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**Abstract.** Magnesium alloys are lightweight materials that have a great potential to be developed because the alloy can reduce the energy consumption and total weight. The alloy is made of magnesium metal as a primary component characterized by a soft and mechanically low-strength. The addition of aluminium in Mg-Al system will form $Mg_{17}Al_{12}$ particles causing grain refining the effect of the α-Mg matrix. Similarly, the addition of Zn in Mg-Zn system increases the strength and hardness of the alloy. Hence, the combined addition of Al and Zn in Mg-Al-Zn system would be interesting for automotive component applications. In this study, we have carried out the casting process for Mg-9Al-1Zn (wt. %) through a gravity of the metal mold with air cooling method. The cast alloy designated as Mg9Al1Zn alloy received a solution treatment at temperature of 415 °C for 2 hours. The microstructure observation for the cast alloy showed the presence of α-Mg as a matrix with the largest fraction and β-$Mg_{17}Al_{12}$ phase as a precipitate. The microstructure also showed the presence of pores indicated by black colour. We have also undertaken microanalysis to each phase present in the sample by EDS that detected all elements. The result of Hardness evaluation confirmed that the solution treated as-cast alloys possessed the hardness value of 65.21. The VHN significantly enhanced when compared with that of original cast-alloy which was only 73.02 VHN. The enhancement of the hardness is discussed in relation with processing method and microstructure development after a solution treatment.

**Keywords:** Magnesium alloy, casting, solution treatment, microstructure, hardness.

## 1. Introduction

Magnesium (Mg) is a lightweight metal and becomes the third most abundant metal crusted after Al and Fe. The weight of Mg is only about 66 % of Al and 25 % of Fe. Hence, the Mg is the lightest weight among the three metals [1]. It is reasonable to introduce Mg for substituting Al in lightweight-based alloys when the total weight becomes a primary consideration in a material selection. Despite Mg has a mild nature, nevertheless, for engineering purposes, the weight is not the only a primary consideration, the other properties like good mechanical properties are also required. Three primary factors that generally determine the weight of the vehicle are Engine (28%), body parts (28%), and vehicle frame (27%) [2]. It has already become a general concern that in the transportation sector, the efficiency of fuel oil usage in the vehicles is the one that needs to be considered. Therefore, the utilization of

lightweight metal materials becomes an option in the future manufacturing of automotive components like the body and frames of the vehicles [3]. The mechanical properties of Mg-substituted lightweight-based alloys must be improved to widen the use of Mg. The addition of various elements to the magnesium alloy is considered necessary to obtain a more efficient magnesium alloy. These elements are Al, Zn, Ca, Ce, Ni, Cu, and Th which have proven to increase the strength and tenacity [4]. Alloying is one method to improve the mechanical properties of magnesium alloys. The alloying elements for magnesium alloys are Ca, Zn and Ca, Ca and Sr, Ca and Re, and Zn and Sn [5]. In addition, the rare earth elements like Y, Nd, Sm, Ce, and particularly Gd have been shown remarkably to improve both strength and high-temperature creep resistance [6]. One of the useful methods to improve the strength and formability of Magnesium alloys is grain refinement. The various grain refiner compounds like TiC, $MgCO_3$, SiC, ZnO have been used to improve the mechanical properties of magnesium alloys [7–10]. The current research work aimed at developing energy efficiency alloys based on a Mg-9Al-1Zn (wt.%) composition. It is a two-phase alloy with α-Mg phase serves as the matrix and an intermetallic $Mg_{17}Al_{12}$ phase acting as a reinforcer and grain refiner that can block the movement of dislocations. In addition to the alloying elements or grain refining agents, the improvement of mechanical properties of Mg-based alloys can also be enhanced by a solution treatment. In this paper, we discuss a hardness enhancement obtained in a cast Mg-9Al-1Zn (wt.%) alloy through a solution treatment. The results are presented and discussed in term of microstructural change after a solution treatment.

## 2. Methods

The Mg-based alloy of Mg-9Al-1Zn (wt.%) composition was prepared through a casting method. The alloy feedstocks were Mg (98.53% purity), 9% wt Al (99.87% purity) and 1% wt Zn (99.62% purity) metal chips. The feedstocks were collected in a stainless steel crucible and melted all together in an electrical furnace until the casting temperature achieved 750 °C. The melting process was carried out in an inert condition under argon gas atmosphere to avoid the oxidation. The electric furnace is equipped with a stirrer to facilitate the stirring carried out in 30 s to allow the homogenization of molten alloy. The molten was then poured into a cylindrical metal mold of 20 mm in diameter and 200 mm length and then cooled in an open-air to produce a cylindrical as-cast sample. The as-cast sample was then processed to a solution treatment at 415 °C for 2 hours [11]. The chemical composition of the treated sample was analyzed by Rigaku Nex CG X-Ray Florence (XRF). The microstructures of solution treated samples were observed by an Olympus BX-60M metallurgical microscope and SEM JEOL type JSM-6510A type equipped with energy analyzer, EDS. The hardness was tested using Metrov Duroline-M micro Vickers hardness tester.

## 3. Results and Discussion

### *3.1. Chemical composition*

Table 1 summarizes the results of element analyzed by XRF in the solution treated sample. The data listed in Table 1 show the minimum and maximum values for each element according to the successive measurements of two different locations. The designated composition of the as-cast sample was a stoichiometry Mg-9Al-1Zn (wt.%). When referring to the values listed in Table 1, the composition of the as-cast sample was over stoichiometry in Mg content and Al content in the sample was found deficit but the Zn was about near stoichiometry. Since the alloy system had α-Mg as the main phase, the as-cast alloy with off-stoichiometry composition would affect only the phase composition of the alloy.

**Table 1.** Chemical composition of the as-cast sample

| Point | Al (wt. %) | Zn (wt. %) | S (wt. %) | Mg (wt. %) | Impurities (wt. %) | Total (wt.%) |
|---|---|---|---|---|---|---|
| 1 | 7.80 | 0.80 | 0.10 | 90.80 | 0.50 | 100.00 |
| 2 | 6.30 | 1.00 | 0.10 | 92.20 | 0.40 | 100.00 |

*3.2. The microstructure of solution treated sample*

The microstructure change was studied through a comparison between the microstructure of the as-cast and solution treatment samples according to the observation under optical and scanning electron microscopes. The latter microscope is equipped with a micro analyzer that facilitates the micro analysis of phases in the sample. The microstructures of the as-cast and solution treated samples observed in transverse and longitudinal direction are shown in Figure 1. Obviously, the two samples had a different microstructure from which the as-cast sample was dominated by a grain boundary phase appearing along and at the grain boundaries. The as-cast sample was a two-phase microstructure consisted of the main phase presence as the equiaxed grains with a relatively large size about 50μm estimated from the bar scale and much finer size of the second phase present along and at the grain boundaries. There was no significant difference in the microstructure observed in longitudinal and transversal directions. This indicated that there was no preferred orientation of grains due to the effect of casting. The phase existence in the as-cast sample can be predicted from the phase diagram of Mg-Al system [12] from which the intermediate α-Mg phase must be a major phase with the largest mass fraction about 80.95 wt.% in addition to the intermediate β-$Mg_{17}Al_{12}$ phase as the minor phase. The mass fraction of the two phases can be estimated by the lever rule [13]. The configuration of microstructure showed in Figure 1a and 1b is somewhat like the composite structure in which the major intermediate phase can be determined as the matrix and that of the minor phase as the filler. Hence, there should be a reason for the enhancement in the hardness value of the alloy with such microstructure, especially when compared with a single phase of intermediate Mg-rich. This matter will be discussed further later. After solution treatment process, the microstructure significantly changed as shown in Figure 1c and 1d. The microstructure of a cross section of the two directions was almost similar confirming there was no preferred grain orientation or no anisotropy effects. However, regarding phase constitution, it seems that the phase constitution of the sample remained the same but with an even larger size of the primary phase (100 μm – 200 μm) than that of the as-cast sample. The second phase present in ultra-fine size precipitated within the grain and at the grain boundaries.

When referring to the phase diagram of Mg-Al system, it can be predicted that the phase existence in the sample during solution treatment at 415 °C, the intermediate α-Mg phase was in equilibrium with the intermetallic β-$Mg_{17}Al_{12}$ phase. During the air-cooling, the solution treated sample to room temperature, the composition of intermediate phase changed according to the solidus line. Meanwhile, there was no compositional change in the intermetallic phase during the cooling. The cooling should then change the composition structure of phase existence in the sample. Based on the phase diagram of the Mg-Al system, the initial formation of the intermetallic β-$Mg_{17}Al_{12}$ occurred at a temperature of about 370 °C during the $Mg_{17}Al_{12}$ phase forming refrigeration process increasing and growing at the grain and grain boundaries [14]. Obviously, the mass fraction of intermediate phase decreased while that of intermetallic increased. The formation of alpha-Mg and intermetallic phase $Mg_{17}Al_{12}$ was formed at Mg plus 9% Al of the weight began to occur at temperature 370 °C and last at 100 °C; the percentage of phase can be predicted based on the lever rule as shown in Figure 2 That produced α-Mg of 80.95% and Intermetallic $Mg_{17}Al_{12}$ of 19.05%. [15]. The intermetallic phase $Mg_{17}Al_{12}$ has an A12 isomorph cubic crystal structure with alpha Mn (c158) with a space group of $I\bar{4}3m$ with a lattice parameter of $a$ = 1.06 nm. The unit cell of $Mg_{17}Al_{12}$ contains 34 Mg and 24 Al atoms. γ-$Mg_{17}Al_{12}$ is the second phase [16] which forms eutectic alloy in Mg-Al alloys and also in Mg-Al-Zn alloys with a high Al:Zn ratio.

In equilibrium solubility, the soluble alpha-matrix phase Mg is saturated in Al, especially in the interdendritic regions that precipitate discontinuous β-$Mg_{17}Al_{12}$ when exposed to high temperatures.

Table 2. listed results of microanalysis that pointed at two different specific points representing each phase exist in the sample. The matrix both in Figure 1a and 1b shows the Mg-rich phase respectively. Al and O are also detected in the phase analysis probably refer to the $Al_2O_3$ phase presence due to the oxidation. The results of Microanalysis for the intermetallic phase are pointed respectively in Figure 1c and 1d showing a major content of Mg and Al. The weight of Mg and Al in the intermetallic phase β-$Mg_{17}Al_{12}$ was 56% of Mg and 44% of Al. Figure 3 represents the results of the hardness number evaluation for the as-cast sample compared with that of a solution treated sample. It indicated the mean hardness number of solutions treated sample was in the range of 67.92-77.93 HV, which was higher than that of as-cast in the range of 61.01-72.59 HV. The average value was 65.21 HV, which was about 11 % less than that of the solution treated sample.

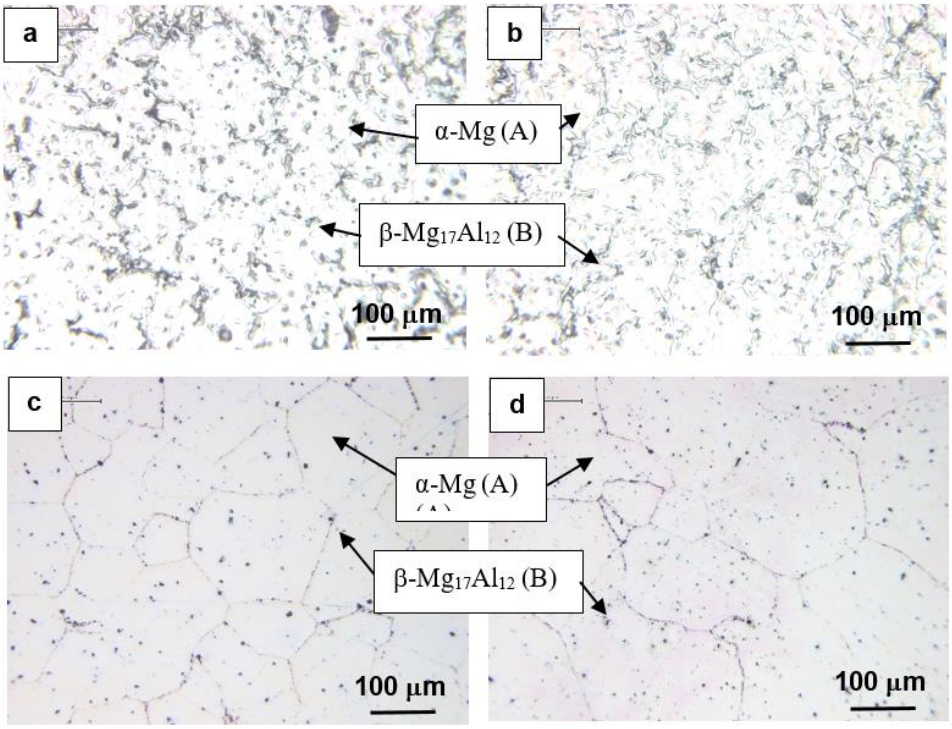


**Figure 1.** The Microstructure of the Mg9-Al1Zn alloy as-cast air cooling a) transversal direction, b) longitudinal direction; the as-cast solution treatment 415 °C at 2 c) transversal direction, d) longitudinal direction (Mag. 200x)

**Table 2.** EDS analysis result of the constitution in the grain and intermetallic compound (wt.%)

| | | Mg | Al | Zn | O |
|---|---|---|---|---|---|
| Figure 1. (a). (b) | Matrix α-Mg (point A) | 84.15 | 3.99 | | 11.85 |
| | Intermetallic phase β-$Mg_{17}Al_{12}$ (point B) | 61.08 | 29.25 | 0.14 | 9.53 |
| Figure 1. (c), (d) | Matrix α-Mg (point A) | 88.85 | 6.11 | | 5.04 |
| | Intermetallic phase β-$Mg_{17}Al_{12}$ (point B) | 62.95 | 21.01 | 0.34 | 15.70 |

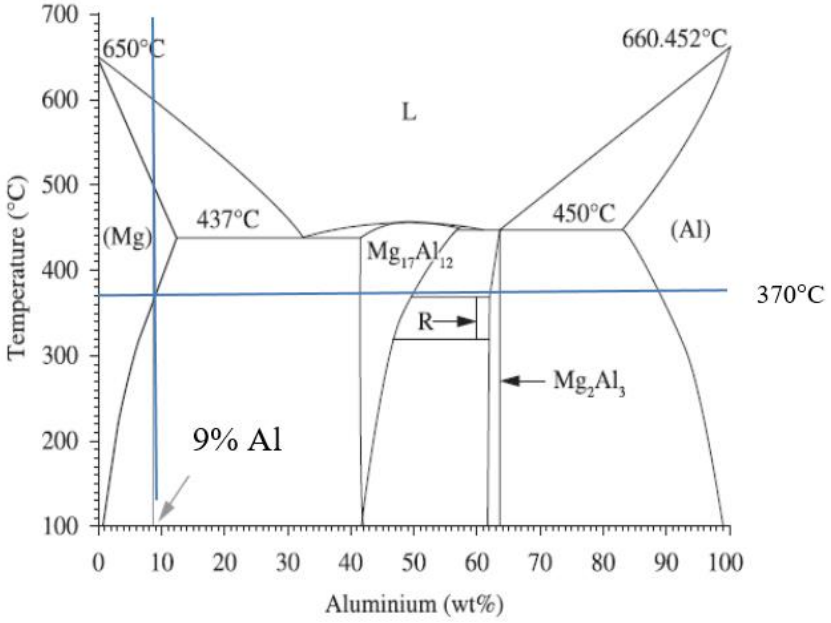


**Figure 2.** A phase diagram of Mg-Al [17]

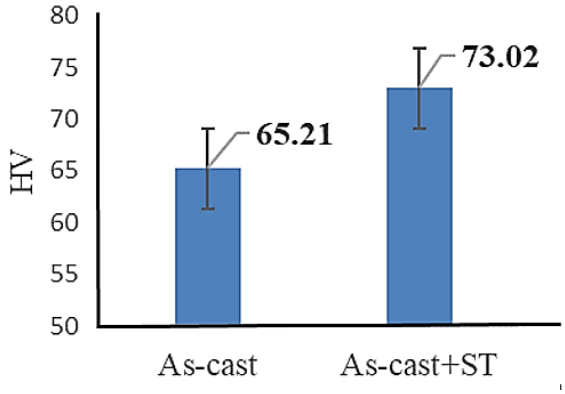


**Figure 3.** The average hardness of solution treatment result compared to the as-cast

The increase in the hardness number of solutions treated sample occurred because of the change in the microstructure after a solution treatment. The change in the microstructure in question is shown previously in Figure 1. The phase formed in both as-cast and as-cast solution treatment had the same stage phase, i.e., the intermediate α-Mg and intermetallic β-$Mg_{17}Al_{12}$ but the mechanism of microstructural change for the two samples was different. The microstructure of the as-cast sample was developed under a slow cooling process in which the process of freezing the molten metal began with the formation of a growing dendritic structure resulting in α-Mg and β-$Mg_{17}Al_{12}$ intermetallic (flake-shaped) intermixed low violence [18]. The microstructure of solution treated sample had equiaxial grain structure morphology with α-Mg phase and intermetallic β-$Mg_{17}Al_{12}$ in the form of ultra-fine grains distributed in the grain and grain boundary as shown in Figure 1c and 1d. The solution treatment had also provided a structural change from a dynamic to an equiaxial caused by the Mg atomic movement forming an equilibrium of the HCP crystallites and clustering into ultra-fine grain structures.

The phases formed in the as-cast sample were equiaxed grains of an α-Mg and irregularly shaped the grain of intermetallic β-$Mg_{17}Al_{12}$. Subject to microhardness evaluation of each phase, the hardness value of α-Mg phase was 66.7 - 72.7 HV and that of the intermetallic β-$Mg_{17}Al_{12}$ hardness was 89.2-92.2 HV. Hence, when the rule of the mixture is applied to calculate the hardness of as-cast samples, the hardness

value will increase with the increase of β-$Mg_{17}Al_{12}$ phase fraction. The previous research work of Ebrahimi et al. [19] showed that the solubility of the β-$Mg_{17}Al_{12}$ precipitate in the α-Mg matrix increased with the holding time during the homogenization process. The 24 hours holding time increased the maximum tensile strength from 62 to 94 MPa due to the gain in phase solubility of the beta precipitate β-$Mg_{17}Al_{12}$ in the α-Mg matrix. The addition of Al alloy elements in the magnesium alloy produced the intermetallic phase of β-$Mg_{17}Al_{12}$. It was also shown that when the solubility of the intermetallic phase and holding time increased, the mechanical properties of hardness and tensile strength increased.

## 4. Conclusion

Based on the analysis and discussion of the results given above, it can be concluded that the change in the microstructure after a solution treatment is responsible for the enhancement in the hardness value of the $Mg_{90}Al_9Zn$ (wt. %) alloy. Hence, the hardness is a microstructure sensitive property. A solution treatment at 415 $^0$C for 2 hours had increased the hardness value of about 11 % above the hardness value of the as-cast sample (65.21 HV).

## References

[1] Uttle C. The Elements Magnesium Benchmark book. Tarrytown New York: 2000.
[2] Mutua, J., Kihiu, M., Rading, G.O, Kimotho JK. Use of Magnesium Alloys in Optimizing the Weight of automobile. Curr Trends Oppor 2011.
[3] James M, Kihiu JM, Rading GO, Kimotho JK. Use of magnesium alloys in optimizing the weight of automobile: Current trends and opportunities n.d.
[4] Yang Z, Li JP, Zhang JX, Lorimer GW, Robson J. Review on Research and Development of Magnesium Alloys. Acta Met Sin(Engl Lett 2008;21:313–28.
[5] Pourbahari B, Emamy M, Mirzadeh H. Progress in Natural Science : Materials International Synergistic e ff ect of Al and Gd on enhancement of mechanical properties of magnesium alloys. Prog Nat Sci Mater Int 2017:1–8.
[6] Mirzadeh H. Quantification of the strengthening effect of rare earth elements during hot deformation of Mg-Gd-Y-Zr magnesium alloy. Integr Med Res 2015:4–7. doi:10.1016/j.jmrt.2015.03.001.
[7] Paramsothy M, Chan J, Kwok R, Gupta M. TiC nanoparticle addition to enhance the mechanical response of hybrid magnesium alloy. J Nanotechnol 2012.
[8] Chen TJ, Jiang XD, Ma Y, Li YD, Hao Y. Grain refinement of AZ91D magnesium alloy by SiC. J Alloys Compd 2010;496:218–25. [9] Kusharjanto, Soepriyanto S, Korda AA, Dwiwanto SA. Effect of ZnO nanoparticles to mechanical properties of thixoformed Mg-Al-Zn alloy. Mater Res Express 2018;5:1–19.
[10] Chen TJ, Jiang XD, Ma Y, Wang RQ, Hao Y. Grain refinement of AZ91D magnesium alloy by MgCO3. Mater Res 2011;14:124–33.
[11] Greger M, Kocich R, Pawlica L, Republic C, Centrum F-SS, Republic C. Structure and properties of alloys of the Mg-Al-Zn system 2009;32:179–87.
[12] Bannour S, Abderrazak K, Mattei S, Masse JE, Autric M, Mhiri H. The influence of position in overlap joints of Mg and Al alloys on microstructure and hardness of laser welds. J Laser Appl 2013;25:032001.
[13] William D. Callister JDGR. Material Science and Engineering an Introduction. Wiley; 2014.
[14] M.Pekguleryuz. Alloying Behaviour of Magnesium and Alloy Design 2013:162–3.
[15] D.Singh, C.Suryanarayana, L.Mertus R-HC. Extended homogencity range of intermetallic phases in mechanically alloyed Mg-Al alloysNo Title. Intermetallic 2003;11:373–6.
[16] Braszczyriska-Malik KN. Precipitates of Mg17Al12 phase in AZ91 alloy. Magnes Alloy Process Prop 2011:95–112.
[17] ASM International. Alloy Phase Diagrams (ASM Handbook). 1998.
[18] Techniques C, Republic C. Influence of Al addition on microstructure of die casting magnesium alloys 2006;19:49–55.

[19] Ebrahimi GR, Maldar AR, Ebrahimi R, Davoodi A. The effect of homogenization on microstructure and hot ductility behaviour of AZ91 magnesium alloy. Kov Mater 2010;48:277–84.

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