

Analysis of heavy alloying elements segregation in gravity cast experimental Mg-Al-Zn-RE alloy

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Abstract

Microstructure of experimental AZ91 alloy with an addition of rare earth elements (RE) at a level of 4 wt.% was examined by means of light microscopy. The investigated AZ91 + 4 wt.% RE alloy was fabricated by adding cerium rich mish metal to molten commercial AZ91 alloy. In the microstructure of the resulting alloy, besides α solid solution, $\alpha + \gamma$ eutectic and discontinuous precipitates of γ phase, also the $Al_{11}RE_3$ phase with needle-like morphology and the polygonal $Al_{10}RE_2Mn_7$ phase were revealed. No segregation of rare earth elements was found in the investigated gravity cast alloy, which was confirmed by statistical analysis of cerium concentrations in selected parts of the cast. Similar results were obtained for manganese. Ce and Mn concentrations were determined by a spectrophotometric method.

Key words: Mg-Al-Zn alloys; Segregation; Rare earth elements

1. Introduction

Magnesium alloys have a variety of useful properties such as high specific strength, good castability and weldability under controlled atmospheres, vibration damping abilities and low toxicity [1-3]. Widely used magnesium alloys belong to Mg-Al-Zn (AZ) series, which have excellent castability and a low cost. However, these alloys exhibit poor mechanical properties, especially at elevated temperatures. To meet the challenges of new applications, mechanical properties of Mg-Al-Zn alloys at high temperatures need to be further improved. Recently, several investigators [4-6] have reported that the addition of rare earth elements (RE) to magnesium alloys turned out to be an effective way improving their mechanical properties.

The beneficial effect of adding rare earth elements to magnesium die casting alloys were reported many years ago,

while recently the alloys of Mg-Al-RE system have been developed, for example AE42 [7]. However, due to a high cost of commercial alloys, nowadays investigations are directed to new experimental alloys with rare earth elements [6,8]. Unfortunately, due to a high density of rare earth elements, some difficulties in introducing them into magnesium can arise, because there is a possibility that during gravity casting rare earth elements may segregate resulting in macro-heterogeneity in casts. Thus, verification of RE contents in different parts of investigated alloys is of primary importance.

In this work, we concentrate on the verification of a RE content within the experimental cast of the commercial AZ91 alloy with the 4 wt.% addition of cerium rich mish metal. The Ce contents were determined by a simple spectrophotometric method [9].

2. Experimental material and procedures

AZ91, with a nominal composition listed in Table 1, was chosen as a master alloy. Rare earth elements were introduced to the alloy in the form of cerium rich mish metal (MM) with the composition shown in Table 2.

Table 1.
Chemical composition of AZ91 alloy according to ASTM B93-94

Alloy	Chemical composition [wt.%] *							
	Al	Zn	Mn	Si max	Fe max	Cu max	Ni max	Others each max
AZ91	8.5- 9.5	0.45- 0.9	0.17- 0.4	0.05	0.005	0.03	0.002	0.02

* Mg rest

Table 2.
Chemical composition of mish metal used in this study

	Chemical composition [wt.%]					
	Ce	La	Nd	Pr	Fe	Mg
mish metal	54,8	23,8	16,0	5,4	0,16	0,19

The experimental material based on AZ91 alloy with the 4 wt.% addition of mish metal was cast into metal moulds in the form of rods with dimensions shown in Fig. 1.

Microstructural analyses were performed by means of light microscopy. A standard metallographic technique was used for sample preparation which includes wet prepolishing and polishing with different diamond pastes. Specimens were examined by a light microscope (NEOPHOT-21, Carl-Zeiss Jena).

To verify contents of RE in different parts of the cast (broken lines in Fig.1) spectrophotometric determination of cerium was carried out. Briefly, weighted specimens were dissolved in sulphuric acid, then cerium(III) ions were oxidized to cerium(IV) by sodium peroxodisulfate with the presence of Ag^+ ions (a catalyst). After that, the absorbance of Ce^{4+} ions at a wavelength of 313 nm was measured. Since peroxodisulfates oxidize Mn^{2+} to MnO_4^- (the experimental alloy contains manganese at a level of 0.2 wt.%), which also absorb light at 313 nm the appropriate correction was introduced. Namely, the absorbance of MnO_4^- ions was measured at 526 nm, where Ce^{4+} ions practically do not absorb light. This absorbance was recalculated on the absorbance of MnO_4^- ions at 313 nm, which was subtracted (assuming the absorbance additivity) from the absorbance value measured originally at this wavelength. The cerium concentration in the analyzed solution can be calculated from the following equation [9]:

$$c_{Ce^{4+}} = \frac{A_{313} - \frac{A_{526}}{\varepsilon_{526,Mn} l_2} \varepsilon_{313,Mn} l_1}{\varepsilon_{313,Ce} l_1} \quad (1)$$

where:

A_{313} - absorbance at $\lambda = 313$ nm,

A_{526} - absorbance at $\lambda = 526$ nm,

$\varepsilon_{313,Mn}$ - molar absorption coefficient of MnO_4^- ions at $\lambda = 313$ nm,

$\varepsilon_{526,Mn}$ - molar absorption coefficient of MnO_4^- ions at $\lambda = 526$ nm

$\varepsilon_{313,Ce}$ - molar absorption coefficient of Ce^{4+} ions at $\lambda = 313$ nm,

l_1 and l_2 - optical path lengths (cuvettes' thicknesses) at which absorbances at 313 and 526 nm were measured, respectively

Spectrophotometric measurements were carried out using UV2-200 spectrometer (ATI Unicam, England). The details of the analytical procedure were described earlier [9].

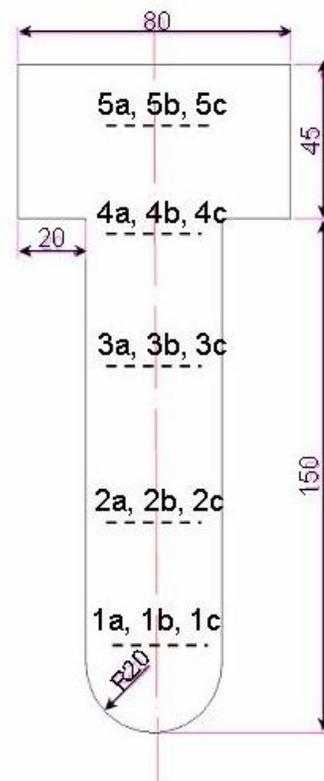


Fig. 1. The cast scheme with marked places where samples for chemical analysis were taken from. All dimensions are expressed in mm

3. Results and discussion

Fig. 2 shows the microstructure of the as-cast AZ91 alloy containing 4 wt.% of RE. The microstructure of AZ91 + 4 wt.% RE, similarly to the initial AZ91 alloy, is consisted of α - Mg matrix (marked as 1 in Fig. 2), $\alpha + \gamma$ eutectic (marked as 2 in Fig.2) and discontinuous precipitates of γ phase (marked as 3 in Fig. 2); where γ is the intermetallic compound $Mg_{17}Al_{12}$.

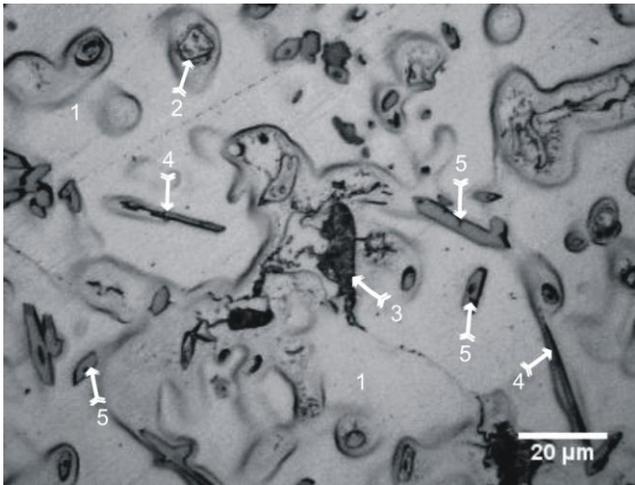


Fig. 2. Microstructure of as-cast AZ91 + 4 wt.% RE

On the other hand, in AZ91 + 4 wt.% RE the volume fraction of $\alpha + \gamma$ eutectic appeared to be smaller and, in comparison with AZ91 solidified at the same conditions, larger amount of discontinuous precipitates of γ phase occurred. Additionally, in the microstructure of AZ91 + 4 wt.% RE alloy the needle-like (marked as 4 in Fig. 2) and polygonal (marked as 5 in Fig. 2) phases were observed. The phase with the needle-like morphology is $Al_{11}RE_3$ and the polygonal phase is a ternary intermetallic compound, which formula can be expressed as $Al_{10}RE_2Mn_7$.

In order to verify the distribution of RE and Mn in the experimental alloy, 3 samples were taken from each of 5 selected parts (Fig. 1) of the cast. The results of spectrophotometric determinations of cerium and manganese contents are shown in Table 3. The total concentrations of RE were calculated from the concentrations of Ce assuming that other rare earth elements were transferred to the alloy proportionally together with Ce. It should be remembered that mish metal used in this work contained 54.8 wt.% Ce. The obtained results show that in different parts of the investigated alloy the total amount of added rare earth elements ranges from 3.5 to 3.9 wt. %. To estimate the significance of the differences between average Ce contents in different parts of the investigated cast, the one-way analysis of variance (ANOVA) was applied [11-13].

The null hypothesis $H_0: y_1 = y_2 = y_3 = y_4 = y_5$, with the alternative hypothesis H_a : at least one inequality between y_j exists, was verified (were y_j is the average Ce content in the j th part of the cast). The test of hypothesis about the equality of means is therefore an F test for the equality of two variances [12]:

$$F = \frac{\sigma_A^2}{\sigma_W^2} \quad (2)$$

where σ_A^2 is the among-group (among the selected parts) variance and σ_W^2 is the within-group (different samples from the same part of the cast) variance. These variances can be estimated by the following equations:

$$\sigma_A^2 = MS_A = \frac{SS_A}{k-1} = \frac{\sum_{j=1}^k n_j (y_j - \bar{y})^2}{k-1} \quad (3)$$

$$\sigma_W^2 = MS_W = \frac{SS_W}{n-k} = \frac{\sum_{j=1}^k \sum_{i=1}^{n_j} (y_{ij} - y_j)^2}{n-k} \quad (4)$$

$$n = \sum_{j=1}^k n_j \quad (5)$$

where \bar{y} is the mean of all concentrations (i.e. all samples in all parts), i.e. the mean of $nk=15$ values, MS – mean sum of squares and SS – sum of squares, n_j - the number of samples taken from the j th part of the cast, k – the number of selected parts in the cast.

Table 3.

Concentrations of cerium and manganese in the selected parts of the investigated cast

No.	Ce content wt. %	average Ce content (± standard deviation) wt. %	expected RE content wt. %	Mn content wt. %	average Mn content (± standard deviation) wt. %
1a	1.91			0.208	
1b	2.10	1.91±0.20	3.50	0.205	0.205±0.00
1c	1.71			0.202	3
2a	2.21			0.207	
2b	2.14	2.15±0.05	3.93	0.205	0.207±0.00
2c	2.12			0.210	3
3a	2.12			0.205	
3b	2.09	2.11±0.01	3.85	0.201	0.203±0.00
3c	2.11			0.202	2
4a	2.11			0.210	
4b	2.04	2.10±0.06	3.83	0.209	0.213±0.00
4c	2.16			0.222	6
5a	2.16			0.214	
5b	2.14	2.10±0.08	3.84	0.204	0.208±0.00
5c	2.02			0.207	5

The F-statistics has Snedecor's distribution with k-1 and n-k degrees of freedom. The calculated F value was compared with critical value $F_{\alpha,4,10} = 3.48$ from the F – Snedecor's distribution table for a significance level, $\alpha = 0,05$ [11-13]. Because $F < F_{\alpha,4,10}$ there is no base to reject H_0 hypothesis, which means that really with the 95% confidence average Ce contents in different parts of the cast are equal. The results suggested that rare earth elements are evenly distributed in the experimental cast without any segregation.

Table 4.
ANOVA for the Ce contents in the investigated cast

Source of variation	Sum of squares (SS)	Degrees of Freedom	Variance	F value
Between different parts of the cast	0.113	4	0.028	2.84
In the same part of the cast	0.100	10	0.010	

It should be also noted that AZ91 alloy contain small amount of manganese. Since this element may also segregate during casting, the spectrophotometric determination of manganese was also carried out. Table 3 shows the values of the determined manganese content. The average content of manganese in different parts of the investigated alloy ranges from 0.203 to 0.208 wt. %. These results were consistent with the data from ASTM B93-94, where AZ91 should contain 0.17 - 0.40 wt.% of Mn.

The distribution of Mn was verified similarly to the distribution of Ce. The ANOVA results for the manganese contents are shown in Table 5. Calculated F value was compared with critical value $F_{\alpha} = 3.48$ from F – Snedecor's distribution table for a significance level, $\alpha = 0,05$ [11-13]. Because $F < F_{\alpha,4,10}$ there is no base to reject the hypothesis about the equality of the Mn contents in the selected parts of the experimental cast, which means that with 95% confidence Mn contents in different parts of the cast are equal. Similarly as cerium, manganese is distributed in the cast evenly with no segregation.

Table 5.
ANOVA for the Mn contents in the investigated cast

Source of variation	Sum of squares (SS)	Degrees of Freedom	Variance	F value
Between different parts of the cast	1.81e-4	4	4.52e-5	2.72
In the same part of the cast	1.66e-4	10	1.66e-5	

4. Summary

The addition of 4 wt.% rare earth elements to AZ91 magnesium alloy causes the formation of the new phases: needle-like $Al_{11}RE_3$ and polygonal $Al_{10}RE_2Mn_7$. The one-way analysis of variance (ANOVA) for concentrations of Ce and Mn (determined in selected parts of the experimental cast) indicates that these elements are evenly distributed in the alloy or, in other words, there is no segregation of these elements.

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