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Influence of cooling rate on crystallization, structure and mechanical properties of MCMgAl6Zn1 alloy

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Abstract

This work presents an influence of cooling rate on crystallization process, structure and mechanical properties of MCMgAl6Zn1 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: mechanical properties, structure, thermal analysis, magnesium alloy

1. Introduction

The growing interest of magnesium alloys in many industrial branches involves necessity of research on optimization of chemical composition and manufacturing technologies in order to obtain the material with most advantageous mechanical properties and in consequence use of modern research methods of magnesium alloys in real time to reach total control over the crystallization process with possibility to make presumable quality corrections of alloy [1÷5].

One of the most common testing methods of alloys in the liquid state before casting is the method of thermal-derivational analysis. This method, thanks to its simplicity, has found wide range of applications in quality evaluation of liquid metal alloys. Basing on theoretical analysis of phase equilibrium systems and practical measurements under industrial conditions, the relationship between nucleation temperature of α phase, solidus temperature, cooling rate and chemical composition of the alloy and its properties can be determined. Peculiar advantage of this method is the short time to obtain data for assessment of tested material [6÷11].

Thermal-derivational analysis is revamped and developed form of commonly known thermal analysis and bases on registration of alloy solidification curve and, basing on that, determination of its first derivative, which represents the change of states of matter and transitions in liquid and solid states. Thermal-derivational analysis method may provide valuable quantitative and qualitative data, difficult or impossible to obtain by other methods. This makes possible better design of alloys, heat treatment processes and allows for more precise estimation [12, 13].

Alloys of Mg-Al-Zn, besides of the three basic elements (magnesium, aluminum and zinc), contain also manganese and

silicon. In the microstructure of MCMgAl6Zn1 foundry alloy occur: solid phase α with precipitates of β phase ($Mg_{17}Al_{12}$) at the grain boundaries and fields of α+β lamellar mixture. There can be also observed fields of as called Abnormal eutectic, precipitation of $MnAl_4$, Al_8Mn_5 phases and precipitation of Mg_2Si Laves phase [14÷16].

The structure of the magnesium alloys, that is fraction, type, distribution, size and shape of crystalline phase obtained in the crystallization process, is determined by crystallization kinetics. Obtained structure of the casting directly influence on the mechanical properties of final products [17]. Due to this fact, the determining factor leading to improve the quality of the products obtained in the casting process is the appropriate use of knowledge about the influence of alloying elements and cooling rate on mechanical properties and structure of magnesium casting alloys.

2. Material and experimental procedure

The experiments have been carried out on MCMgAl6Zn1 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 compositions of the investigated materials are 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.
Chemical composition of MCMgAl6Zn1alloy

Al	Zn	Mn	Cu	Si	Fe
5.624	0.46	0.16	0.0024	0.034	0.07

The thermal analysis during melting and solidification cycles was carried out using the Universal Metallurgical Simulator and Analyzer (UMSA) (Fig. 1) [18]. 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 in the form of heating and cooling curves was recorded during the melting and solidification cycles. The temperature vs. time and first derivative vs. temperature as well as fraction solid vs. temperature were calculated. The cooling rates for these experiments were determined using the following formula:

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.

$$CR=(T_{Liq}-T_{Sol})/(t_{Sol}-t_{Liq}) \quad (°C/s) \qquad (1)$$

were T_{liq} and T_{sol} are the liquidus and solidus temperatures (°C), respectively, and t_{liq} and t_{sol} the times from the cooling curve that correspond to liquidus and solidus temperatures, respectively.

Fig. 1. UMSA apparatus - (1) sample chamber, (2) supervisory computer, (3) temperature control, (4) gas flow control

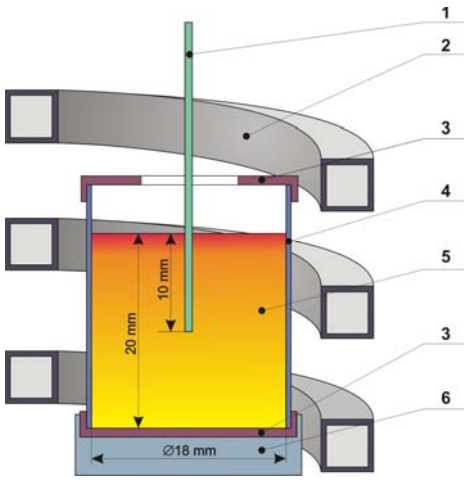

Fig. 2. Schematic of the UMSA Thermal Analysis Platform experimental set-up: 1 – low thermal mass thermocouple, 2 – heating and cooling coil, 3 – thermal insulation, 4 – steel foil, 5 – test sample, 6 – ceramic base

The experiments were performed using a pre-machined cylindrical test sample with a diameter of ϕ=18mm and length of l=20mm taken from the ingot (Fig. 2). 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 Oxford EDS LINK ISIS 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 XPert 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. Results and discussions

According to the X–ray phase analysis, the investigated MCMgAl6Zn1 alloy cooled with solidification rate: 0.6, 1.2 and 2.4. ºC/s is composed of two phases (Fig. 3.): α–Mg solid solution as matrix and β($Mg_{17}Al_{12}$).

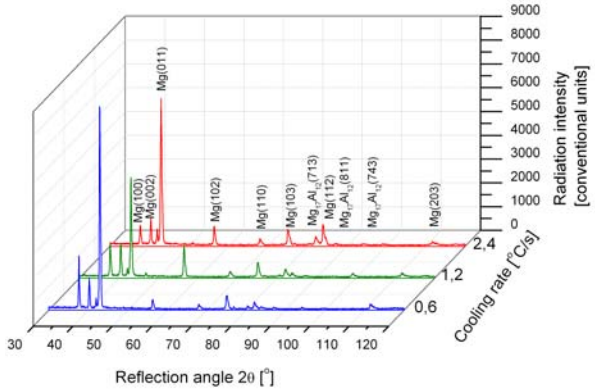

Fig. 3. XRD pattern of MCMgAl6Zn1 casting alloy at various solidification conditions

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 change of solidification rate don't influence on 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%.

Figures 4 shows the solidification microstructures of MCMg6Zn1 alloys at different cooling at 2.4°C/s, which consisted of α-Mg solid solution, $Mg_{17}Al_{12}$ 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, shows that the grain size decreases with increasing cooling rate.

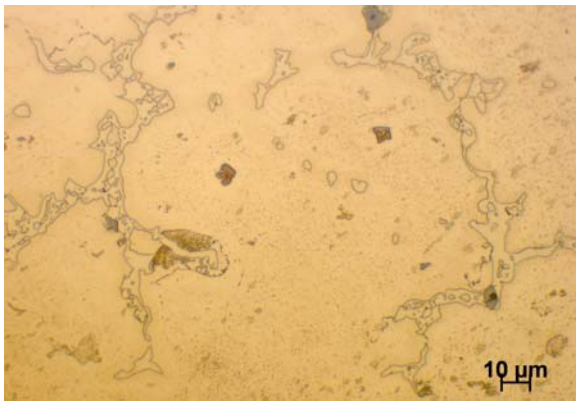

Fig. 4. Microstructure of MCMgAl6Zn1 alloy cooled at 2,4°C/s, mag. 500x.

SEM micrographs of MCMgAl3Zn1 cast after thermal analysis are shown in Figs. 5. 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.

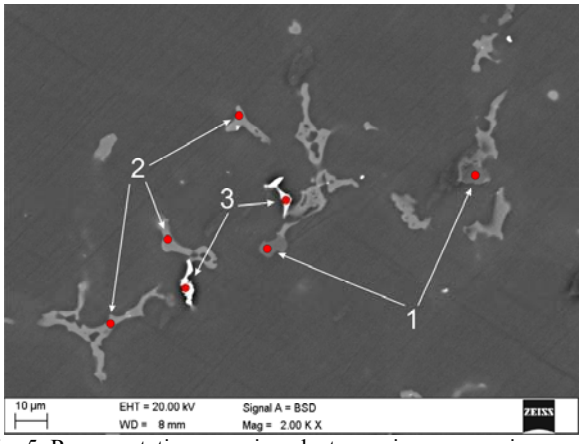

Fig. 5. Representative scanning electron microscope micrograph of magnesium alloy that solidified with cooling rate 2.4°C/s.

Table 2.
Pointwise chemical composition analysis from Fig. 5

	Element	*The mass concentration of main elements, %*	
		weight %	*atomic %*
1	Mg	72.81	75.58
	Si	27.19	24.42
2	Zn	4.38	1.73
	Mg	65.66	69.64
	Al	29.96	28.63
3	Mg	14.93	20.53
	Al	43.88	54.39
	Mn	41.19	25.08

The cooling curves recorded for MCMgAl6Zn1 alloy at various cooling rates are shown in Fig. 6. It is seen that formation temperatures of the various phases are changed when the cooling rate is increased. The shift magnitude increases with an increasing cooling rate. This shift changes the characteristic parameters of thermal analysis particularly in the liquidus region.

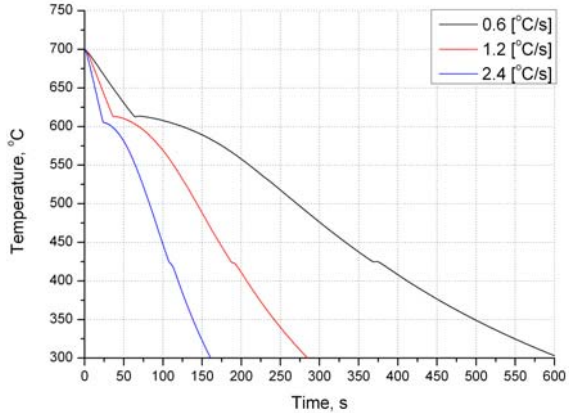

Fig. 6. Cooling curves of MCMgAl6Zn1 alloy at various cooling rates

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.

Figure 7 shows the variation of the magnesium nucleation temperature as a function of cooling rate and the variation of the Mg nucleation undercooling temperature. Standard errors calculated for each measured data point have also been included in the graph. It is evidence from the plot, that the Mg nucleation temperature increase with increase cooling rate from 0.6 to 2.4ºC/s, the Mg nucleation temperature increases from 615.88°±1C to 619.77±1.2°C. Increasing the cooling rate increases the heat extraction. Due to the increase the cooling rate, the nucleation undercooling increases from 4 to 10°C.

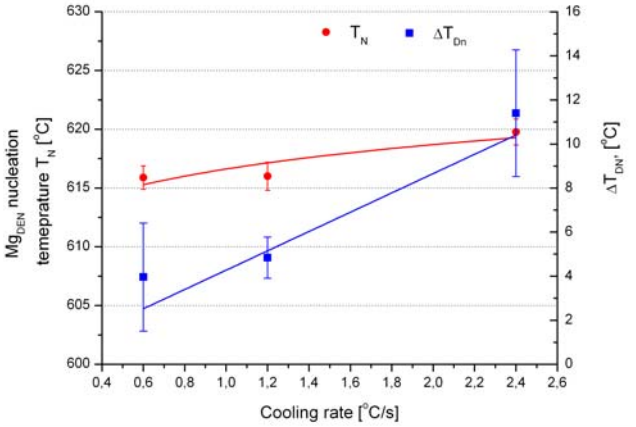

Fig. 7. Variation of the Mg nucleate temperature as a function of cooling rate and variation of the Mg nucleate undercooling temperature as a function of cooling rate

Figure 8 presents a variation of the solidus temperature as a function of cooling rate and variation of the α+β eutectic nucleation temperature as a function of cooling rate.

The α+β eutectic nucleation temperature increase with increase cooling rate from 0.6 to 2.4°C/s, the α+β eutectic nucleation temperature increases from approximately 429,45±1,2°C to 432,99±1°C. Due to the increase of the cooling rate the solidus temperatures decrease. When the cooling rate is increased, the solidification temperature is decreased from 419,47±3,26°C for the 0.6°C/s cooling rate to 401,66±4°C. for 2.4°C/s cooling rate.

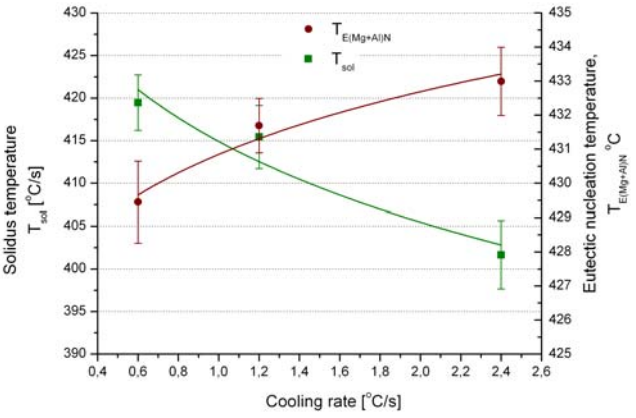

Fig. 8. Variation of the eutectic nucleation temperature and solidus temperature as a function of cooling rate

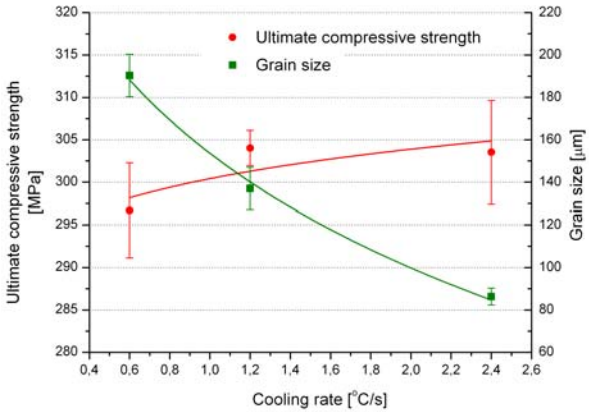

Fig. 9. Variation of the grain size and ultimate compressive strength as a function of cooling rate of analyzed magnesium alloy

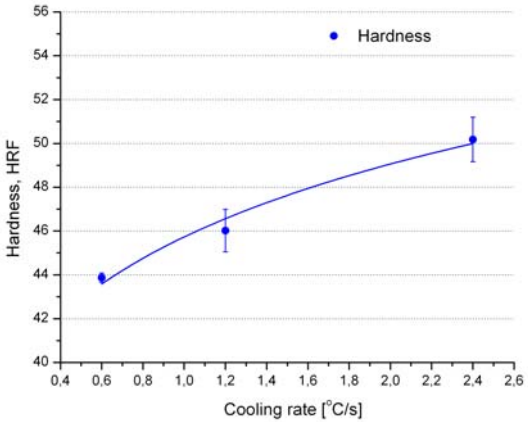

Fig. 10. Variation of the hardness as a function of cooling rate

The variations of grain size and ultimate compressive strength have been showed graphically in Figure 9. Grain size is strictly depending on the cooling rate. For the sample that was cooled with lowest cooling rate, the grain size is approximately 190,3±10µm. Increases cooling rate cause decrease of grain size to 86,28±4µm.

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 296,71±5,59 MPa for lowest cooling rate to 303,53±6,12 MPa for highest cooling rate (Figure 9).

Figure 10 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 43.87±0.23 HRF for lowest cooling rate to 50.18±1.02 HRF for highest cooling rate. Measuring errors occurred during testing did not exceed 5%.

4. Conclusions

The results are summarized as follows:

1. Solidification parameters are affected by the cooling rate. The formation temperatures of various phases are changed with an increasing cooling rate.
2. Increasing the cooling rate increases significantly the Mg nucleate temperature, α+β eutectic nucleation temperature and decreases the solidus temperature simultaneously widens a solidification range.
3. Mechanical properties of the magnesium alloy are strongly dependent on the effect of cooling rate. Ultimate compressive strength and hardness increases with increasing of the cooling rate.
4. Changes of cooling rate don`t have an influence on phases composition of investigated alloy.

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