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Effect of Gadolinium on the Microstructure of Magnesium Alloy AZ91

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Abstract

The paper presents the results of research related to the possibility of inoculation of the AZ91 magnesium alloy casted into ceramic moulds by gadolinium. Effects of gadolinium content (0.1–0.6 wt%) on microstructure of the AZ91 alloy under as-cast state were investigated. The influence of the inoculator on the formation of the microstructure investigated by means of the thermal and derivative analysis by analysing the thermal effects arising during the alloy crystallization resulting from the phases formed. The degree of fragmentation of the microstructure of the tested alloys was assessed by means of the light microscopy studies and an image analysis with statistical analysis was performed. Conducted analyses have aimed at examining on the effect of inoculation of the gadolinium on the differences between the grain diameters and average size of each type of grain by way of measuring their perimeters of all phases, preliminary α_{Mg} and eutectics $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ in the prepared examined material..

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

1. Introduction

Since 1920s, when the strength-to-weight ratio was developed, there has been a tendency to reduce the mass of objects while maintaining their strength properties, especially in the automotive, aircraft and military industry [1]. Insufficiently high mechanical properties often constitute a limitation in the applicability of magnesium alloy casts [2-3].

The pursuit of obtaining magnesium alloy casts characterizing in possibly high mechanical properties has contributed to intensive adaptation and development of pressure technologies dedicated for the mentioned alloys [4]. On a smaller scale, magnesium alloy casts are also made in ceramic moulds. One of the methods of improving the properties of those alloys is rapid removal of heat from the mould and the casts as a result of intensive cooling, which, in consequence, leads to fragmentation of the microstructure [5,6]. Another method of changing the microstructure of magnesium alloys is introduction of alloy additions as well as application of modification processes with the use of various compounds [7-14].

A special attention should be paid to modifying magnesium alloys with gadolinium (Gd). Gadolinium significantly changes the microstructure and properties of magnesium alloys. In the study of Nan J. et. al. [15], introducing gadolinium and neodymium in the concentration of 0.6% resulted in the highest strength properties in the examined alloys. Miao Y. et al. [16] introduced gadolinium in the amount of 1% into alloy AM50, which also led to an increase of the strength properties as well as corrosion resistance. Mingbo et. al.[17] compared the additions of cerium, yttrium and gadolinium in the amount of about 0.8% on the mechanical properties and the microstructure of alloy Mg-3Sn-1Mn. Sumida M. et. al. [18] examined the effect of a high amount of gadolinium, of the order of 20%, on the heat parameters, including the thermal conductivity, as well as microstructure of magnesium alloy AZ91. It can be inferred from the performed literature analysis that it is possible to perform a modification process of a magnesium alloy with the use of gadolinium.

The aim of the study was to examine the effect of gadolinium on the process of crystallization and solidification as well as microstructure formation of casts made of alloy AZ91 obtained in ceramic moulds.

2. Experimental

The investigations included the preparation of 7 melts for alloy AZ91, which were subjected to modification with gadolinium. The melt schedule is presented in Table 1. Exactly the same mass percentage of the inoculant was used in all the melts.

Table 1.
Melt schedule

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

For the examinations, alloy AZ91 was selected, the composition of which is shown in Table 2. The composition of the examined alloy is in accordance with the standard PN-EN 1753:2001 [20].

Table 2.
Chemical composition of alloy AZ91

Chemical composition, % mass					
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 moulds – DTA samplers preheated to 180 °C. 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 [19]. 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 [6,21], and on the test bench presented in [19].

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:

Pk – 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 were carried out by means of a computer 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 gadolinium.

3. Results and discussion

3.3. DTA test

Figure 1 shows exemplary of the DTA characteristics for the alloy AZ91+0.2% (mass) Gd, whereas Table 3 compiles the coordinates of the characteristic points and their values for alloy AZ91.

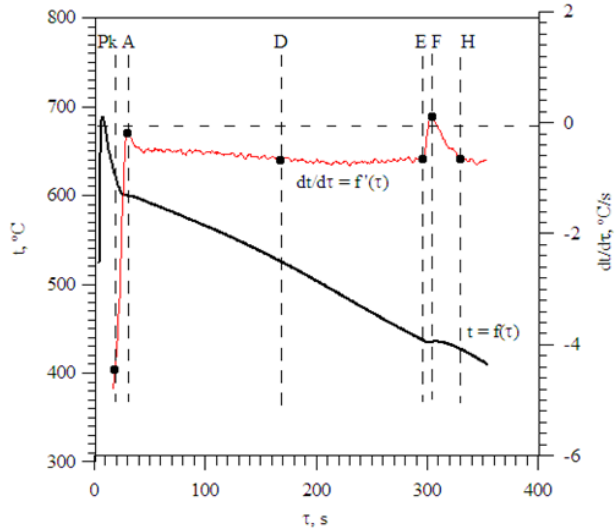

Fig. 1. DTA characteristics of non-modified representative example alloy AZ91+0.2%Gd solidifying in a ceramic sampler ATD10C-PŁ

Table 3.
Characteristics DTA points of non-modified alloy AZ91+0.2% (mass) Gd

Point	τ, s	t, °C	dt/dτ, °C/s	crystallizing phase
P_k	18.56	625.3	-4.4587	α_{Mg}
A	30.08	599.7	-0.1852	
D	167.7	525.8	-0.6760	
E	295.7	436.9	-0.6563	$\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$
F	304.0	434.9	0.1164	

H	330.2	426.5	-0.6551

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 the 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.

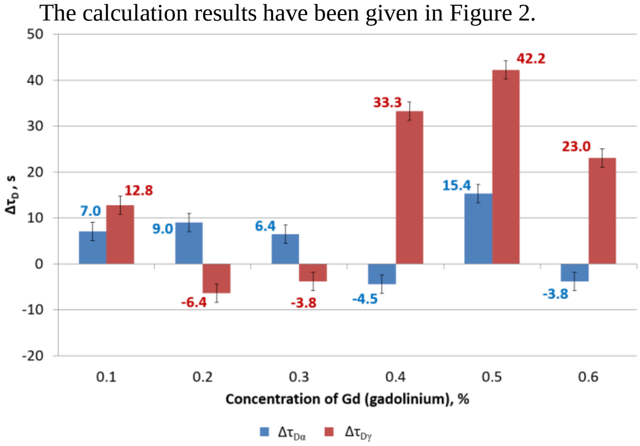

Fig. 2. Difference in the solidification time of phase α_{Mg} and eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$of modified alloys Gd in reference to the initial alloy AZ91

It can be inferred from the diagram presented in Figure 2 that introducing gadolinium into alloy AZ91 changes the crystallization time of both primary phase α_{Mg} and eutectic phase $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$. The crystallization time of phase α_{Mg} became longer for the concentrations from 0.1% to 0.3% as well as for the concentration of 0.5%, reaching its highest value of 15.4 s for the Gd concentration of 0.5%. In turn, for the Gd concentration of 0.4% and 0.6%, the crystallization time of phase α_{Mg} was shortened by about 4 seconds. The crystallization time of phase $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ became shorter for the concentrations of 0.2% and 0.3%. In the case of the remaining examined concentrations, the crystallization time of eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ was prolonged. The crystallization time of the eutectic increased the most for the gadolinium concentration equaling 0.5%. The total crystallization time became longer in all the examined samples. The highest prolongation of the total crystallization time $\Delta\tau = 57.6\ s$ was observed for the gadolinium concentration of 0.5%, whereas the lowest increase of the total crystallization time $\Delta\tau$=2.6 s was recorded for the inoculant concentrations of 0.2% and 0.3%.

3.2. Microstructure analysis

Metallographic tests were performed on the analyzed alloys. For the obtained microstructures, photographs were taken, which were then subjected to an image analysis described in section 3.3. Figure 3 shows the microstructure of non-modified alloy AZ91, whereas Figure 4 presents an exemplary microstructure of modified alloy AZ91+0.3%(Gd) and AZ91+0.4%(Gd). It can be inferred from the performed metallographic tests that, with the increase of the gadolinium concentration, the precipitates of primary phase α_{Mg} increased as well, whereas the precipitates of eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ became refined.

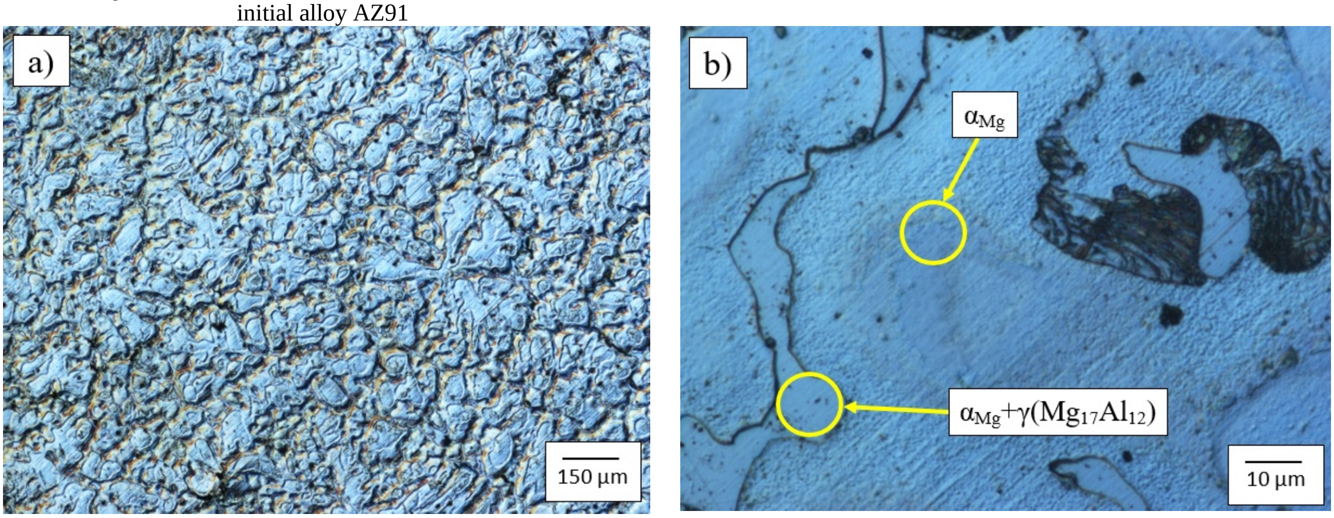

Fig. 3. Microstructure of AZ91 alloy

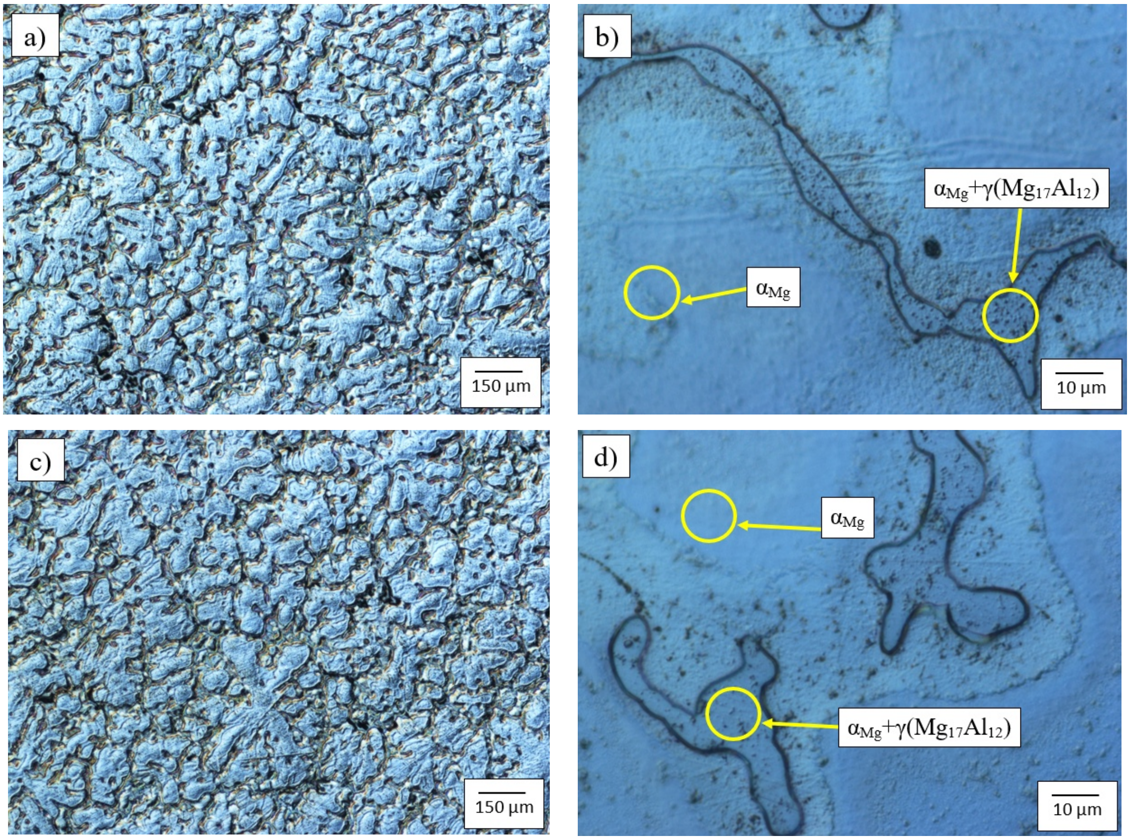

Fig. 4. Microstructure of representative examples AZ91+0.3%(Gd) – a, b and AZ91+0.6%(Gd) – c, d

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 average change in the grain size of primary phase α_{Mg} and eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ in reference to non-modified alloy AZ91. In order to present the effect of the inoculant addition on the mean sizes of primary phase α_{Mg} and eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ precipitates, measurements of the average values of the perimeters and diameters of the particular phases were performed. The percentage difference in the perimeters P_D of the analyzed phases α_{Mg} as well as eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ for the modified alloys in reference of non-modified alloy AZ91 was calculated from the relation:

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

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:

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

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

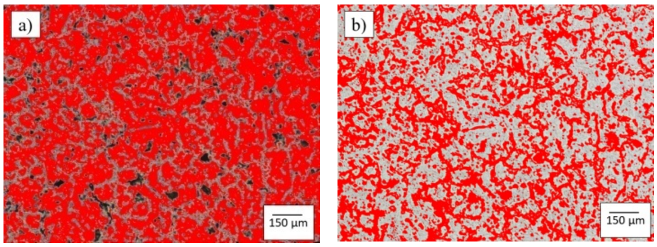

Fig. 5. Microstructure of representative sample AZ91+0.2Gd afterimage; a – preliminary phase α_{Mg}, b – eutectic$\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$

Figure 6 shows the value of index P_D calculated from relation 1. It can be inferred from the diagram that, for the inoculant concentrations of 0.1% and 0.5%, the mean perimeters of primary phase α_{Mg} and eutectic $\alpha Mg+\gamma(Mg_{17}Al_{12})$ precipitates become larger. For the gadolinium concentrations in the range of 0.1–

0.3% as well as for the concentration of 0.5%, the average perimeters of primary phase α_{Mg} precipitates became larger, reaching the highest value of 9.2% for the gadolinium addition in the amount of 0.2%. For the remaining examined concentrations, the phase α_{Mg} precipitaes became smaller about 8.1% for the Gd concentration of 0.4%. In the case of phase $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ for the gadolinium concentration of 0.1% as well as in the range from 0.4 to 0.6%, the mean perimeters of the precipitates became larger, reaching the highest value of 9.4%. In turn, for the inoculant concentrations in the range of 0.2–0.3%, the value of mean perimeters became lower, whereas the highest reduction of the mean perimeters about 10.6% was observed for the gadolinium concentration of 0.2%.

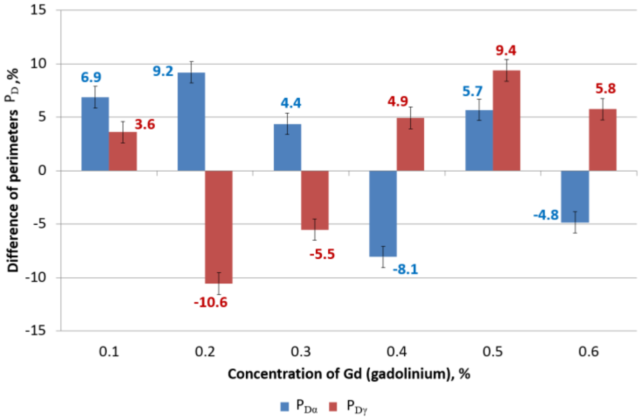

Fig. 6. Change of the grain perimeters of phase α_{Mg} and $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ in samples inoculated in reference to AZ91

Figure 7 shows the value of index D_D calculated from relation 2.

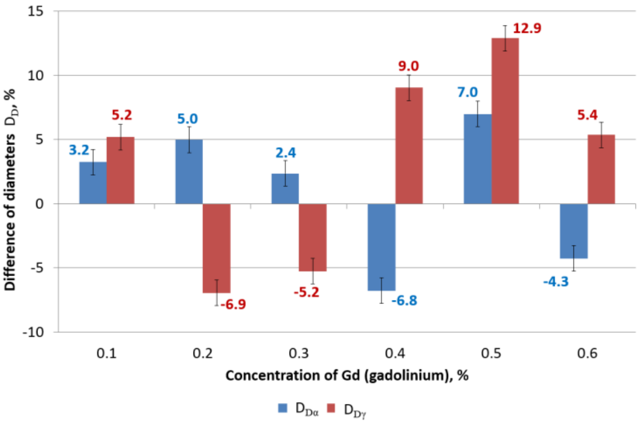

Fig. 7. Change in the mean diameters of phase α_{Mg} and $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ in inoculated samples in reference to AZ91

It can be inferred from the presented diagram that a gadolinium addition in the concentrations of 0.1% and 0.5% causes a simultaneous increase of the mean diameter values of phase α_{Mg} and phase $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ precipitates. It was also observed that, for the gadolinium concentrations in the range of 0.1%–0.3% as well as the concentration of 0.5%, an increase of the mean grain diameter values of primary phase α_{Mg} occurred. For the remaining two examined concentrations, the value of mean diameters became lower. The highest increase of the mean diameters for the primary phase equalled 7.0%, whereas the lowest value of the mean grain diameters of the primary phase equalled 0.4%. In the case of eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$, a reduction of the average grain diameters was observed for the concentrations of 0.2% and 0.3%, with the lowest reached value about 4.9%. For the remaining examined concentrations, an increase of the average grain diameters of the eutectic was observed. The highest increase of the mean diameters was recorded for the gadolinium concentration of 0.5%, reaching the value of 12.9%.

3.4. Chemical composition analysis

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

Table 4.
Chemical composition of analysed alloys

	Chemical composition, % mass				
Melt no.	**Mg**	**Al**	**Zn**	**Mn**	**Si**
II	90.8	8.48	0.442	0.164	0.0290
III	90.8	8.46	0.467	0.177	0.0330
IV	90.8	8.51	0.485	0.162	0.0198
V	91.7	7.57	0.446	0.174	0.0174
VI	91.3	7.94	0.478	0.165	0.0190
VII	91.8	7.53	0.440	0.171	0.0152

4. Conclusions

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

1. An addition of the inoculant in all the examined concentrations led to a prolonged total solidification time of the analyzed alloys, reaching its maximum equalling 57.6 s for the gadolinium concentration of 0.5%.
2. An introduction of the inoculant in the concentrations of 0.2% and 0.3% prolonged the solidification time of the alloy to the least degree in relation to non-modified alloy AZ91, by the value of 2.6 s.
3. An addition of gadolinium in the concentrations of 0.1% and 0.5% causes a simultaneous increase of the mean grain perimeters and diameters of primary phase α_{Mg} as well as eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$.
4. An introduction of the inoculant in the amount of 0.1–0.3% as well as 0.5% increases the values of the average perimeters and diameters of phase α_{Mg} precipitates in reference to non-modified alloy. For the remaining examined concentrations, the effect is reverse.

5. The application of gadolinium in the concentrations of 0.2% and 0.3% causes a reduction of the mean perimeters and diameters of the eutectic grains in reference to non-modified alloy.
6. For the inoculant concentrations equalling 0.1% as well as in the range of 0.4–0.6%, an increase in the values of mean perimeters and diameters of the eutectic grains was observed.
7. Based on the performed research, the optimal modifying effect in respect of microstructure fragmentation as well as crystallization time is obtained with the gadolinium concentration at the level of 0.3%.

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