Faculty Of Engineering

Investigation of Hardness and Corrosion Properties on Graphene Nanoplatelets Reinforced Magnesium Composite

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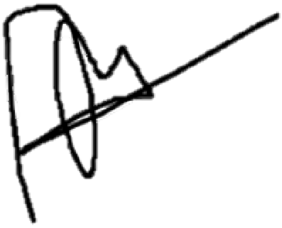
DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. Except where due acknowledgements have been made, the work is that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.



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ABSTRACT

Magnesium (Mg) has been used for many decades in various applications. This metal has attractive mechanical properties such as strength and hardness. Although Mg is lightweight and has high strength, one of the major limiting factors in using Mg includes its corrosion resistance. In the natural environment, the poor corrosion resistance of Mg and Mg alloys in saline and physiological environments remains a constant threat for Mg and Mg alloys as potential automotive parts, aerospace materials or biomedical implants. This research is done to study the hardness and corrosion properties of Mg and Mg-based composites. The hardness was determined using the Vickers microhardness test. Based on the results, Mg0.2%Mn%6%Zn-1% GNPs had the highest hardness at 48 HV, followed by Mg0.2%Mn%6%Zn-0.5% GNPs at 45 HV, Mg0.2%Mn%6%Zn at 44 HV, and HP Mg at 34 HV. Increasing GNP content with zinc and manganese reinforcement is important for improving hardness in sintered Mg-based GNPs composites. An immersion test on GNP-reinforced Mg composites showed that Mg0.2%Mn%6%Zn-1% GNPs had the highest corrosion resistance (PW=17.546mm/y), followed by Mg0.2%Mn%6%Zn-0.5% GNPs (PW=19.770mm/y), Mg0.2%Mn%6%Zn (PW=22.958mm/y), and HP Mg (PW=90.3146mm/y). GNPs also lowered the corrosion rate in saline solution. Corrosion morphology and type were determined by 3D optical microscope, SEM, and EDX. Overall, this study has managed to fabricate Mg-based composites using the powder metallurgy method. Adding GNP as reinforcement has increased hardness and corrosion properties significantly, thus proving the strengthening effect of corrosion resistance by GNPs in Mg-based composites.

Keywords: Magnesium-based composites; graphene nanoplatelets; powder metallurgy; microhardness test; corrosion immersion test

Penyiasatan Tentang Sifat Kekerasan Dan Pengaratan Bagi Komposit Magnesium Dengan Nanoplatelet Graphene

ABSTRAK

Magnesium (Mg) telah digunakan selama beberapa dekad dalam pelbagai aplikasi. Logam ini mempunyai sifat mekanikal yang menarik seperti kekuatan dan kekerasan. Walaupun Mg ringan dan mempunyai kekuatan tinggi, salah satu faktor pengehad utama dalam menggunakan Mg termasuk rintangan pengaratanya. Dalam persekitaran semula jadi, rintangan pengaratan yang lemah bagi aloi Mg dan Mg dalam persekitaran masin dan fisiologi kekal sebagai ancaman berterusan bagi aloi Mg dan Mg sebagai bahagian automotif yang berpotensi, bahan aeroangkasa atau implan bioperubatan. Penyelidikan ini dilakukan untuk mengkaji kekerasan dan sifat pengaratan komposit berasaskan Mg dan Mg. Kekerasan ditentukan menggunakan ujian microhardness Vickers. Berdasarkan kajian, Mg0.2%Mn%6%Zn-1% GNP mempunyai kekerasan tertinggi pada 48 HV, diikuti oleh Mg0.2%Mn%6%Zn-0.5% GNP pada 45 HV, Mg0.2%Mn %6%Zn pada 44 HV dan HP Mg pada 34 HV. Peningkatan % GNP dengan tetulang zink dan mangan adalah penting untuk meningkatkan kekerasan dalam komposit GNP berasaskan Mg tersinter. Ujian rendaman ke atas komposit Mg bertetulang GNP menunjukkan bahawa Mg0.2%Mn%6%Zn-1% GNP mempunyai rintangan kakisan tertinggi (PW=17.546mm/y), diikuti oleh Mg0.2%Mn%6%Zn-0.5% GNP (PW=19.770mm/y), Mg0.2%Mn%6%Zn (PW=22.958mm/y) dan HP Mg (PW=90.3146mm/y). GNP juga menurunkan kadar kakisan dalam larutan garam. Morfologi dan jenis pengaratan ditentukan oleh mikroskop optik 3D, SEM, dan EDX. Secara keseluruhannya, kajian ini telah berjaya menghasilkan komposit berasaskan Mg menggunakan kaedah metalurgi serbuk. GNP sebagai tetulang telah *meningkatkan kekerasan dan sifat pengaratan dengan ketara, sekali gus membuktikan kesan pengukuhan rintangan pengaratan oleh GNP dalam komposit berasaskan Mg.*

Kata kunci: *Komposit berasaskan magnesium; graphene nanoplatelet; metalurgi serbuk; ujian mikro kekerasan; ujian pengaratan rendaman*

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LIST OF ABBREVIATIONS

$AgNO_3$	Silver Nitrate
Al	Aluminium
BCC	Body Centred Cubic
CNT	Carbon Nanotubes
CO_2	Carbon Dioxide Gas
Cr_2O_3	Chromium (III) Oxide
Cu	Copper
EDX	Energy Dispersive X-ray Spectroscopy
FCC	Faced Centred Cubic
GNPs	Graphene Nanoplatelets
H	Hydrogen
H_2	Hydrogen Gas
HCP	Hexagonal Closed Packed
HP Mg	High Purity Magnesium
Mg	Magnesium
$Mg(OH)_2$	Magnesium Hydroxide
MgCl	Magnesium Chloride

MMC	Metal Matrix Composites
Mn	Manganese
NaCl	Sodium Chloride
Ni	Nickel
O	Oxygen
O_2	Oxygen Gas
RE	Rare Earths Metals
SEM	Scanning Electron Microscope
Ti	Titanium
VHN	Vickers Hardness Number
Zn	Zinc
Zr	Zirconium

CHAPTER 1

INTRODUCTION

1.1 Study Background

Magnesium (Mg) is widely used in industrial applications due to its lightweight properties. This lightweight property of Mg in industrial applications, mainly automotive, can increase the power-to-weight ratio, reducing fuel consumption and increasing fuel efficiency (Romanowski, 2019). Meanwhile, Mg is used for medical applications that are less dense for implants (Witte, 2010). Despite having some exclusive properties in terms of mechanical properties, Mg has a critical limitation on its corrosion resistance. Mg is one of the most reactive metals towards corrosion in most metals. The corrosion of Mg can be happened either by generalised corrosion, localised corrosion, galvanic corrosion, or environmental cracking (Atrens et al., 2011).

Mg-based composites are one of the interests of researchers for automotive applications other than Mg-based alloys. This development is made to enhance the mechanical properties and the resistance toward corrosion of Mg. One of the latest developments of Mg in engineering applications is fabricating magnesium reinforced with graphene nanoplatelets composite. Graphene nanoplatelets (GNPs) is a thin graphite sheets with a thickness of less than 100 nm, made from nanosized graphene particles. Graphene is a single freestanding monolayer of graphite that originates from carbon. It is the first 2D material ever manufactured by humankind, having a thickness of one atom (0.34 nm) and lateral size orders of magnitudes larger than graphite (Cataldi et al., 2018).

Recent research studies by Rashad, Tang, et al. (2015) and Rashad, Asif, et al. (2014) show that magnesium-reinforced graphene nanoplatelets composites have superior properties compared to magnesium alloys and other magnesium-based composites. Rashad et al., 2015 reported that the magnesium composite with the addition of graphene nanoplatelets helps maintain the lightweight property as the density of magnesium is not influenced. Therefore, Mg-reinforced GNPs composite gives identical mass value with Mg.

Another study by Arab and Marashi (2019) stated that GNPs could help increase the hardness by 14% by applying friction stir processing and by 41% by adding GNPs due to grain refinement, dynamic recrystallisation and pinning effect of GNPs. Besides that, other mechanical properties such as universal tensile strength, elongation, Vickers hardness and porosity have improved on Mg-reinforced GNPs composites using the thixomoulding process found by Chen et al. (2019). They also reported that the GNPs' mechanical properties significantly improved on AZ91D-GNPs composites compared with AZ91D Mg alloy. The thixomoulding process is well known for common industry manufacturing, promising the production of Mg-based composites. This is due to the shortened process time to show that this method can produce large-scale production in the future.

Under a corrosive environment, Mg reacts in an aqueous solution to form magnesium hydroxide ($Mg(OH)_2$) as a corrosion product at the end of the reaction. It protects Mg from further corrosion by forming a thin layer that is formed on the surface. After all, these $Mg(OH)_2$ films are only limited to alkaline solutions as a protective layer. They can break through immediately in non-alkaline, which are neutral, acidic, or saline solutions. These solutions can cause catastrophic corrosion to occur. In a saline environment, especially in sodium chloride solution, the $Mg(OH)_2$ layer is removed as the chloride ions convert $Mg(OH)_2$ to form magnesium chloride (MgCl) soluble salt (Pourbaix, 1974).

Many researchers investigated the corrosion behaviour of Mg and its alloys, including the heat treatment of Mg alloys. The most prevalent type of corrosion that happens in Mg is galvanic corrosion. Galvanic corrosion occurs when Mg is coupled with other more cathodic metals than magnesium. Alloying of Mg can also induce galvanic corrosion when alloyed with more anodic alloying elements such as aluminium and accelerates the corrosion rate faster when the iron is the impurity of magnesium alloys (Guangling Song, Hapugoda et al. 2004). Comprehensive and detailed research on the corrosion of Mg and its alloys demonstrates that high-purity magnesium has a lower corrosion rate than Mg alloys. Several methods, such as weight loss measurement, hydrogen evolution and electrochemical measurement, such as Tafel extrapolation, were used to determine the corrosion rate (Qiao, Hort, Zainal Abidin, et al., 2012; Shi, Liu, & Atrens, 2010).

The mechanical properties and corrosion resistance are much better in Mg-based composites than in non-reinforced Mg for future applications in automotive and biomedical (Rashad, Pan, Tang, et al., 2015). Some properties, such as strength and hardness, are better with 0.3% GNPs with the semi-powder metallurgy method. Further research was also done by Rashad, Pan, et al. (2017) to study the corrosion resistance of Mg-reinforced GNPs using the stir casting method. Although their results reveal that the presence of GNPs in different matrices decreases the corrosion resistance of composites, this finding might be improved by adjusting the parameters of the experimental methods, such as using the powder metallurgy technique and adding other metals in synthesising the composite.

1.2 Problem Statement

In the automotive, aerospace, and medical industry specifically, the challenge nowadays is to fabricate materials which have high hardness with better corrosion resistance. Magnesium and its alloys are the material that fulfil requirements which attract many engineers and technologists for applications in automotive and medical. Despite magnesium-based alloys having superior mechanical properties and hardness to pure magnesium, the corrosion resistance of magnesium alloys is worse than pure magnesium as the reactions with other alloying elements influence the corrosion properties. On the other hand, pure Mg gives better corrosion resistance compared with some Mg-based alloys with the limitation on the mechanical properties' superiority. Thus, several improvements have to be made for Mg-based alloys limitations by the researchers.

1.3 Objectives

The objectives of this research are:

1. To investigate the effect of different GNPs compositions towards the hardness properties of GNPs reinforced Mg composites.
2. To investigate the effect of different GNPs compositions towards the corrosion behaviour of GNPs reinforced Mg composites.
3. To study the microstructure and composition of fabricated GNPs reinforced Mg composites.

1.4 Scope of Project

In this research project, the composition of alloying elements in the Mg sample is the primary concern. This investigation is to observe how the difference in the design of magnesium composites can affect the mechanical properties and corrosion behaviour. This research focused on Mg composites with 6% of zinc and 0.2% of manganese compositions of the metal matrix. Meanwhile, the percentage of the reinforcement used GNPs ranged from 0%, 0.5% and 1%. Besides that, the fabrication method used on GNPs reinforced Mg composites that utilise the powder metallurgy method. The materials characterisation of the area using the 3D optical microscope, scanning electron microscope and energy dispersive X-ray spectroscopy. Furthermore, the hardness testing uses the Vickers microhardness test, and the corrosion test is conducted by the immersion test. The corrosion rate was determined using hydrogen evolution and weight loss measurement.

1.5 Chapter Summary

This thesis outline explains the summary of each chapter from Chapter 1 to Chapter 5.

Firstly, Chapter 1 is an introduction which describes the background of the research topic, problem statement, objectives, and the scope of the research project.

Chapter 2 describes the literature review, which focuses more on the importance of the proposed research topic with previous relevant research that the researchers had done. This chapter first describes magnesium and its alloys. Further description is focused more on magnesium and its alloys in automotive applications and alloying of magnesium. The heat treatment is described further to know the limitation of the heat treatment toward magnesium-based alloys. Meanwhile, magnesium-based composites mainly focus on the type of magnesium-based composites with the explanation of mechanical properties and corrosion resistance. Other than that, the corrosion behaviour of magnesium is discussed further. Lastly, this chapter also describes magnesium's powder metallurgy in fabrication.

Next, Chapter 3 is the methodology part of the research project. This chapter describes the research's materials, equipment, and step-by-step procedures. This chapter also highlights the mechanical and corrosion test of the composites conducted on the project.

Chapter 4 is the part where all the results and observations of the test conducted on the samples were obtained. The results and observations include the data in figures, tables, graphs and more. The discussion of the results obtained is also portrayed in this chapter.

Lastly, the last chapter is Chapter 5. This chapter concludes with the hardness and corrosion properties of graphene nanoplatelets-based reinforced magnesium composites. Besides that, the recommendation for the research project is also included in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Magnesium and its Alloys

Magnesium (Mg) is one of the most abundant metals present in the Earth's crust. It can be found in seawater at approximately 2.8% and other ore forms such as dolomite ($CaMg(CO_3)_2$), magnesite ($MgCO_3$) and carnallite ($KMgCl_3.6H_2O$). In the periodic table, Mg is in group 2, period 3 element known as alkaline earth metals. Mg is the lightest of all the engineering metals, having a 1.74 g/cm3 density. 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 is also categorised as light metal, apart from aluminium and titanium. Mg has proven to become desirable engineering material in many applications, especially in the automotive, aerospace, and biomedical industries, with its low density, adequate specific strength, stiffness, and excellent damping capacity.

Mg is an excellent engineering metal widely used due to its significant properties and is readily available commercially. Mg is readily available for industries in various primary foundry forms such as bar, billet, foiled, rolled, and more, as shown in Figure 2.1. However, the applications of pure Mg in these industries still need to be improved due to poor corrosion resistance, relatively low strength, and low ductility, as mentioned by (Blawert, Hort, & Kainer, 2004).

Figure 2.1: Magnesium metals in various forms available commercially. (Courtesy from Press Metal Berhad)

In most applications, Mg is stronger per unit than aluminium (Al), titanium (Ti) or iron (Fe). Mechanical properties such as strength and stiffness are important for automotive applications. Some properties that are important for Mg compared with other metals for scientific and engineering research and applications are shown in Table 2.1.

Table 2.1: Comparison between properties of Mg, Ti, Al, and Fe (Kulekci, 2008)

Property	Magnesium	Titanium	Aluminium	Iron
Crystal Structure	HCP	HCP	FCC	BCC
Density at 20°C (g/cm^3)	1.74	4.54	2.70	7.86
Coefficient of thermal expansion 20–100°C (×10^6/C)	25.2	8.6	23.6	11.7
Young's modulus of elasticity (MPa)	44.126	113.8	68.947	206.842
Tensile strength (MPa)	240 (for AZ91D)	880 (for Ti-6Al-4V)	320 (for A380)	350
Melting point (°C)	650	1668	660	1536

2.1.1 Magnesium and its Alloys in Industry

Nowadays, many industries, such as the automotive industry, lead engineers and technologists from various car manufacturers. They realised the demand for cars with superior properties, strong, stiff, and high corrosion resistance. Mg has been widely used as a suitable metal for the automotive industry because of its lightweight property. Besides, Mg and its alloys are preferred and commonly used in the automotive industry due to their high specific strength and excellent cast ability (Rashad et al., 2017). The weight reduction in automobiles saves energy required for the car to accelerate and thus reduces greenhouse gas and carbon dioxide CO_2 emissions that can pollute the environment. Reducing the automotive weights will result in a significant percentage of improvement in fuel economy and efficiency (Atrens et al., 2015). For high-performance cars, such as racing cars, the body framework must be light to accelerate faster within an abbreviated period (Easton et al., 2008). Light weighting provides up to a 7% improvement in fuel economy for each 10%