Identification of Ageing Behavior of Mg-Al-Zn and AZ91 Reinforced Carbon Nanotube at Evaluated Temperature

by

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LIST OF ABBREVIATIONS

Al	Aluminum
AZ91	Composition of Element (Mg 90%, Al 9%, Zn 1%)
CNT	Carbon Nanotube
DSC	Differential Scanning Calorimeter
EDS	Energy Dispersive Spectroscopy
FESEM	Field Emission Scanning Electron Microscope
JMA	Johnson Mehl-Avrami
Mg	Magnesium
MPa	Megapascal
OM	Optical Microscope
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction
Zn	Zinc

LIST OF SYMBOLS/NOMENCLATURE

nm	Nanometers
α	Acceleration (ms^{-2})
Ω	Resistance (ohm)
T1	Sintering
T6	Ageing Treatment

Pengenalpastian kelakuan Penuaan Mg-Al-Zn dan Tiub Nano Karbon Bertetulang AZ91 pada Suhu Ternaik

ABSTRAK

Aloi magnesium ialah bahan komposit berpotensi yang boleh digunakan untuk aplikasi kejuruteraan struktur ringan kerana kekuatan khususnya dalam sifat mekanikal dan fizikal. Walau bagaimanapun, bahan komposit ini kehilangan sifat kekuatan dan rintangan rayapan apabila terdedah pada suhu tertentu. Dilaporkan bahawa dengan menambah aloi AZ91 dan AZ91 dengan tiub nano karbon bertetulang (CNT) akan meningkatkan sifat mekanikal dan fizikalnya. Namun begitu, kerja mengenai kesan rawatan haba dan ramalan sifat kelkuan penuaan AZ91 dan AZ91 diperkukuh dengan CNT masih kurang dan berpotensi untuk diterokai. Mg-Al-Zn (AZ91) dan AZ91 diperkukuh dengan karbon tiun nano (CNT) telah difabrikasi menggunakan kaedah metalurgi serbuk. Sampel dipelbagaikan dengan peratus berat CNT dengan 0, 0.3, 0.6 dan 0.9 wt.%. Sampel dicampur melalui pengisar planet selama 20 jam dan dipadatkan pada 400 MPa, bentuk palet dengan diameter 12 mm. Semua sampel menjalani pensinteran pada 450 ˚C kemudian menjalani rawatan haba T4 (Rawatan larutan) pada 415 °C dan T6 (Penuaan) pada 175 °C, 210 °C dan 300 °C. Struktur mikro AZ91 dan AZ91+ CNT telah diperhatikan dengan menggunakan mikroskop optik (OM) dan Mikroskop Elektron Pengimbasan (SEM). Kesemua sampel AZ91 dan AZ9 +CNT telah menjalani analisis fasa dengan menggunakan pembelau sinaran-X (XRD). Sementara itu, sifat fizik dicirikan menggunakan alat pcynometer untuk menentukan ketumpatan sampel. Kajian sifat mekanikal dilakukan dengan menggunakan ujian kekerasan Rockwell dan ujian mampatan melalui Mesin Pengujian Universal (UTM). Akhir sekali, ramalan tenaga pengaktifan dan kekerasan komposit AZ91 dan AZ9+CNT dinilai dengan mengubah suai dan menambah baik model separuh empirik John Mehl-Avrami. Daripada keputusan, didapati bahawa CNT telah tertabur secara homogen ke dalam matriks AZ91 kerana kejayaan pengaloian mekanikal menggunakan pengisar planet. Ketumpatannya ialah 1.98 g/m^3 untuk AZ91 dan 1.87 g/m^3 untuk AZ91+ 0.3% CNT. Manakala, kekuatan mampatan yang diperolehi ialah 26.8 MPa untuk AZ91 dan 47.1 MPa untuk AZ91+CNT. Penambahan CNT memberikan kesan pelembutan untuk komposit AZ91 + 0.3% CNT dan kesan positif untuk komposit AZ91 + 0.6% CNT dan AZ91 + 0.9% CNT. Komposit AZ91 + 0.6% CNT dan AZ91 + 0.9% CNT menunjukkan penuaan dipercepatkan dan mencapai kekerasan usia puncak pada masa penuaan 4 jam. Kesan positif pengerasan dijangka disebabkan oleh pemendakan Mg17Al12. Siasatan menunjukkan signifikan masa dan suhu adalah peranan utama dalam proses pengerasan kerpasan nanokomposit. Didapati bahawa kekerasan berkurangan apabila suhu meningkat dan kekerasan meningkat seiring dengan masa penuaan. Keputusan ramalan yang menggalakkan diperhatikan apabila dibandingkan dengan data eksperimen pada masa dan suhu tertentu. Kajian kinetik menunjukkan tenaga pengaktifan 21kJ/mol nanokomposit AZ91. Tujuan kajian ini adalah untuk menentukan parameter rawatan haba optimum untuk menghasilkan komposit AZ91 berkekuatan tinggi, yang merupakan komponen bahan kritikal untuk blok enjin yang digunakan dalam sektor automobil.

Identification of Ageing Behavior of Mg-Al-Zn (AZ91) and AZ91 Reinforced with Carbon Nanotube (CNT) at Elevated Temperatures

ABSTRACT

Magnesium alloys are potential composite materials that can be applied for lightweight structural engineering applications due to its specific strength in mechanical and physical properties. However, these composite materials lose its strength and creep resistance properties when exposing at certain temperature. It is reported that by adding minor alloy AZ91 and composite AZ91 with reinforced carbon nanotubes (CNT) will improve its mechanical and physical properties. Nevertheless, the work on the effects of heat treatment and prediction of ageing behaviour properties and activation energy of AZ91 and composite AZ91 reinforced with CNT still less and potential to be explored. Mg-Al-Zn (AZ91) and composite AZ91 reinforced with carbon nanotube (CNT) were fabricated using powder metallurgy method. The composite samples were varied with the weight percent of CNT with 0, 0.3, 0.6 and 0.9 wt.%. The samples were mixed via planetary mill for 20 hours and compacted at 400 MPa, pallet shape with diameter 12 mm. All samples undergo sintering at 450 ˚C then undergo T4 heat treatment (solution treatment) at 415 °C and T6 (artificial ageing) at 175 °C, 210 °C and 300 °C. Microstructure of AZ91 and AZ91+ CNT composites were observed by using an optical microscope (OM) and Scanning Electron Microscope (SEM). All samples AZ91 and AZ9+CNT composites were undergone phase analysis by using X-Ray Diffraction (XRD). Meanwhile physical properties were characterized using pycnometer instrument to determine the density of the samples. Mechanical properties studies were performing by using Rockwell hardness test and compression test via Universal Testing Machine (UTM). Finally, the activation energy and hardness prediction of AZ91 and AZ9+CNT composites were evaluated by modifying and improving John Mehl-Avrami Semi-Empirical Model. From the analyses, it was found that CNT were homogeneously distributed into the matrix of AZ91 composites due to successfully mechanical alloying using planetary mill. Their densities were 1.98 g/m^3 for AZ91 and 1.87 g/m^3 for AZ91+ 0.3% CNT. Meanwhile, the compressive strength obtained were 26.8 MPa for AZ91 and 47.1 MPa for AZ91+CNT. The addition of CNT gives softening effect for composite AZ91 + 0.3% CNT and positive effect for composites AZ91 + 0.6% CNT and AZ91 + 0.9% CNT. Composites AZ91 + 0.6% CNT and AZ91 + 0.9% CNT show accelerated ageing and achieve peak aged hardness at 4 hour of ageing time. The positive effect of hardening is expected due to the precipitation of $Mg_{17}Al_{12}$. The investigation shows the significant of time and temperature are the main role in the precipitation hardening process of the nanocomposite. It is found that the hardness decreases when the temperature is increases and the hardness is increases together with ageing time. Encouraging prediction results are observed when compared with experimental data at a specific time and temperature. Kinetics study show an activation energy of 21kJ/mol of the AZ91 nanocomposite. The purpose of this study is to determine the optimal heat treatment parameter for producing a high-strength AZ91 composite, which is a critical material component for engine blocks used in the automobile sector.

CHAPTER 1 : INTRODUCTION

1.1 Background

Magnesium alloys are utilized in engineering application for lightweight structural and functional parts in aircrafts, automotive applications, electronics, and other industrial fields due to the corresponding high specific strength, light specific weight, high damping capacity, recyclability, and electromagnetic shocks shielding ability (Chen et al., 2017). In contrast, magnesium and its alloy were essentially deforming via its basal slip and twinning at room temperature, which limits their formability. Consequently, thermomechanical commonly rejected at high temperature (Li et al., 2012). It is generally considered that additional slip systems (prismatic and pyramidal) contribute significantly to deformation when the temperature is higher than 300°C, namely, when the associated critical resolved shear stresses properties are comparable (Li et al., 2012).

According to Yulin Zhu et al. 2020 in the literature, pre-plastic deformation may be used to magnesium alloy in order to boost the ageing reaction and, as a result, improve its mechanical characteristics. According to Lou et. al. (2018), the combination application of pre-deformation and ageing treatment significantly increased the strength of AZ80 Mg alloy sheet, which was previously considered weak. Several twins were introduced during the pre-deformation process, which encouraged continuous precipitation (CP) and prevented discontinuous precipitation (DP) during the following ageing treatment, it was stated.

The good specific strength and specific modulus of magnesium alloys be features that are a priority for the automobile industry for reducing fuel consumption at once can reduce environmental impact. Among the cast magnesium alloys, AZ91 (Mg–9Al–1Zn) is the most sought alloy because of its good casting properties (Pai et al. 2012). However, this alloy loses its strength and creep resistance properties when exposing to the temperature at about 120 ˚C and above due to softening of the β- phase ($Mg_{17}Al_{12}$). It also reports that when minor alloy addition or constituent into AZ91 it can improve the strength. For example, additions of Ca to AZ91 alloy to the levels of about 0.4 wt.% increased the ambient and high-temperature strength of the base alloy (Pai et al. 2012).

The melting temperature of pure magnesium is 650°C. The solubility of magnesium in the aluminium melt reaches a maximum of 18.9 at. % at the 450°C eutectic temperature. Composition in magnesium alloy is important and can give distinct properties to the composite. All of the trait possess from original constituent thus giving magnesium alloy an improved properties compared to the other lightweight metal (Liu and Guo 2020), (Esmaily et al. 2017). The maximum solubility of aluminum in magnesium at the eutectic temperature is 11.8 at. %. Figure 1.1 show Mg-Al binary phase diagram.

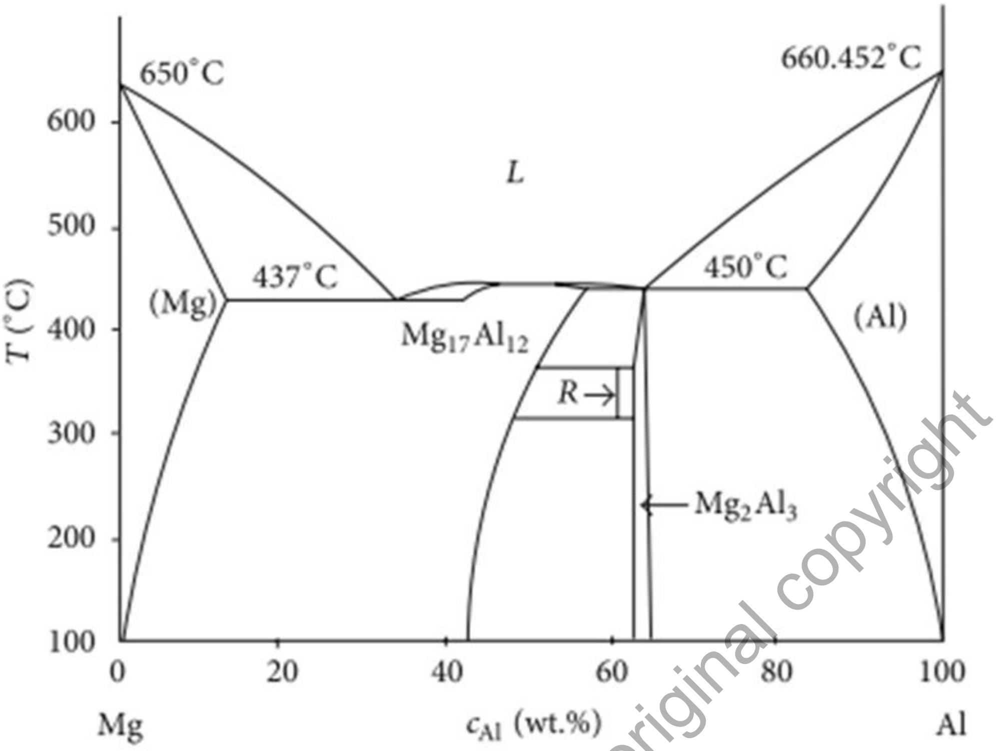

Figure 1.1: Mg-Al binary phase diagram (Djurdjević et. al, 2013)

Figure 1.2 describes element, alloying quantity and heat treatment used in designation AZ91. Aluminum is used as stabilizer in magnesium alloys due reasonable mechanical properties.

The concentrated solid solubility of aluminium in Mg is 12.7 wt.% at 437°C (Sahu, 2015). Al delivers solution solidification, β phase precipitation more than 2 wt. % will boosts hardening. Aluminium improves the cast ability and fluidity. However, the drawback are it can rises the trend for micro porosity shrinkage up to 9% and then decreases. Zinc influence solidification pattern of AZ91 and form porosity at micro level. Zn also amplifies α-Mg and β-$Mg_{17}Al_{12}$ phase field which effect in a higher precipitation and strength in age hardened alloys. Zinc also responsible to speed up amount of precipitation in age hardening.

The tensile strength of AZ91 alloy is also lower than that of AZ92 alloy with higher Zn content (Kim, Sang-Hoon;Moon, Byoung-Gi;You, Bong-Sun;Park 2017). These drawbacks limit the applications of the alloy as a structural component requiring higher ductility and tensile strength. Lightweight Mg-Al-Zn/CNT nanocomposites could be a promising alternative to address the tensile strength problem (Yuan et al., 2016). Incorporation of a few CNT into Mg alloys leads to the formation of performance and functional nanocomposites with enhanced mechanical and physical properties and reduced weight (Yuan et al., 2016). The heat treatment can affect wear through changes in the species and amounts of the reinforcing phase, along with the nature of the interface between the reinforcement and the matrix. As one of the widely utilized magnesium alloys, the AZ91 alloy usually contains high quantities of the β-phase ($Mg_{17}Al_{12}$), distributed along the grain boundaries. The microstructure, the morphology, and the volume fraction of the β-phase could be changed by both solid solution and ageing treatment, which could prominently affect the wear resistance (Chen et al., 2017).

Powder metallurgy metal matrix composites based on AZ91 alloy matrix reinforced with 0.3, 0.6 and 0.9 weight percent of multiwall carbon nanotube (CNT) were investigated from the point of view of their response to artificial ageing as compared to the unreinforced AZ91 matrix alloy.

1.2 Problem Statement

Compared to monolithic magnesium or magnesium alloys, magnesium matrix composites are the lightest metal structural material and have a number of benefits over them, including a high modulus of elasticity, high strength, and outstanding creep and wear resistance at extreme temperatures (Dey & Pandey, 2015). However, due to their poor ductility and fracture toughness, the practical applicability of these materials is severely restricted (Zeng, Zhang & Wu, 2003). As an added bonus, due to the existence of a hexagonal lattice structure (HCP) that resists plastic deformation, the use of magnesium alloys has been restricted. The decreased temperature formality of an HCP structure with insufficient slip systems is not met, and the strength of the structure is poor as a result of the ease with which the basal slip is activated (Kumar, Sasanka, Ravindra, & Suman, 2015; You et al., 2017)AZ91 is a magnesium alloy that possess dendritic structure with relatively coarse grain size. It contains high quantities of β-phase ($Mg_{17}Al_{12}$) distribute along grain boundaries, which is responsible for improving hardening properties. In AZ91 reinforced with carbon nanotubes (CNT), the presence of carbon will further increase the strength of AZ91 (Zhao & Li, 2016).

Heat treatment is an important stage in powder metallurgy to enhance the structural properties of the alloy. The most versatile and promising method of heat treatment is ageing process because it has the ability to restructure the phase element of the alloys so that to enhance the mechanical properties (Rajan Soundararajan et al. 2021). However, there is lack of study focusing on the ageing behaviour properties of AZ91 and AZ91 reinforced with CNT (Huang, Abbas, and Ballóková 2019), particularly on the optimum temperature to achieve the strength for AZ91 alloy (Yuan et al. 2019) and on the optimum weight percentage of CNT as reinforcement into the magnesium alloy (Radhamani, Lau, and Ramakrishna 2018).

Among popular fabrication method is powder metallurgy due to its capability to produce stable, lightweight alloys (Suprapedi et al. 2020). However, it was reported that the main problem for AZ91 reinforced CNT to be applied as an industrial reinforcement for composites is their poor mixing in the matrix. This is caused by agglomerates that easily occur due to strong Van Der Waals forces between carbon atoms (Kondoh et al., 2010). Previous method of mixing using roll mill needs to be improvised to produce more homogenous mixing.

Predictive model validation is an important process to ensure accuracy of ageing treatment. However, the current existing work on hardness aging prediction is limited to certain parameters and selected data range (Saboori et al. 2017). Nevertheless, to improve accuracy and robustness, the model prediction can be exploited with the consideration of new parameters and extended data range using semi empirical approach.

1.3 Objective of Research

The objectives of the research are:

1. To determine the optimum weight percent of CNT (0.3, 0.6 and 0.9) as an additive into AZ91 matrix with regards to its physical and mechanical properties.

2. To investigate the effect of ageing temperature (175ºC, 210ºC and 300ºC) with respect to the microstructure and hardness properties of AZ91 and AZ91/CNT.
3. To evaluate the activation energy and predict the hardness value of the heat treated AZ91 and AZ91/CNT composite by modifying and improving semi-empirical model based on Johnson Mehl-Avrami equation.

1.4 Scope of Study

Mg-Zn-Al (AZ91) and AZ91 nanocomposite were prepared by using planetary mill for 20 hours and compact the powder mixture at 400 MPa. Then, the sample was sintered at 450˚C for 2 hours. After 2 hours, the samples were taken out from the furnace and were hold at about 2 hours in open air. Then, the samples were undergone solution treatment at 415 ˚C temperature for 2 hours. Then samples were undergoing quenching where all of the samples were immediately immersed in water. Then, all the sample were put on the strainer for the drying process.

After past through T4 process, the samples were continued with artificial ageing, T6. The samples were sintered using 10 ˚C/min, the parameter for temperature are 175 ˚C, 210 ˚C and 300 ˚C for 36 hours and taken every 2 hours. Finally, the samples were characterized and tested for phase element analysis, morphology observation, porosity and density measurement, physical and mechanical properties.

CHAPTER 2 : LITERATURE REVIEW

2.1 Introduction

Magnesium alloy is one of the most promising lightweight metals for structural applications due to its strong, low density and high damping capacity (You, Huang, Kainer, & Hort, 2017). Magnesium alloys have advantages over conventional metallic materials, ceramics and biodegradable polymers for biomedical applications (Li & Zheng, 2013). Magnesium alloys are used in a variety of applications including automotive, aerospace equipment.

The use of a magnesium alloy becomes important due to a magnesium density one-third lower than that of aluminum, improved damping capacity, increased corrosion resistance and better mechanical properties (Barrena, Gómez De Salazar, Matesanz, & Soria, 2011). Magnesium matrix composites are the lightest metal structural material and offer many advantages over monolithic magnesium or magnesium alloys, such as high modulus of elasticity, high strength, and excellent creep and wear resistance at elevated temperatures (Dey & Pandey, 2015).

However, commercial application of these materials is severely limited by their low ductility and fracture toughness (Zeng, Zhang & Wu, 2003). Moreover, application of magnesium alloy are limited due to presence of hexagonal lattice structure (HCP) which resist the plastic deformation. HCP structure with inadequate slip systems does not satisfy reduced temperature formality and its strength is also low due to the easy activation of the basal slip (Kumar, Sasanka, Ravindra, & Suman, 2015; You et al., 2017)