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Effect of Inoculant Emgesal® Flux 5 on the Microstructure of Magnesium Alloy AZ91

C. Rapiejko *, D. Mikusek, A. Andrzejczak, T. Pacyniak
Lodz Univeristy of Technology, Department of Materials Engineering and Production Systems,
ul. Stefanowskiego 1, 90-924 Łódź, Poland
* Corresponding author. E-mail address: cezary.rapiejko@p.lodz.pl

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Abstract

This work presents the results of the research of the effect of the inoculant Emgesal Flux 5 on the microstructure of the magnesium alloy AZ91. The concentration of the inoculant was increased in samples in the range from 0.1% to 0.6%. The thermal processes were examined with the use of Derivative and Thermal Analysis (DTA). During the examination, the DTA samplers were preheated up to 180 °C. A particular attention was paid to finding the optimum amount of inoculant, which would cause fragmentation of the microstructure. The concentration of each element was verified by means of a spark spectrometer. In addition, the microstructures of the samples were examined with the use of an optical microscope, and an image analysis with a statistical analysis using the NIS–Elements program were carried out. Those analyses aimed at examining the differences between 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 an introduction to a further research of grain refinement in magnesium alloys, especially AZ91. Another purpose of this research is to achieve better microstructure fragmentation of magnesium alloys without the related changes of the chemical composition, which should improve the mechanical properties.

Keywords: Metallography, Solidification process, Magnesium alloys, Emgesal® Flux 5, 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]. This is caused by the fact that magnesium alloys characterize in low specific gravity as well as relatively good mechanical properties. Despite the fact that investigations of magnesium alloys have been performed since the moment this element was discovered, the real full potential of these alloys still remains unknown. Magnesium alloys are currently viewed as the lightest construction alloys. They occupy the top third position in respect of the extent of application, right after steels and aluminium alloys.

The properties of magnesium alloys depend on the technology of obtaining the casts. The best properties of magnesium alloy casts are obtained with the use of the pressure casting technology [3]. Magnesium alloy casts are also made in ceramic moulds, moulds made of synthetic moulding sands, as well as by means of die casting, yet at a smaller scale. In order to improve the mechanical properties of magnesium alloy casts, intensive cooling of the moulds is applied [4,5]. Another way of improving the properties of these alloys is changing their microstructure with the use of alloy additions and inoculants [6–11].

In the recent years, the researchers have been largely interested in modifying magnesium alloys with calcium. Ca, together with other elements, changes the microstructure and properties of magnesium alloys. A simultaneous introduction of Ca and Y significantly improves the tensile strength and creep resistance [12]. A Ca and La addition in the amount of approximately 2% also increases the tensile strength, yield point and elongation at room temperature as well as the temperature elevated to 175 °C [13]. In the case of AZ31 alloys, a 0.5% Ca addition reduces the tensile strength and yield point with a simultaneous increase of elongation at room temperature [14], whereas for the Mg–2Zn alloy, the tensile strength, the yield point and the elongation reached the highest values for the calcium concentration of 0.2% [15].

Commercial applications use compounds which modify the alloy and create a protective atmosphere during the melting process. Such compounds include Emgesal® Flux 5.

The aim of the study was to examine the effect of the Emgesal® Flux 5 concentration on the microstructure of AZ91alloy casts obtained in ceramic moulds.

2. Experimental

For the sake of the research, 7 melts of alloy AZ91 were performed, the alloy being modified with the Emgesal® Flux 5 compound of different percentage concentrations. The Emgesal® Flux 5 compound is a commercial product of Rheinkalk HDW GmbH & Co KG, the Lhoist group. It is a compound which reduces the degree of impurities of magnesium alloys containing 5% CaF_2 and with the density of 2.22 g/cm^3 and the freezing point of 384 °C [16]. The schedule of the melts has been presented in Table 1.

Table 1.
Melt schedule

Melt number	Melt's chemical composition
I	AZ91
II	AZ91+0.1% (5%CaF_2)
III	AZ91+0.2% (5%CaF_2)
IV	AZ91+0.3% (5%CaF_2)
V	AZ91+0.4% (5%CaF_2)
VI	AZ91+0.5% (5%CaF_2)
VII	AZ91+0.6% (5%CaF_2)

Alloy AZ91 was elected for the tests. Its chemical composition has been given in Table 2.

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 steel 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 avoid oxidation of the magnesium alloys, sulphur dust was used. The casts were then cooling at room temperature.

The casts were made in ceramic DTA samplers, which were preliminarily heated to 180 °C. Inside the samplers, there were quartz tubes, closed at one end, which served as protection for the measuring thermocouple type S (Pt-PtRh10). The samplers were made according to the technology described in [17]. The tests of the solidification and crystallization process of the examined alloys performed with the use of the DTA method were carried out by means of the methodology described in [4], with the use of the test bench presented in [18].

Within the research, the DTA method was used to perform an evaluation of the cooling ($t=f(\tau)$) and the kinetics ($dt/d\tau=f'(\tau)$) of the crystallization processes. On the derivation curve ($dt/d\tau=f'(\tau)$), the following thermal effects have been determined for the examined magnesium alloys:

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 examined with the use of a spark spectrometer SPECTROMAXx – Spectro. Before the microstructure was examined, the polished and ground surfaces of the samples underwent etching with the use of a formulation containing 1 ml acetic acid, 50 ml distilled water and 150 ml ethyl alcohol. The microstructure analysis was performed by means of an optical microscope Nikon Eclipse Ma 200, and the image analysis combined with a statistical analysis were carried out with the use of the NIS–Elements program cooperating with the microscope. The DTA analysis results and the statistical image analysis for the modified samples have been given in reference to the initial AZ91 alloy without modification.

3. Results and discussion

3.1. DTA tests

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

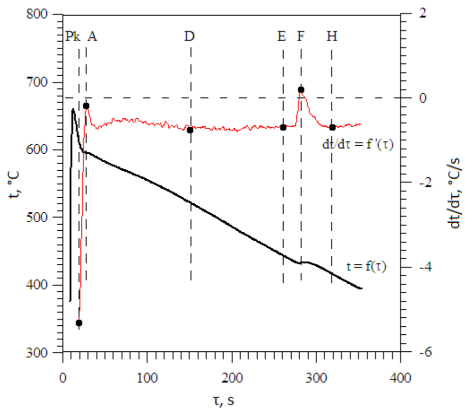

Fig. 1. DTA characteristics of non-modified AZ91 alloy solidifying in a ceramic ATD10C-PŁ sampler

Table 3.
Characteristic DTA points of non-modified AZ91

Point	τ, s	t, °C	dt/dτ, °C/s	Crystallizing phase
P_k	19.8	611.9	-5.32	
A	28.2	595.0	-0.20	α_{Mg}
D	151.7	521.1	-0.75	
E	260.5	443.8	-0.70	
F	281.6	432.6	0.20	α_{Mg}+ $\gamma(Mg_{17}Al_{12})$
H	301.4	428.2	-0.56	

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

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

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

- 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 α_{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 results of the performed calculations have been presented in Figure 2.

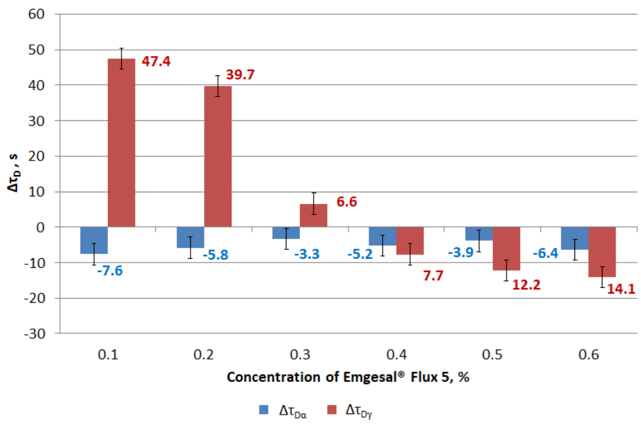

Fig. 2. Difference in the solidification time of phase α_{Mg} and eutectic α_{Mg}+$\gamma(Mg_{17}Al_{12})$ of modified alloys in reference to the initial AZ91 alloy

It can be inferred from Figure 2 that introducing the CaF_2 compound into the AZ91 alloy changes the crystallization time of both the primary phase α_{Mg} and the eutectic phase α_{Mg}+$\gamma(Mg_{17}Al_{12})$. The crystallization time of phase α_{Mg}, depending on the amount of the introduced inoculant, changed in respect of the initial AZ91 alloy. It was noticed that the introduced inoculant shortens the crystallization time of phase α_{Mg}. The strongest effect of the Emgesal® Flux 5 modification on the crystallization time of phase α_{Mg} of the AZ91 alloy was observed in the alloy containing 0.1% of the inoculant. The crystallization time of phase α_{Mg} was reduced by $\Delta\tau_{\alpha}$ = 7.6 s. The weakest effect of the inoculant on the crystallization time of phase α_{Mg} was observed for the concentration of 0.3% and 0.5%, for which the crystallization time $\Delta\tau_{\alpha}$ was shortened by approximately 4 s.

As a result of the performed research, it was established that the discussed inoculant significantly affects the formation of the eutectic phase α_{Mg}+$\gamma(Mg_{17}Al_{12})$. Introducing the inoculant in the amount of 0.1–0.3% increased the crystallization time of eutectic α_{Mg}+$\gamma(Mg_{17}Al_{12})$ by $\Delta\tau_{\gamma}$ = 47.4 s, 39.7 s and 6.6 s. The inoculant introduced in the amount of 0.4–0.6% shortened the crystallization time of the discussed phase, with the highest values of the time reduction - of over 10 s - recorded for the concentration of 0.5% and 0.6%.

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 the non-modified alloy AZ91 and an exemplary microstructure of the modified alloy AZ91+0.4%(5%CaF_2). It can be inferred from the performed metallographic tests that the precipitations of the primary phase α_{Mg} were reduced, whereas, depending on the amount of the introduced inoculant, eutectic α_{Mg}+$\gamma(Mg_{17}Al_{12})$ was expanded or refined, at the same time becoming more branched.

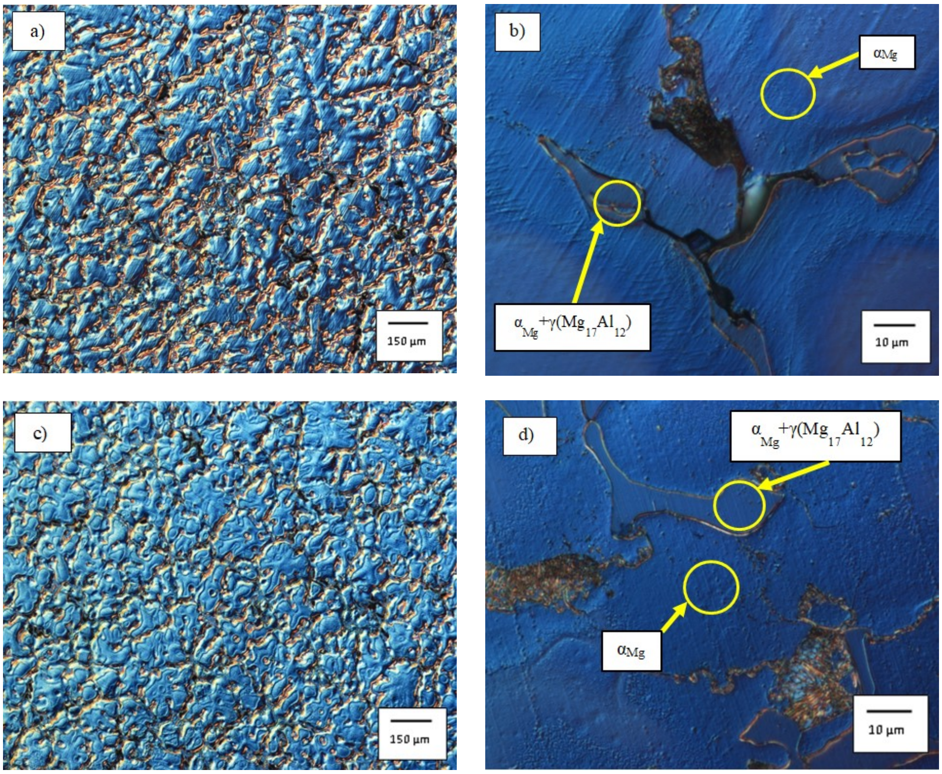

Fig. 3. Microstructure of non-modified alloy AZ91 (a, b) and alloy AZ91+0.4%(CaF_2) (c, d)

3.3. Image analysis

Figure 4 shows exemplary microstructure images subjected to a statistical image analysis. The aim of the analysis was to compare the average change of the grain size of the primary phase α_{Mg} and eutectic α_{Mg}+γ($Mg_{17}Al_{12}$) in respect of 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 α_{Mg}+γ($Mg_{17}Al_{12}$), measurements of the mean values of the perimeters and diameters of the particular phases were made. The percentage difference of the perimeters P_D of the analyzed phases α_{Mg} and eutectic α_{Mg}+γ($Mg_{17}Al_{12}$) for the modified alloys in reference to the non-modified alloy AZ91 were calculated from the Equation:

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

where:

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

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

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

where:

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

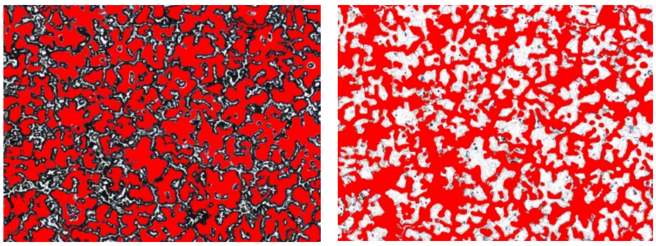

Fig. 4. Microstructure subjected to a statistical image analysis of alloy AZ91+0.6%(5%CaF_2); a – phase α_{Mg}, b – eutectic α_{Mg}+γ($Mg_{17}Al_{12}$)

Figure 5 shows the value of index P_D calculated from Equation 1. It can be inferred from the diagram that introducing the inoculant in the amount of 0.1% into alloy AZ91 reduces the average perimeters of phase α_{Mg} by about 6%. It was observed that the inoculant introduced in the amount of 0.2% and 0.3% significantly reduced the average perimeters of the primary phase (by over 50%) in reference to the mean perimeters of phase α_{Mg} of the non-modified alloy AZ91. Introducing the inoculant in the amount of 0.4% reduces the average perimeters of phase α_{Mg} by about 37%, whereas the inoculant addition of 0.5% and 0.6% reduces the mean perimeters by less than 20%.

The inoculant addition in the scope of 0.1–0.3% increases the mean perimeters of eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$, whereas an additon of the inoculant in the amount of 0.4–0.6% reduces the mean perimeters of the eutectic phase. The smallest perimeters of phase $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ were observed for the inoculant concentration of 0.4%; the change, in comparison with the sample of non-modified AZ91, equals about 28%.

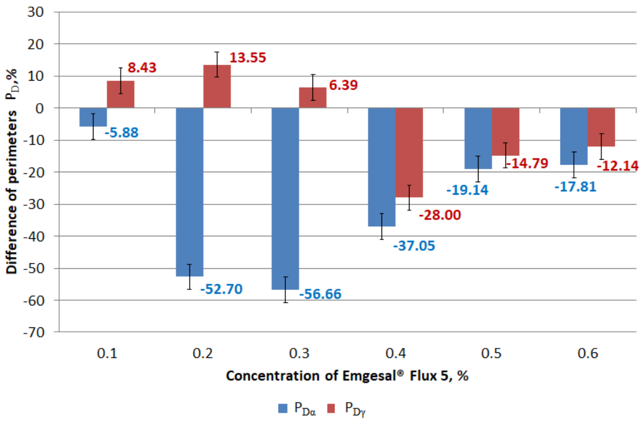

Fig. 5. Change of the grain perimeters of phase α_{Mg} and $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ in modified samples in relation to AZ91

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

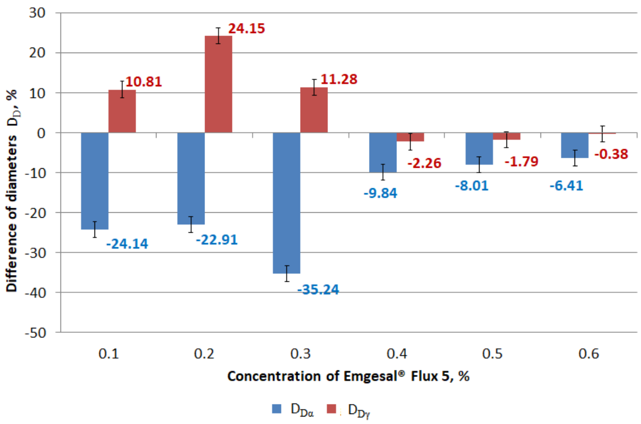

Fig. 6. Change of the mean diameters of phase α_{Mg} and $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ in modified samples in relation to AZ91

It can be inferred from the presented diagram that an addition of Emgesal® Flux 5 in the scope of 0.1–0.2% significantly reduced the average values of the diameters of phase α_{Mg} precipitations (by over 20%). Introducing the inoculant in the amount of 0.3% causes a reduction of the precipitation diameter by about 35%. The inoculant introduced in the scope of 0.4–0.6% reduces the values of the mean diameters of α_{Mg} primary phase precipitations by less than 10%.

The introduction of Emgesal® Flux 5 in the amount of 0.1–0.3% causes an increase of the value of the mean diameter of eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ precipitations by about: 10%, 24 % and 11%, respectively. The inoculant added in the scope of 0.4–0.5% reduces the value of the mean diameter of the eutectic precipitation by about 2%, whereas Emgesal® Flux 5 in the amount of 0.6% had practically no effect on the diameter of phase $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ precipitations.

3.4 Chemical composition analysis

Table 4 provides a compilation of the results of the chemical composition analysis performed on the examined samples. The chemical composition of all the trials is in accordance with the standard PN-EN 1753:2001 [19].

Table 4.
Chemical composition of the analysed alloys

	Chemical composition, % wt.				
Melt no.	Mg	Al	Zn	Mn	Ca
II	90.7	8.51	0.453	0.189	0.0048
III	89.9	9.26	0.487	0.238	0.0022
IV	90.5	8.73	0.437	0.243	0.0040
V	90.0	9.20	0.482	0.239	0.0040
VI	90.0	9.22	0.449	0.224	0.0015
VII	89.8	9.42	0.517	0.159	0.0016

4. Conclusions

The investigations were carried out as an introduction to more extensive studies aiming at refining the microstructure 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 test results made it possible to draw the following conclusions:

1. The application of an inoculant shortens the crystallization time of phase α_{Mg} in each concentration, while prolonging the crystallization time of phase $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ in the concentration of 0.1–0.3%, whereas in higher concentrations, it shortens the crystallization time of the eutectic, which also causes the corresponding changes in the microstructure.
2. The use of Emgesal® Flux 5 in the amount of 0.4–0.6% shortens the alloy's total crystallization time in a ceramic ATD sampler.
3. Introducing Emgesal® Flux 5 in the amount of 0.1–0.3% causes an increase of the perimeters and diameters of the $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ eutectic grains.
4. The inoculant addition of 0.4–0.6% reduces the perimeters of the precipitations of phase α_{Mg} and eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ as well as the values of mean diamteres.
5. The use of an inoculant reduces the value of the mean diameter of phase α_{Mg} precipitations with a simultaneous reduction of their perimeters.
6. The strongest effect of refinement of primary phase α_{Mg} was observed in samples enriched with the inoculant in the amount of 0.2–0.4%.

7. The introduction of Emgesal® Flux 5 to alloy AZ91 in the concentration of 0.1–0.3% increases the value of the mean diameter of eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$, whereas its concentrations of 0.4–0.6% causes a reduction of the value of the eutectic's mean diameter.
8. It was observed that a mutual refinement of phase α_{Mg} and eutectic $\alpha_{Mg}+\gamma(Mg_{17}Al_{12})$ in alloy AZ91 occurred after the introduction of 0.4% of the inoculant.

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