Al-Khwarizmi Engineering Journal, Vol. 7, No. 2, PP 75 - 82 (2011)

Al-Khwarizmi Engineering Journal

Effect of Lanthanum Addition on the Microstructure of Mg-4Al Alloy

Ahmed A. Moosa

Department of Production and Metallurgy Engineering/ University of Technology
Email: ahmedmuot@yahoo.com

(Received May 2010; accepted 17 February 2011)

Abstract

This research was to determine the effect of rare earth metal (REM) on the as-cast microstructure of Mg-4Al alloy. The rare earth metal used here is Lanthanum to produce Mg-4Al-1.5La alloy. The microstructure was characterized by optical microscopy. The phases of this alloy were identified by X-ray diffraction. The microstructure of Mg-4Al consists of α-Mg and grain boundaries with precipitated phase particles. With the addition of Lanthanum, three distinct phases were identified in the X-ray diffraction patterns of the as cast Mg-4Al-1.5La: Mg, $Al_{11}La_3$, Al_4La. The $Mg_{17}Al_{12}$ phase was not detected. The addition of Lanthanium increases the hardness and decrease the wear rate of Mg-4Al.

Keywords: *Metallic alloys, magnesium-aluminum-rare earth alloys, microstructure.*

1. Introduction

Light-weight magnesium alloys have attracted increasing interest in recent years for applications in the automotive, aircraft and electronic industries.

Magnesium alloy die-castings are very suitable for automotive applications because vehicle weight reduction and consequently energy saving are becoming the world focus. Magnesium is one-third less dense than Aluminum and four-fifths less dense than iron [1, 2].

A major development in creep-resistant magnesium alloys has been the emergence of rare-earth (RE)–containing alloys. This group of Mg-Al-RE alloys contains at least one and, in general, a mixture of RE elements, as aPrecipitate. This alloy system exhibits a major improvement in creep resistance. These alloys did not find their place in industry due to various reasons such as poor castability and low strength.[3,4]

In Mg-Al-REM alloys however, under slow solidification rates (sand and permanent mold casting), it was discovered that the rare earth reacted preferentially with aluminum and favored Al_2RE formation with no improvement in creep resistance. Under die-casting conditions (higher solidification rates), Al_4RE formation was favored and improved creep resistance was achieved [1, 5].

Recently developed alloys containing one or more rare earths have been found to possess improved properties over the early mischmetal alloys like AE42 alloy (Mg - 3.74Al - 0.87Ce - 0.43 La -0.26 Nd- 0.08 Pr) [6]. The AE42 casting alloy (Mg-4Al-2REM) was developed for high temperature applications. Aluminum is added to improve castability and room temperature mechanical properties while REM addition is for creep resistance. However, the properties of AE42 deteriorate rapidly when the temperature is above 150 °C. Therefore, there still remains a limitation to its use at high temperatures [6].

A certain dependence of the solubility of REM in magnesium on the atomic size of lanthanides has been established. It correlates with the change in the atomic radii of REM, which grows with growth in the atomic number and closeness to the atomic radius of magnesium [7]. It is well established that REM of the yttrium subgroup (Y, Gd, and Lu) posses a considerably higher solubility in solid magnesium than REM of the cerium subgroup (La, Ce, Pr,) [7, 8].

Many studies have been conducted on the effects of RE on microstructures of Mg-REM alloys, but different phases were reported [9-12]. High-pressure die-cast Mg–4Al–4RE–0.4Mn (RE = La, Ce) magnesium alloys were studied by Zhang et al.[13] . Two binary Al–Ce phases, $Al_{11}Ce_3$ and Al_2Ce, are formed mainly along grain boundaries in Mg–4Al–4Ce–0.4Mn alloy, while the Mg–4Al–4La–0.4Mn alloy contains only α-Mg and $Al_{11}La_3$. The results of the theoretical calculation showed that the stability of $Al_{11}La_3$ is the highest among four Al–RE intermetallic compounds supports the experimental results further [13].

Powell et al. [1] studied the Microstructure and Creep Behavior in AE42 Magnesium Die-Casting Alloy. A lamellar-phase $Al_{11}RE_3$, which dominates the interdendritic microstructure of the alloy, partly decomposes above 150°C into Al_2RE and Al (forming $Mg_{17}Al_{12}$). Die-cast Mg –4Al–4RE–0.4Mn (RE = Ce-rich mischmetal) and Mg –4Al–4La–0.4Mn magnesium alloys have been investigated by Zhang et al.[14] **.** The results show that the two phases, $Al_{11}RE_3$ and Al_2RE, are formed along grain boundaries in Mg –4Al–4RE–0.4Mn alloy, while the phase compositions of Mg –4Al–4La–0.4Mn alloy mainly consist of α- Mg phase and $Al_{11}La_3$ phase. The $Al_{11}La_3$ phase occupies a large grain boundary area of the alloy microstructure and grows with complicated morphologies.

Li et al. [15] found that there are some grain refinement and thinning of β-$Mg_{17}Al_{12}$ phase in AZ91D alloy containing Calcium (0.1- 1.0 wt. %). Increasing Ca content resulted in the formation of Al_2Ca phase as well as in the reduction in quantity of β-$Mg_{17}Al_{12}$ phase. The ultimate tensile strength and relative elongation worsened which was explained by the presence of Al_2Ca phase on the grain boundaries.

In this work REM, La, will be added to Mg-4Al to study the influences of Al–REM phases on the microstructures of Mg-4Al-1.5La cast alloy.

2. Experimental Methods

The Mg-Al alloy (Mg-4Al) and Mg-4Al-1.5 La alloy were prepared from commercially pure ingots of magnesium, aluminum and lanthanum. To minimize the amount of inclusions or oxides films in the specimen during alloy preparation, a special melting crucible was used. A schematic drawing of the equipment used is shown in Figure(1). Each alloy was first prepared by melting the desired amount of materials in a stainless steel crucible in an electric resistance furnace under Argon gas. Two stainless steel crucibles were used, the inner melting crucible and the second outer crucible. The outer crucible has two tubes at the upper cover, one tube through which argon gas passes and the second tube for argon gas outlet. Type -K thermocouple was inserted through the cover of the outer crucible for recording real temperature near inner crucible with a controlled temperature ± 2 °C.

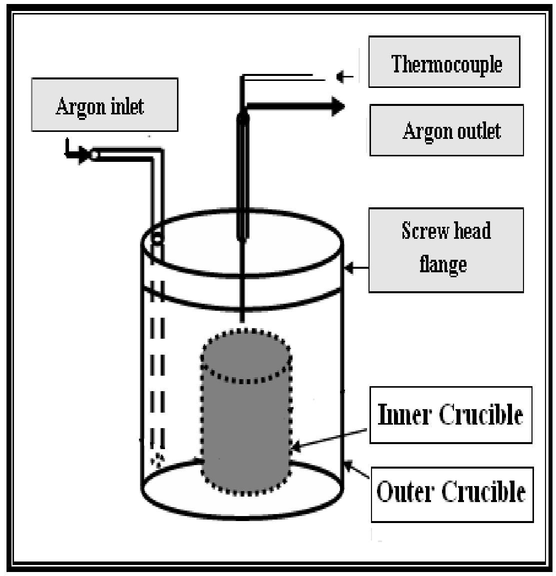

Fig.1. Schematic Diagram for Melting Crucible for Mg Alloys.

Magnesium (99.5% purity), Aluminum (99.9% purity) and Lanthanum (99.9% purity, MTI Co. China) were used. Each metal was weighed using digital balance (Precisa, Model XB220A, Swiss) with accuracy ±100 µg. Mg - 4Al – 1.5 La alloy was prepared by wrapping the Magnesium and Lanthanum in a piece of Aluminum foil which was first put in the inner stainless steel crucible. This inner crucible was then put inside the outer stainless steel crucible. This combined system was then put in an electrical holding furnace under an argon atmosphere with a flow rate of 1.5 L /min . At 900◦C, the melt was purged for about 5 min. After purging, the melt was held for 15 min. The ingot was remelted three times under argon to insure homogeneity. The ingot was furnace cooled under argon atmosphere to room temperature. Molten magnesium and its alloys are volatile substances that have a tendency to oxidize explosively in air and require surface protection in casting processes. Thus, argon gas was used as a cover gas for the molten Magnesium alloys to prevent the rapid surface oxidation and possible burning or igniting explosively in air.

Each ingot was cut into 1cm x 1cm x 0.5cm and then cleaned with ultrasonic bath using alcohol. Each sample was then ground using silicon carbide paper (200, 500,800, 1000 and 1200) grits , washed with water and then polished using cloth with alumina suspension (particle size 0.3 µm). Samples were then ultrasonically cleaned , dried and then etched using enching solutions : Glycol solution : 1 ml HNO3 (conc.), 24 ml water, 75 ml ethylene glycol for (3-5) seconds and then with Acetic-picral solution : 5 ml acetic acid, 6 gm picric acid, 10 ml H2O, 100 ml ethanol (95%)for (3-5) seconds [13]. The microstructure was analyzed by Optical Microscopy, (Olympus, Japan). Vickers hardness test is done by using Digital Micro Vickers Hardness Tester (Type TH715, Beijing, Time High Technology Ltd). For the purpose of accurate readings, an average of ten readings was taken at each point for each sample with 2.94 N load.

The X-ray diffraction for Mg-4Al-RE alloy was carried out using Cu Kα radiation at 40 KV and 30 mA was (XRD 6000 Shimadzu). The sample was machined in the form of disc (3.8 mm thickness and 10 mm diameter). In order to identify the phase present, the sample was continuously scanned within Bragg angle range of (20-50°).

Dry sliding wear tests were conducted on Mg-4Al and Mg-4Al-1.5La specimens on the pin-on-disc apparatus. The wear specimens were cylindrical with a diameter of 10 mm and a height of 20 mm. The specimen slides on a carbon steel disc with a hardness of 38 HRC. The applied load used in this test was 10 N.

Wear rate is calculated from the following formula

$$\text{Wear rate (Wr)} = \Delta w / 2\pi RN\rho_t t \qquad \ldots(1)$$

$$\text{And} \qquad \Delta w = w_1 - w_2 \qquad \ldots(2)$$

where

Wr : wear rate (cm^3/cm)

w_1 : specimen weight before the wear test (gm).

w_2 : specimen weight after the wear test(gm).

R : the distance from the center of the specimen to the center of the steel disc = 7 cm.

N : the rotational speed for the steel disc = 277 rpm.

ρ_t : the density of the Mg-4Al and Mg-4Al-1.5La alloy (1.745 and 1.844 gm/cm^3 respectively).

t : the sliding time = 10 minutes.

3. Results and Discussion

3.1. Microstructure

Pure magnesium had long columnar grains growing from the edge toward the center. The addition of Al caused significant grains refinement. Addition of 4% Al produced a transition to equiaxed grains and a significant reduction in grain size. The microstructure of Mg-4Al alloy composed of the primary α- Mg matrix, and a secondary phase that exists in two kinds of morphologies, i.e., a discontinuous network of coarse particles along grain boundaries, and many spherical particles that distributed both inside grains and at grain boundaries as shown in Figure.2.

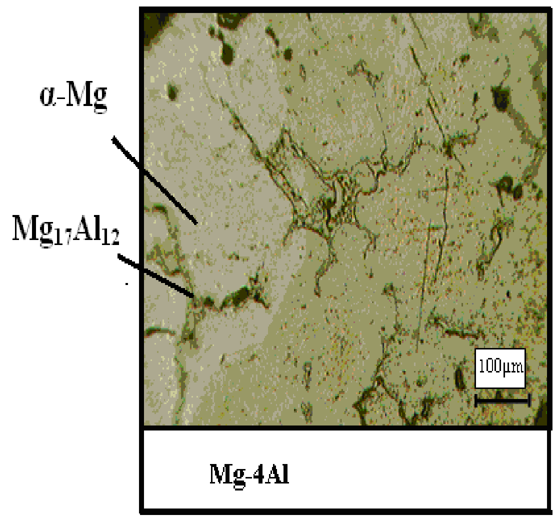

Fig. 2. Optical Micrograph of as Cast Mg-4Al alloy with α-Mg plus Al12Mg17.

Aluminum increases the hardness of Mg , with the strengthening effect being based on solid-solution formation α-Mg and with large β- phase particles, $Mg_{17}Al_{12}$ phase. This is in agreement with the findings of other studies [11, 12] where at high aluminum contents, an interdendritic $Mg_{17}Al_{12}$ grain boundary phase is formed, which lowers the strength at application temperatures beyond 120 °C. The weakening effect of the $Mg_{17}Al_{12}$ phase on the grain boundaries has been invoked as the limiting factor for creep resistance of AZ91alloy (Mg-9Al-1Zn) as reported by Fan et al.[11]. Besides improving the mechanical properties, Aluminum significantly enhances the castability of magnesium.

Chinese Script is also observed in Mg- 4Al alloy as shown in Figure 3. When a eutectic composition solidifies, both α and β solid phases must deposit on the grain nuclei until all of the liquid is converted to solid. This simultaneous deposition results in microstructures made up of distinctively shaped particles of one phase in a matrix of the other phase, or alternate layers of the two phases. Chinese script is one of the characteristic eutectic microstructures. Each eutectic alloy has its own characteristic microstructure when slowly cooled. More rapid cooling, however, can affect the microstructure obtained [16].

The addition of La to Mg-4Al alloy will lead to grain refinement as shown in Figure 4. The mechanism of grain refinement by lanthanum has not been identified [17]. However, the effect of La on growth kinetics can be understood by the growth restriction effect of La rejected ahead of the solid/liquid interface. Because its solid solubility in magnesium is relatively small, rapid enrichment of solute in the liquid ahead of the growing interface would be expected during solidification. Gruzleski and Aliravci [18] proposed a grain refinement mechanism in Mg – Sr system. In this mechanism, Sr may poison the grain surface or poison the fast growing directions of the grains by preferential adsorption of Sr at these sites.

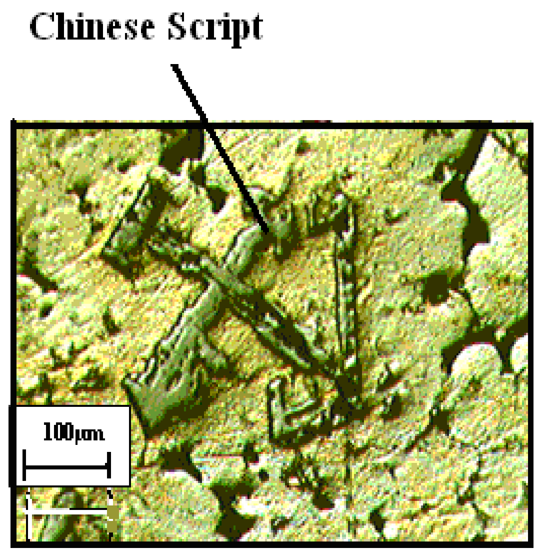

Fig.3. Optical Micrograph of as Cast Mg-4Al Alloy Showing Chinese Script. Etched with (75glycol +24 H_2O +1 HNO_3) Solution.

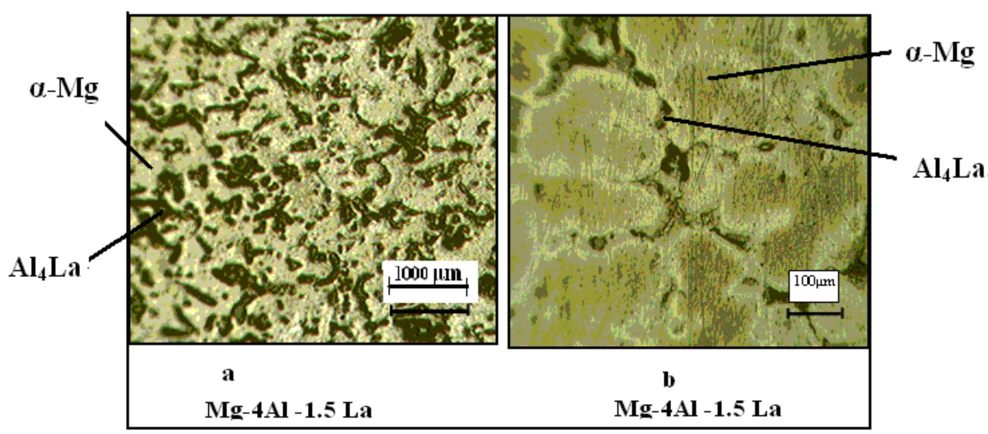

Fig.4. Mg-4Al-1.5 La as Cast Alloy; a) Showing Mg, and Other Al-La Compound ; b) Higher Magnification.

3.2. X-Ray Diffraction

X-ray diffraction patterns of the Mg - 4Al – 1.5 La alloy is shown in Figure 5. Three distinct phases were identified in the patterns: Mg, $Al_{11}La_3$, and Al_4La. The major phase is magnesium. Although there is some disagreement in the literature as to whether $Al_{11}La_3$ and Al_4La are the same phase [19, 20]. In this work they are different. Details of the effects of rare earth additions on phases present in Mg-alloys are listed in Table 1. The formation of α- Mg and $Al_{11}RE_3$ phases in this work are in agreement with many researchers. The discrepancies are in the formation of Al_2RE, Al_4RE or Al_3RE. The formation of either $Al_{11}RE_3$ or Al_4RE is sensitive to the individual rare earth element as evidenced by a relationship between the relative amounts of $Al_{11}RE_3$ versus Al_4RE. The $Mg_{17}Al_{12}$ phase was not observed in Mg-4Al- 1.5 La alloy.

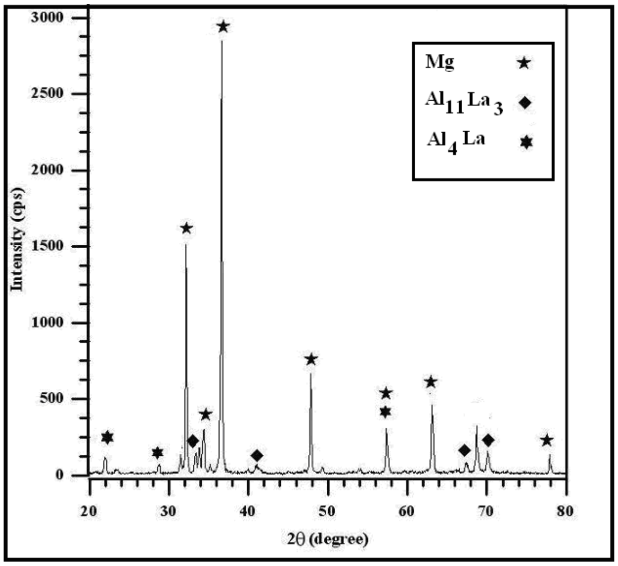

Fig.5. X-Ray Diffraction of Mg-4Al-1.5 La.

Table 1,
Effect of Rare Earth Addition on Phases Present in Mg-4Al Alloys.

	Alloy	Phases	Reference
AE42	Mg-4Al -2RE	Mg, $Al_{11}La_3$	Sun et al. [Ref. 12]
AZL2	Mg-9Al-0.7Zn-2L	Mg, $Mg_{17}Al_{12}$, $Al_{11}La_3$,Al_8LaMn_4	Fan et.al. [Ref 11]
AE42	Mg-4Al -2RE	Mg, $Al_{11}RE_3$, Al_2RE	Powell et al. [Ref. 1]
AE42	Mg-4Al -2RE	Mg,$Mg_{17}Al_{12}$	Rzychoń et al. [Ref.9]
AE44	Mg-4Al -4RE	Mg, $Al_{11}RE_3$, Al_3RE	Rzychoń et al [Ref.9]
	Mg-5.5Al -1Ce	Mg, $Mg_{17}Al_{12}$,Al_4Ce	Zhou et al.[ref 10]
AE44	Mg-4Al -4La	Mg, $Al_{11}La3$	Zhang et al.[Ref 13]
AE44	Mg-4Al -4Ce	Mg, $Al_{11}Ce3$, Al_2Ce	Zhang et al.[Ref 13]

In order to suppress the eutectic reaction to form ($Mg_{17}Al_{12}$) phase in Mg – Al – La system , then the element La should react with aluminum and form an Al_zLa_w intermetallic(where z,w are constants). This is true only if the affinity of the element La for Al is higher than its affinity for Mg; then the formation of Al_zLa_w will be preferred to Mg_x La_y. Analyzing the known diagrams of binary Mg – La and Mg – Al systems [16], it is clear that only rare-earth metals (RE), alkaline-earth elements, and transition elements of the third group of the Periodic System possess such affinity.

The reason for the absence of $Mg_{17}Al_{12}$ in our results may be attributed to the higher content of rare **earth elements** (i.e., La) in the alloy. Most Al is present in the form of $Al_{11}La_3$ and Al_4La, with little Al sequestered as solute in the α-Mg matrix. The maximum solid solubility of La in Mg is about (0.79 wt %), consequently more La atoms are utilized in the formation of intermetallic compounds [13].

The Solid solubility of REM in magnesium is very low, which is further reduced by the presence of Al [14]. Because of the high chemical stability of $Al_{11}RE_3$ and Al_4RE phases, rare earths are combined with Al and form $Al_{11}RE_3$ until all the available rare earths are used without any formation of pseudo-binary Mg-RE or Mg-Al phase or pseudo-ternary Mg-Al- RE phase [13].

Depending on the composition, precipitates of other types of compounds have also been mentioned in the literature. Pettersen et al. [21] suggested that when RE/Al weight ratio is above 1.4 all of the aluminum will be tied up as $Al_{11}RE_3$ in which case further precipitation of other phases such as anot Pekguleryuz et al. [22] report that the alloys show different microstructures based on the Sr/Al ratio. For Sr/Al ratio below about 0.3, Al_4Sr intermetallic is the only second phase in the structure. When the Sr/Al ratio is higher, a second intermetallic phase (a ternary Mg-Al-Sr phase) is also observed. Sr/Al controls the formation of $Mg_{17}Al_{12}$ as well. When the Sr/Al ratio is very low, there would be insufficient amount of Sr to bind all Al and the excess Al would form the $Mg_{17}Al_{12}$ phase.

In the alloy of this research more aluminum atoms were consumed by the formation of $Al_{11}La_3$ and Al_4La phases. It leads additionally to decreasing of aluminum content in solid solution α-Mg and this alloy probably will be better to work at elevated temperature, her type of Al-Re phase or $Mg_{12}RE$ becomes possible.

3.3. Hardness and Wear Rate

The hardness of Mg-4Al and Mg-4Al -1.5 LA alloys were measured using Vickers hardness (2.94 N). The overall hardness of Mg-4Al increases with La addition as shown in Figure 6. The increase in the hardness due to La addition is due to the refining of the microstructure due to nucleation of $Al_{11}La_3$ phases.

The wear rate of Mg-4Al and Mg-4Al -1.5 La alloys were measured using pin on disk apparatus. The load applied is 10 N and the duration is 10 min. It is clear from Figure 7, that the wear rate for Mg-4Al -1.5 La is lower than that for Mg-4Al. This is in agreement with the hardness measurement where the La addition increases the hardness of the alloy.

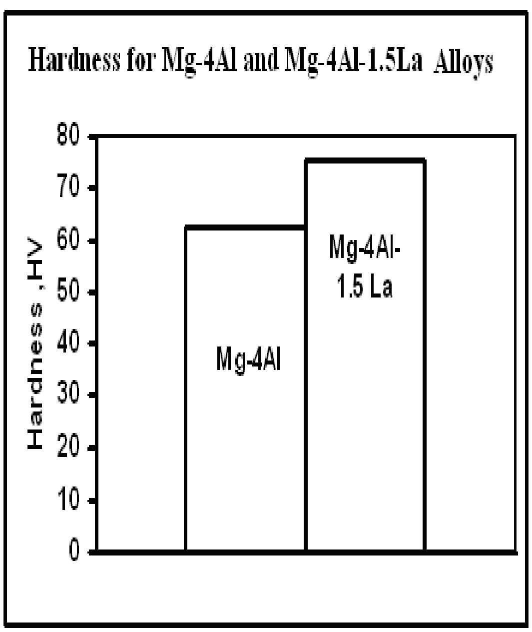

Fig.6. Vickers Hardness of Mg-4Al and Mg-4Al-1.5La Alloys.

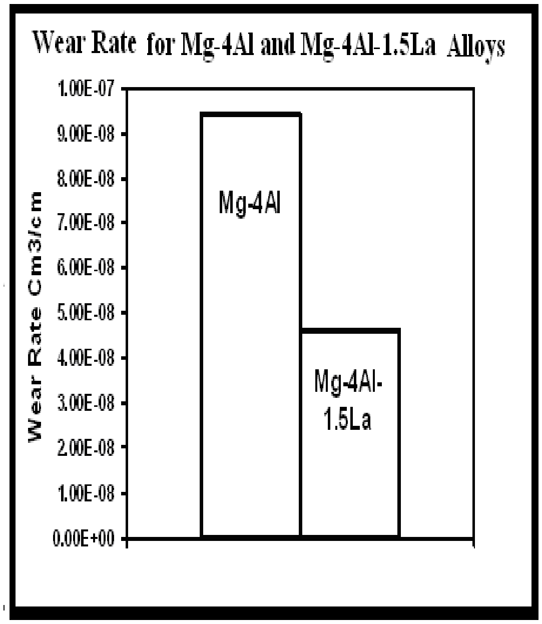

Fig.7. Wear Rate of Mg-4Al and Mg-4Al-1.5La Alloys.

4. Conclusions

1- In the as-cast condition the microstructure of Mg-4Al alloy consists of primary α- grains with the grain boundaries precipitates of large β- phase particles.
2- The addition of lanthanum refined β- phase and formed $Al_{11}La_3$ strengthening phase, which improved the hardness and wear resistance of the Mg-4Al- 1.5La alloy.
3- With the addition of lanthanum, the $Mg_{17}Al_{12}$ phase was not detected.

5. References

[1] Bob R. Powell, Vadim Rezhets, Michael P. Balogh, and Richard A. Waldo, Microstructure and Creep Behavior in AE42 Magnesium Die-Casting Alloy, J. of Metals , Vol.54 , August 2002, pp.34-38
[2] Y. Xu, L.S. Chumbley, G.A. Weigelt, and F.C. Laabs, Analysis of interdiffusion of Dy, Nd, and Pr in Mg, J. Mater. Res., Vol. 16, No.11, Nov. 2001, p. 3288
[3] M.O. Pekguleryuz and A.A. Kaya: in Magnesium Alloys and Their Applications, K.U. Kainer, ed., Wiley-VCH Verlag GmbH, Germany, 2003, pp. 74–93.
[4] F. Khomamizadeh, B.Nami, and S. Khooshkhooei , Effect of Rare-Earth Element Additions on High-Temperature Mechanical

Properties of AZ91 Magnesium Alloy, Metallurgical and Materials Transaction A, Vol. , 36A, Dec., 2005, pp. 3489-3494.

[5] E.G. Sieracki, J.J. Velazquez, and K. Kabiri, "Compressive Stress Retention Characteristics of High Pressure Die Cast Magnesium Alloys," SAE Technical Publication No. 960421 (Warrendale, PA: TMS, 1996).

[6] A. A. Luo, and M. O. Pekguleryuz, "Cast Magnesium Alloys for Elevated Temperature Applications," J. Mat. Sci., vol. 29, 1994, pp. 5259-5271.

[7] L. L. Rokhlin, Magnesium Alloys Containing Rare Earth Metals.Structure and Properties, Taylor and Francis, London – NewYork (2003).

[8] L. L. Rokhlin , Structure and Properties of Alloys of the Mg-REM system , Metal Science and Heat Treatment, Vol. 48, Nos. 11 – 12, 2006, pp. 487-490.

[9] T. Rzychoń, A. Kiełbus ,Effect of rare earth elements on the microstructure of Mg-Al alloys, Journal of Achievements in Materials and Manufacturing Engineering,Vol. 17,No. 1-2, July-August,2006, pp. 149-152.

[10] H. Zhou, X. Zeng, L. Liu, Y. Zhang, Y. ZHU, W. Ding, Effect of cerium on microstructures and mechanical properties of AZ61 wrought magnesium alloy, J. OF MAT. SCI. Vol. 39, 2004, pp.7061 – 7066.

[11] Y. Fan , G. Wu , H. Gao , G. Li , C. Zhai, Influence of lanthanum on the microstructure, mechanical property and corrosion resistance of magnesium alloy , J. Mater Sci, Vol. 41,2006, pp. 5409–5416.

[12] Y. Sun, S. Xue, J. Bai, F. Xue, Heat Resistant Magnesium Alloys With Rare Earth and Alkaline Additions, Materials Forum ,Vol.29 , 2005 , pp. 311-317.

[13] J.Zhang , D.Zhang , Z.Tian , J.Wang, K.Liu , H. Lu, D.Tang , J.Meng, Microstructures ,Tensile properties and Corrosion Behavior of Die Cast Mg-4Al-Based Alloys Containing La and /or Ce , J. Mater. Sci. Eng. A, vol., 489, 2008, pp.113-119.

[14] J. Zhang, P. Yu, K. Liu, D. Fang, D. Tang, and J. Meng, Effect of substituting cerium-rich mischmetal with lanthanum on microstructure and mechanical properties of die-cast Mg –Al–RE alloys, Materials and Design, Vol.30,No.7, August 2009, pp. 2372-2378 .

[15] P. Li, B. Tang, E.G. Kandalova, Microstructure and properties of AZ91D alloy with Ca additions, Materials Letters, Volume 59, Issue 6, March 2005, pp. 671-675.

[16] ASM. VOL.9, "Metallography and Microstructures" and Vol.3 "Alloy Phase diagrams" Metal Park OH, USA. 2004.

[17] Y.C. Lee, A.K. Dahle, and D.H. StJohn, "The Role of Solute in Grain Refinement of Magnesium", Metallurgical and Materials Transaction A, Vol. 31A, Nov. 2000, pp. 2895-2909.

[18] J.E. Gruzleski and C.A. Aliravci: Low Porosity, Fine Grain Sized Strontium-Treated Magnesium Alloy Casting, U.S. Patent No. 5,143,564, 1992.

[19] L.Y. Wei and G.L. Dunlop: "Precipitation Hardening in a Cast Mg-Rare Earth Alloy," Magnesium Alloys and Their Applications, ed. B.L. Mordike and F. Hehmann , Verlag, Germany,1992, pp. 335–342.

[20] A.H. Gomes de Mesquita and K.H.J. Buschow, "The Crystal Structure of So-Called alpha-LaAl4," Acta Cryst., 22 (1967), pp. 497–501.

[21] G. Pettersen, H. Westengen, R. Hoier and O.Lohne, Microstructure of a pressure die cast magnesium-4wt.% aluminium alloy modified with rare earth additions", Mat. Sci. and Eng., A207, 1996, pp. 115-120.

[22] M. Pekguleryuz, P. Labelle, E.Baril, D. Argo, ''Magnesium Diecasting Alloy AJ62x with Superior Creep Resistance and Castability," 2003 Magnesium Technology, TMS, San Diego, March 2003, pp. 201-207.

تاثير اضافة معدن اللنثانيوم على خصائص سبيكة المغنسيوم - ٤% المنيوم

احمد علي موسى
قسم هندسة الإنتاج والمعادن/ الجامعة التكنولوجية
البريد الالكتروني: ahmedmuot@yahoo.com

الخلاصة

يهدف هذا البحث الى دراسة تاثير اضافة عناصر الارض النادرة على سبائك (Mg-4Al) والحيلولة دون اكسـدة المغنيسيوم أو احتراقه وأنتاج سبيكة (Mg-4Al-1.5 La).

كما تضمن البحث الفحوصات المجهرية وفحص الأشعة السينية لمعرفة الأطوار الناتجة في سبيكة (Mg-4Al-1.5 La).

أظهرت النتائج أن سبيكة (Mg-4Al) تحتوي على الطور (α- Mg) مع وجود ترسبات على الحدود البلورية .

اما الاطوار في سبيكة (Mg-4Al-1.5 La) فهي $Mg, Al_{11}La_3, Al_4La$ مع عدم ظهور الطور $Mg_{17}Al_{11}$ ان اضافة اللنثانيوم يؤدي الى زيادة الصلادة وانخفاض معدل البلى .