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Microstructural Characterization of the As-cast AZ91 Magnesium Alloy with Rare Earth Elements

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Abstract

Microstructural analysis of as-cast Mg-9Al-0.9Zn-xRE (x = 0, 1, 2, 3, 5 wt.%) magnesium alloys is presented. Light microscopy (LM) and scanning electron microscopy (SEM+EDX) were used to characterized the obtained material. The results revealed that the as-cast AZ91 alloy consists of α – Mg matrix, binary eutectic α + γ (where γ is $Mg_{17}Al_{12}$). While rare earth elements were introduced to the Mg-Al-Zn alloy new $Al_{11}RE_3$ phase was formed. Additionally, in the experimental alloys instead of Al-Mn phase, ternary Al-Mn-RE compound was observed. What is more, the influence of RE addition on the area fraction of eutectic and needle-like phase was analysed. With increasing addition of RE, the amount of γ phase decreased, but the amount of $Al_{11}RE_3$ phase increased.

Keywords: Mg-Al-Zn alloy; Rare earth elements; Microstructure;

1. Introduction

Magnesium alloys are lightweight structural material with low density, good die-castability and recyclability. These properties make them attractive in the automotive, aerospace and communication industries [1÷3].

Most commercial magnesium alloys are based on Mg-Al system, in particular AZ and AM alloy series with the most popular AZ91 alloy. The equilibrium microstructure (according to Mg-Al equilibrium phase diagram) for commercial Mg-Al alloys is 100% α – magnesium, but due to non-equilibrium solidification conditions, metastable eutectic α + γ (where γ is the intermetallic compound $Mg_{17}Al_{12}$) forms and is present in the as-cast microstructure down to about 2 wt.% Al [4]. This ternary magnesium alloy contains about 9 wt.% Al and 1 wt.% Zn, with 0.4 wt.% Mn for corrosion resistance improvement. In comparison with binary Mg-Al alloys, new phases do not appear in ternary alloys Mg-Al-Zn, when Al to Zn ratio is greater than 3:1. In this case, Zn substitutes Al in $Mg_{17}Al_{12}$ phase and creates ternary compound ($Mg_{17}(Al, Zn)_{12}$ or $Mg_{17}Al_{11.5}Zn_{0.5}$ type) [5]. However, the applications of magnesium-aluminium alloys are limited due to the poor mechanical properties above 393K. These poor elevated temperature properties are related to the occurrence of the low-melting γ phase. It is commonly known that the addition of rare earth (RE) elements is an effective way to improve the mechanical properties of magnesium alloys at elevated temperatures [6]. Rare earth elements are added to magnesium alloys either as single element, mishmetal or didymium [7÷10]. Mishmetal is a mixture of rare earths containing mainly cerium, lanthanum and neodymium; didymium is a natural mixture of approximately 85% neodymium and 15% praseodymium. RE introduced to the magnesium alloys caused the formation of the highly thermal stable $Al_{11}RE_3$ intermetallic compound. Typical representative of Mg-Al-RE system is AE44 die casting alloy with good creep resistance due to the presence of high-melting $Al_{11}RE_3$ phase and absence of $Mg_{17}Al_{12}$ compound [11, 12].

Earlier studies allowed to introduce successfully rare earth elements into AM50 and AZ91 magnesium alloys [13, 14]. In the present work, different amounts of RE were added to AZ91 alloy and their influence on the area fraction of eutectic was studied.

2. Experimental material and procedures

The common commercial AZ91 magnesium alloy was chosen as a base alloy. Different amount of rare earth elements (RE) were added to the AZ91 melt in the form of cerium-rich mishmetal (with the composition: 54.8 wt.% Ce, 23.8 wt.% La, 16.0 wt.% Nd,5.4 wt.% Pr, 0.16 wt.% Fe, 0.19 wt.% Mg). The chemical composition of the investigated alloys is listed in Table 1. The melt was held for 10 minutes to make sure that RE's were completely dissolved and stirred to ensure homogenous distribution of introduced elements. The experimental alloys were cast using permanent mold casting. During the melting process a protective argon atmosphere was employed. The melt was poured into a steel mold and then cooled down to room temperature by air cooling.

A standard metallographic technique was used for sample preparation. To reveal microstructure the specimen surfaces were etched with 4% nital solution.

Table 1.
Chemical composition of the investigated alloys

	Chemical composition [wt.%][1)]				
Alloy	**Al**	**Zn**	**Mn**	**Si**	**RE**
AZ91	8.5÷9.5	0.45÷0.9	0.17÷0.40	0.05	-
AZE-1	8.5÷9.5	0.45÷0.9	0.17÷0.40	0.05	1
AZE-2	8.5÷9.5	0.45÷0.9	0.17÷0.40	0.05	2
AZE-3	8.5÷9.5	0.45÷0.9	0.17÷0.40	0.05	3
AZE-5	8.5÷9.5	0.45÷0.9	0.17÷0.40	0.05	5

[1)] Mg rest

The microstructure was examined using a light microscope (LM - Neophot-21, Carl-Zeiss Jena) and scanning electron microscope (SEM). SEM investigations were perform using a Jeol JSM – 6610LV equipped with energy dispersive X-ray spectrometer, with the accelerating voltage of 20kV.

To measure the stereological parameters a program for image analysis ImageJ was used. The most important part of quantitative description of Mg-Al-RE alloys – area fraction of eutectic and area fraction of dominant intermetallic compound $Al_{11}RE_3$ was analysed. Measurements of area fraction in each sample were performed on 10 random images. Images for the analysis were registered at 500x magnification. It should be noted, that both eutectic and $Al_{11}RE_3$ phase are characterized by unsharp interface boundaries, so manual correction was performed.

3. Results and discussion

Fig. 1 shows the microstructure of as-cast AZ91 alloy. It is composed of α solid solution of alloying elements in magnesium (point 1 in Fig. 1) and divorced binary eutectic α + γ in the interdendritical spaces (point 2 in Fig. 1). Strong dendritic segregation of alloying elements is characteristic for majority as-cast Mg-Al alloys due to relatively wide temperature spans between liquidus and solidus curves. Small amount of manganese caused the formation of precipitates with polygonal shape (point 3 in Fig. 1).

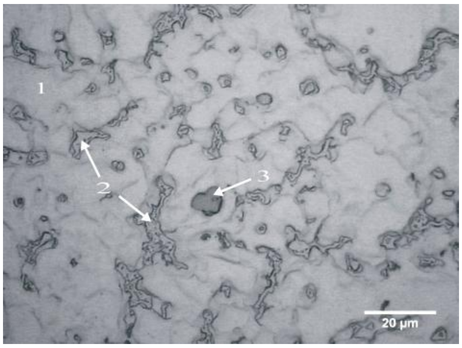


Fig. 1. Microstructure of as-cast AZ91; LM

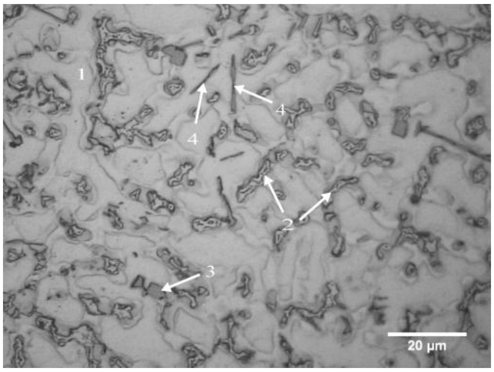
The microstructure of AZ91 with 1, 2 and 3 wt.% rare earths addition is shown in Fig 2a, 2b and 2c respectively. Similarly to as-cast AZ91 alloy, the α solid solution (marked as 1 in Figs. 2a, 2b and 2c) and eutectic α + γ (marked as 2 in Figs. 2a, 2b, 2c) are observed. Additionally, in the experimental alloys new, needle-like phase was observed.

Further SEM observations confirm the occurrence of α +γ eutectic (point 2 in Fig. 3a) and solid solution of aluminium in magnesium (α phase, point 1 in Fig. 3a). The EDX analysis of AZ91 alloy with rare earth elements (Fig. 3b) reveals that the solubility of RE in α-Mg matrix is negligible, due to the great difference between the atomic radius of these elements and Mg (1.6Å for Mg and 1.84Å for Ce). It can be clearly seen that RE elements have been concentrated in the needle-like (point 4 in Fig. 3a) and polygonal (point 3 in Fig. 3a) phases. Moreover, polygonal phase except from aluminium and RE contains also manganese and can correspond to $Al_{10}RE_2Mn_7$.

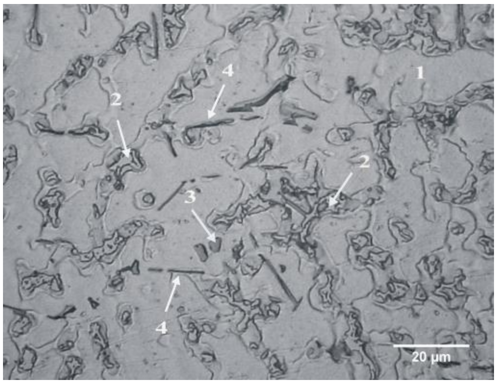
In order to study the influence of rare earth elements introduced to AZ91 alloy on the area fraction of the α + γ eutectic a quantitative evaluation of the microstructure was used. The influence of RE addition on the area fraction of binary eutectic and $Al_{11}RE_3$ phase in AZ91 was presented in Fig. 4. The area fraction of eutectic decreased while the area fraction of the needle-like phase increased with increasing RE content.

The formation temperature of $Al_{11}RE_3$ compound is much higher than that of γ, which means that the formation of Al-RE phase precedes that of $Mg_{17}Al_{12}$. Therefore, during the solidification of $Al_{11}RE_3$ consumes Al atoms and reduces the precipitation of γ phase.

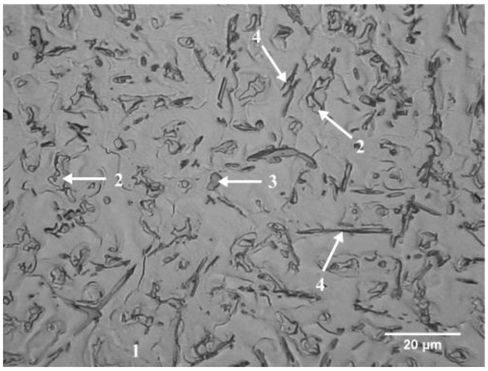
a)



b)



c)



d)

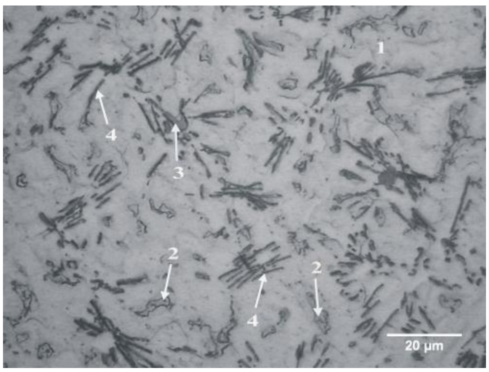
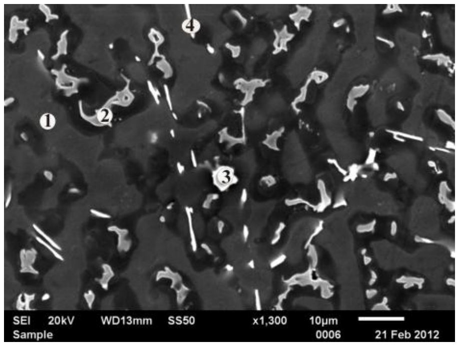


Fig. 2. Microstructure of as-cast a) AZE -1; b) AZE-2, c) AZE-3; d) AZE-5 alloys, LM

a)



b)

Point	Element	wt.%	at.%
1	Mg	96.23	96.59
	Al	3.77	3.41
2	Mg	73.99	77.54
	Al	22.23	20.99
	Zn	3.78	1.47
3	Mg	6.63	11.33
	Al	37.18	57.23
	Mn	32.14	24.30
	La	4.24	1.27
	Ce	17.33	5.14
	Pr	2.48	0.73
4	Mg	72.69	81.89
	Al	15.40	15.76
	La	4.76	0.95
	Ce	7.15	1.41

Fig. 3. a) SE image of AZE-1 alloy; b) element distribution in different areas of AZE-1 structure from the image a

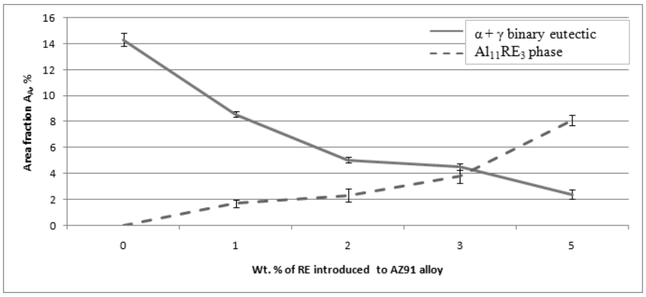


Fig. 4. Influence of RE addition on the area fraction of binary eutectic and $Al_{11}RE_3$ phase in investigated alloys

The statistical analysis was used to verify the obtained results. Barlett's test confirmed the assumed homogenity of variance in investigated alloys (p_e=0.256, p_i=0.621, α=0.05 where index e – eutectic, i – intermetallic compound $Al_{11}RE_3$) and it was possible to carry out a homogenity test for five means. In the homogenity test for five means the relations $p_e<\alpha$ and $p_i<\alpha$ occurred, so the hypothesis assuming that the average area fraction of eutectic and $Al_{11}RE_3$ phase in alloys with different RE content are identical was rejected. The results obtained in test confirmed a significant difference in area fraction of binary eutectic and $Al_{11}RE_3$ phase in the alloys with different rare earth elements content.

4. Summary

The microstructure analyses of AZ91 and AZ91+xRE (where x = 1, 2, 3 and 5 wt.%) were presented. The results revealed that the AZ91 is characterized by the α – Mg matrix and eutectic α + γ. Addition of RE to the AZ91 alloy caused the formation of $Al_{10}RE_2Mn_7$ phase and precipitates of $Al_{11}RE_3$ compound, which is the dominant intermetallic phase. The amount of γ phase decreased with increasing addition of RE, on the other hand, the amount of $Al_{11}RE_3$ phase increased.

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