


Figure 1: SEM micrograph of graphene nanosheets

sheet of graphite paper was placed between the punch and the powders as well as between the die and the powders for easy removal. The compact Mg-Gr composite billets were vacuum hot pressed at 610 °C for 1.5 h under a pressure of 25 MPa using powder metallurgy. The Mg-Gr composite with 2.0 % mass fraction of graphene nanosheets was rolled at 400 °C with a thickness reduction of 10 % per pass. The rolling-wheel pressure was 40 t, and the rolling-wheel temperature was 25 °C. The as-rolled composites were heat treated at 350 °C for (1, 2 and 3) h, respectively.

The microstructures of the as-sintered composites were observed with an X-ray diffractometer of Rigaku Ultima IV with $\text{Cu-K}\alpha$ radiation at 40 kV and 40 mA, and a scan rate of 0.02 °/s in a 2θ range of 20–90°. The surface morphology was observed with an S-3400N scanning electron microscope (SEM) equipped with an energy-dispersive spectrometer (EDS) and a Carl Zeiss Axiovert200MAT optical microscope. The density was measured using Archimedes' method. Theoretical densities of the composites were calculated using rules of mixtures.

3 RESULTS AND DISCUSSION

The typical microstructures of the graphene observed with SEM are shown in **Figure 1**. The graphene nanosheets, having a feather-like, translucent structure, show that their thickness is very thin. The radial size is in the micron order. These nanosheets have the typical characteristics of a folded structure.

The ball-milling time and the graphene content have an important influence over the morphology, powder size, microstructure and physical properties of Mg-Gr composites. **Figures 2 to 4** show a comparative analysis for the sintered composites with different milling times and graphene contents. **Figure 2** shows the effect of the graphene content (taking 0.5, 1 and 2 % as the examples) on its dispersion for the ball-milling time of 6 h. It can be found that the graphene nanosheets are mainly distributed at the magnesium grain boundaries, showing no obvious agglomeration for the graphene content of 0.5 %. However, there is an obvious agglomeration of the graphene nanosheets in the Mg matrix when the content of graphene in the Mg-Gr composites is up to 1.0 %. This is because magnesium grains cannot be completely coated when the content of graphene is less than 1.0 %. The graphene is distributed intermittently at the grain boundaries. When the graphene content is 1.0 %, its presence at the grain boundary can be observed (**Figure 2b**); and when the content of graphene is increased, the graphene nanosheets at the magnesium grain boundaries gradually increase. A serious agglomeration of the graphene nanosheets is observed in the Gr composites containing 2.0 % of mass fractions of Mg, as shown in **Figure 2c**.

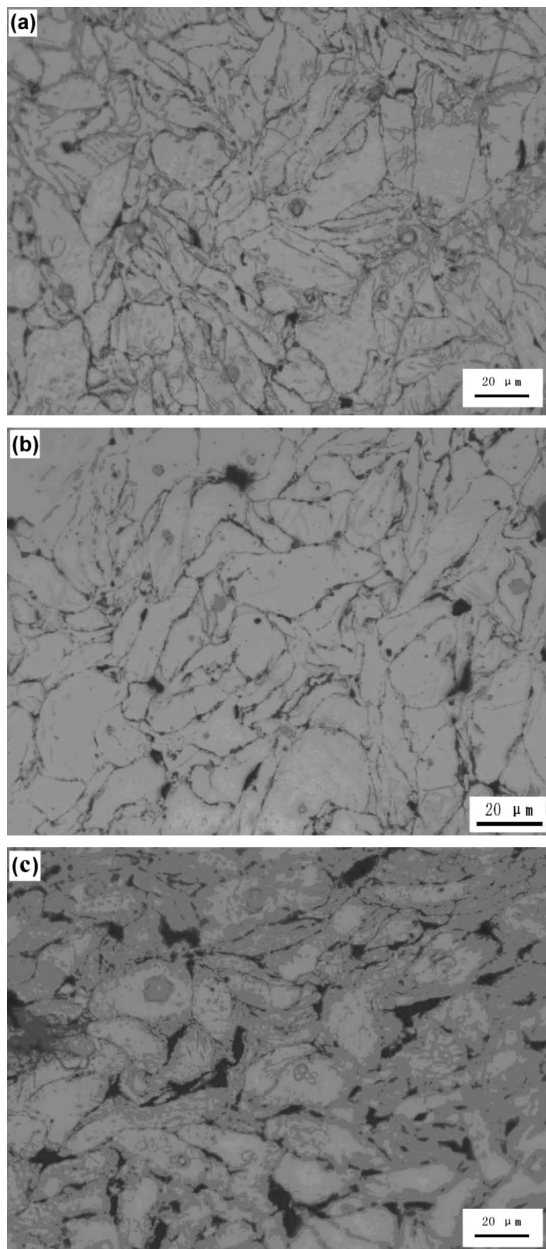


Figure 2: Microstructures of the composites with different graphene contents for the ball-milling time of 6 h: a) 0.5 %, b) 1.0 %, c) 2.0 %

In order to obtain a uniform dispersion of graphene in the magnesium matrix for a higher content of graphene, the milling time was increased to 72 h. We tried to carry out ball-milling tests at 12 h, 24 h and 48 h, respectively. However, the agglomeration was still present in the composites with 1.0 % graphene. Then the milling time was further extended to 72 h. Figure 3 shows the microstructures of the sintered composites with 1.0 % and 2.0 % graphene contents for the ball-milling time of 72 h. It is found that the graphene nanosheets at the magnesium grain boundaries gradually tend to be uniform for the composites with the 1.0 % graphene content. The figure indicates an excellent dispersion of the graphene in the magnesium matrix after the ball-milling period of 72 h.

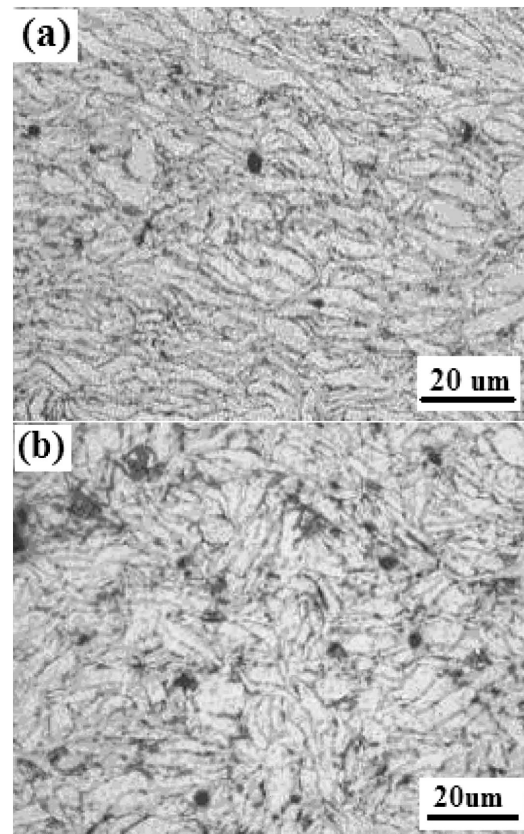


Figure 3: Microstructures of the sintered composites with different graphene contents for the ball-milling time of 72 h: a) 1.0 % of mass fraction, b) 2.0 % of mass fraction

However, clusters of graphene nanosheets are still visible after 72 h in the composites with the 2.0 % graphene content (**Figure 3b**). No experiment with a longer milling time was performed in this study.

In order to eliminate the porosity of the composites, improve the density of the composites and refine the grain size of the composites, hot rolling and heat treatment were successively performed. Optical micrographs of the Mg-Gr composite with the graphene content of 1.0 % in hot-rolling and heat-treatment conditions are presented in **Figures 4** and **5**, respectively. It is found that the grains of the as-rolled composite are elongated along the rolling direction, as shown in **Figure 4**. The graphene nanosheets are still distributed mainly along the grain boundaries. Compared with **Figure 2b**, it is important to note that a coordinated deformation of the multilayer graphene nanosheets occurs with the deformation of the surface grains, which may cause a significant reduction in the number of layers of the graphene nanosheets. It can be explained that the refinement of the grains on the surface greatly increases the number of grain boundaries, which can cause a reduction of the thickness of the graphene nanosheets. A recovery and recrystallization of the microstructure appear at an aging temperature of 350 °C, as shown in **Figure 5**. The microstructure of the composite tends toward homogenization

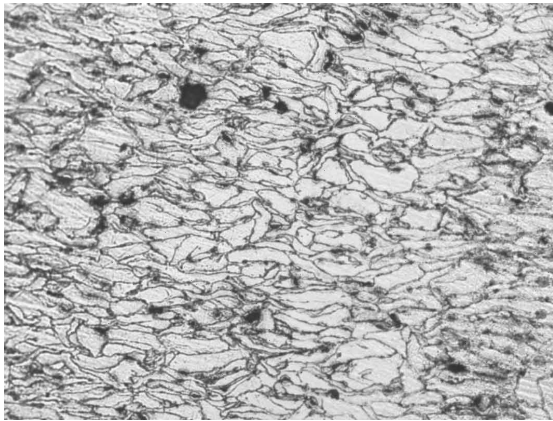


Figure 4: Microstructure of the as-rolled composite with 1.0 % of mass fraction of graphene content

after an aging time of 3 h. This is expected to improve the mechanical properties of the composite. The investigation in this field will be implemented in the future.

The theoretical solid density of magnesium is 1.74 g/cm³. The density of the sintered sample, ρ_{ac} , was measured using Archimedes' method. The mixture density, ρ_{th} , was calculated with the rule of mixtures, using the theoretical density of 1.74 g/cm³ for the pure magnesium powder and 2.25 g/cm³ for the graphene nanosheets,¹⁸ as follows in Equation (1):

$$\rho_{th} = \frac{100}{\frac{W_{mg}}{\rho_{mg}} + \frac{W_g}{\rho_g}} \quad (1)$$

where ρ_{mg} and ρ_g are the specific weights of the base magnesium powder and graphene nanosheets, respectively; W_{mg} and W_g indicate the weight percentage of the magnesium powder and graphene nanosheets, respectively. The relative density representing the quality of powder metallurgy, ϕ , is defined in Equation (2):

$$\phi = \frac{\rho_{ac}}{\rho_{th}} \times 100\% \quad (2)$$



Figure 5: Microstructure of the as-rolled composite with 1.0 % of mass fraction of graphene content after the aging time of 3 h

Based on Equation (1), the densities of the magnesium-based composites reinforced with graphene nanosheets were expected to be increased compared with the density of the pure magnesium powder.

Theoretical, experimental and relative densities of the Mg-Gr composites with different graphene contents are shown in **Figure 6**. It is found that the relative densities of the composites are more than 99.8 %, which shows that the sintered composites are dense. The relative density of the Mg-Gr composites shows a decrease with the increase in the amount of graphene nanosheets in the Mg matrix (**Figure 6a**). This may be attributed to the fact that the dispersion of the graphene nanosheets in a Mg matrix becomes poor and the microvoid increases with the increase in the amount of the graphene nanosheets. The increase in the amount of the graphene nanosheets causes a poor combination of magnesium particles, which results in an increase in the porosity of the composites leading to a poor relative density of the composites. **Figure 6b** shows the variation in the theoretical density and experimental density with the variation in the graphene content in the Mg-Gr composites. The theoretical density follows the rule of mixture, showing a linear increase with the addition of the graphene nanosheets. However, the experimental density is slightly lower than the theoretical density and the difference bet-

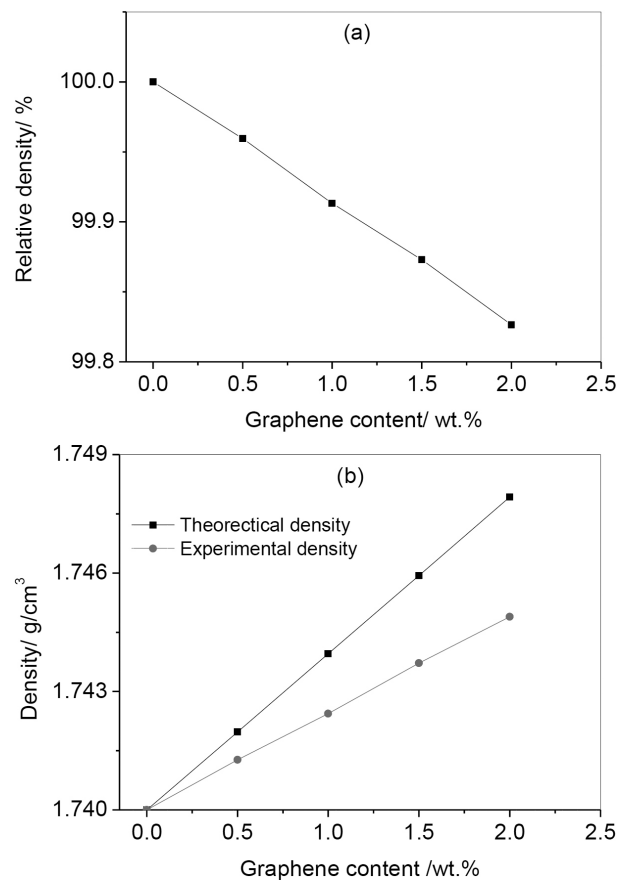


Figure 6: Variation of: a) relative density, b) theoretical density and experimental density of pure Mg and various Mg-Gr composites

ween them becomes large with the increase in the addition of the graphene nanosheets to the Mg matrix. This may lead to a reduction in the mechanical properties.

4 CONCLUSIONS

In this work, Mg-Gr composites were fabricated with ball-milling mixing of a pure magnesium powder and graphene nanosheets, followed by hot pressing, rolling and, finally, heat treatment. The contents of the graphene nanosheets were varied from 0.5 % to 2.0 % mass fraction in the magnesium matrix. The microstructures of the as-sintered and as-rolled composites were analyzed; the densities of the Mg-Gr composites in the as-rolled state were tested. Experimental results revealed that the graphene nanosheets were gradually dispersed in the magnesium matrix by increasing the ball-milling time, and a uniform dispersion was achieved after 72 h. No obvious agglomeration of graphene was observed in the as-sintered and as-rolled composites with the contents of the graphene nanosheets of up to 1.0 % mass fraction. A coordinated deformation of the multilayer graphene nanosheets occurs with the deformation of the surface grains during rolling, which may cause a significant reduction in the number of layers of the graphene nanosheets. By increasing the graphene content, the density of the Mg-Gr composites shows an increase.

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