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Thermal Analysis of the ZnAl10 Alloy Modified by Ti Additions in AlTi5C0.15 and ZnTi3.2 Inoculants

G. Piwowarski*, J. Buraś, W.K. Krajewski, P.K. Krajewski**
AGH University of Science and Technology.
Faculty of Foundry Engineering – Department of Engineering of Foundry Processes,
23 Reymonta Street, 30-059 Krakow, Poland
*Corresponding author. E-mail address: *piwgrz@agh.edu.pl; **krajwit@agh.edu.pl

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Abstract

Cast alloys on the Zn matrix and of an increased Al content are characterised by good technological and mechanical properties, due to which they should meet special, more demanding requirements. However, the basic problem in these alloys technology, apart from a high tendency for gases pick-up and oxidation of liquid metals, is a tendency to form coarse-grained dendritic structures in castings solidifying in sand moulds, what - in turn - unfavourably influences their plastic properties [1, 2, 7, 11]. Therefore several treatments aimed at obtaining fine-grained structure and improving plastic properties are applied in these alloys technology. The presented study concerns the modification process of binary, middle-aluminium Zn alloys performed by additions of inoculants containing titanium and investigations of these modifications influence on the structure refinement degree. The Zn-10wt% Al (ZnAl10) alloy modified, before pouring into a sand mould, either by addition of the traditional inoculant i.e. Al-3wt% Ti-0.15wt% C (AlTi3C0.15 – TiCAl) or the new inoculant Zn-3.2wt% Ti (ZnTi3.2) was tested. Within investigations the thermal analysis was performed, especially cooling curves and their first derivatives, and also measurements by means of the differential scanning calorimetry (DSC), with a purpose of determining the modification influence on undercooling degree changes. Microstructures of the tested alloy were observed by the light microscopy (LM). The applied modification of middle-aluminium zinc alloys by AlTi3C0.15 and ZnTi3.2 inoculants causes a significant refinement of the alloy structure. Inoculants applied in investigations have a strong nucleating activity, which is confirmed by decreasing of undercooling and the temperature recalescence in cooling curves, which occurs simultaneously with grain refinements.

Keywords: medium-aluminium zinc alloys, grain refinement, thermal analysis

1. Introduction

A grain-refinement of casting alloys before pouring into a mould is a generally applied practice, which allows to increase grain population in the structure and favourably influences plastic properties of alloys [3, 4]. It is known from the scientific literature that casting alloys on the Zn-Al base have potentially significant possibilities of the practical utilisation due to their universality and the ability of being processed by the most modern techniques such as suspension pouring or squeeze casting [3, 4]. Zn alloys of the Al content increased to 8-40 wt.% deserve special attention due to good mechanical properties and very good casting properties, which allows to qualify these materials to the group of promising future materials. However, castings of these alloys made in sand moulds are characterised by a coarse-grained structure, obtained at a slow cooling in the mould, which unfavourably influences their plastic properties.

Currently performed investigations lead mainly towards ensuring optimal properties of high-aluminium Zn alloys at a simultaneous application of the environment friendly and energy-saving technological solutions [5, 6, 8, 10]. The hereby study is devoted to investigations aimed at the determination of the modification process influence on the degree of fineness of the middle-aluminium Zn alloys structure. The traditional TiCAl inoculant and the new ZnTi3.2 inoculant, were applied.

The Zn - 10wt% Al alloy (ZnAl10) was investigated. Before pouring into the sand mould it was modified by additions of the traditional modifying inoculant of the type: Al-3wt% Ti–0.15wt % C, marked as AlTi3C0.15 - TiCAl and the new inoculant: ZnTi3.2. Both inoculants were introducing into the metal bath approximately 100 ppm Ti. The thermal analysis, especially cooling curves and their first derivatives were performed as well as measurements by means of the differential scanning calorimetry (DSC). The light microscope (LM) was used for assessment of the refinement of macrostructure grains of the alloy being investigated.

2. Materials and methodology

The investigation results obtained for ZnAl10 alloy are presented in the paper. This is the middle-aluminium alloy, representing the group of alloys: ZnAl8 and ZnAl12. The initial alloy was obtained from electrolytic zinc and aluminium, of both elements purity being 99.999 %. The ZnAl10 alloy melted from pure components was cast in a form of rollers of a mass app. 0.5 kg. The material prepared in such way was then re-melted and subjected to modifications before pouring into the mould. Melts were performed in the graphite crucible in the resistance furnace. Samples for tests were cast as rollers of a diameter 32 mm and a height app. 80 mm. Samples were cast in dried moulds made of the classic bentonite moulding sand. The AlTi3C0.15 inoculant and inoculant ZnTi3.2 were applied as the modifying factors. Both inoculants are good carriers of titanium, the strongly nucleating element. The sand mould application allowed to eliminate - to a high degree - the influence of the cooling rate on the casting grains refinement, which occurs when metal mould is used and makes difficult the modifier effectiveness assessment.

Two measuring techniques were applied in the thermal analysis. Measurements of cooling curves in the sand mould, which schematic presentation is given in Figure 1. Measurements by means of the differential scanning calorimetry (DSC).

In the sand mould cavity, intended for casting of samples intended for structure and thermal analyses (Fig. 1) two thermoelements type K (NiCr-NiAl0.5) of Ø 0.20 mm were mounted from the top. These thermoelements were in protective, double-bore ceramic tubes of external diameter 1.2 mm, produced by Degussit, Germany. Temperature values were recorded by the measuring instrument Agilent 34980A, produced by Agilent Technologies Inc., USA.

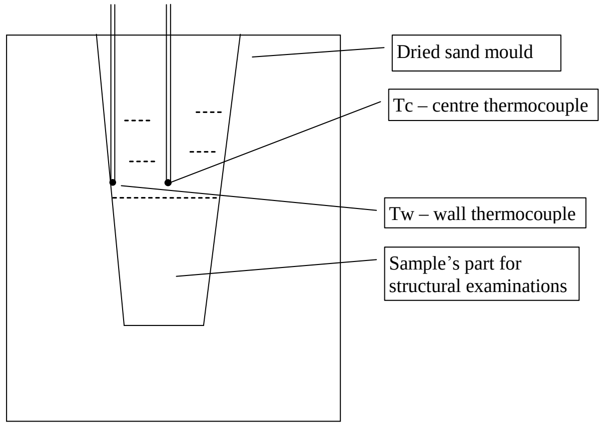

Fig. 1. Schematic presentation of the sand mould

The obtained temperature-time data were transferred, via interface into the computer, where they were further processed by means of the calculation sheet Excel. On the bases of the recorded temperature changes $\boldsymbol{T}$ as a time $\boldsymbol{t}$ function, the first derivatives $\boldsymbol{dT/dt}$, were calculated.

The temperature corresponding with the beginning of the alloy crystallisation, was determined from the first derivative, from the breakdown curve related to the crystallisation heat emission and the abrupt change of the derivative value, as well as from the analogous breakdown in the temperature difference curve in the casting centre, Tc and in the vicinity of the casting-mould wall, Tw.

The thermal DSC analysis was performed by means of the microcalorimeter SDT Q600, produced by TA Instruments, USA. The temperature range to app. 500 °C was used in investigations. Samples heating and cooling processes were performed with the rate of 5 K min^{-1}.

Crucibles made of Al_2O_3, supplied by the device producer, were used. One crucible contained the tested sample, while another was empty and served as the reference material. Samples for DSC tests were cut out from the cast rollers, and weighted app. 40 mg. Before measurements the temperature calibration was performed by means of high purity Zn, Al, Cu and Ni, and also the mass, base DTA line and heat flow calibrations, were done. The analysis of DSC tracks was performed by the internal software of the TA Company, which allowed to determine points of the transformation start and finish in the DSC curve, as well as areas of peaks corresponding with these transformations.

3. Description of achieved results of own researches

Cooling curves of the initial, not modified ZnAl10 alloy and after the modification are presented in Figure 2. It can be noticed that both modifying inoculants cause shifting the crystallisation start temperature in the direction of higher temperatures and cause decreasing and decaying of undercooling. Cooling curves for the alloy modified by addition of 100 ppm Ti introduced in the AlTi3C0.15 inoculant, are presented in Figure 3. The diagram presents cooling curves measured at sample axis, Tc and at its wall, Tw. Curves corresponding to the first derivative dT/dt and difference between Tc and Tw temperatures, are also in this diagram. Breakdowns in these curves allow to determine the temperature of the crystallisation start. Analogous series of data are presented in Figure 3b, however they show the modification treatment when 100ppm of Ti was introduced in the ZnTi3.2 inoculant.

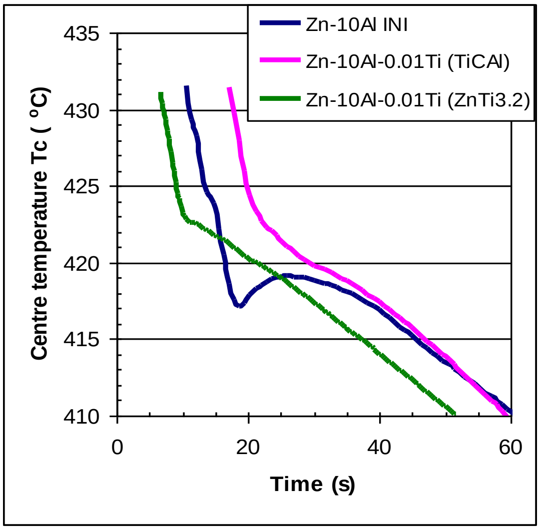

Fig. 2. Comparison of cooling curves first periods for the not modified and modified ZnAl10 alloy

The temperature of the crystallisation start read-out from the diagram for the initial ZnAl10 alloy equals app. 423 °C. The DSC investigation, the results of which are presented in Figure 4, indicates the similar crystallisation temperature. The determined temperature constitutes a point of departure for the determination of the efficiency of casting grains fragmentation by the applied inoculants.

When comparing cooling curves (Fig. 3a) and DSC curves diagrams (Fig. 5), it is possible to determine the temperature of the beginning of crystallisation for the alloy modified by the AlTi3C0.15 inoculant. It is equal app. 428 °C. In a similar way, from the comparison of curves in Figures 3b and 6, it is easy to determine the temperature for the ZnTi3.2 inoculant, which equals 427 °C. Thus, it can be seen from the performed analyses and from comparisons of curves - mentioned above - that both inoculants by introducing Ti in the amount corresponding to 100 ppm cause increasing the crystallisation start temperature by app. 5°C. Such change has an essential influence on the crystallisation course and causes increased number of crystallisation nuclei, which - in turn - leads to increased grains number and to a general intensive structure refinement. The results of microscopic observations are presented in Figure 7 and 8. The modification influence on the alloy microstructure (Fig. 7) is mainly manifested by limiting the dendrite growth and by increasing their numbers. Their shapes are also changing. From strongly branched they are becoming more coagulated and compact. The eutectic fraction in also increased.

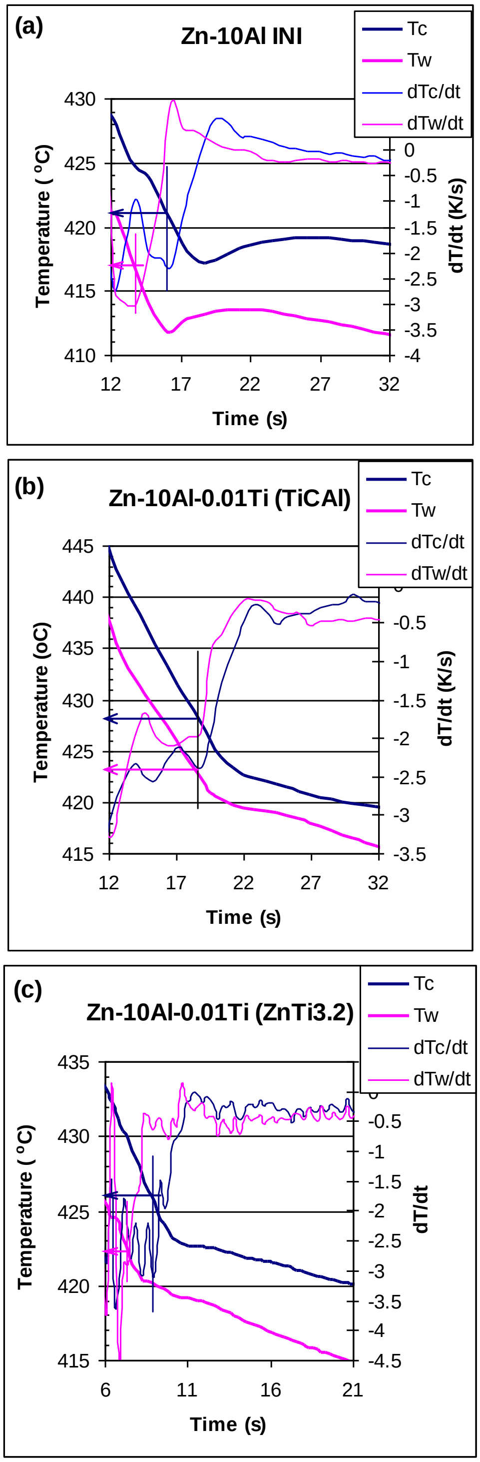

Fig. 3. Cooling curves and the first derivative for: a) initial non inoculated ZnAl10 alloy, b) ZnAl10 alloy inoculated by 100 ppm Ti in the AlTi3C0.15 refiner alloy, c) ZnAl10 alloy inoculated by 100 ppm Ti in the ZnTi3.2 refiner

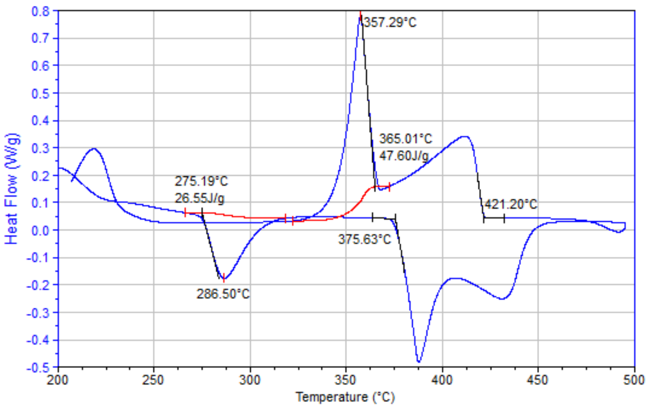

Fig. 4. DSC curves for the ZnAl10 alloy

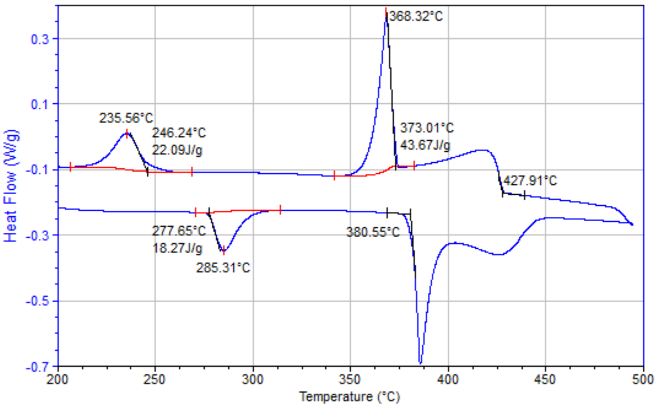

Fig. 5. DSC curves for the ZnAl10 alloy modified by 100 ppm Ti in the AlTi3C0.15 inoculant

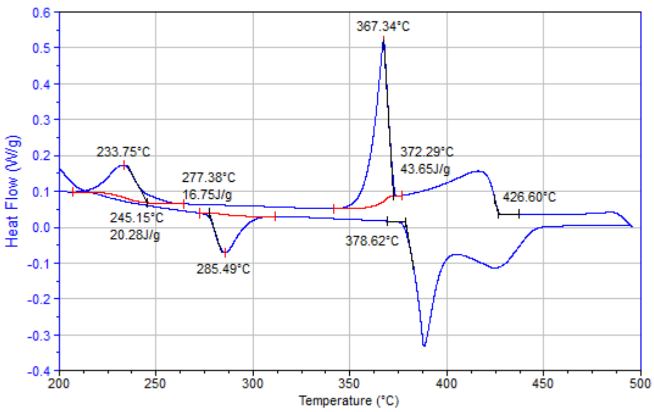

Fig. 6. DSC curves for the ZnAl10 alloy modified by 100 ppm Ti in the ZnTi3.2 inoculant

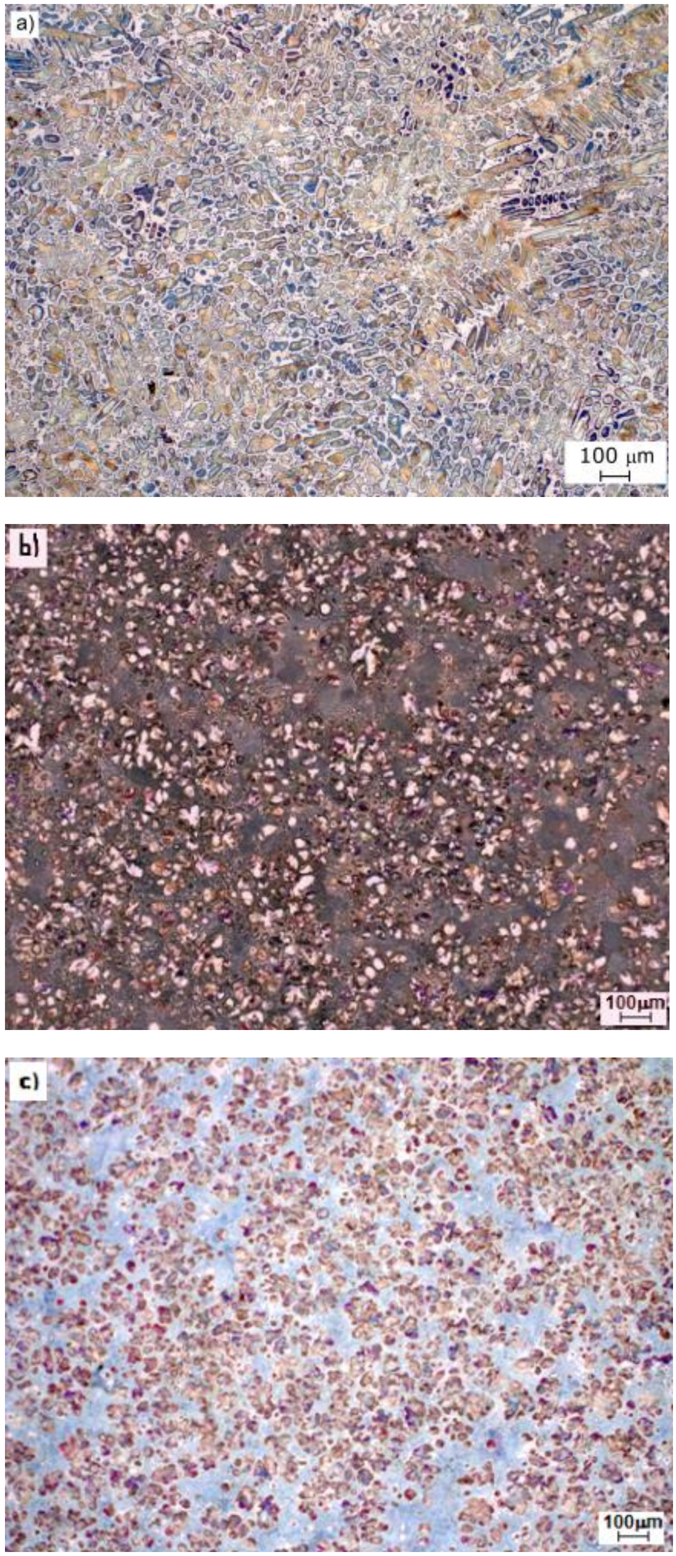

Fig. 7. Microstructures of the ZnAl10 alloy: a) Initial, not modified, b) Modified by 100 ppm Ti in the ZnTi3.2 inoculant, c) Modified by 100 ppm Ti in the AlTi3C0.15 inoculant

Applying polarised light, pictures of the macrostructure of the ZnAl10 alloy not modified and after modification procedures (Fig. 8) were obtained. Due to the structure specificity of the ZnAl alloys the detailed analysis of pictures is rather difficult. These analyses allow to draw the general conclusion that subjecting these alloys to modifying process with the application of inoculants used in investigations causes intensive refinement of grains.

4. Conclusions

On the bases of the performed investigations and obtained results it can be stated that the application of the modification process of middle-aluminium zinc alloys by the addition of 100 ppm of Ti in the AlTiC0.15 and ZnTi3.2 inoculants causes a significant refinement of the structure components. As can be seen from Fig. 3 the crystallisation starts at a temperature higher by app. 5 °C in comparison with the initial, not modified alloy, which is also indicated by nearly complete decaying of undercooling. In addition on the recorded cooling curves the temperature recalescence occurring simultaneously with grains refinement, is clearly seen. The obtained results allow to state that creation of new crystallisation nuclei in the modified alloy occurs according to the heterogeneous nucleation mechanism. The detailed analysis of macro- and microstructures confirms nucleating activity of inoculants used in investigations. However, comparing the influence of both inoculants it is difficult to state explicitly which has the better nucleating activity. The obtained results indicate that the achieved effects are comparable. The fact that the ZnTi3.2 inoculant is zinc based and due to that such parameters as the melting temperature and density are similar to the ones of alloys in which this inoculant is used, can be in its favour. These properties, in turn, cause good and fast dissolving of the ZnTi3.2 inoculant in the metal bath as well as prevents out-flowing of inoculant pieces on the metal bath surface during their introduction, as it happens when the traditional AlTi3C0.15 inoculant - based on the aluminium matrix - is introduced.

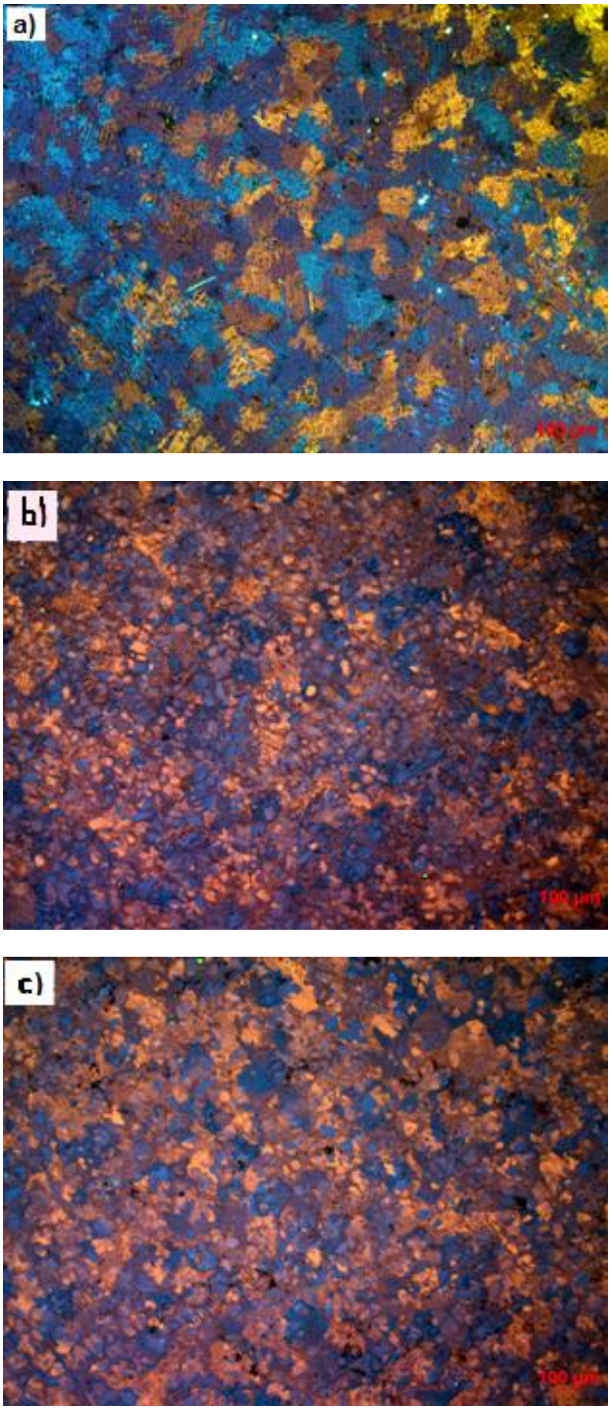

Fig.8. Macrostructures of the ZnAl10 alloy: a) Initial, not modified, b) Modified by 100 ppm Ti in the ZnTi3.2 inoculant, c) Modified by 100 ppm Ti in the AlTi3C0.15 inoculant

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