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Effect of Mischmetal on the Microstructure of the Magnesium Alloy AZ91

D. Mikusek *, C. Rapiejko, D. Walisiak, T. Pacyniak
Department of Materials Engineering and Production Systems of Lodz University of Technology,
Stefanowskiego 1/15, 90-924 Łódź, Poland
* Corresponding author. E-mail address: dominik.mikusek@edu.p.lodz.pl

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Abstract

In this paper is discussed the effect of the inoculant mischmetal addition on the microstructure of the magnesium alloy AZ91. The concentration of the inoculant was increased in the samples within the range from 0.1% up to 0.6%. The thermal process was performed with the use of Derivative and Thermal Analysis (DTA). A particular attention was paid to finding the optimal amount of the inoculant, which causes fragmentation of the microstructure. The concentration of each element was verified with use of a spark spectrometer. In addition, the microstructures of every samples were examined with the use of an optical microscope and also was performed an image analysis with a statistical analysis using the NIS–Elements program. The point of those analyses was to examine the differences in the grain diameters of phase α_{Mg} and eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ in the prepared samples as well as the average size of each type of grain by way of measuring their perimeters. This paper is the second part of the introduction into a bigger research on grain refinement of magnesium alloys, especially AZ91. Another purpose of this research is to achieve better microstructure fragmentation of magnesium alloys without the relevant changes of the chemical composition, which should improve the mechanical properties.

Keywords: Metallography, Solidification process, Magnesium alloys, Mischmetal, DTA process

1. Introduction

In the recent years, it has been possible to observe a significant increase in the interest in magnesium alloys in applications for the automotive, aerospace, electronics and aircraft industry [1–3]. Their low specific gravity as well as quite good mechanical properties causes magnesium alloys to find new applications, with a simultaneous optimization of the microstructure and the chemical composition. Magnesium alloys are currently viewed as the best construction alloys; in respect of the degree of their use in the industry, they are placed as third, behind steels and aluminum alloys.

The technology used to obtain magnesium alloy casts determines their subsequent properties. At present, the best properties of magnesium alloys are obtained with the application of pressure casting [4]. Magnesium alloy casts are also made in casting technologies using ceramic moulds, synthetic sandmix moulds, or dies, but at a smaller scale. Improving the mechanical properties of casts made of, among others, magnesium alloys is realized by way of intense cooling of the mould [5]. Another way of improving the properties of those alloys is changing their microstructure through the use of alloy additions and inoculants [6–14].

One of the techniques is modifying magnesium alloys with mischmetal. Mischmetal significantly changes the microstructure and properties of magnesium alloys. Introducing mischmetal in the concentration of 2.5% increases the tensile strength by about 10% at ambient temperature [15], whereas an addition of mischmetal based on cerium in the amount of 1.5% into alloy ZK60 causes a decrease of the Young's modulus, hardness and tensile strength as a result of the abundant formation of the intermetallic compound $MgZn_2Ce$ [16]. A lower amount of the added mischmetal, at the level of 0.4%, causes a decrease of the tensile strength, proof stress and elongation [17]. A cerium addition,

which is the main component of mischmetal, in the amount of about 4%, increases the tensile strength, yield point and elongation by a few percent [18]. Industrial applications take advantage of compounds which modify the alloy and create a protective atmosphere during the melting process.

The aim of the study was to examine the effect of the mischmetal concentration on the microstructure of casts made of alloy AZ91 obtained in ceramic moulds.

2. Experimental

The investigations included the preparation of 7 melts for alloy AZ91, which was subjected to modification with mischmetal (MM). The chemical composition of used MM is ~50% Ce, ~30% La, ~10% Nd, ~6% Y and ~3% Pr [19]. The melt schedule has been presented in Table 1. To melts was used exactly the same mass percentage of inoculant.

Table 1.
Melt schedule

Melt number	Melt's chemical composition
I	AZ91
II	AZ91+0.1% (mass) MM
III	AZ91+0.2% (mass) MM
IV	AZ91+0.3% (mass) MM
V	AZ91+0.4% (mass) MM
VI	AZ91+0.5% (mass) MM
VII	AZ91+0.6% (mass) MM

For the examinations, alloy AZ91 was selected, the composition of which has been shown in Table 2. The composition of the examined alloy is in accordance with the standard [20].

Table 2.
Chemical composition of alloy AZ91

Chemical composition, % wt.					
Mg	Al	Zn	Mn	Ca	Si
90.6	8.69	0.424	0.248	0.0011	0.0225

Each time, the alloy was melted in a crucible, which was heated in a resistance furnace SNOL 8,2/1100 UMEGA AB to the temperature of 740 °C ±5 °C. In order to prevent oxidation of the magnesium alloys, sulphur powder was applied. After the examined alloys were cast, they were cooled down at room temperature.

The casts were made in ceramic DTA samplers preheated to 180 °C. An image of an exemplary DTA sampler has been shown in Figure 1. Inside the samplers, a quartz pipe, sealed on one side, served as a shield for a measuring thermocouple type S (Pt-PtRh10). The samplers were made according to the technology described in [21]. The investigations of the solidification and crystallization of the examined alloys were performed by means of the DTA method, according to the methodology described in [5,22], and on the test bench presented in [21].

An evaluation of the cooling ($t=f(\tau)$), kinetics ($dt/d\tau=f'(\tau)$) and crystallization process was made by the DTA method. On the derivation curve ($dt/d\tau=f'(\tau)$), the following thermal effects for the examined magnesium alloys were marked with points:

P_k – A – D – crystallization of primary phase α_{Mg},

D – E – F – H – crystallization of eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$.

The chemical composition of the samples was tested with the use of a spark spectrometer SPECTROMAXx – Spectro. In order to reveal the microstructure of the ground and polished samples, the latter was subjected to etching. For the etching, a formulation containing 1 ml acetic acid, 50 ml distilled water and 150 ml ethyl alcohol was used. The microstructure test was performed with the use of an optical microscope Nikon Eclipse Ma 200, and the image analysis combined with a statistical analysis was carried out by means of a program working with a NIS–Elements microscope. The results of the DTA analysis and the statistical analysis for the modified samples were presented in reference to the initial alloy AZ91, not modified with mischmetal.

3. Results and discussion

3.1. DTA test

Figure 1 shows exemplary DTA characteristics for alloy AZ91, whereas Table 3 compiles the coordinates of the characteristic points and their values for alloy AZ91.

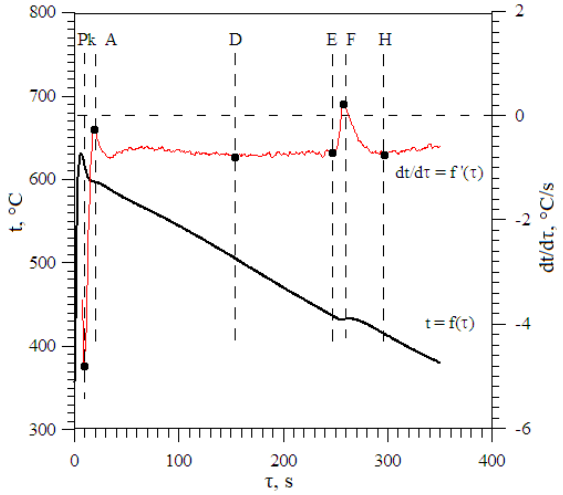

Fig. 1. DTA characteristics of non-modified alloy AZ91 solidifying in a ceramic sampler ATD10C-PŁ

Table 3.
Characteristics DTA points of non-modified alloy AZ91

Point	τ, s	t, °C	dt/dτ, °C/s	Crystallizing phase
P_k	9.6	616.6	-4.8154	α_{Mg}
A	19.2	596.7	-0.2637	
D	154.2	504.6	-0.7915	
E	247.0	436.0	-0.7060	$\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$
F	257.9	432.1	0.2051	
H	297.0	414.1	-0.7493	

For the examined alloys, the DTA characteristics were recorded and the values for the particular characteristic points of the microstructure crystallization were determined. Based on the DTA data, the solidification times for primary phase α_{Mg} and eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ were calculated. The calculations were made from the relation:

- Solidification time of phase α_{Mg}: $\Delta\tau_\alpha=\tau_D-\tau_{pk}$,
- Solidification time of eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$: $\Delta\tau_\gamma=\tau_H-\tau_D$.

In order to present the effect of modification on the DTA characteristics in reference to the non-modified alloy AZ91, the differences in the crystallization times of primary phase α_{Mg} and eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ were calculated from the relation:

- Difference in the solidification time of phase α_{Mg}: $\Delta\tau_{D\alpha}=\Delta\tau_{\alpha AZ91}-\Delta\tau_{\alpha AZ91inX}$,
- Difference in the solidification time of eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$: $\Delta\tau_{D\gamma}=\Delta\tau_{\gamma AZ91}-\Delta\tau_{\gamma AZ91inX}$.

Where: *inX* denotes the amount of the introduced inoculant.

The calculation results have been given in Figure 2.

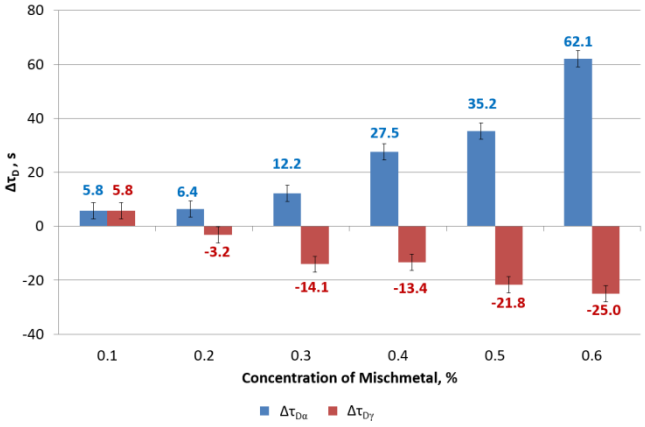

Fig. 2. Difference in the solidification time of phase α_{Mg} and eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ of modified alloys MM in reference to the initial alloy AZ91

It can be inferred from Figure 2 that introducing mischmetal into alloy AZ91changes the crystallization time of both the primary phase α_{Mg} and the eutectic phase $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$. The crystallization time of phase α_{Mg} , depending on the amount of the introduced inoculant, increases. It was noticed that, together with the increase of the amount of the introduced mischmetal, the crystallization time of the eutectic decreases. An exception is the crystallization time of phase $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ for the alloy containing 0.1% of inoculant, for which the crystallization time of the eutectic phase was increased by 5.8 s. The biggest increase of the crystallization time of phase α_{Mg} equaled $\Delta\tau_\alpha$ = 62.1 s for the inoculant concentration 0.6%. The highest reduction of the crystallization time of the eutectic equaled $\Delta\tau_{\alpha+\gamma}$= 25.0 s and it was reached for the mischmetal concentration of 0.6%. The inoculant concentration of 0.2% had the least effect on the crystallization time of the eutectic, causing a reduction of the solidification time of phase $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ by $\Delta\tau_{\alpha+\gamma}$ = 3.2 s. The total crystallization time becomes longer in most of the examined samples, except for the alloy with the mischmetal concentration of 0.3%, for which the total crystallization time shortened by 1.9 s.

3.2. Microstructure analysis

Metallographic examinations were performed for the analyzed alloys. For the obtained microstructures, photographs were taken, which then underwent the image analysis described in section 3.3. Figure 3 shows the microstructure of the non-modified alloy AZ91, whereas Figure 4 presents an exemplary microstructure of the modified alloy AZ91+0.3%MM and AZ91+0.5%MM. It can be inferred from the performed tests that, with the increase of the mischmetal concentration, the precipitations of primary phase α_{Mg} became bigger, whereas the size of the precipitations of eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ became reduced.

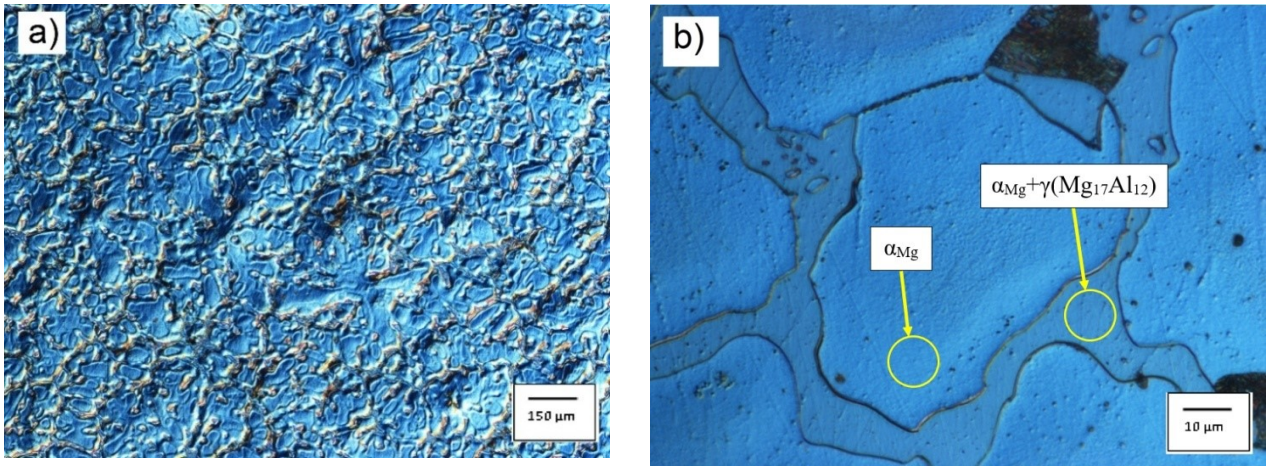

Fig. 3. Microstructure of non-modified alloy AZ91

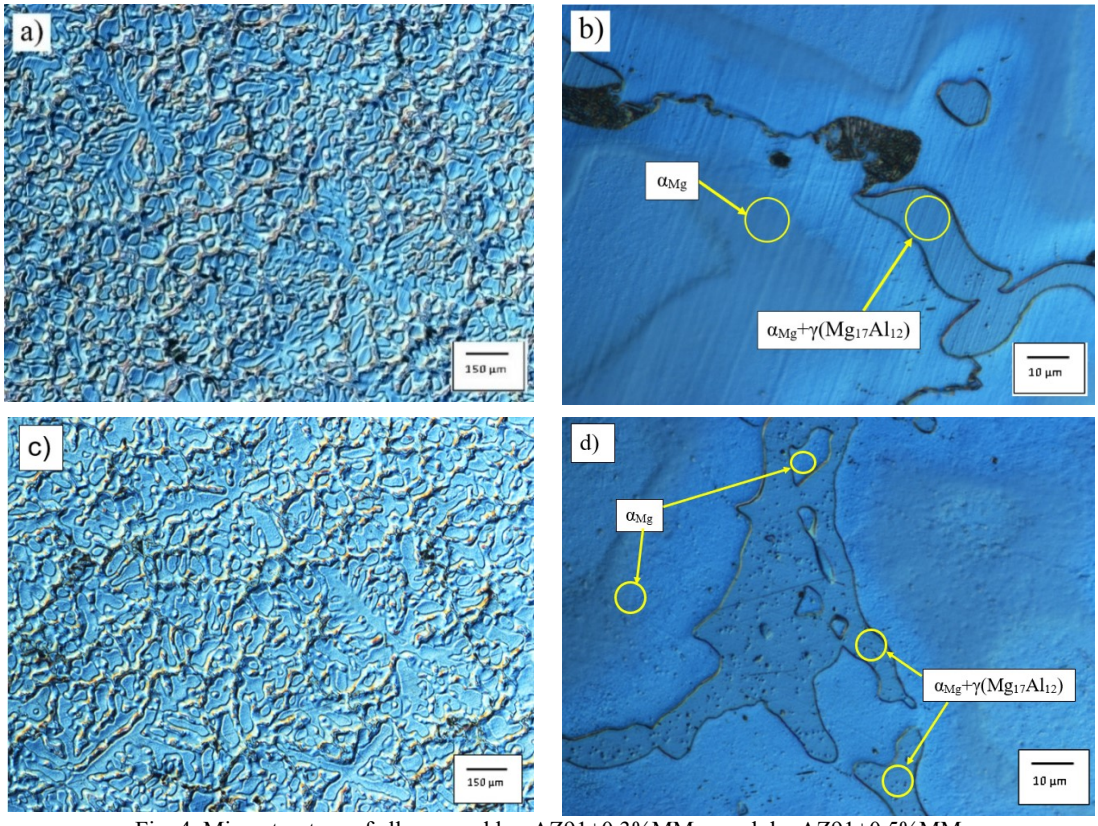

Fig. 4. Microstructure of alloy: a and b – AZ91+0.3%MM, c and d – AZ91+0.5%MM

3.3. Image analysis

Figure 5 shows exemplary microstructure images subjected to a statistical image analysis. The aim of the analysis was to compare the mean change in the grain size of primary phase α_{Mg} and eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ in reference to the non-modified alloy AZ91. In order to present the effect of the inoculant addition on the mean sizes of the precipitations of phase α_{Mg} and eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$, measurements of the mean perimeter and diameter values for the particular phases were made. The percentage difference of the perimeters P_D of the analyzed phases α_{Mg} and eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ for the inoculated alloys in reference to the non-inoculated alloy AZ91 was calculated from the relation:

$$P_D = \frac{\overline{P_{in}}-\overline{P_B}}{\overline{P_B}} \cdot 100\% \quad (1)$$

where:

P_D – calculated difference of perimeters, %
$\overline{P_{in}}$ – average perimeter of phases α_{Mg} and $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ of inoculated alloys, µm
$\overline{P_B}$ – average perimeter of phases α_{Mg} and $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ of AZ91, µm

Additionally, the percentage change in the diameter D_D for the particular phases was calculated from the relation:

$$D_D = \frac{\overline{D_{in}}-\overline{D}}{\overline{D_B}} \cdot 100\% \quad (2)$$

where:

D_D – calculated difference of diameters, %
$\overline{D_{in}}$ – average diameter of phases α_{Mg} and $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ of inoculated alloys, µm
$\overline{D_B}$ – average diameter of phases α_{Mg} and $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ of AZ91, µm

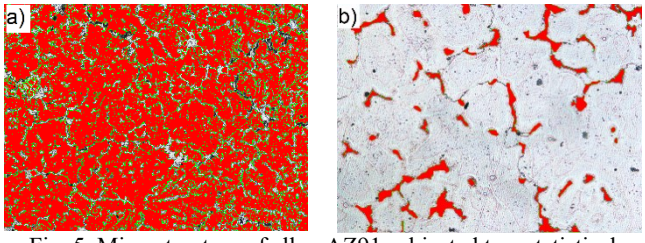

Fig. 5. Microstructure of alloy AZ91 subjected to a statistical image analysis: a – primary phase α_{Mg} magnification x50, b – eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ magnification x200

Figure 6 shows the value of the index P_D calculated from relation 1. It can be inferred from the diagram that, for the inoculant concentration of 0.1%, the mean perimeters of the primary phase precipitations increase by nearly 3% with a simultaneous increase of the eutectic perimeters by almost 6%. In the inoculant concen-

tration range of 0.2–0.6%, together with the increase of the amount of the inoculant introduced into alloy AZ91, the mean perimeters of the primary precipitations of phase α_{Mg} increase. In the same mischmetal concentration range, it was observed that, with the increase of the amount of the introduced inoculant, the mean perimeters of the precipitations of phase $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ become decreased. The highest increase of the mean perimeters for the primary phase was observed for the alloy inoculated with mischmetal in the conetrtation of 0.6%, for which the mean perimeters increased by nearly 36% compared to alloy AZ91. For the same inoculant concentration, the highest reduction of the mean perimeters of the eutectic was observed, equaling 16.30%, compared to the non-inoculated alloy.

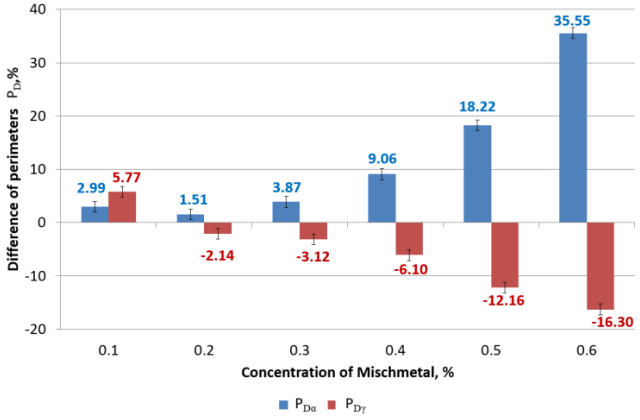

Fig. 6. Change of the grain perimeters of phase α_{Mg} and $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ in samples inoculated in reference to AZ91

Figure 6 shows the value of index D_D calculated from relation 2.

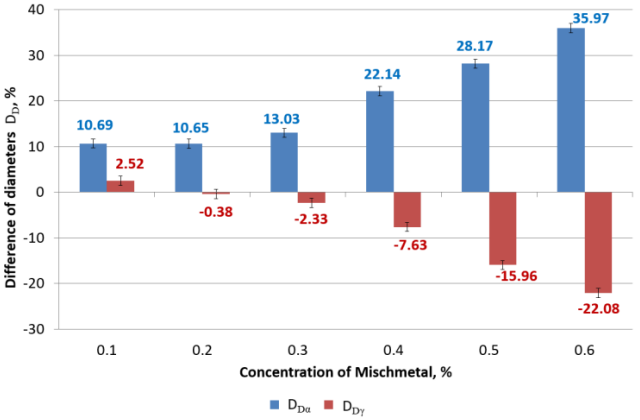

Fig. 7. Change in the mean perimeters of phase α_{Mg} and $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ in inoculated samples in reference to AZ91

It can be inferred from the presented diagram that the mischmetal addition in the concentration of 0.1% causes a simultaneous increase of the mean perimeter value for the precipitations of phase α_{Mg} and $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$. Together with the increase of the inoculant concentration in the scope of 0.3–0.6%, we observe a decrease of the diameter of the eutectic precipitations. Introducing the inoculant in the amount of 0.2% has practically no effect on the diameter of the eutectic precipitations. The highest decrease of the eutectic precipitations' diameters equals about 22% and it was reached for the inoculant concentration of 0.6%.

Introducing mischmetal in the amount of 0.1–0.2% causes an increase of the mean value of the α_{Mg} precipitations diameter by the approximate value of: 10.69% and 10.65%, respectively. The inoculant addition in the scope of 0.4–0.6% increases the mean diameter value of the primary precipitations by over 20%, reaching the highest value 35.97% for the inoculant concentration equaling 0.6%.

3.4. Chemical composition analysis

Table 4 compiles the results of the chemical composition analysis for the examined samples.

Table 4.
Chemical composition of analyzed alloys

Chemical composition, % mas					
Melt no.	**Mg**	**Al.**	**Zn**	**Mn**	**Si**
II	91.2	8.07	0.485	0.174	0.0129
III	91.4	7,86	0.446	0.181	0.0136
IV	91.7	7.55	0.421	0.208	0.0164
V	91.2	7.90	0.478	0.199	0.0131
VI	91.7	7.58	0.423	0.203	0.0162
VII	90.7	8.07	0.481	0.241	0.0191

4. Conclusions

The performed investigations are an introduction into a broader research aiming at microstructure refinement of casts made of magnesium alloy AZ91, which, in consequence, will improve the mechanical properties of the casts without a significant effect on the alloy's chemical composition. The analysis of the obtained investigation results made it possible to draw the following conclusions:

1. The application of the inoculant in the concentration of 0.1% prolongs the crystallization time of phase α_{Mg} and $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$, whereas in the concentration range of 0.2–0.6%, the crystallization time of the eutectic becomes shorter, with a simultaneous prolongation of the primary phase crystallization time.
2. The application of mischmetal in the amount of 0.3% shortens the total crystallization time of the alloy in a ceramic ATD sampler. For the remaining inoculant concentrations, the total crystallization time increases.
3. Introducing mischmetal in the concentration of 0.1% causes an increase of the mean perimeters and mean diameters of the grains of primary phase α_{Mg} and eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$.
4. An inoculant addition in the amount of 0.2–0.6% increases the mean perimeters and mean diameters of phase α_{Mg} precipitations compared to the non-inoculated alloy.
5. The use of the inoculant in the concentration of 0.2% has practically no effect on the mean diameters of the eutectic

precipitations, with a simultaneous decrease of the mean perimeters of the discussed phase.

6. The application of mischmetal in the scope of 0.3–0.6% causes a simultaneous decrease of the mean perimeters and mean diameters of phase $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ precipitations.
7. It was observed that introducing mischmetal in the amount of over 0.3% into the alloy causes microstructure refinement inside the massive precipitations of eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$.

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References

[1] Dieringa, H. et al. (2018). Mg Alloys: Challenges and Achievements in Controlling Performance, and Future Application Perspectives. Orlov D., Joshi V., Solanki K., Neelameggham N. (Eds.) *Magnesium Technology 2018*. Cham. The Minerals, Metals & Materials Series.

[2] Brown, R.E (2009). Magnesium in the 21 century. *Advanced Materials and Processes*. 167(1), 31-33.

[3] Luo, A.A. (2013). Magnesium casting technology for structural applications. *Journal of Magnesium and Alloys.* 1, 2-22 DOI: 10.1016/j.jma.2013.02.002.

[4] Mordike, B.L. & Ebert, T. (2001) Magnesium. Properties – applications – potential. *Materials Science and Engineering*. A302. 37-45. DOI: 10.1016/S0921-5093(00)01351-4.

[5] Rapiejko, C., Pisarek, B. & Pacyniak, T. (2017). Effect of intensive cooling of alloy AZ91 with a chromium addition on the microstructure and mechanical properties of the casting. *Archives of Metallurgy and Materials.* 62(4), 2199-2204. DOI: 10.1515/amm-2017-0324.

[6] Rapiejko, C., Pisarek, B. & Pacyniak, T. (2014). Effect of Cr and V alloy additions on the microstructure and mechanical properties of AM60 magnesium alloy. *Archive of Metallurgy and Materials*. 59(2), 761-765. DOI: 0.2478/amm-2014-0128.

[7] Lin, H., Yang, M., Tang, H. & Pan, F. (2018). Effect of minor Sc on the microstructure and mechanical properties of AZ91 Magnesium Alloy. *Progress in Natural Science: Materials International*. 28, 66-73. DOI: 10.1016/j.pnsc.2018.01.006.

[8] Kasinska, J. (2016). Modification influence of mischmetal on fractography fracture of G17CrMo5-5 cast steel samples after the three-point bending test. *Metalurgija–Sisak then Zagreb*. 55(4), 749-752.

[9] Kasinska, J. & Skrzypczyk, A. (2018). Fracture energy and fracture morphology after three-point bending test of welded joints made of cast steel designed for use in power sector, with and without the addition of rare earth metals. *Metals*. 8(2), 115-130. DOI: 10.3390/met8020115.

[10] Yu, Z., Xiaofeng, H., Ya, L., Zhenduo, M., Ying, M. & Yuan, H. (2017). Effects of samarium addition on as-cast microstructure, grain refinement and mechanical properties of Mg-6Zn-0.4Zr magnesium alloy. *Journal of Rare Earths.* 355(5), 494-502. DOI: 10.1016/S1002-0721(17)60939-6.

[11] Zhang, Y., Huang, X., Ma, Y., Chen, T., Li, Y. & Hao, Y. (2017). Effects of Cu addition on microstructure and mechanical properties of as-cast Mg-6Zn magnesium alloy. *China Foundry*. 14(4), 251-257. DOI: 10.1007/s41230-017-6094-2.

[12] Zhang, Y. et al. (2017) The influences of Al content on the microstructure and mechanical properties of as-cast Mg-6Zn magnesium alloys. *Materials Science & Engineering A*. A686, 93-101. DOI: 10.1016/j.msea.2016.12.122.

[13] Zhi, H., Qun, H., Hong, Y., Xiaoping, J. & Yuansheng, R. (2016). The influences of Al content on the microstructure and mechanical properties of as-cast Mg-6Zn magnesium alloys. *Rare Metal Materials and Engineering*. 45(9), 2275-2281. DOI: 10.1016/S1875-5372(17)30016-4.

[14] Liu, L. et al. (2017). Rare Earth Element Yttrium Modified Mg-Al-Zn Alloy: Microstructure, Degradation Properties and Hardness. *Materials*. 10(5), 477-487. DOI: 10.3390/ma10050477.

[15] Silva, E.P., Buzolin, R.H., Callegari, B., Warchomicka, F., Requena, G.C. & Pinto, H.C. (2017). Effect of mischmetal additions and solution heat treatments (T4) on the Microstructure and Mechanical Properties of Thixocast ZK60-RE Magnesium Alloys. *Trans Tech Publications*. 879, 2300-2305. DOI: 10.4028/www.scientific.net/MSF.879.2300.

[16] Silva, E.P., Marques, F., Nossa, T.S., Alfaro, U. & Pinto, H.C. (2018). Impact of Ce-base mischmetal on the microstructure and mechanicalbehavior of ZK60 magnesium casting alloys. *Materials Science & Engineering A*. 723, 306-313. DOI: 10.1016/j.msea.2018.02.024.

[17] Xu, Y., Zhang, K. & Lei, J. (2016). Effect of mischmetal on mechanical properties and microstructure of die-cast magnesium alloy AZ91D. *Journal of Rare Earths*. 34(7), 742-746. DOI: 10.1016/S1002-0721(16)60086-8.

[18] Tardif, S., Tremblay, R. & Dubé, D. (2010). Influence of cerium on the microstructure and mechanical properties of ZA104and ZA104 + 0.3Ca magnesium alloys. *Materials Science & Engineering A*. 527, 7519-7529. DOI:10.1016/j.msea.2010.08.082.

[19] Pietrowski, S. (2000). Knowledge compedium of vermicular cast iron. *Soldification of Metals and Alloys*. 2(44). 279-292

[20] PN-EN 1753:2001. Magnesium and magnesium alloys. Magnesium alloy ingots and castings.

[21] Rapiejko, C., Pisarek, B, Czekaj, E. & Pacyniak, T. (2014). Analysis of AM60 and AZ91 Alloy Crystallisation in ceramic moulds by thermal derivative analisys (TDA). *Archive of Metallurgy and Materials*. 59(4), 1149-1455. DOI: 10.2478/amm-2014-0246.

[22] Król, M., Tański, T., Matula, G., Snopiński, P. & Tomiczek, A.E. (2015). Analysis of crystallisation process of cast magnesium alloys based on thermal derivative analysis. *Archives of Metallurgy and Materials*. 60(4), 2993-2999. DOI 10.1515/amm-2015-0478.