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The Effect of Graphene Nanoplatelets Content on the Hardness of Mg6%Zn0.2%Mn Composites

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ABSTRACT

The effect of graphene nanoplatelets (GNPs) content on the hardness of magnesium-based composites was studied. A magnesium-based composite, Mg6%Zn0.2%Mn with graphene nanoplatelets (GNPs), was fabricated via powder metallurgy process at room temperature and compressive pressures of 50kN for 20 minutes, which was then sintered at 500°C for 2 hours. It produced significant grain refinement microstructure. The change in microstructure was examined by 3D microscope analysis, and the hardness value was evaluated using the Vickers microhardness apparatus. This study demonstrated the importance of GNPs reinforcement with zinc and manganese for microhardness analysis in the sintered Mg-based GNPs composites. It also portrayed their influence on grain refinement of the microstructure. The hardness results agreed with the microstructure results, proving that the presence of GNPs increases the hardness of the Mg-based composites.

Keywords: Graphene nanoplatelets, magnesium-based composites, microhardness test, powder metallurgy

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INTRODUCTION

Magnesium (Mg) is one of the most abundant metals present in the Earth's crust. Mg is the lightest of all the engineering metals, having a density of 1.74 g/cm^3. It is 35% lighter than aluminium (2.7 g/cm^3), 60% lighter than titanium and over four times lighter than steel (7.86 g/cm^3) (Mordike & Ebert, 2001). Mg has become desirable engineering material in every specific application, especially in automotive industries, with its low density, specific strength, stiffness, and excellent damping capacity. Mg has been used widely in industrial applications due to its lightweight properties. This lightweight property of Mg in industrial applications, especially the automotive perspective, can increase the power-to-weight ratio, reducing fuel consumption and increasing fuel efficiency. Besides that, Mg is used for medical applications that are less dense for body implants than titanium. Despite having some exclusive mechanical properties, Mg has a critical limitation on its resistance towards corrosion. Mg is identified as one of the metals that is reactive to corrosion. The corrosion of Mg can occur either by generalised corrosion, localised corrosion, galvanic corrosion, or environmental cracking (Prasad et al., 2022). Additionally, Mg is chemically unstable and extremely susceptible to corrosion in a marine environment. It is known that the corrosion is most likely due to impurities in the metal rather than having an inherent characteristic.

Besides using Mg-based alloys as an engineering material, Mg-based composites are one of the interests of researchers for automotive applications up until this date. This development is made to enhance the mechanical properties of Mg apart from utilising alloying and heat treatment processes. One of the latest developments of Mg in engineering applications is fabricating magnesium reinforced with graphene nanoplatelets. Graphene nanoplatelets, also known as GNPs, are a form of graphene made in the large-scale production of the graphene layer. Meanwhile, single graphene is a monolayer of graphite that has a 2-dimensional (2D) geometry structure with a thickness of one atom (0.34 nm) (Cataldi et al., 2018). Graphene possesses a remarkably high elastic modulus of 1 TPa and yield strength (YS) of 130 GPa, which has been considered a promising candidate for enhancing composite materials (Meng et al., 2018). A research study by Rashad et al. (2014) showed that magnesium-reinforced graphene nanoplatelets composite has superior properties to magnesium alloys and other magnesium-based composites. They reported that adding graphene nanoplatelets into magnesium composite helps maintain the lightweight property as the density of magnesium is not influenced. Therefore, the Mg-reinforced GNPs composite gives an identical mass value to Mg.

Another study conducted by Arab and Marashi (2019) stated that GNPs could help to increase the hardness of Mg-based composite. It can be achieved by applying friction stir processing that can increase the hardness up to 14% and further improve the hardness by 41% via adding GNPs. GNPs help with grain refinement, dynamic recrystallisation and pinning effect of AZ31 Mg GNPs composite. Besides that, other mechanical properties such as universal tensile strength, elongation, Vickers hardness, and porosity have enhanced Mg-reinforced GNPs composites fabricated using the thixomoulding process. Chen et al. (2019) reported that GNPs affect mechanical properties significantly, enhancing AZ91D-GNPs composites compared with AZ91D Mg alloy. The thixomoulding process is well known in common industry manufacturing, thus promising the production of Mg-based composites. It is due to the shortened process time on production that enables large-scale production via this method.

It is known that Mg in its pure form needs to be improved for better performance in various applications. The hardness of Mg must be improvised by selecting the fabrication and choosing the best ways of treatment, such as alloying, heat treatment or fabrication of Mg-based composites. Rotary parts, especially automotive, railway and aerospace parts, need materials with high hardness to withstand plastic deformation over time. Therefore, Mg-reinforced GNPs composites were fabricated using the powder metallurgy method in this study. The powder metallurgy method comprises three primary operations: powder mixing, powder compacting, and sintering. The powder metallurgy method offers a homogeneous and uniform distribution of reinforcement particles in the matrix for composite synthesis (Rashad et al., 2015). Powder metallurgy can also help to control the metal porosity, perform well under stress and increase mechanical properties such as hardness and wear resistance (Boopathy et al., 2011). In another research by Rodzi and Hussain (2018), the powder metallurgy method on Mg-based composites can improve mechanical properties. These results proved that the powder metallurgy technique with ball mill treatment might help increase strength due to the dispersion of the elements of Mg-based composites more evenly. In this research, the presence and increase in the weight percentage of GNPs within Mg-based composites will help refine the Mg matrix's grain boundary and increase the hardness. The increase in hardness is important in Mg-based composites as it enables them to resist deformation, bending, scratching, abrasion or cutting on specific moving parts such as gears and motors.

MATERIALS AND METHODS

Materials

In this research, commercially available Mg powder (>99% purity), Mn powder, Zn powder (−325 mesh, ≥99% trace metals basis) and GNPs powder (5 μm particle size with a surface area of 120-150 m^2/g) were used as starting materials. The Merck Company supplied all these powders. For the fabrication of MgMnZn mixture powder, 93.8wt.% of magnesium powders, 0.2wt.% of manganese and 6wt.% of zinc powders were stirred first, while graphene nanoplatelets were sonicated before being stirred with mixed MgMnZn-based powder.

Methods

Powder Metallurgy. To fabricate a pallet sample of Mg0.2Mn6.0Zn-1% GNPs composite, 0.03 g of GNPs powder was mixed with 40 ml of ethanol in a beaker. The mixture was then sonicated using a bath sonicator for about 1 hour. 2.784 g of Mg powder, 0.18 g of

Zn powder and 0.006 g of Mn powder were added to 40 ml of ethanol in a beaker, and the mixture was stirred on a magnetic stirrer for 2 hours. GNPs and Mg mixture solutions were mixed and stirred for another 1 hour. The mixed and stirred solution was then filtered using filter paper. The filtered mixture was left to dry in an oven at a fixed temperature of 50°C until it was completely dry. 1 g of dried powder mixture was taken and was then compressed by using a hydraulic compressor with a pressure of 50kN for 20 minutes to produce a cylindrical shape from pallet. Then, the obtained cylindrical pallet was sintered using the tube furnace under an inert argon gas environment and was heated at a temperature of 500°C with a heating rate of 10°C/min for 2 hours to enhance the bonding between Mg mixtures and GNPs. As a precautionary step, the sintered pallet would be taken out after the furnace was cooled down completely. This sample fabrication method was repeated similarly for Mg0.2Mn6.0Zn-0.5% GNPs, Mg6%Zn0.2%Mn and high purity (HP) Mg, respectively.

Microstructure Observation. The microstructural observation was conducted to study the characteristic of the grain boundary, interface integrity between matrix and reinforcement, the presence of porosity and the grain size of the composite samples. This characterisation process was conducted under a 3D optical microscope.

After the composite samples were fabricated, all the composites were ground with 1000 to 2000 grit of silicon carbide (SiC) abrasive paper and polished with alumina suspension until mirror-like surfaces were obtained. Then, the polished composites were washed with distilled water and were allowed to dry using high-pressure air. After that, the samples were etched using a 3% nital (nitric acid mixed with ethanol) solution. The composite samples were dipped into the etching solution for only 2 seconds to prevent over-etching on the surface of the samples.

All the composite samples were observed using a 3D optical microscope. A 3D optical microscope was used as it gave higher resolution when the samples were zoomed at 1000x magnification using high brightness light emitting diode (HB-LED) support. Besides that, the image produced would have a significantly high dynamic range (HDR). The observed images and analysis of the microstructure of the composites were obtained and recorded.

Hardness Test. The hardness test is a measurement of the resistance of a material against plastic deformation. The hardness of a metal is measured by forcing an indenter onto the composite surface. In the process of testing hardness, a known load is applied to indent slowly at 90° onto the tested surface of a sample. After the indentation is done, the indenter is withdrawn from the surface. The hardness measurement is then calculated based on the cross-sectional area and depth of indentation, depending on the type of hardness machine used.

In this study, the hardness test of the composite samples was done using the Vickers microhardness test. The fabricated samples were indented with a load of 5 kgf for 10 seconds. The diamond shape indentation on the surface was then measured and recorded. For the Vickers hardness test, the indenter has a pyramidal with a square base shape and a semi-apex angle of 68◦. The corresponding hardness number HV is a calculated function of the contact area, d^2. The test was repeated, with three readings recorded for the samples. Then, the average of the readings was calculated as the hardness of the samples. The indention results were then calculated based on the following equation:

$$Vickers\ Hardness(HV) = \frac{Applied\ Load}{Surface\ Area\ of\ Depression}$$

$$= \frac{2Psin\left(\frac{136°}{2}\right)}{d^2}$$

$$= 1.854\ \frac{P}{d^2}$$

Where,

$P =$ Applied Load (kgf)

$d = \frac{d_1 + d_2}{2}$

RESULTS AND DISCUSSION

Microstructure Observations

Figure 1 shows the microstructure of HP Mg, Mg0.2%Mn6.0%Zn, Mg0.2%Mn6.0%Zn-0.5% GNPs and Mg0.2Mn6.0Zn-1% GNPs sample that was obtained from 3D optical microscope after grinding, polishing, and etching, respectively.

The samples for all the grains of samples were equiaxed and irregular in shape based on Figure 1. The 3D optical microscope images showed that HP Mg in Figure 1a has the largest grain size, followed by Mg0.2%Mn6.0%Zn in Figure 1b, Mg0.2%Mn6.0%Zn-0.5% GNPs in Figure 1c, and Mg0.2%Mn6.0%Zn-1% GNPs in Figure 1d. The addition of Zn in the composite caused the coarsening of the grain size (Budinski & Budinski, 1999). Besides Zn, the addition of Mn helps in reducing grain size. After adding 0.2 wt% of Mn, the grain size was slightly reduced by about 25% to 35% with the sample without adding Mn. Mn's effect on grain refinement is gradually weakened when the Mn content exceeds 1.3 wt% (Zhao et al., 2019). GNPs in the composite successfully suppressed the growth of the grain size. Grain boundaries contribute primarily to the diffusion channels of Mg0.2%Mn6.0%Zn

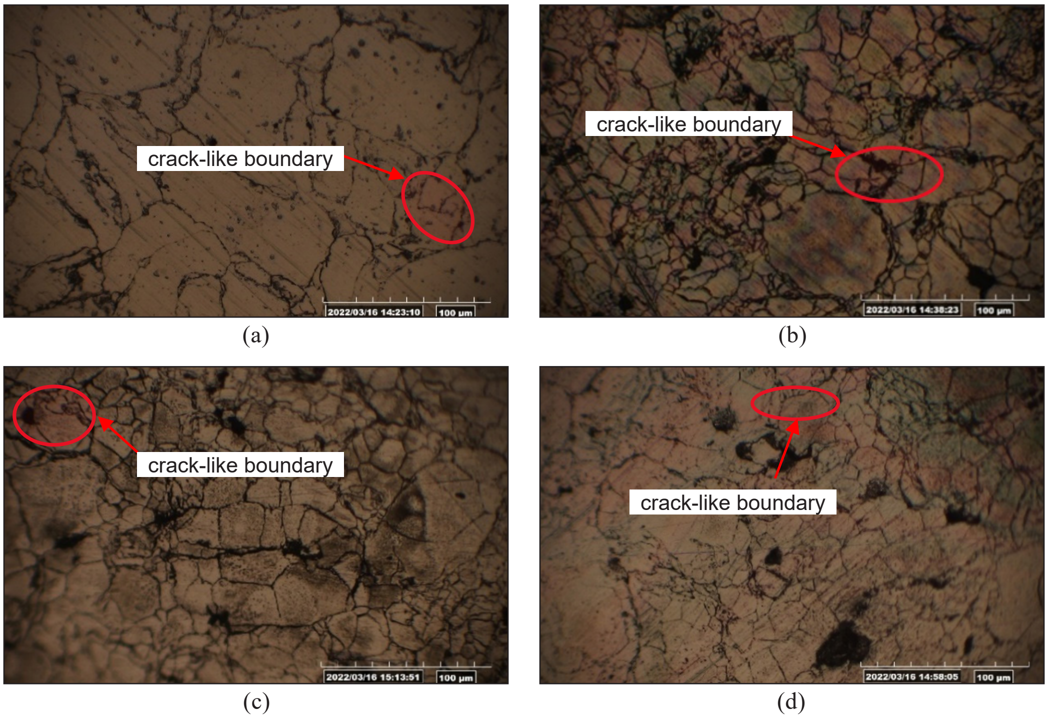

Figure 1. Microstructure of: (a) HP Mg; (b) Mg6%Zn0.2%Mn; (c) Mg6%Zn0.2%Mn-0.5% GNPs composite; (d) Mg-6%Zn0.2%Mn-1% GNPs composite was observed under 3D optical microscope with 1000× magnification

alloy matrix and GNPs in the nucleation sites formation, thus reducing the grain size. The heterogeneous nucleation mode promoted the formation of a tight mechanical interfacial bonding between the GNPs and Mg0.2%Mn6.0%Zn matrix. With the increase in GNPs content, more heterogeneous nucleation substrates were provided, leading to more crystal nuclei of Mg on the GNPs. Hence, the increase in nucleation rate can effectively refine the Mg crystal grains at a given Mg0.2%Mn6.0%Zn matrix (Sun et al., 2020). It implies that GNPs can act as nucleation sites and grain refiners in magnesium-based composites. Besides, it shows further results in more refined grains than Mg0.2%Mn6.0%Zn (Rashad et al., 2016). It was observed that the Mg0.2%Mn6.0%Zn-0.5% GNPs and Mg0.2%Mn6.0%Zn-1% GNPs produced almost equal size of the grains with the help of GNPs that reinforced the Mg alloy matrix.

Many crack-like boundaries were observed in all samples, as highlighted in Figure 1, which differed from the grain boundaries. These crack-like boundaries were formed as transgranular crack boundaries. A more severe transgranular crack happens with the presence of GNPs, especially where the GNPs concentration in the area is high. Due to the residual thermal stress and pressure during compaction, the crack will be pinned down in the grain boundary and defected into the grain. Then, the transgranular crack will occur. It needs more additional external stress to promote crack propagation. In general, the change in crack fracture mode is also related to the strength of the interface because cracks tend to propagate along with the weaker interfaces (Fan et al., 2019).

Vickers Microhardness Test

The samples were tested using 5kgf of load for 10 seconds in this test. The Vickers hardness for HP Mg, Mg0.2%Mn6.0%Zn, Mg0.2%Mn6.0%Zn-0.5% GNPs and Mg0.2%Mn6.0%Zn-1% GNPs composite were recorded, while the average of Vickers Hardness Number (VHN) and standard deviation were calculated and shown in Table 1.

Table 1
Vickers hardness test

Type of sample	Sample	VHN 1	VHN 2	VHN 3	Average VHN	Standard Deviation
HP Mg	1	34.2	34.4	34.2	34.27	0.094
	2	34.6	34.6	34.3	34.50	0.141
Mg0.2%Mn6.0%Zn	1	44.3	44.5	44.6	44.47	0.125
	2	44.5	44.2	44.3	44.33	0.125
Mg0.2%Mn6.0%Zn-0.5%GNPs	1	45.5	45.4	45.7	45.53	0.126
	2	45.6	45.5	45.3	45.47	0.124
Mg0.2%Mn6.0%Zn-1%GNPs	1	48.6	48.4	48.6	48.53	0.094
	2	48.2	48.2	48.4	48.27	0.095

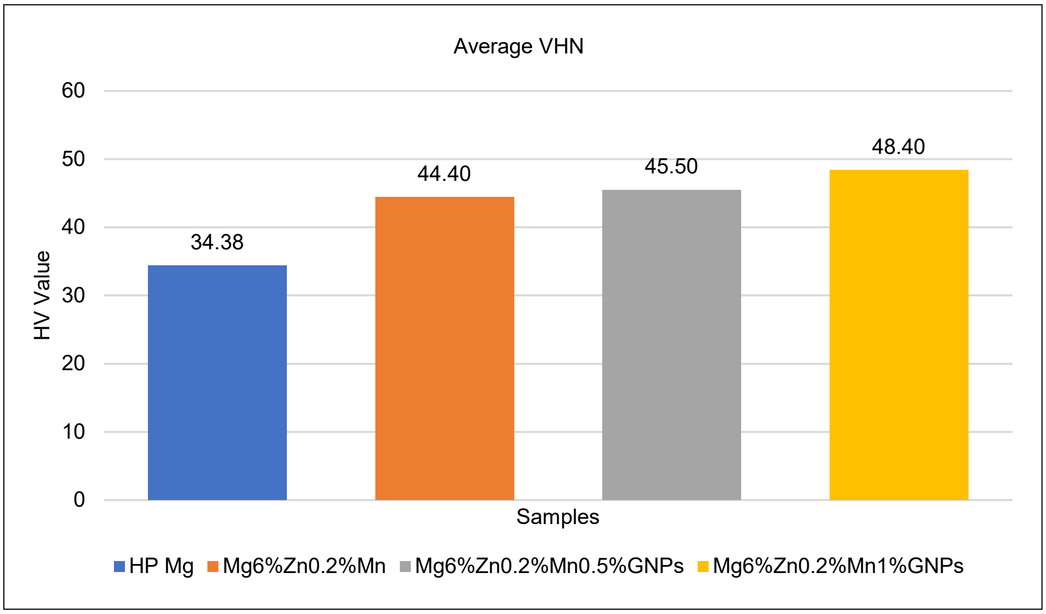

Figure 2. Bar chart of average Vickers hardness of the samples

Three measurements and readings were applied during the test and the average values of each composite were considered. From the result obtained, Mg0.2%Mn6.0%Zn-1% GNPs showed the highest value of VHN, giving it the highest hardness sample among the other samples. For Mg0.2%Mn6.0%Zn-0.5%, GNPs offered higher hardness than Mg0.2%Mn6.0%Zn, and the material that had the least hardness was HP Mg. In comparison, Mg0.2%Mn6.0%Zn-1% GNPs give an increase of hardness by 33.87%, followed by Mg0.2%Mn6.0%Zn-0.5% GNPs hardness with an increase of 27.84% and Mg0.2%Mn6.0%Zn with an increase of 25.55%.

Other than that, the Mg0.2%Mn6.0%Zn-1% GNPs had shown higher hardness than Mg0.2%Mn6.0%Zn without GNPs by 9.52%. From the bar chart shown in Figure 2, the alloying of Mg with Mn and Zn can give better hardness than the HP Mg by 24.54%. These results were supported by previous research with other micro constituents, which mentioned that adding graphene nanoplatelets into the magnesium matrix could increase its hardness. It is confirmed because the GNPs restrict the dislocation movement of the Mg and the constituents present in Zn and Mn as alloying elements. Zn and Mn improve the mechanical properties by reducing the grain size of Mg alloy and introducing dislocations in the microstructure (Shuai et al., 2018; Wang et al., 2019). Due to the hindrance in dislocation movement, the surface hardness increased at a high concentration of reinforcements. Rajaganapathy et al. (2020) also found that adding graphene into AA6082 aluminium-based composites could increase the graphene from 1% to 5%, gained from 86HV to 107HV with an increment of 24.08%. However, the hardness of the composites is improved by the existence of a comparatively more rigid reinforcement. Besides that, Liu et al. (2017) discussed that the mechanical properties of alloys and composites could change due to the high-temperature diffusion rate during the sintering process. Hence, the reinforcement particle of the composite in the matrix can make the distance between particles closer due to thermal diffusion on compacted powdered samples.

CONCLUSION

Overall, Mg0.2%Mn6.0%Zn-based reinforced GNPs composites with the powdered structure were fabricated via a feasible method and showed exceptionally enhanced hardness through powder metallurgy. GNPs were dispersed uniformly on the Mg0.2%Mn6.0%Zn matrix. The following mixing and sintering processes promoted the distribution of GNPs. GNPs reinforcements were well embedded into the Mg matrix and formed good bonding with the Mg0.2%Mn6.0%Zn matrix. The reduced grain size structure that was induced by the introduction of GNPs suppressed the grain localisation movement. It promoted an increase in grain boundary; thus, increasing the hardness of the composite up to 41% is beneficial compared with HP Mg. This research study highlighted the significance of the distribution design of nanoscale carbon-based reinforcement, such as GNPs reinforcements, in fabricating metal matrix composites in terms of hardness and enhancing other mechanical properties with suitable fabrication methods in the future.

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