Optimisation of the Hardness AZ31B Reinforced with Lead and Carbon Nanotubes using the Response Surface Method

M F Abdullah1*, S Abdullah2, M S Risby1, M Z Omar2 and Z Sajuri2

1Department of Mechanical Engineering, Faculty of Engineering, Universiti Pertahanan Nasional Malaysia, Kem Sg. Besi 57000 Kuala Lumpur, Malaysia
2 Centre for Materials Engineering and Smart Manufacturing, Faculty of Engineering & Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

Abstract. This paper presents the optimisation of the hardness of the material, AZ31B, reinforced with a percentage of lead and carbon nanotubes (CNTs). Currently, the new automotive era is focusing on lighter and stronger materials. Therefore, in this study, although magnesium alloy showed characteristics of high strength, yet it still needed to be enhanced in terms of strength and elongation. Hence, AZ31B was selected to enhance the strength through the addition of lead and CNT reinforcement particles. The Response Surface Method (RSM) was used to optimise the percentage composition of lead and CNT. From the RSM, a mathematical model can be obtained for the optimization of the given parameter. The RSM method was validated through an experimental analysis using the Disintegrated Melt Deposition (DMD) technique for the sample preparation. From the results, it was shown that the optimised composition due to the addition of lead was between 1% and 5%, while with CNT it was between 0.1% and 0.5%. The suggested reinforcement materials increased the material hardness of the AZ31B material by up to 27%. Hence, the proposed RSM was suitable for the optimization of the reinforcement materials.

1. Introduction

The demand for lightweight materials for automotive applications is very high because these materials can reduce the load of the vehicle and, at the same time, save on fuel costs [1]. One of the most important material properties in automotive applications is the strength, which allows the device to withstand the effects of various conditions. The strength of this material is also directly proportional to the hardness of the material [2]. Therefore, the development of such a composite was switched to that of an alloy composite, namely magnesium alloy, as the lightweight material. Magnesium alloy is used mostly in the automotive and aerospace industry and falls within the AZ31B alloy series, which provide suitable strength properties for various applications [3].

Magnesium has a hexagonal close-packed structure (HCP). This structure affects the strength and ductility of materials because there are voids between the molecules [4]. Therefore, it is necessary to have a material that is able to fill these voids in order to prevent the structural collapse of the material. The most suitable materials to fill those voids are carbon nanotubes (CNTs). CNTs have unique characteristics that can generate strong materials with enhanced energy absorption properties [5], and many researchers have acknowledged that CNTs can improve the strength of materials. CNT materials are produced from nano-technology for the purpose of filling the voids in structures and producing van der Waals bonds within them [6]. In addition, lead (Pb) materials are also being used extensively to increase the absorption of energy as well as to enhance the ductility of materials. Since an increase in the ductility of a material is directly proportional to the elasticity of the material, an increase in the lead content can have an effect on the enhancement of the ductility of AZ31B [7].
Magnesium alloy, AZ31B, is a material with high-energy absorption. However, this material is weak in terms of its ductility and hardness. The addition of CNT to a material can increase the strength and hardness of that material, while its ductility can be increased by the addition of lead. These additions can improve the material properties of magnesium alloy, making it better than the original material. Therefore, this study was conducted to obtain the optimum hardness by adding a percentage of CNT and lead to AZ31B using the RSM. The addition of an optimum percentage of CNT and lead can increase the hardness of the experimental materials.

2. Methodology

2.1. Sample preparation

The matrix material used was the magnesium alloy, AZ31B, in the form of an ingot. CNT, with an external diameter of 10-30 nm, density of 2.1 g/cm³ and a purity of more than 90%, was added to the AZ31B. Besides that, the lead powder that was added had a purity of 99.9%, with a density of 11.342 g/cm³. This process of adding foreign substances into the AZ31B is known as the Disintegrated Melt Deposition (DMD) method. In this case, the AZ31B ingot was heated in an induction furnace until it melted. This heating was conducted in a chamber where the air had been sucked out to create a partial vacuum before argon gas was piped through the combustion chamber at a speed of 25 mm/min [8]. When the ingot had melted, the CNT and lead compositions were channelled into the chamber concerned. The percentage of CNT and lead that was added depended on the experimental design, as shown in Table 1. Figure 1 shows the machine induction furnace where the substances were added to the melted magnesium alloy.

Figure 1: Induction furnace for melting magnesium alloy and reinforcement materials.

2.2. Matrix combination for Response Surface Method

The development of the magnesium alloy, which involves the addition of CNT and lead, uses a statistical method known as the Response Surface Method (RSM). RSM is a practical and economical process that is used by many researchers to obtain the optimum parameters for an experiment [9]. The mathematical model that is generated by the RSM gives the relationship between the response and the given input as equation (1):

\[ y = f(x_1, x_2, ..., x_k) + \varepsilon \] (1)

where \( y \) is the response, \( f \) is the unknown function of the response, \( x_1, x_2, ..., x_k \) are the independent variables, also known as the original variables, \( \varepsilon \) is the statistical error that represents a variable source that has not been taken into account in the function, \( f \). \( \varepsilon \) is usually regarded as a normal distribution with a min variation of zero.

Table 1 gives the parameters that were tested in the RSM experiment. Five factors were involved, namely the CNT percentage, lead percentage, temperature, endurance duration and mixing speed. All the factors were tested at two levels, that is, the minimum and maximum levels.
Table 1: Main parameters and their important levels that were affected

| Parameter               | Level codes | Maximum | Minimum |
|-------------------------|-------------|---------|---------|
| Percentage of CNT       |             | 0.5     | 0.1     |
| Percentage of Lead      |             | 5.0     | 0.5     |
| Temperatures (°C)       |             | 660     | 750     |
| Holding time (s)        |             | 1800    | 900     |
| Stirrer speed (rpm)     |             | 500     | 250     |

The parameters that were obtained were based on an earlier study by Katsuyoshi et al. (2010) [10], which found that a suitable composition of CNT for their study was around 0.5%. Srinivasan et al. (2007) showed that an increase in the lead content by as much as 5% of the original composition of the material would have a positive effect on the energy absorption [7]. The temperature parameter was taken into account based on the melting point of magnesium and on the study by Nguyen et al. (2008), which used a superheated temperature of 750 °C [8]. Other parameters were also discussed by previous researchers.

2.3. Hardness Observation
A hardness test was carried out to determine the change in the hardness of the alloy due to CNT and lead. A Vickers hardness (HV) test was conducted using a power scale of 300 gf in reference to the ASTM E384 standard [11]. Figure 2 shows the hardness testing machine that was used in this experiment.

![Figure 2: (a) Vickers tester used for hardness characterization, (b) view of placed sample](image)

3. Results and discussion
Table 2 shows the number of runs obtained in the RSM with regard to the response to the hardness of the material. There were 25 runs altogether, which gave different hardness results. This RSM table used a model with one midpoint and three replications to get a significant comparison in the statistical analysis. Figure 3 shows a comparison of the percentage increase and decrease in the hardness of each material with the parameters as set out in Table 2 against that of the original material. The original hardness of the AZ31B was 57.7 HV for a scale of 300 gf. From the hardness test conducted, some materials experienced a reduction in hardness, while others experienced an increase. It was observed that the highest reduction in hardness was at run 7, i.e. 46.7 with a reduction of -19.1%. The highest increase in hardness was at run 22, i.e. 72.9 with an increase of 26.3% compared to the original material. The median of increase in hardness was at run 12, i.e. 62.0 with an increase of 7.5% compared to the original material. According to the DOE table that was obtained, run 8 was the run at the midpoint of the model. Run 8 had a hardness of 65.5, i.e. 13.5% higher than that of the original material, AZ31B.
Table 2: Number of DOE Runs for RSM

| Run Order | Hardness | Run Order | Hardness |
|-----------|----------|-----------|----------|
| 1         | 57.2     | 14        | 55.0     |
| 2         | 56.6     | 15        | 68.1     |
| 3         | 65.7     | 16        | 63.3     |
| 4         | 60.2     | 17        | 70.0     |
| 5         | 60.2     | 18        | 60.1     |
| 6         | 68.2     | 19        | 65.3     |
| 7         | 46.7     | 20        | 53.8     |
| 8         | 65.5     | 21        | 61.7     |
| 9         | 66.2     | 22        | 72.9     |
| 10        | 55.4     | 23        | 70.4     |
| 11        | 67.7     | 24        | 64.4     |
| 12        | 62.0     | 25        | 65.8     |
| 13        | 66.0     |           |          |

Figure 4 shows the normal probability graph for the hardness of each AZ31B composite with a combination of CNT and lead. This normal probability uses the P-value as its reference point. The P-value taken for this experiment was 0.001. The P-value is important for determining whether the data has a normal distribution or not. From the data taken for 25 runs, the P-value for hardness was 0.025. The P values obtained for the hardness was much higher than the P-value reference point, thus indicating that the hardness data for the magnesium alloy had a normal distribution. The hardness of the magnesium alloy had an average value, $\mu$, of 63.87 HV and a standard deviation, $\sigma$ of 5.088. From Figure 4, it can be seen that the hardness data for magnesium alloy was located in the border area distribution with a 95% confidence level. A normal distribution was important at the start of the statistical analysis to ensure that the data that was obtained fulfilled the statistical conditions for the next stage of the analysis, i.e. the RSM analysis.

Figure 3: Percentage increase in hardness compared to AZ31B
In the next analysis, the hardness data for the material was employed for the optimization using the RSM. The RSM is a practical, economical and relatively easy method, and many researchers utilize it for the modelling process. It is also successfully used for applications in composite material science [12]. The calculated data was used with a regression method to construct a mathematical model. This mathematical model was taken as the objective function and could be optimized using any mathematical or analytical approach to obtain the appropriate process parameters.

Figure 5 shows the contour plot for the effects of hardness on the percentage composition of CNT and lead in AZ31B. It can be seen that the hardness of the material increased with the addition of CNT in the initial stage, but started to decrease when it exceeded the optimum content for CNT. The percentage increase in lead, on the other hand, did not have a significant impact, as the change that occurred in the hardness was not extreme. This response towards hardness was in the form of a curve, which can be clearly seen in Figure 6, which depicts the plot of the surface hardness towards the percentage increase in CNT and lead. These contours and surface plots took into consideration the midpoint factors that were given, namely a temperature of 705 °C, duration of 22.5 minutes and rotational speed of 375 rpm.

Figure 4: Normal hardness probability graph for each AZ31B composite containing CNT and lead

Figure 5: Contour plot for hardness in relation to percentage increase in CNT and lead
From the estimated regression coefficient for hardness and based on the factors given in this experiment, the regression model equation (2) can be derived as follows:

\[
\text{Hardness} = -32.529 + 25.917(CNT) + 11.769(Pb) + 0.118(\text{Temp}) \\
+ 0.328(\text{Duration}) + 0.009(\text{Speed}) - 42.500(CNT \times CNT) \\
- 0.014(Pb \times \text{Temp}) - 0.005(Pb \times \text{Speed}) 
\]  

The composition of this material could also be optimised with regard to the response of the material using the RSM. Figure 7 shows the optimum percentage content of CNT and lead in the AZ31B composite. It was learned that the optimal content for this response was 0.306 % CNT and 0.5 % lead at a temperature of 750 °C, duration of 30 minutes and rotational speed of 500 rpm. This provided the optimal hardness of 73.70 HV, which was 27.7 % higher than the hardness of the original material, AZ31B.

Figure 8 shows the correlation between the experiment and the simulation for the material hardness. The correlation plot showed that a very high $R^2$ value of 0.9054 was obtained, which approached the ideal precision value of 1.0. This showed that the experiment generated a hardness equation that could be used in this study.
4. Conclusions
The increase in the percentage of CNT and lead can enhance the hardness of the magnesium alloy, AZ31B. These additions took into account other side factors such as temperature, the melt duration and the rotational velocity during the blending. These factors resulted in a combined hardness from the percentage of CNT and lead. These factors indirectly contributed to the change in the nature of the material being studied. The use of the RSM statistical analysis method enabled the optimum value for the percentage increase in the composition to be known. The optimum composition for CNT and lead was 0.306% and 0.5 %, respectively, which served to increase the hardness by as much as 27.7 % compared to the original material, AZ31B. The hardness that was obtained enhanced the properties of the AZ31B magnesium alloy. This resultant increase in hardness will extend the use of the magnesium alloy, giving rise to a higher level of energy absorption by the magnesium alloy upon impact at high speeds.

Acknowledgments
The authors would like to express their gratitude to Ministry of Higher Education Malaysia via Universiti Kebangsaan Malaysia and Universiti Pertahanan National Malaysia (Research funding: LRGS/2013/UPNM-UKM/DS/04) for supporting this research.

References
[1] Bakshi S R, Lahiri D and Agarwal A 2010 Carbon nanotube reinforced metal matrix composites—a review. International Materials Reviews vol 55 (1). Pp 41-64
[2] Saad A, Alsubaie, Yi Huang Terence and Langdon G 2017 Hardness evolution of AZ80 magnesium alloy processed by HPT at different temperatures. Journal of Materials Research and Technology 6 (4): 378-384
[3] Watari H, Davey K, Rasgado M T and Izawa S 2004 Semi-solid manufacturing process of magnesium alloy by twin-roll casting, J. Material Processing Technology, Vol 155-156: 1662-1667
[4] Jena P K, Kumar K S, Krishna V R, Singh A K and Bhat T B 2008 Studies on the role of microstructure on performance of a high strength armour steel. Engineering Failure Analysis 15 1088–1096
[5] Muhammad R, Mahesh H, Shaik Z, Uday V, Arefin T, Ashok K, Jonathan T and Shaik J 2013 Effects of amino-functionalized MWCNTs on ballistic impact performance of E-glass/epoxy composites using a spherical projectile. International Journal of Impact Engineering 57 108-118.
[6] Selvamani S T, Premkumar S, Vigneshwara M, Hariprasath P and Palanikumard K 2017 Influence of carbon nano tubes on mechanical, metallurgical and tribological behavior of magnesium nanocomposites Journal of Magnesium and Alloys 5 (3): 326-335

[7] Srinivasan A, Pillai U T S and Pai B C 2007 Effect of Pb addition on ageing behavior of AZ91 Magnesium alloy Material Science and Engineering 452-453 p87-92

[8] Nguyen Q B and Gupta M 2008 Increasing significantly the failure strain and work of fracture of solidification processed AZ31B using nano-Al2O3 particulates Journal of Alloys and Compounds 459 (1–2), p244–250

[9] Shokuhfar A, Khalili S M R, Ghasemi A F, Malekzadeh K and Raissi S 2008 Analysis and optimization of smart hybrid composite plates subjected to low-velocity impact using the response surface methodology (RSM) Thin-Walled Structures 46: 1204 – 1212

[10] Katsuyoshi K, Hiroyuki F, Junko U, Hisashi I, Bunshi F and Morinobu E 2010 Microstructural and mechanical analysis of carbon nanotube reinforced magnesium alloy powder composites Materials Science and Engineering A 527 : 4103–4108

[11] ASTM E384-2011 standard test method for knoop and vickers hardness of materials P 43

[12] Shokuhfar A, Farsani R, Raissi S and Sedghi A 2007 Optimization of carbon fibers made up of commercial polyacrylonitrile fibers using screening design method. Mater Sci: An Interdiscip J Phys, Chem Technol. Mater 25(1):113–20