ASM Sc. J., 12, Special Issue 3, 2019 for ICST2018, 34-39

The Effect of Ca and Zn on Microstructure and Hardness Properties of Mg-10Al-1Zn and Mg-10Al-5Ca-2Zn Alloy

Rosmamuhamadani Rami[1#] , Mohd Muzamir Mahat[1], Sabrina M. Yahaya[1] and Mahesh Kumar Talari[2]

[1] *School of Physics and Materials Studies, Faculty of Applied Sciences, Universiti Teknologi MARA, Shah Alam, Selangor, Malaysia.*

[2] *Department of Metallurgical and Materials Engineering, National Institute of Technology, Warangal, Telangana 506004, India.*

Magnesium (Mg) alloys are well known for their superior specific strength and good machinability with ubiquitous applications in automobile and aerospace industries. In addition, these lightweight alloys demonstrate good surface finish and high specific strength. In this research, the microstructures and mechanical properties of Mg-10Al-1Zn were compared with those from Mg-10Al-5Ca-2Zn composite alloy. Scanning electron microscopy (SEM) was employed to observe the microstructure. The samples were ground and polished with diamond slurry. The resulting morphology of these composites was then observed. X-ray diffraction (XRD) was used to analyze the peak and phase distribution while Vickers hardness tester was used to determine the hardness of these composite alloys. Results showed that the average grain size of Mg-10Al-5Ca-2Zn was smaller than those from Mg-10Al-1Zn composite alloys. The addition of calcium (Ca) to Mg-10Al-1Zn composite alloys improved its microstructural properties. For Mg-10Al-1Zn composite alloy, primary α-Mg and β-$Mg_{17}Al_{12}$ were observed whereas for Mg-10Al-5Ca-2Zn alloy, both α-Mg and Al_2Ca were observed. XRD analysis showed that the addition of Ca to Mg-10Al-1Zn composite alloy reduced the peak and pattern in the Mg-10Al-5Ca-2Zn alloy. The hardness of Mg-10Al-1Zn composite alloy increased with the addition of Ca element. The hardness value of Mg-10Al-1Zn and Mg-10Al-5Ca-2Zn were 70.54 and 86.82, respectively.

Keywords: magnesium alloy; Mg-10Al-1Zn composite alloy: microstructure; hardness property; x-ray diffraction (XRD)

I. INTRODUCTION

A. Mg alloy

Magnesium (Mg) is the lightest structural metal with a hexagonal closed packed lattice structure. Pure Mg is rarely used for engineering application except when it is alloyed with other metals. Alloying is one of the most practical approaches to improve the properties of the metal. Mg alloys are an inexpensive light-weight material with high specific strength (Kainer, 2013). Besides that, Mg alloys exhibit low Young's modulus, high stiffness, low density with high specific strength. You *et. al.* (2017) highlighted that Mg alloys in structural application have promising lightweight properties of metals provided with its high specific strength, low density and high damping capacity. Due to its low melting point at 650 °C, Mg has the ability to creep under load at elevated temperature. Alloying the Mg improves its creep performance which can be achieved by controlling its grain-boundary collision between each other.

Among the Mg alloys, Mg-Al-Zn composite alloy has a widespread application in the automotive industry due

*Corresponding author's e-mail: rosma614@salam.uitm.edu.my

to the presence of $Mg_{17}Al_{12}$. This alloy offers the advantages of room temperature strength, ductility, corrosion resistance and excellent castability (Son *et. al.* 2008). According to Geranmayeh *et. al.* (2014), when Mg-Al alloys are exposed to a temperature of 393K and above, the alloys are susceptible to softening due to the low melting point (723K) of intermetallic phase $Mg_{17}Al_{12}$ at the grain boundaries and inter dentritic regions. The addition of Ca into Mg alloys can improve the properties of these alloys such as improved tensile strength at elevated temperature and ambient temperature due to grain refinement Hakamada *et. al.* (2008). In other words, even something as small as modifications to these alloys' grain structure will be translated to improvements on their overall properties and performance.

Mg alloys are widely used in the automobile industry because of their lightweight properties which contribute to reduced fuel consumption and pollution (Wan *et. al.* 2013). According to Kulekci (2008), the application of Mg in automotive industries saw its debut in the Volkswagen Beetle. An estimate of 22 kg of Mg alloys is accounted for in each Beetle. Although Mg alloys have excellent strength, they cannot tolerate load at high temperature. Besides having a low elastic modulus, Mg alloys also have limited strength and creep resistance at elevated temperature. To improve these properties, an alloying element such as Ca, Zn, and Al can be added. In this study, Mg-10Al-1Zn composite alloy with the addition of Ca and Zn were prepared. Its resulting hardness was measured with Vickers hardness tester. Microstructural properties of the alloy were investigated with SEM and XRD.

B. Mg-Al system

The Mg-Al system in general has included Mg alloys. Overall, the strength, castability and corrosion resistance of Mg will be improved when it is alloyed with Al. According to You *et. al.* (2017), the (β)-$Mg_{17}Al_{12}$ phase that is formed along grain boundaries has a relatively low melting temperature (710 K). The presence of this phase caused microstructure instability due to grain boundaries sliding which compromises the mechanical properties of Mg-Al alloy at temperatures more than 120° C (Kainer, 2013). A few elements can be used to improve the microstructure of Mg-Al alloys such as Zn and Ca. Al alloys are widely used in automobile and aerospace industry because of their superior properties such as high specific strength, chemically inert and good performance at a low temperature. Mg-Zn-Al alloys have ternary phase diagram, ternary intermetallic compounds of ternary phase, τ-phase (Mg_{32} (Al, Zn)$_{49}$), Mg-rich φ-phase ($Mg_5Zn_2Al_2$) and a binary intermetallic compound of ε-phase.

According to Son *et. al.* (2008), the addition of Ca in Mg alloys will improve their creep resistance and strength at high temperature. Further quaternary addition can improve the alloys at a low cost. Apart from that, the addition of Ca may improve the mechanical properties of Mg alloys at high and ambient temperatures due to grain refinement (Hakamada *et. al.* 2008). However, the addition of Ca also has its drawback through the potential manifestations of crack or void. According to You *et. al.* (2017), the addition of Ca to Mg-Al alloys can give rise to thermally stable Al_2Ca phase with a higher T_m of around 1352 K. The presence of this particular phase can augment the strength and creep properties of Mg-Al alloys. In the development of Mg-Al-Ca alloys, the addition of Ca in high quantity is meant to suppress the formation of β-$Mg_{17}Al_{12}$ phase. It was used as micro-alloying element in the heat resistance of Mg-Zn-Al based alloys. Therefore, the microstructure and the mechanical properties of Mg-Al-Zn-Ca alloys system are reported with simultaneously high Ca and Zn contents (Kulekci, 2008).

II. METHODOLOGY

A. Sample preparation

Mg-Al-Ca-Zn and Mg-Al-Zn composite alloys were prepared for this study. The nominal compositions of the samples are shown in Table 1. The raw materials were cut with a handsaw. 99.95% pure Mg and 70% Mg - 30% Ca master alloys were used.

Table 1. The composition of alloy in (wt. %)

Alloy	Elements			
Mg-10Al-1Zn	Mg	Al	Ca	Zn
Mg-10Al-5Ca-2Zn	83	10	5	2

B. Melting

Before the melting process, the chamber was cleaned thoroughly with laboratory tissues that were soaked in acetone to eliminate contaminants. After chamber decontamination, the samples and Ti getter were placed inside the chamber on a Cu plate. The chamber was vacuumed for 10 minutes to eliminate atmosphere gases followed by argon gas purging into the chamber. Argon gas was used to ensure an absence of reaction between the gas and samples during the melting process. Since Ti is highly reactive with oxygen and nitrogen, the Ti getter was melted first before the samples were melted. The melting of the Ti getter also served a purpose of absorbing impurities in the gas. This was crucial to prevent oxidation of the samples. The alloys melting was prepared in arc melting furnace on a water-cooled Cu hearth in Argon (Ar) atmosphere. The arc melting furnace was powered by Miller Dynasty 350 power source. The power supply operated in both AC and DC mode for different purposes. The DC power supply was used to melt the titanium (Ti) getter while the AC power supply was used to melt the Mg alloys. The Ca and Zn elements ware added at 650 ◦C and the melt of the Mg alloy was refined at 720 ◦C and then held for 20 minutes before pouring. The samples were melted five times to ensure homogeneity of the samples.

C. Cold mounting

Cold mounting was performed to ease the handling of the samples during sectioning, grinding, and polishing process. PVC mold was used as the mold. Before inserting the samples in the mold, the surface of the PVC mold was inspected to ensure a clean, flat, and smooth contour. After grinding, the inside of the mold was coated with silicon mold release or Vaseline so that the samples did not stick to the mold. This cold mounting process required an epoxy to hardener ratio of 9:1. The mixture was stirred gently to avoid air bubbles in the mixture. Next, the mixture was poured into the mold cavity and left intact for 24 hours to cure the samples.

D. Polishing and etching

The samples surface was polished with 6µ to 1µm diamond slurry. The diamond slurry was applied on a damp polishing cloth in a mechanical polishing process. Water-based solution is known to provide a surface with fewer scratches. Different polishing cloth was used with different sizes of diamond slurry. Napped cloth was avoided because it can cause problems with excessive relief and drag. The etching process was performed to reveal the finer details of the microstructure. After polishing, the surface of the samples was exposed to acidic or basic chemical solution for microscopic examination. 2% Nital with a composition of 2 ml nitric acid (HNO_3) and 98 ml ethyl alcohol was employed as the etchant. The etching process lasted for 15 seconds. After the etching process, the sample was immediately rinsed with distilled water and left to dry.

E. Hardness property

The Vickers hardness tester was used to measure the hardness of the materials. Hardness means that the materials have a resistance to permanent deformation like abrasion, scratch, wear and indentation. In Vickers test, it involves a diamond indenter in the form of square-based pyramid. This method measures the permanent depth of indentation that has produced by a force or load on an indenter. The samples were tested using 500 g load and dwell for 15 seconds. The Vickers hardness number, H_v was determined by the ratio F/A, where F is the force applied to the diamond in kilograms-force and A is the surface area of the resulting indentation in square millimeters ASTM E-92. (2003).

F. Microstructure analysis

Microstructural examination of samples was conducted by using (SEM). SEM (INCA, SUPRA 40V 40VP) Zeiss was used in order to observed the microstructure of that composites. The standard grinding and polishing method were used to prepare the sample for SEM observation. The sample were grind using silicon carbide paper from 120 grit to 1200 grit and then followed by polishing process that use diamond slurry from 6 µm to 1 µm. During microscopic examination or microstructure analysis, the structure of material was studied under different magnification. This process determines the properties of materials and these properties are dependent on the material's structure. The images were taken at 2000 x magnification.

III. RESULTS AND DISCUSSION

A. Microstructure observation

Based on the SEM result, it was found that the size of grain boundaries varied with different magnification. The microstructures of the experimental alloys are shown in Figure 1 and 2. The microstructure pointed to the presence of α-Mg solid solution primary phase which was surrounded by a eutectic region of intermetallic and α-Mg. There were slight differences in dendritic cell size due to the grain boundaries on the surface of the structure. The average grain size of Mg-10Al-5Ca-2Zn was lower compared to those from Mg-10Al-1Zn composite alloy due to the addition of Ca and Zn in the former.

Figure 1(a) shows the SEM microstructure of Mg-10Al-1Zn composite alloy at 2000x magnification. Two phases were observed, which are α-Mg (primary phase) and β-$Mg_{17}Al_{12}$ (secondary phase). These phases can be distinguished by their contrast. The bright contrast and dark contrast represents β-$Mg_{17}Al_{12}$ phase and α-Mg phase, respectively. Besides that, change of eutectic structure from divorced to lamellar was observed when Ca was added to the Mg-10Al-1Zn composite alloy. Wang *et. al.* 2017) reported that when Ca composition is increased, the cell size and size of $Mg_{17}Al_{12}$ on the grain boundaries will be reduced. This is parallel to the findings of Qudong *et. al.* (2001). Figure 1(b) shows the SEM microstructure of Mg-10Al-5Ca-2Zn alloy at 2000x magnification. The existence of Al_2Ca phase was evident from this microstructure. According to Srinivasan *et. al.* (2013), the formation of Al_2Ca is due to the addition of Ca to Mg-10Al-1Zn composite alloy.

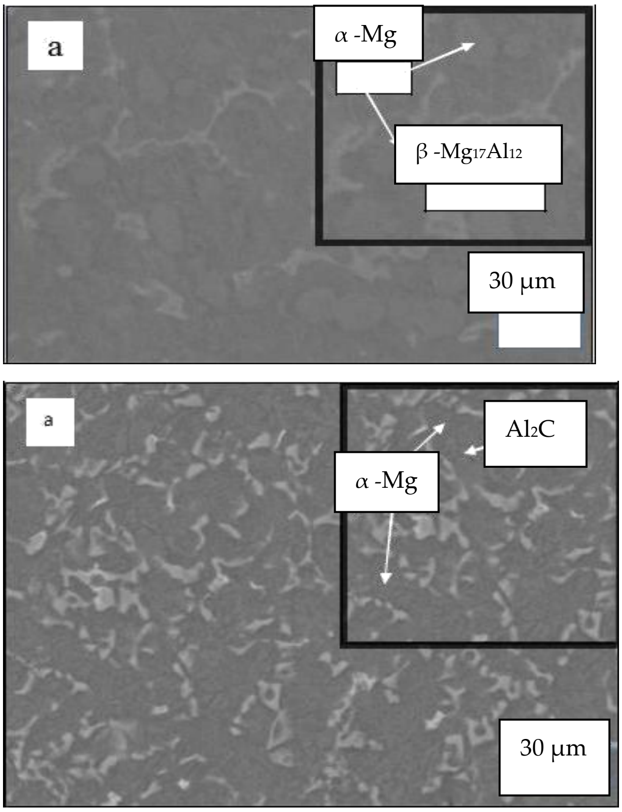

Figure 1. SEM micrograph of (a) Mg-10Al-1Zn composite alloy, and (b) Mg-10Al-5Ca-2Zn composite alloy with 2000x magnification

B. Characterization of the crystal structure

Phase and peak distribution measurements of the Mg composites alloys were performed with XRD that was equipped with Cu-Kα radiation. In addition, XRD was used to determine the presence of a crystalline compound in the samples. During the analysis, the sample was measured at 45 kV and 20 mA. The XRD spectra are.

The Mg-10Al-5Ca-2Zn alloy showed a better phase identification compared to the Mg-10Al-1Zn composite alloy due to the addition of Ca in the former. In Mg-Al alloy, the $Mg_{17}Al_{12}$ phase was reduced with increment in Ca composition. According to Srinivasan *et. al.* (2013), XRD results proved that the $Mg_{17}Al_{12}$ phase will be suppressed whenever the composition of Ca is higher than 2%. Furthermore, the contiguous eutectic network will increase with the continuous addition of Ca.

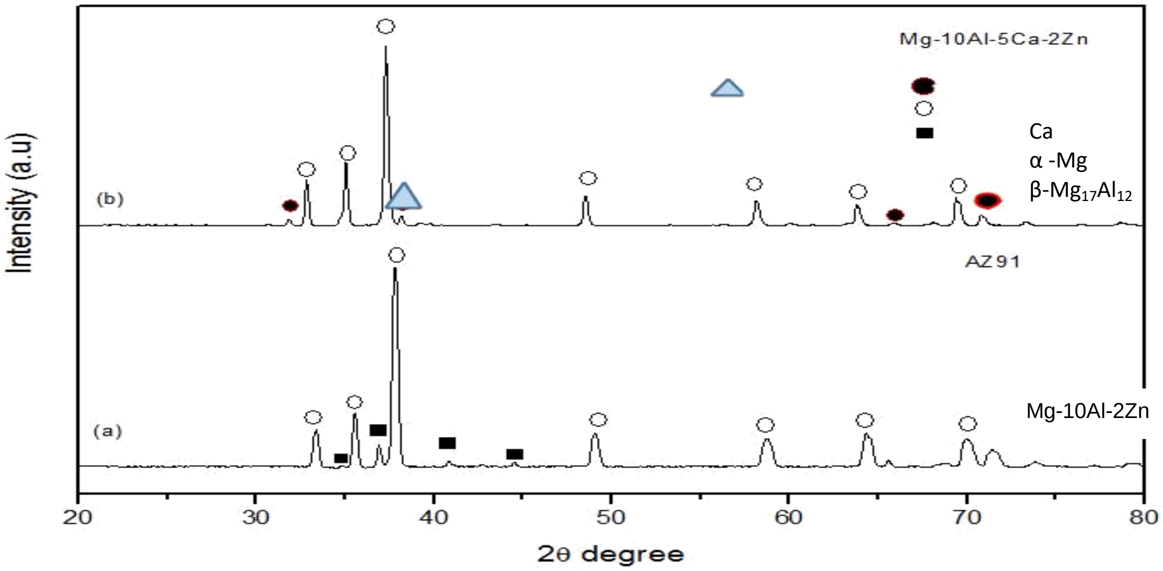

Figure 2. XRD patterns of (a) Mg-10Al-1Zn, and (b) Mg-10Al-5Ca-2Zn composite alloys

Based on the XRD results, the intense and sharp peaks suggested that the alloys have a crystalline structure. Mg-10Al-1Zn composite alloy displayed a peak that corresponded to $Mg_{17}Al_{12}$ phase. This phase is also known as β-phase. However, when Ca was added to Mg-10Al-1Zn composite alloy, the $Mg_{17}Al_{12}$ peak was apparently less intense in Mg-10Al5Ca-2Zn alloys. From Figure 2, the α-Mg phase was detected at 2θ =32.84°, 35.55°, 37.80°,49.09°, 58.65°, 64.36°, and 69.93°. The Al_2Ca phase was detected at 38.163°. As seen in Figure 2(a) the β-$Mg_{17}Al_{12}$ phase appeared at 2θ=34.21°, 37.11°, 40.86°, and 44.54°. The Ca element appeared at 2θ =31.89°, 65.78° and 76.77°. All these peaks corresponded to (200), (400) and (420).

C. *Hardness Property*

The Vickers hardness tester was used to measure the micro hardness in different phases under a load of 0.5 kg with a dwell time of 15 seconds. A minimum of 5 time of 15 seconds. A minimum of 5 indentations was performed to measure the hardness of Mg-10Al-1Zn and Mg10Al-5Ca-2Zn composite alloys and their average value was quantified. The hardness value for Mg-10Al-5Ca-2Zn and Mg-10Al-1Zn composite alloy were 86.82 and 70.54 H_v, respectively. This suggests that the hardness of Mg alloy increases with the addition of Ca, with the addition of Zn causing a specific effect of precipitation hardening. The results of this hardness study are in line with the results of Kompel *et. al.* (2009) who studied the hardness properties of Mg-Ca alloy as a function of Zn addition. Gao *et. al.* (2005) also reported a significant increase in the hardness of Mg-Ca alloy with Zn addition.

IV. CONCLUSION

The addition of Ca and Zn improved the microstructural properties and hardness value of Mg-10Al-1Zn composite alloy. Primary α-Mg and β-Mg17Al12 were observed in Mg-10Al-1Zn composite alloy whereas for Mg-10Al-5Ca-2Zn alloys, α-Mg and Al_2Ca were observed. Mg17Al12 phase was reduced while Al2Ca phase increased with the addition of Ca in Mg-10Al-1Zn composite alloy. The hardness value for Mg-10Al-5Ca-2Zn was higher than Mg-10Al-1Zn composite alloy. The values were 86.82 H_v± 2 and 70.54 H_v± 2, respectively. Therefore, it was proven that the addition of Ca and Zn will increase the hardness of Mg composite alloy.

VI. ACKNOWLEDGEMENTS

The authors would like to thank Research Management Institute (RMI) and Faculty of Applied Sciences for their financial support (600-IRMI 5/3/GIP (049/2018) and facilities.

V. REFERENCES

[1] ASTM E-92 2003, 'Standard Test Method for Vickers Hardness of Metallic Materials', *Annual Book or ASTM Standards*, American Society for Testing and Materials 82.

[2] Gao, XS, Zhu, SM, Muddle, BC and Nie, JF 2005, 'Precipitation-hardened Mg-Ca-Zn alloys with superior creep resistance', *Scripta Materialia*, vol. 53, no. 12, pp. 1321-1326.

[3] Geranmayeh, AR and Mahmudi, R 2014, 'Indentation creep of a cast Mg-6Al-1Zn-0.7Si alloy', *Materials Science and Engineering* A, vol. 614, pp. 311-318.

[4] Hakamada, M, Watazu, A, Saito, N and Iwasaki, H 2008, 'Tensile Properties of Forged Mg-Al-Zn-Ca Alloy', *Materials transactions*, vol. 49, no. 3, pp. 554-558.

[5] Kainer, KU (Ed.) 2013, *'Magnesium Alloys and Technology'*, John Wiley & Sons. New Magnesium Alloys with High Elastic Modulus Young, vol. 3, no. 1.

[6] Kompel, N, Lohmüller, A, Krause, A and Singer, RF 2009, 'Comparison of conventional Mg alloys with Mg-Al-Ca-Zn and Mg-Al-Sr-Zn alloys processed by injection molding', *Proceedings of the 8th International Conference on Magnesium Alloys and their Applications, Weimar,* pp. 67-74.

[7] Kulekci, MK 2008, 'Magnesium and its alloys applications in automotive industry', *The International Journal of Advanced Manufacturing Technology,* vol. 39, no. 9, pp. 851-865.

[8] Qudong, W, Wenzhou, C, Xiaoqin, Z, Yizhen, L, Wenjiang, D, Yanping, Z and Mabuchi, M 2001, 'Effects of Ca addition on the microstructure and mechanical properties of AZ91 magnesium alloy', *Journal of Materials Science*, vol. 36, no. 12, pp. 3035-3040.

[9] Son, HT, Lee, JS, Oh, IH, Kim, DG, Yoshimi, K and Maruyama, K 2008, 'Microstructure and mechanical properties of Mg-Al-Ca-Nd alloys fabricated by gravity casting and extrusion process', *Materials Transactions*, vol. 49 no. 5, pp. 1025-1031.

[10] Srinivasan, A, Ajithkumar, KK, Swaminathan, J, Pillai, UTS and Pai, BC 2013, 'Creep behavior of AZ91 magnesium alloy', *Procedia Engineering* vol. 55, pp. 109-113.

[11] Wan, XF, Ni, HJ, Huang, MY, Zhang, HL and Sun, JH 2013, 'Microstructure, mechanical properties and creep resistance of Mg-(8%-12%) Zn-(2%-6%) Al alloys', *Transactions of Nonferrous Metals Society of China,* vol. 23 no. 4, pp. 896-903.

[12] Wang, F, Hu, T, Zhang, Y, Xiao, W and Ma, C 2017, 'Effects of Al and Zn contents on forged Mg-Al-Zn-Ca alloy', *Materials Transactions*, vol. 49 no.3, pp.554-558.

[13] You, S, Huang, Y, Kainer, KU and Hort, N 2017, 'Recent research and developments on wrought magnesium alloys', *Journal of Magnesium and Alloys,* vol.5 no.3, pp. 239-253.