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# Structure and Properties Investigation of MCMgAl12Zn1 Magnesium Alloy

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## Abstract

This work presents an influence of cooling rate on crystallization process, structure and mechanical properties of MCMgAl12Zn1 cast magnesium alloy. The experiments were performed using the novel Universal Metallurgical Simulator and Analyzer Platform. The apparatus enabled recording the temperature during refrigerate magnesium alloy with three different cooling rates, i.e. 0.6, 1.2 and 2.4°C/s and calculate a first derivative. Based on first derivative results, nucleation temperature, beginning of nucleation of eutectic and solidus temperature were described. It was fund that the formation temperatures of various thermal parameters, mechanical properties (hardness and ultimate compressive strength) and grain size are shifting with an increasing cooling rate.

**Keywords:** Thermal analysis, Microstructure, Mechanical properties, Magnesium alloy

## 1. Introduction

Magnesium has the best strength to weight ratio of common structural metals, and it has exceptional die-casting characteristics. This makes magnesium alloys particularly attractive for transportation applications such as in the automotive and aircraft industries for weight reduction and higher fuel efficiency. The rapid growth in the magnesium consumption has highlighted the need for a greater understanding of factors that influence the properties of magnesium alloys and industry's increasing demands for a wider range of magnesium alloys with lower thermal expansion, higher fatigue strength, higher creep strength, and better corrosion resistance [1, 2]. The current use of magnesium in automotive applications is limited to noncritical parts because of its restricted creep properties [3].

The growing interest of many branches of industry magnesium alloys involves the need to carry out research on the optimization of chemical composition and manufacturing technology in order to obtain material which is characterized by the most favourable mechanical properties, and thus the use of modern methods of research of magnesium alloys in real time, in order to achieve full control over the process of crystallization and to make possible the improvement of quality alloy [4, 5].

One of the most common methods for the study of alloys in a liquid state before pouring method of analysis used thermal-derivation. This method is due to its simplicity, has found wide application in assessing the quality of liquid metal alloys. Based on theoretical analysis of phase equilibrium systems, and practical measurements in industrial conditions, can be determined between the temperature dependence of nucleation phase, solidus temperature, cooling rate and chemical composition of the alloy and its properties. A special feature of this method is the short time in which to obtain data to evaluate the test material [6-9].

The derivative thermal analysis is a modernized and extended form commonly known thermal analysis. Registration involves an alloy solidification curve and determining on the basis of the first derivative, which represents the change of state and changes in a liquid state and solid. Thermal derivation analysis can provide valuable derivation of quantitative and qualitative information that are difficult or impossible to obtain by other methods. This

allows for better design of alloys, their heat treatment and allows more accurate their assessment.

Thermal derivation analysis is very broad scope in both research and industrial practice. The most common application concerns a field of quality management because it allows rapid assessment of concentrations of certain elements in alloys, evaluation of some mechanical and technological properties, which in turn determines the quality of alloys. Thermal analysis is possible to perform alloy just before casting into the mould to make any adjustments to the quality of molten metal, e.g. for subsequent heating or cooling. The particular advantage this method is not only the opportunity to evaluate alloy with the chemical composition, but also the opportunity to evaluate the same process of measuring many of the details of the kinetics of crystallization of primary or secondary. Obtain as much information on interest in such a short time (2-5 minutes) allows for an immediate decision to improve the quality or the motivates greater technical discipline process. This is so the best and easiest way to improve the quality of foundry and metallurgical deciding the degree of reliability of machines and equipment [10-13].

## 2. Investigation methodology

Research has been done on MCMgAl12Zn1 magnesium alloys in as-cast made in cooperation with the Faculty of Metallurgy and Materials Engineering of the Technical University of Ostrava and the CKD Motory plant, Hradec Kralove in the Czech Republic. The chemical composition of the investigated material is given in Table 1. A casting cycle of alloys has been carried out in an induction crucible furnace using a protective salt bath Flux 12 equipped with two ceramic filters at the melting temperature of 750±10ºC, suitable for the manufactured material. In order to maintain a metallurgical purity of the melting metal, a refining with a neutral gas with the industrial name of Emgesalem Flux 12 has been carried out. To improve the quality of a metal surface a protective layer Alkon M62 has been applied. The material has been cast in dies with betonite binder because of its excellent sorption properties and shaped into plates of 250x150x25. The cast alloys have been heated in an electrical vacuum furnace Classic 0816 Vak in a protective argon atmosphere.

Table 1.
Average chemical composition (wt. %) of the MCMgAl12Zn1 alloy

| Al | Zn | Mn | Cu | Si | Fe |
|---|---|---|---|---|---|
| 11.894 | 0.55 | 0.22 | 0.0064 | 0.05 | 0.02 |

The thermal analysis during melting and solidification cycles was carried out using the Universal Metallurgical Simulator and Analyzer (UMSA) (Fig. 1) [14]. The melting and solidification experiments for the magnesium alloy were carried out using Argon as cover gas. The data for Thermal Analysis (TA) was collected using a high-speed National Instruments data acquisition system linked to a personal computer. Each TA trial was repeated three times to stabilize a process.

The TA signal was recorded during the melting and solidification cycles. The temperature vs. time and first derivative vs. temperature were calculated.

The procedure comprised of the following steps. First, the test sample was heated to 700±2°C and isothermally kept at this temperature for a period of 90s in order to stabilize the melt conditions. Next, the test sample was solidified at cooling rate of approximately 0,6°C/s, that was equivalent to the solidification process under natural cooling conditions. To achieve an intentional cooling rate:

- 0.6°C/s sample was cooled without forces air
- 1.2°C/s sample was cooled in airflow 30 l/min,
- 2.4°C/s sample was cooled in airflow 125 l/min.

The experiments were performed using a pre-machined cylindrical test sample with a diameter of $\phi$=18mm and length of l=20mm taken from the ingot. In order to assure high repeatability and reproducibility of the thermal data, the test sample mass was 9.1g within a very closely controlled range of ±0,1g. Each sample had a predrilled hole to accommodate a supersensitive K type thermocouple (with extra low thermal time constants) positioned at the center of the test sample to collect the thermal data and control the processing temperatures.

Metallographic samples were taken from a location close to the thermocouple tip. Samples were cold mounted and grounded on 240, 320, 400, 600 and 1200 grit SiC paper and then polished with 6μm, 3μm and 1μm diamond paste. The polished surfaces were etched with a solution of 2g oxalic acid, 100ml water, with fresh alcohol blotted repeatedly onto the surface to prevent residue deposits.

Microstructure features were characterized using light optical microscope Leica Q-WinTM image analyzer.

The X-ray qualitative and quantitative microanalysis and the analysis of a surface distribution of cast elements in the examined magnesium cast alloys have been made on the Opton DSM-940 scanning microscope with the TRIDENT XM4 (EDS, WDS, EBSD) EDAX dispersive radiation spectrometer at the accelerating voltage of 20 kV. Phase composition and crystallographic structure were determined by the X-ray diffraction method using the X`Pert device with a copper lamp, with 40 kV voltages. The measurement was performed by angle range of 2θ: 30º-120º.

Rockwell F–scale hardness tests were conducted at room temperature using a Zwick HR hardness testing machine.

Ultimate compressive test were made on universal testing machine Zwick ZHR 100. Compression and hardness specimens were tested corresponding to each of the three cooling rates.

## 3. Investigation results

According to the X–ray phase analysis, the investigated MCMgAl12Zn1 alloy cooled with solidification rate: 0.6, 1.2 and 2.4. ºC/s is composed of two phases (Fig. 1.): α–Mg solid solution as matrix and γ($Mg_{17}Al_{12}$). In the diffraction pattern of the matrix, the {011} Mg–diffraction line has very intensity. Based on the X–ray phase analysis was found, that changing the cooling rate does not change the phases composition of investigated alloy. The X–ray phase analysis don't ravel occurring of $Mg_2Si$ and phases

contains Mn and Al, what suggested that the fraction volume of these phases is below 3%.

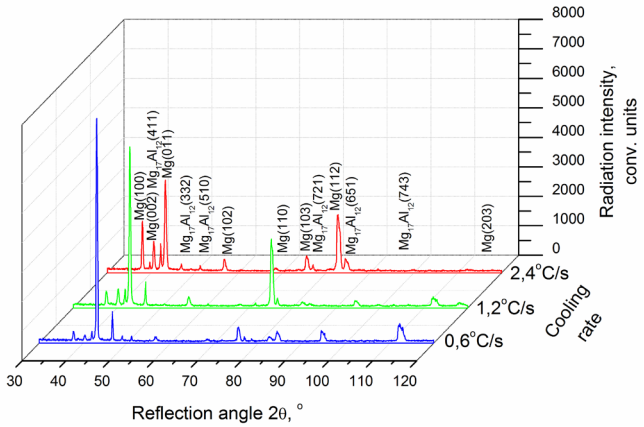



Fig. 1. XRD pattern of MCMgAl12Zn1 casting alloy at various solidification conditions

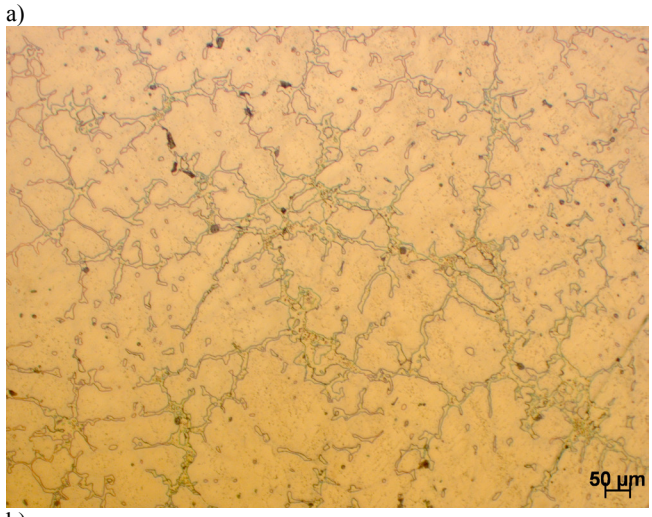
Figures 2 shows the microstructures of MCMgAl12Zn1 alloys at cooled with different cooling rates. Microstructures consisted of α-Mg solid solution, $Mg_{17}Al_{12}$ phase compound located in grain edge, $Mg_2Si$ and phases contains Mn and Al. The structure configurations at different experimental cooling rates were similar. The cooling rate had obvious effect on grain size of solidification microstructure. The grain size of magnesium alloy was determined by image analysis and shows that the grain size decreases with increasing cooling rate.

SEM micrograph of MCMgAl12Zn1 magnesium alloy after thermal analysis are shown in Fig. 3. Results from EDS analysis are shown in Table 2. EDS spectra for all samples confirms that, the matrix is α-Mg, and intermetallics phases mostly likely $Mg_2Si$, and Al-Mn (it could be a mixture of $Al_8Mn_5$, $MnAl_4$). Because the size of particular elements of the structure is, in a prevailing measure, smaller than the diameter of the analyzing beam, the obtained at the quantitative analysis chemical composition may be averaged as a result of which some values of element concentrations may be overestimated.

The cooling curves recorded for MCMgAl12Zn1 alloy at various cooling rates are shown in Fig. 4. Thermal analysis of the magnesium alloys have been presented on Fig. 5. The cooling rate is proportional to the heat extraction from the sample during solidification. Therefore, at a low cooling rate (0.6 ºC/s), the rate of heat extraction from the sample is slow and the slope of the cooling curve is small. So, it creates a wide cooling curve. But, at a high cooling rate (2.4 ºC/s) the rate of heat extraction from the sample is fast, the slope of the cooling curve is steep and it makes a narrow cooling curve. Two visible temperatures were observed on the cooling curves.

More information about the liquidus and solidus temperatures and nucleation of eutectic were characterized based on the first derivative curves (Fig. 5). Thermal analysis of magnesium alloy revealed that the solidify process of material cooled at 0.6°C/s (Fig. 4, line a) started at 583.01± 9.18°C (point 1) and was completed at 420.07±2.97°C (point 3) where fraction solid obtained a 100%.

a)




b)


c)

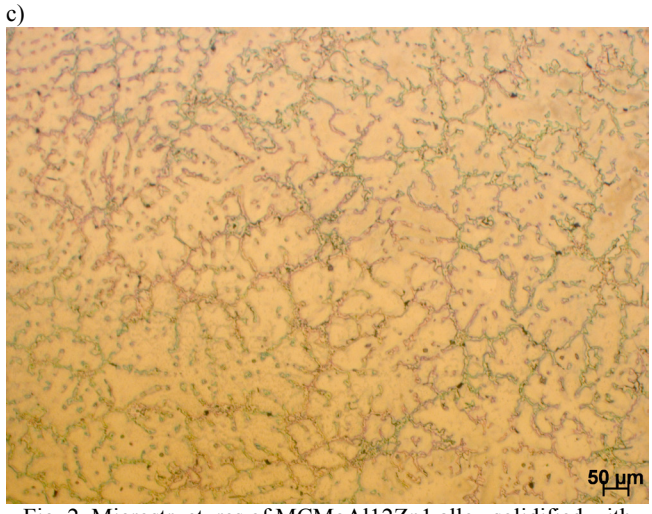



Fig. 2. Microstructures of MCMgAl12Zn1 alloy solidified with cooling rate: a) 0.6°C/s, b) 1.2°C/s, c) 2.4°C/s. Magnification 100x.

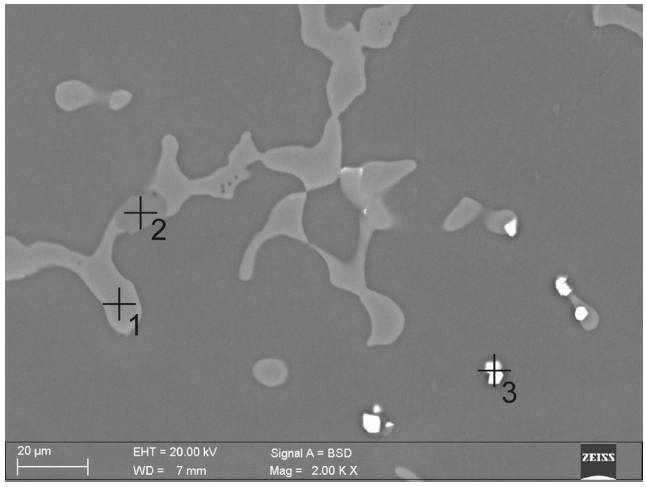



Fig. 3. Representative scanning electron microscope micrograph of magnesium alloy that solidified with cooling rate 0.6°C/s

Table 2.
Pointwise chemical composition analysis from Fig. 3

| | *Element* | *The mass concentration of main elements, %* | |
|---|---|---|---|
| | | *weight %* | *atomic %* |
| 1 | Zn | 4.17 | 1.65 |
| | Mg | 61.97 | 65.9 |
| | Al | 33.87 | 32.45 |
| 2 | Mg | 65.86 | 69.02 |
| | Si | 34.14 | 30.98 |
| 3 | Mg | 8.47 | 12.47 |
| | Al | 41.29 | 54.79 |
| | Mn | 50.24 | 32.74 |

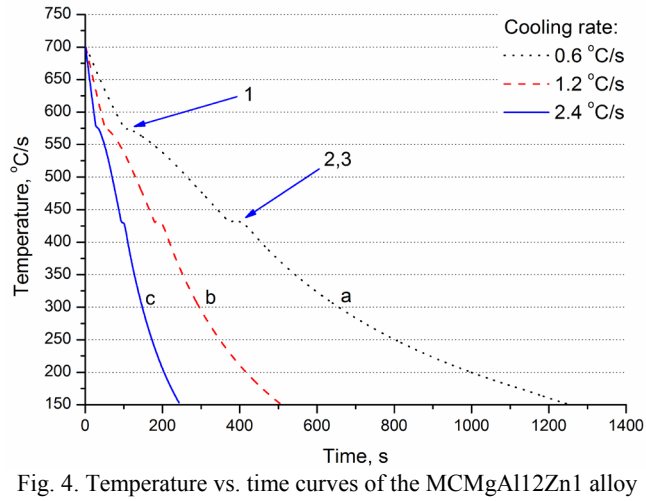



Fig. 4. Temperature vs. time curves of the MCMgAl12Zn1 alloy test samples recorded during solidification at 0.6°C/s (line a), 1.2°C/s (line b) and 2.4°C/s (line c). The numbers correspond to the various metallurgical reactions as presented in Table 3.

Next change on the first derivative curve, at 432.55± 0.64°C was observed and corresponded to the nucleation of the α(Mg)-γ(Mg-$Mg_{17}Al_{12}$) eutectic (Fig. 4, point 2). The cooling curve for the MCMgAl12Zn1 alloy that solidified under a 1.2°C/s solidification rate is presented in (Fig. 4, line b). Alloy started solidify at 582.4±1.98°C and finished at 414.03±3.84°C. The nucleation of the α(Mg)-γ(Mg-$Mg_{17}Al_{12}$) eutectic was observed at 436.05±0.83°C.

The non-equilibrium liquidus temperature of MCMgAl12Zn1 alloy that solidified under a 2.4°C/s (Fig. 4, line c) was found approximately at 592.28±4.64°C. A further decrease in the temperature resulted in nucleation of the α(Mg)-γ(Mg-$Mg_{17}Al_{12}$) eutectic at 441.87±2.24°C. The solidification process finished approximately at 415.42±0.93°C when the fraction solid obtained a 100%.

Table 3.
Non-equilibrium thermal characteristics of the MCMgAl12Zn1 alloy test samples obtained during the solidification process at 0.6°C/s, 1.2°C/s and 2.4°C/s solidification rates

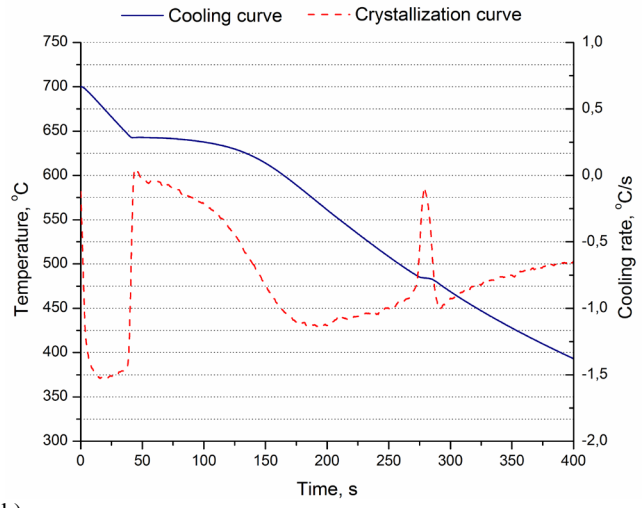
| Characteristic point | Solidification rate,°C/s | | |
|---|---|---|---|
| | 0.6 | 1.2 | 2.4 |
| | Temp., °C | Temp., °C | Temp., °C |
| 1 | 583.01± 9.18 | 582.4±1.98 | 592.28±4.64 |
| 2 | 432.55± 0.64 | 436.05±0.83 | 441.87±2.24 |
| 3 | 420.07±2.97 | 414.03±3.84 | 415.42±0.93 |

The variations of grain size and ultimate compressive strength have been showed graphically in Fig. 6. Grain size is strictly depending on the cooling rate. For the sample that was cooled with lowest cooling rate, the grain size is approximately 110.4±20 µm. Increases cooling rate cause decrease of grain size to 84.5±8 µm.

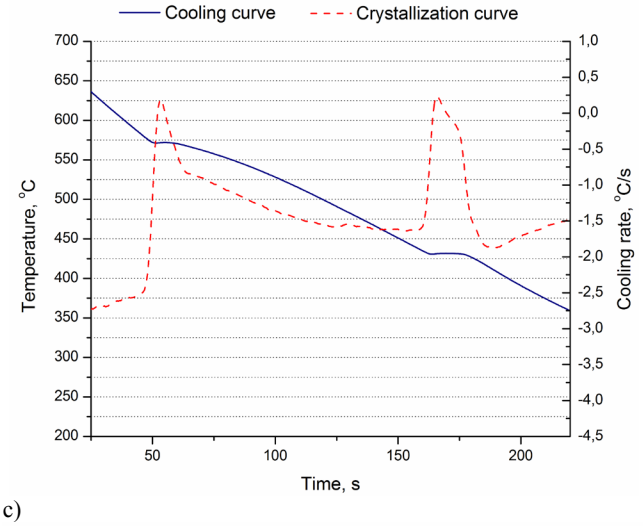
Mechanical properties of the magnesium alloy are strongly dependent on the effect of grain size. Ultimate compressive strength increases with a decrease the grain size. Investigations results shows, the increase the cooling rate from 0.6ºC/s to 2.4ºC/s influence on the reduction of the grain size, what have influence on the ultimate compressive strength. The ultimate compressive strength increase from 256.1±9 MPa for lowest cooling rate to 273.7±1 MPa for highest cooling rate (Figure 6).

Figure 7 presents a variation of the hardness as a function of cooling rate. The hardness grows with increment of the cooling rate. The hardness increases from 71.5±1.6 HRF for lowest cooling rate to 74.2±1.8 HRF for highest cooling rate. Measuring errors occurred during testing did not exceed 5%.

a)




b)




c)

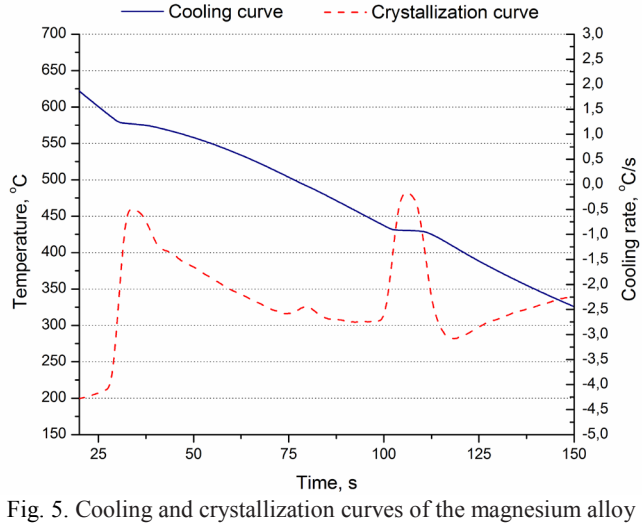



Fig. 5. Cooling and crystallization curves of the magnesium alloy solidified with cooling rate: a) 0.6°C/s, b) 1.2°C/s, c) 2.4°C/s

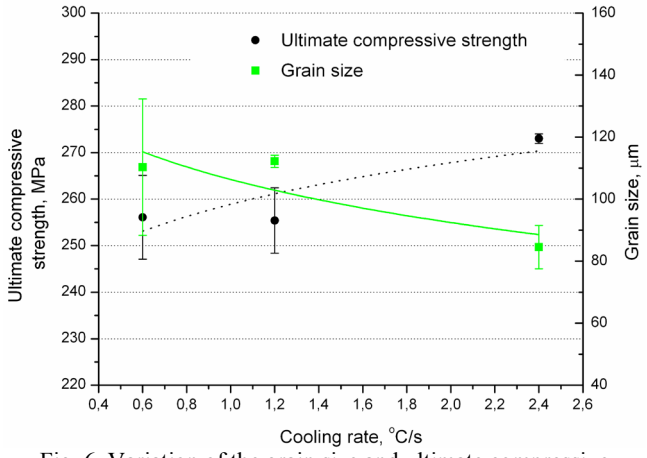



Fig. 6. Variation of the grain size and ultimate compressive strength as a function of cooling rate of analyzed magnesium alloy

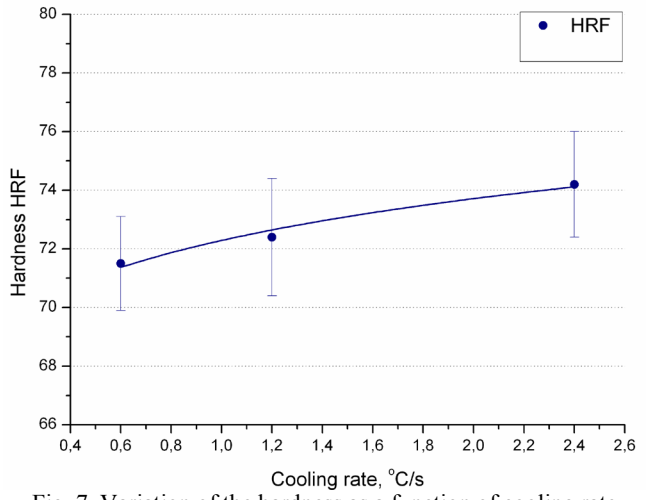



Fig. 7. Variation of the hardness as a function of cooling rate

# 4. Conclusions

The thermal derivative analysis demonstrates, that diversification of obtained values of phases transformation temperatures, occurring during crystallization and registered on graphs of thermal derivative analysis, are result of changes used cooling rate. Increase of cooling rate causes increase of α phase nucleation temperature and decrease of solidus temperature, causing the increase of temperature range of solidifying alloys.

The α primary solid solution together with the γ-($Mg_{17}Al_{12}$) phase precipitations located mainly in the grains boundaries, α+γ eutectic occurring near $Mg_{17}Al_{12}$ precipitates and $Mg_2Si$ phases ones as well as phases containing Mn and Al make the structure of the examined Mg-Al-Zn cast alloys. The X–ray phase analysis don't ravel occurring of $Mg_2Si$ and phases contains Mn and Al, what suggested that the fraction volume of these phases is below 3%. Change of cooling rate does not result in changes phases compositions of examined alloys. Increase of cooling rate from

0.6°C/s to 2.4°C/s cause decrease of grain size, and thus increase of hardness and ultimate compressive strength.

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