PREPARATION AND CHARACTERIZATION OF MAGNESIUM MATRIX COMPOSITES REINFORCED WITH GRAPHENE NANO-SHEETS

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Graphene/magnesium composite materials (Mg-Gr) are prepared by the combination of powder metallurgy and rolling methods. The effects of the graphene nano-sheets content, sintering temperature and ball-milling time on the microstructures of the composites were investigated. It is indicated that the a uniform dispersion of graphene nano-sheets in Mg matrix are achieved when the graphene content increases from 0.5 wt.% to 2.5 wt.% with increasing the ball-milling time. And no obvious agglomeration of graphene is observed in as-sintered and as-rolled composites for the contents of graphene nano-sheets up to 2.5 wt.%. The coordinated deformation of multilayer graphene nano-sheets occurs with the deformation of the surface grains during rolling, which may cause a significant reduction in the number of layers of graphene nano-sheets.

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1. Introduction

With increasing importance of light-weight and energy efficient systems in aerospace, weaponry and automotive applications, magnesium and its alloys have attracted great research attention due to their low density (about 35% and 80% lighter than aluminum and steel, respectively), high specific strength, and good formability and damping ability. However, wider utilization of Mg and its alloys in practical applications is severely limited due to their lower strength. It is required to improve its mechanical properties such as strength and ductility by developing traditional alloys and composite materials [1].

In past decades, many attempts have been made to improve mechanical properties of magnesium and it's alloys by developing magnesium-based composites, such as SiC_p/Mg [2,3], TiC/Mg [4,5], B_4C/Mg [6,7], Al_2O_3/Mg [8,9], Y_2O_3/Mg [10,11] etc. Recently, the researchers focused their attention on the lighter reinforcements, such as graphene and carbon nanotube (CNT), to enhance the mechanical properties of Mg alloys [12,13].

Graphene, a single atomic layer of sp^2 hybridised carbon, has extraordinary electrical, thermal, and physical properties. The nanometric nature and high specific surface area allow a great interaction of 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 [14-16]. Compared to one-dimensional carbon nanotubes, two dimensional graphene is much easier to be controlled and dispersed in metal matrix. Furthermore, graphene can be prepared in large quantities by chemical exfoliation of graphite [17]. Therefore, graphene is considered as an ideal reinforcement in metal matrix composites.

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In the past few years, research results on nanoscale graphene-reinforced aluminum matrix composites have been reported [18-20]. The tensile strength of aluminum alloy reinforced with 0.3 wt.% graphene nano-sheets increased 62% [18]. The yield strength and tensile strength of aluminum alloy reinforced with 0.5 wt.% of graphene nano-sheets increased 49.1% and 25.20%, respectively [19]. Rashad et al. reported that the yield strength and tensile strength of pure aluminum reinforced with 0.3 wt.% of graphene nano-sheets increased 14.7% and 11%, respectively [20]. However, the Mg composites reinforced with graphene nano-sheets are relatively limited. The existing results in the literature indicate that graphene has incomparable advantages in solving the dispersion and wettability conundrums, compared with carbon nanotubes, there is an obvious reinforcement effect and has potential applications as the ideal reinforcement in graphene reinforced magnesium matrix composites [21-23].

In this study, magnesium matrix composites (Mg-Gr) reinforced with graphene nano-sheets were prepared by high-energy ball-milling, hot-press sintering and hot rolling. The morphologies and structures of the composites were characterized. Meanwhile, the effects of graphene nano-sheets on the microstructure of the composites were also investigated.

2. Experimental details

2.1 Materials

Graphene nano-sheets used in our experiments were prepared by modified hummers method as reported previously [24]. The experimental material is natural graphite with particle size of about 45 um. Natural graphite was reduced at 95 ℃ for 24 hours by using hydrazine hydrate. Graphene nano-sheets with the thickness of several atomic layers were obtained. The preparation method was similar to that of Ref. [24]. Magnesium powder with 99.5% purity was bought from Henan Jianglang metal powder, Inc. , China with an average particle size of 20 um was used as matrix material. And the densities of magnesium powder and graphene nanonano-sheets were 1.74 g/cm^3 and 2.25 g/cm^3 respectively.

2.2 Synthesis of composites

Pure magnesium powders were initially mixed with 0.5, 1.5, 2.5wt.% as-prepared graphene nano-sheets in a conventional rotating ball milling machine using the stainless jar and balls. Ball milling was carried out in argon atmosphere at a rotating speed of 90 rpm for 2-96 hours with ball-to-powder weight ratio of 3:1. No process control agent was used. The milling was paused for 5 minutes after every 40 minutes to prevent heating. The above prepared Mg-Gr powders were loaded into a graphite die with a diameter of 50 mm. A sheet of graphitic 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 560-610℃ for 1.5 hours under a pressure of 25 MPa by powder metallurgy. The Mg-Gr composite with 0.5 wt.% graphene nano-sheets was rolled at 400 ℃ with thickness reduction of 10% one pass. The rolling wheel pressure is 40 tons, and the rolling wheel temperature is 25℃. As-rolled composite was heat treated at 350℃ for 1, 2 and 3 hours, respectively.

2.3 Characterization

The surface morphology of as-sintered composites was observed by a scanning electron microscopy (SEM) of S-3400N equipped with energy-dispersive spectrometer (EDS) and an optical microscope of Carl Zeiss Axioert200MAT.

3. Results and discussion

Typical microstructures of pure magnesium powder and graphene observed by SEM are shown in Fig. 1. The particle shape of magnesium is irregular lamellar. The mean size of the particles appears to be ～60um with some smaller particles of 10-20 um and some larger particles of about 80 um (Fig.1 (a)). Graphene nano-sheets showing a feather like, translucent, show that the thickness is very thin. The radial size is in micron order. And they have the typical characteristics of the folded structure (Fig.1 (b)).

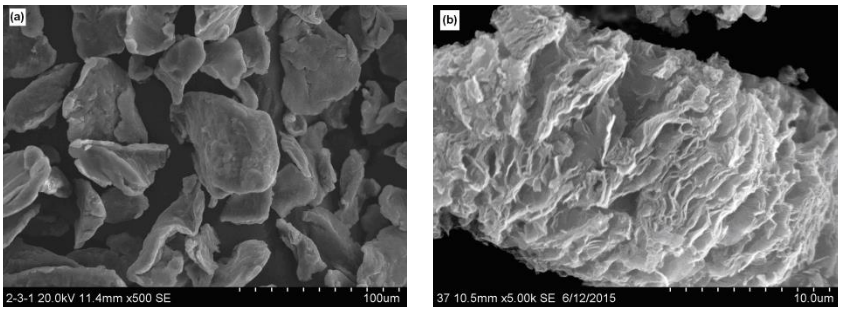
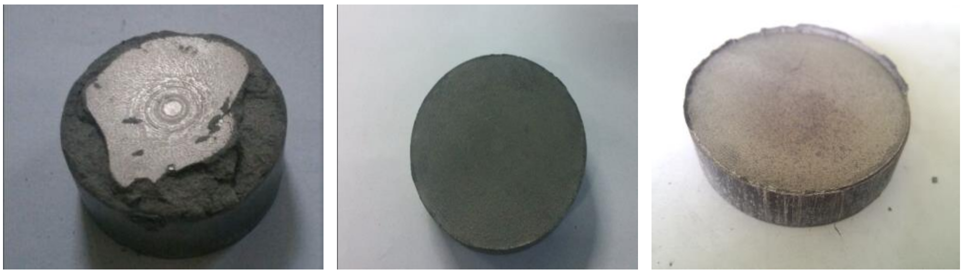


Fig. 1. SEM micrograph of powders used, (a) pure magnesium powder, (b) Graphene nano-sheets

Hot-pressed sintering temperature, ball-milling time, and graphene content have an important influence over morphology, powder size, microstructure and physical properties in Mg-Gr composites. Fig. 2 shows the effect of sintering temperature on the process quality of composites. It is found that there is a unfavourable effect on the process quality of composites for the lower or higher temperature. The suitable sintering temperature is 595 ℃ for this work.



(a) (b) (c)

Fig.2 the sintered composite with 0.5 wt.% graphene content for different sintering temperature: (a) 560℃, (b) 595 ℃ and (b) 610 ℃.

Fig. 3-5 show a comparative analysis for sintered composites with different milling time and graphene content. Fig.3 shows the effect of ball-milling time on the microstructures of the sintered composite with 0.5 wt.% graphene content. It is found that the graphene nano-sheets on the magnesium grain boundaries gradually tend to be uniform with the increase of ball-milling time. It is important to notice that clusters of graphene nano-sheets are not visible beyond 6 hours during ball-milling for 0.5 wt.% graphene content. It indicates an excellent dispersion of the graphene in the magnesium matrix in short periods of milling time (6 hours) by using ball milling. However, the agglomerate of graphene nano-sheets are visible at 6 hours during ball-milling for 1.5 wt.% and 2.5 wt.%, shown in Fig. 4 (a) and (b), respectively. It is needed for Longer milling times to improve the dispersion of graphene nano-sheets in magnesium matrix for higher graphene content. Fig. 5 shows the conjunct effect of graphene content and ball-milling time on the dispersion of graphene nano-sheets. It can be found that graphene nano-sheets mainly distributed on the magnesium grain boundaries, and show no obvious agglomeration of graphene nano-sheets for the content of graphene in the Mg-Gr composites is 1.5 wt% and 2.5 wt.% under 72h and 96h, respectively. Moreover, it can be seen that the black ribbons distribute on grain boundaries from Fig.5 (a) and Fig.5 (b). We deduce that the black ribbons are graphene nano-sheets. However, this phenomenon does not appear in Fig. 3(c). The reason is that the content of graphene is low in Mg-0.5wt.%Gr composite. Magnesium grains can not be completely coated.

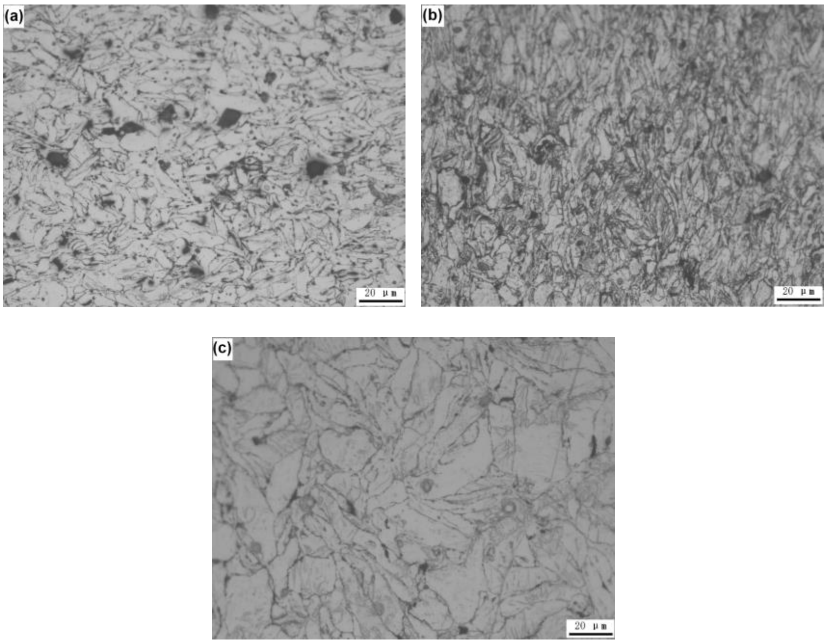


Fig.3 The microstructures of the composites with different graphene content ball-milling time for graphene content of 0.5%, (a) 2h, (b) 4h, and (c) 6h.

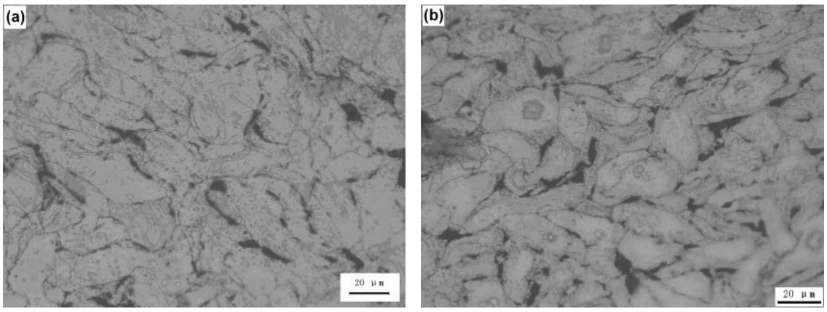


Fig. 4 The microstructures of the composites with different graphene content for ball-milling time of 6h, (a) 1.5 wt.%, (b) 2.5 wt.%.

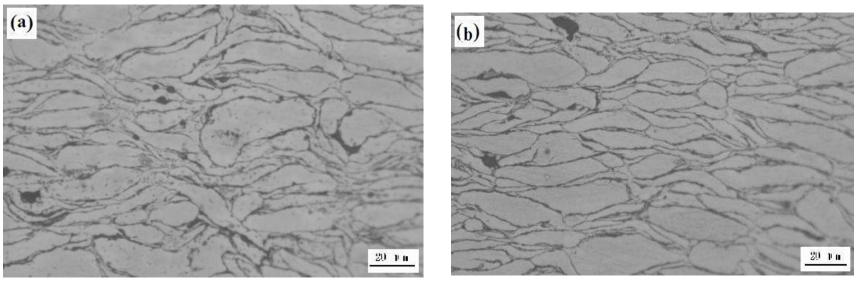


Fig. 5 The microstructures of the composites with different graphene content and ball-milling time (a) 1.5 wt.% for 72h, (b) 2.5 wt.% for 96h.

In order to confirm the presence of graphene nano-sheets on the magnesium grains boundary of the sintered composite, the composite microstructure of 1.5 wt.% graphene content under ball milling time of 72h is analyzed by SEM, shown in Fig.6. It is found that there is a continuous network structure at the grain boundaries of the magnesium in Fig. 6(a). In the high magnification (Fig. 6(b)) there are a lot of pieces in Mg mtrix. This is attributed to the disformation of the graphene during polishing. EDS and it's mapping analysis are also preformed for the sintered composite, as shown in Fig. 7. The EDS analysis corresponding to selected area confirmed the presence of carbon material, graphene nano-sheets (Fig.7 (a) and (b)). The Fig. 7 (c) and (d) show the EDS mapping where graphene nano-sheets are homogeneously embedded in the Mg matrix.

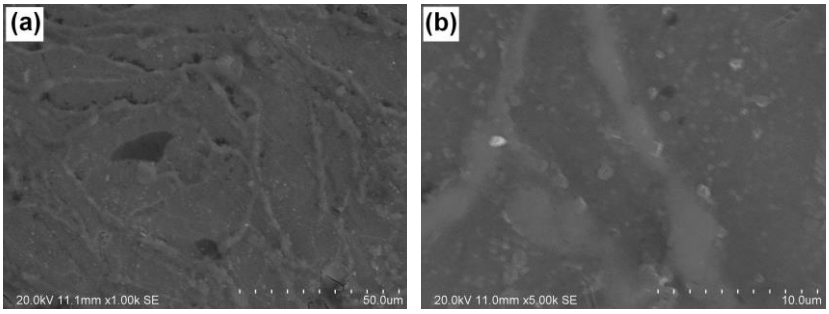


Fig.6 The SEM images of composite with 1.5 wt.% graphene nano-sheets, (a) low-time, (b) high-time.

In order to eliminate the porosity in the composites, improve the density of the composites, and refine the grain size of the composites, the hot rolling and heat treatment were proformed. Optical micrographs of Mg-Gr composite with graphene content of 1.5 wt.% in hot rolling and heat treatment conditions were presented in Fig. 8.

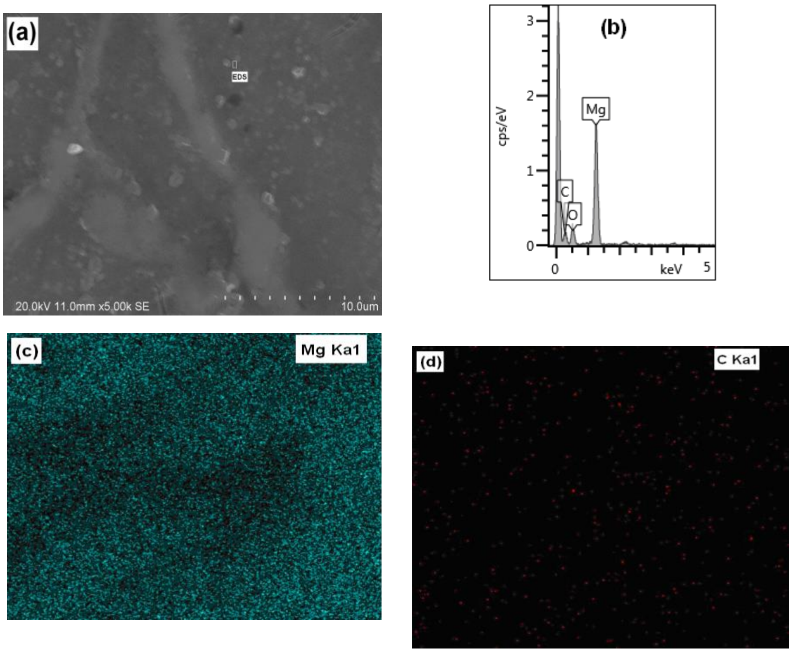


Fig. 7 (a) SEM image of composite surface with 1.5 wt.% graphene nano-sheets; (b) the EDS of the selected area in (a); (c-d) SEM mapping of composite: (c) magnesium; (d) graphene nano-sheets.

It is found that the grains of as-rolled composite are elongated along the rolling direction. Graphene nano-sheets are still distributed mainly along the grain boundaries. Compared with Fig. 3 (c), it’s important to note that coordinated deformation of multilayer graphene nano-sheets occurs with the deformation of the surface grains, which may cause a significant reduction in the number of layers of graphene nano-sheets. It can be explained that the refinement of grain on the surface greatly increases the number of grain boundaries which can cause a reduction of thickness of the graphene nano-sheets. The recovery and recrystallization of the microstructure appear at the aging temperature of 350 ℃. As the aging time increases, the microstructur of the composite tends to homogenization. This is expected to improve the mechanical properties of the composite. The investigation in this field will be implemented in the future.

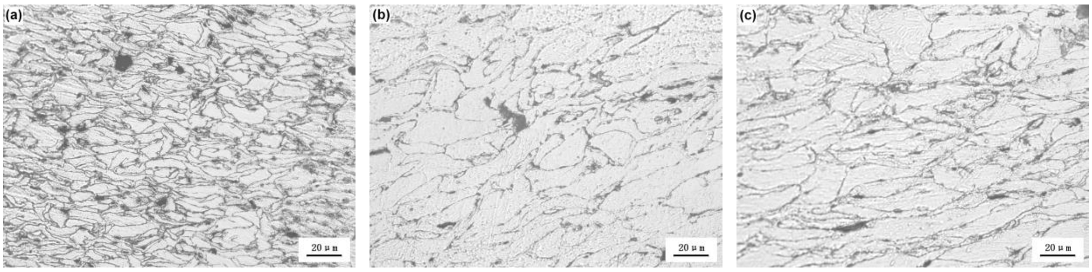


Fig.8 The microstructures of as-rolled composite with 1.5 wt.% graphene content under different aging time, (a) 1h, (b) 2h and (c) 3h.

4. Conclusions

In this paper, the Mg-Gr composites were fabricated by ball-milling mixing of pure magnesium powder and graphene nano-sheets, followed by hot-pressing, sintering, and finally by rolling. The microstructures of as-sintered and as-rolled composites were analzsed.

Experimental results revealed that the graphene nano-sheets are gradually dispersed into the magnesium matrix with increasing the ball-milling time and a uniform dispersion is achieved for the graphene content of 0.5 wt.%, 1.5 wt.% and 2.5 wt.% corresponding to 6 h, 72h and 96h, respectively. And no obvious agglomeration of graphene is observed in as-sintered and as-rolled composites for the contents of graphene nano-sheets up to 2.5 wt.% in applied process parameters. The coordinated deformation of multilayer graphene nano-sheets occurs with the deformation of the surface grains during rolling, which may cause a significant reduction in the number of layers of graphene nano-sheets.

Acknowledgements

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