Solidification, Microstructure and Mechanical Properties of Mg-2.8Nd-1.5Gd-0.5Zn-0.5Zr Cast Alloy with Erbium Addition

R. Ahmad[1], A.M.M. Elaswad[1], M. Z. Hamzah[1], N. R. Shahizan[1]

[1]*Department of Manufacturing and Industrial Engineering, Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia, Parit Raja, 86400, Johor, Malaysia*

Abstract. The thermal parameters of Mg-2.8Nd-1.5Gd-0.5Zn-0.5Zr cast alloy with 0.25 wt.% of erbium (Er) were evaluated by the computer-aided cooling curve thermal analysis(CA CCTA), whereas the microstructure analysis was investigated by the optical microscope and scanning electron microscopy. Results from the cooling curve and microstructure analysis showed that Er altered the grain size of the alloys. In addition, the grain size was reduced by approximately 19.6% with the addition of Er. Scanning electron microscopy results showed that Er formed an Mg-Zn-Nd-Er phase which distributed along the grain boundaries. Furthermore, the mechanical properties were investigated by hardness and tensile tests with Er addition. The addition of 0.25 wt.% of Er significantly improved the ultimate tensile strength and yield strength. In addition, the hardness value of Mg-2.8Nd-1.5Gd-0.5Zn-0.5Zr increased by 13.9% with Er addition.

1 Introduction

The request of weight reduction for structural materials has become increasingly strong in recent years[1]. Magnesium light alloys have aroused increasing interest in recent years for applications in aerospace, aeronautics and automotive [2],due to their high strength weight ratio and low density excellent castability and good machinability [3, 4].Rare-earth (RE) metals are added to Mg alloys to improve their strength, microstructure and creep resistance. Two groups of RE elements considered for Mg alloys are yttrium (Y), gadolinium (Gd), Erbium (Er) and dysprosium (Dy), which are highly soluble, and neodymium (Nd), cerium (Ce), and lanthanum (La), which are less soluble; both groups are used to improve the properties of Mg alloys [5]. Rare earth Er has a large solubility in Mg (6.56 at.%), whose beneficial effects in aluminium alloys has been recently identified [6]. In recent years, some novel magnesium alloys containing heavy rare earth elements such as Mg-Gd-Y-Zr, Mg-Dy-Gd-Nd, and Mg-Dy-Gd-Zr alloys have been developed [7]. It has been reported that the content variation of rare earth elements (RE) and element Er in the alloys can influence the phase formation and mechanical properties greatly [8]. The hard eutectic phases that formed as a result of rare earths addition also strengthen the alloy. Generally, magnesium strengthening through rare earth addition results from grain boundary strengthening caused by precipitates and solid solution. Mg–RE alloys are used in military aircrafts and aerospace applications [9]. Adding Erbium into a Mg–Zn–Zr alloy improves the deformability of the latter and leads to the formation of a fine and uniform microstructure. In addition, erbium can increase the thermal stability and improve the mechanical properties of the alloy structure [10]. This research aims to investigate the addition of Er separately on solidification ehaviour, microstructure and mechanical properties of Mg-Nd-Gd-Zn-Zr cast alloy.

2 Experiment procedures

Magnesium cast alloy Mg-2.8Nd-1.5Gd-0.5Zn-0.5Zr has been used as a base alloy, 0.25 wt.% Erbium (Er) was separately added to the molten metal. The casting was carried out in an electric resistance furnace for a steel crucible under the protection of 2% SF6 and Ar [11, 12]. After the addition, the melt was stirred for approximately 5 min to ensure dissolution of the alloying elements [13]. The molten metal was then poured at 750 ° C ±10 into a preheated steel mould. The mould was then immediately covered to protect the metal from each reaction with air, while the temperature-time data was recorded during cooling to room temperature. The cooling-curve parameters (i.e., temperature and time) for the formation of the phases and the solidification behavior of the modified and unmodified alloys were determined by CA-CCTA. A K-type thermocouple was immersed from the top of the preheated stainless steel mold and placed at the center (Fig.1). The temperature–time data were recorded using a high-speed data acquisition system (EPAD-TH8-K) connected to a computer running the DEWE Soft 7.5 package at a dynamic rate of 100 Hz per channel. The smoothing and plotting of the first derivative of the cooling curves were carried out using the FlexPro 9.0 data analysis software for determining the phase solidification characteristics data. In order to ensure the reliability of the results, the thermal analysis was repeated three times for each composition. The samples for microstructure of the alloys were analysed using an Olympus optical microscope (OM) and scanning electron microscope (SEM). The grain size was evaluated using the linear intercept method, according to ASTM E112-10 and the values of the volume fraction evaluated by an image analysis method specified in ASTM E112-04. The standard of grinding and polishing were used on the specimens for OM observation and etched in (5 Ml acetic acid, 6g picric acid, 10 Ml distilled water and 100 Ml ethanol). The castings were machined and milled to obtain the precise specimen dimensions for the cylindrical tensile test according to ASTMB577M.

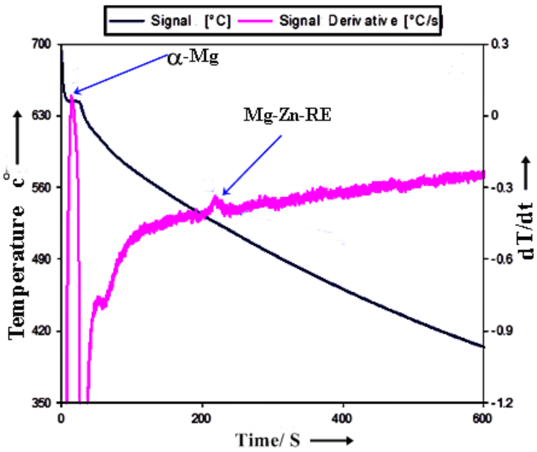

Figure 1. Illustration of mean solidification phases of Mg-2.8Nd-1.5Gd-0.5Zn-0.5Zr.

Table 1. Solidification characteristics of parameters determined during solidification of Mg-2.8Nd-1.5Gd-0.5Zn-0.5Zr alloy

Symbol	Description
$T_S^{\alpha\text{-Mg}}$	Start of α-Mg nucleation (liquidus) / °C
$T_{EU}^{\alpha\text{-Mg}}$	Eutectic growth temperature of dendrite α-Mg
$T_{Eu}^{Mg\text{-}Zn\text{-}RE}$	Formation of eutectic growth phase (Mg-Zn-RE) / °C
Te	End of solidification (solidus) / °C
ΔT	The total solidification temperature $\Delta T = (T_S^{\alpha\text{-Mg}} - Ts)$
Δt	The total solidification time $\Delta t = (t_S^{\alpha\text{-Mg}} - ts)$

3 Result and discussion

3.1 Cooling curves analysis

The obtained cooling curves were analyzed to identify the phase evolution of the base alloy systems during solidification with and without Er addition. The main cooling-curve parameters of the base alloy and Er containing alloys are listed in Table 2.

Table 2. Cooling-curve parameters of the base alloy and the base alloy with Er additions

Parameters	Alloys	
	0 wt.% Er	0.25 wt.% Er
$T_S^{\alpha\text{-Mg}}$ / °C	645.8	643.8
$t_S^{\alpha\text{-Mg}}$/s	11.01	10.01
$T_{EU}^{\alpha\text{-Mg}}$/ °C	635.9	627.7
$t_{EU}^{\alpha\text{-Mg}}$/s	29.18	25.34
$T_{EU}^{Mg\text{-}Zn\text{-}RE}$ / °C	526.8	526
$T_{EU}^{Mg\text{-}Zn\text{-}RE}$/s	218.7	201.9
$T_{S/\,°C}$	521.4	506.1
$t_{S\,/S}$	231.57	203.1

The solidification process of Mg alloys starts with the nucleation and growth of the primary α-Mg phase, followed by other phases containing the alloying elements. As shown Table 2, the α–Mg phase of base alloy was formed at 635.9 °C , and the solidification beginning at 645.8 °C ($T_S^{\alpha\text{-Mg}}$). The experimental results showed that when 0.25 wt.% Er is added, the nucleation temperature of α-Mg phase decreases, which obtained at 643.8 °C. It is reported that the addition of erbium into Mg–Zn alloys facilitated the formation of the α-Mg phase at around 638°C, and this phase appeared as the first peak, which corresponded to the solidification of the magnesium matrix [9, 14].

The eutectic growth temperatures of α-Mg phase $T_{EU}^{\alpha\text{-Mg}}$ decreased by addition of 0.25 wt. % of Er, which obtained at 627.7 °C. The decrease in the nucleation growth of α-Mg phase led to the decrease in the solidus temperature and simultaneously widened the solidification range [9].

Formation of the Mg-Zn-RE secondary phase is the last stage of solidification. The main characteristic parameters of the Mg-Zn-RE phase were determined using the first derivative and included the eutectic growth temperature $T_{EU}^{Mg\text{-}Zn\text{-}RE}$ and time $t_{EU}^{Mg\text{-}Zn\text{-}RE}$. Since the liquidus projection represents only the primary phase formed, it is necessary to know the primary and liquid phases in order to understand the solidification path, including which eutectic transformation takes place [15]. The results showed that the Mg-Zn-RE phase of base alloy was formed at 526.8 °C and With addition of 0.25 wt.% Er, the $T_{Eu}^{Mg\text{-}Zn\text{-}RE}$ temperature of Mg-Zn-RE phase decreased by 0.8 °C. The smaller magnitude of this effect compared with that of the previous addition may be due to the Er content in the intermetallic secondary phase [9].

The effect of Er addition on frozen time was obtained by, solidification time, $\Delta t = (t_S^{\alpha\text{-Mg}} - ts)$. The analysis results of the cooling curve parameters showed that the frozen time (solidification time) of the base alloy decreased from 220.56 s to 193.09 s with Er addition. This result is similar to that obtained by Fletcher, M., et al. [16], who reported that the decrease in liquid temperature was reflected on the grain size of the α-Mg phase. Er has an important effect on the solid solubility of

Zn in the matrix, which changes as a result of the decrement of the solidus curve that shortens the nucleation time and reduces the grain size [8].

3.2 Microstructure analysis

The optical microstructures of the base alloy (a) and base alloy treated with Er (b) are shown in Figure 2. With Er, it greatly refines grain size of Mg-2.8Nd-1.5Gd-0.5Zn-0.5Zr alloy.

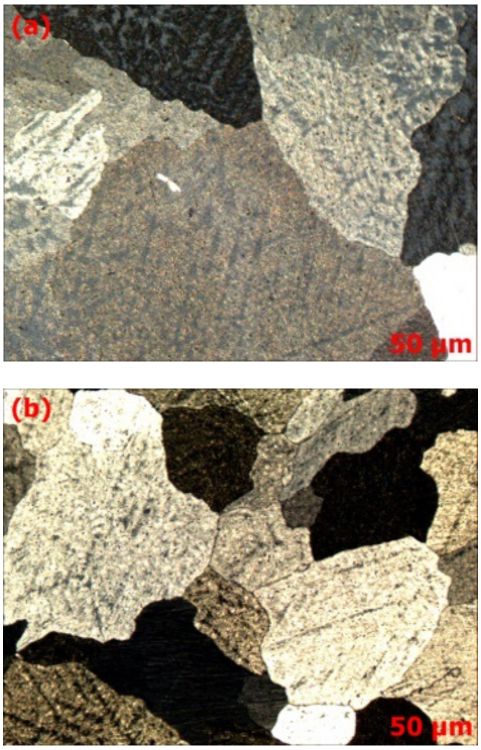

Figure 2. Microstructure images of (a) base alloy and (b) Er-modified alloy.

The addition of Er significantly decreased grain size from 316.8 µm to 254.4 µm. This grain refinement is due to the reduction of the liquid temperature and solidification time [17]. Similar observations were previously reported by Seetharaman, S., et al. [18], who reported that adding Er to the Mg–Al alloys significantly decreased the average grain size. Previous studies reported that the microstructures of Mg alloys could be refined by adding Er, which is a surface reactive element that restrains the growth of the secondary phase and thus reduces the solidification time [10, 14, 19]. These findings were confirmed by frozen time results in this investigation.

In addition, Er increased the volume fractions of the intermetallic secondary phase from 23.6% to 28.1%. The primary α-Mg grains were then enveloped by continuous networks of eutectic compounds, which have a strong tendency to detach when the grains are refined. Scanning electron microscopic (SEM) observations of base alloy treated with 0.25 wt.% of Er is shown in Figure 3. The SEM image of 0.25 wt.% Er shows the new intermetallic phase (Mg-Zn-Nd-Er) crystallized along the grain boundaries. These results can be attributed to the extremely low solubility of RE elements in the solid solution. The presence of these elements in Mg decreases the solubility of Zn in Mg. Thus, during solidification, the RE elements form the Mg–Zn–RE phase until the available RE is used without any formation of other compounds [20, 21].

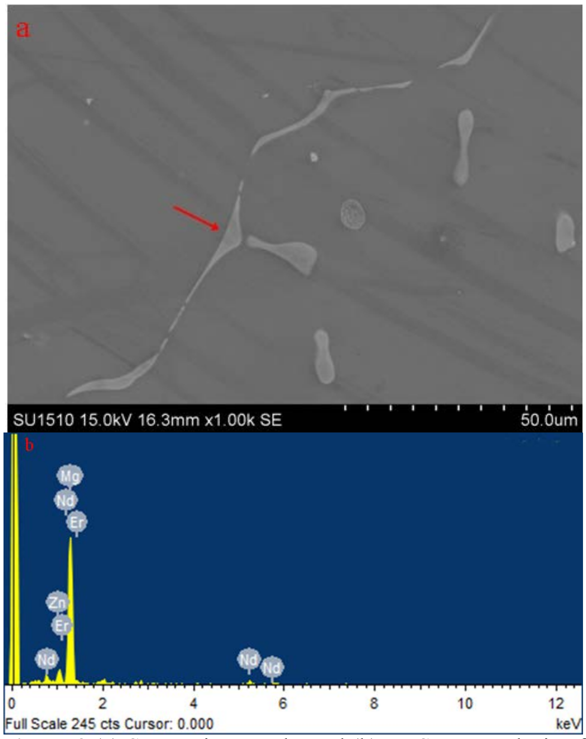

Figure 3 (a) SEM Micrographs and (b) EDS spot analysis of 0.25 Er containing alloy.

3.3 Mechanical properties

The effect of 0.25 wt.% Er on the tensile properties of the Mg-2.8Nd-1.5Gd-0.5Zn-0.5Zr alloy is shown in Table 3. The tensile strength had increase with 0.25 wt.% Er, which was improved by around 13.6%. Acceptable yield strength (YS) was also achieved, as shown in Table 3. The YS value reflects the alloy ductility, where it improved by 6 %. Moreover, the elongation index degraded 0.25 wt.% Er was added. The mechanical properties of the Mg alloys can be extensively influenced by alloying elements. Moreover, the strength of cast Mg alloys can be obtained through solid solution hardening, grain refinement, age hardening, and dispersion hardening [22, 23]. The solute atoms of Er in the Mg matrix can exert dragging forces on the grain boundary motion and decrease the recrystallization kinetics. The improved microstructure and mechanical properties can be attributed to the dissolved Er in the Mg matrix [14]. The tensile properties of Mg–Zn alloys are improved with the Er content. Er is highly soluble in Mg, which has a compact hexagonal structure. The solid solubility of Er in Mg decreases at decreasing temperatures. The atomic radius of Er is 29.2% larger than that of Mg, and thus Er addition leads to intensive solution strengthening in Mg. Increased solution strength and dispersion strength result in further increase in strength [8, 19].

Table 3. Tensile properties of base alloy treaded with Er.

Alloys	UTS, Mpa	YS, Mpa	EL %
0 wt.% Er	109	82.09	5.934
0.25 wt.% Er	123.91	87.04	3.843

The base alloy samples as cast and with 0.25 wt. % Er was examined to obtained the hardness value. However, it has indicated that the hardness value increases from 48.33 Hv for base alloy to 55.08 Hv for 0.25 wt.% Er respectively. The strengthening of Mg alloys is due to the solid solution of the borderline-sized RE atoms and second-phase hardening attributed to the Mg12RE intermetallic phase [24]. The mechanical properties of the Mg alloys are strongly influenced by their microstructure properties, such as grain size, volume fraction, and distribution of intermetallic phases [25].

4 Conclusions

The effect of the addition of 0.25 wt.% Er on the solidification characteristics, microstructure, and mechanical properties of Mg-2.8Nd-1.5Gd-0.5Zn-0.5Zr cast alloy was investigated. From the analysis, the following can be summarized:

1-The computer-aided cooling curve thermal analysis and microstructure results showed that Er improve solidification time and grain refinement.

2-Er decreased the solidification time of alloys by approximately 12% and thus decreased the grain size by 19.6%.

3-The mechanical properties of Mg-2.8Nd-1.5Gd-0.5Zn-0.5Zr had improved. The UTS improved by 13.6% and Ys improved by 6%. Moreover, the hardness value of the alloys increased with Er addition.

References

1. Zhang, Li, Zhang, Jinghuai, Leng, Zhe, Liu, Shujuan, Yang, Qiang, Wu, Ruizhi, and Zhang, Milin. "Microstructure and mechanical properties of high-performance Mg–Y–Er–Zn extruded alloy," Materials & Design (1980-2015). 256, **54**.(2014).
2. Wang, Qu Dong, Li, Da Quan, Li, Qiang, and Ding, Wen Jiang. "Effects of Er on Microstructure and Mechanical Properties of Mg-Zn-Er-Zr Magnesium Alloys," Materials Science Forum. 105, **546-549**.(2007).
3. Zhang, Jinyang, Xu, Min, Teng, Xinying, and Zuo, Min. "Effect of Gd addition on microstructure and corrosion behaviors of Mg–Zn–Y alloy," Journal of Magnesium and Alloys. 319, **4**.(2016).
4. Ma, Yutao, Zhang, Xingguo, Liu, Hongbin, and Meng, Linggang. "Effects of Er on the microstructure and properties of AZ31 magnesium alloy prepared via the EMS process," Rare Metals. 339, **29**.(2010).
5. Z. M. Sheggaf, R. Ahmad, M.B.A. Asmael, and A.M.M. Elaswad, and 1). "Solidification, microstructure, and mechanical properties of the as-cast ZRE1 magnesium alloy with different praseodymium contents," International Journal of Minerals, Metallurgy, and Materials**24**.(2017).
6. Rosalbino, F., Angelini, E., De Negri, S., Saccone, A., and Delfino, S. "Effect of Erbium addition on the corrosion behaviour of Mg–Al alloys," Intermetallics. 55, **13**.(2005).
7. Zhang, Jing, Zhang, Xu Feng, Pan, Fu Sheng, Liu, Chuan Pu, and He, Qu Bo. "Microstructure and Mechanical Properties of an Mg-Zn-Zr Alloy Modified by Rare Earth of Erbium," Materials Science Forum. 810, **610-613**.(2009).
8. Li, Han, Du, Wenbo, Li, Shubo, and Wang, Zhaohui. "Effect of Zn/Er weight ratio on phase formation and mechanical properties of as-cast Mg–Zn–Er alloys," Materials & Design. 259, **35**.(2012).
9. Ahmad, R, Sheggaf, ZM, and Asmael, MBA. "Effect of praseodymium and erbium additions on solidification characteristics, microstructure and mechanical properties of as–cast ZRE1 magnesium alloy," Materialwissenschaft und Werkstofftechnik. 218, **48**.(2017).
10. Zhang, Jing, Ma, Qi, and Pan, Fusheng. "Effects of trace Er addition on the microstructure and mechanical properties of Mg–Zn–Zr alloy," Materials & Design. 4043, **31**.(2010).
11. Pekguleryuz, Mihriban O, Kainer, Karl, and Kaya, A Arslan, 2013, Fundamentals of magnesium alloy metallurgy, Elsevier.
12. Katsarou, Lydia, Mounib, Maher, Lefebvre, Williams, Vorozhtsov, Sergey, Pavese, Matteo, Badini, Claudio, Molina-Aldareguia, Jon Mikel, Jimenez, Carmen Cepeda, Prado, Maria Teresa Pérez, and Dieringa, Hajo. "Microstructure, mechanical properties and creep of magnesium alloy Elektron21 reinforced with AlN nanoparticles by ultrasound-assisted stirring," Materials Science and Engineering: A. 84, **659**.(2016).
13. Sun, Ming, Hu, Xiaoyu, Peng, Liming, Fu, Penghuai, and Peng, Yinghong. "Effects of Sm on the grain refinement, microstructures and mechanical properties of AZ31 magnesium alloy," Materials Science and Engineering: A. 89, **620**.(2015).
14. Zhang, Jing, Li, Weiguo, Zhang, Baoxiang, and Dou, Yuchen. "Influence of Er addition and extrusion temperature on the microstructure and mechanical properties of a Mg–Zn–Zr magnesium alloy," Materials Science and Engineering: A. 4740, **528**.(2011).
15. Suzuki, A., Saddock, N. D., Jones, J. W., and Pollock, T. M. "Solidification paths and eutectic intermetallic phases in Mg–Al–Ca ternary alloys," Acta Materialia. 2823, **53**.(2005).
16. Fletcher, M, Bichlerl, L, Sediako, D, and Klassen, R, 2011, Compressive Creep Behaviour of Extruded Mg Alloys at 150° C.
17. Sheggaf, ZM, Ahmad, R, Asmael, MBA, and Elaswad, AMM. "Solidification, microstructure, and mechanical properties of the as-cast ZRE1 magnesium alloy with different praseodymium contents," International Journal of Minerals, Metallurgy, and Materials. 1306, **24**.(2017).
18. Seetharaman, Sankaranarayanan, Blawert, Carsten, Ng, Baoshu Milton, Wong, Wai Leong Eugene, Goh, Chwee Sim, Hort, Norbert, and Gupta, Manoj. "Effect of

erbium modification on the microstructure, mechanical and corrosion characteristics of binary Mg–Al alloys," Journal of Alloys and Compounds. 759, **648**.(2015).
19. ZHANG, Jing, HE, Qu-bo, PAN, Fu-sheng, ZHANG, Xu-feng, and LIU, Chuan-pu. "Effects of erbium on microstructure and mechanical properties of as-cast Mg-7Zn-3Al alloy," Transactions of Nonferrous Metals Society of China. s22, **18**.(2008).
20. Rzychoń, Tomasz, Szala, Janusz, and Kiełbus, Andrzej. "Microstructure, castability, microstructural stability and mechanical properties of ZRE1 magnesium alloy," Archives of Metallurgy and Materials. 245, **57**.(2012).
21. Rzychoń, T, Kiełbus, A, and Szala, J. "Microstructure and fluidity of sand cast ZRE1 alloy," Journal of Achievements in Materials and Manufacturing Engineering. 135, **26**.(2008).
22. Pekguleryuz, Mihriban O, Kainer, Karl, and Kaya, Aslan, 2013, Fundamentals of magnesium alloy metallurgy, Elsevier.
23. Friedrich, Horst E, and Mordike, Barry L, 2006, Magnesium technology, Springer.
24. Yang, Zhong, Li, JP, Zhang, JX, Lorimer, GW, and Robson, JAMSEL. "Review on research and development of magnesium alloys," Acta Metallurgica Sinica (English Letters). 313, **21**.(2008).
25. Muraliraja, R, Vettrivel, H, and Elansezhian, R. "Synthesis and Characterization of Magnesium Alloy added with Yttrium and To Study the Microstructure and Mechanical Properties," International Journal of Engineering and Innovative Technology. 338, **2**.(2013).