Thermal analysis and microstructural characterization of Mg-Al-Zn system alloys

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Abstract. The influence of Zn amount and solidification rate on the characteristic temperature of the evaluation of magnesium dendrites during solidification at different cooling rates (0.6-2.5°C) were examined by thermal derivative analysis (TDA). The dendrite coherency point (DCP) is presented with a novel approach based on second derivative cooling curve. Solidification behavior was examined via one thermocouple thermal analysis method. Microstructural assessments were described by optical light microscopy, scanning electron microscopy and energy dispersive X-ray spectroscopy. These studies showed that utilization of $d^2T/dt^2$ vs. the time curve methodology provides for analysis of the dendrite coherency point

1. Introduction

The magnesium alloys are an attractive alternative to aluminum alloys for lightweight applications. Mg alloys are widely applied to the production of engines and gearbox housings. However, the magnesium alloys compared to aluminum alloys are inferior casting properties. Castability depends significantly on the dendrite coherency point that represents the temperature, time and the percentage of solid state at which an interlocking solid network forms during solidification. An increase in the solid state at coherence may improve the casting properties of the alloy and reduce casting defects. The thermal analysis technique is a technique used for long time, both in ferrous and nonferrous industries to assess the quality of the melt prior to casting. However, obtaining the appropriate microstructure of a standard cup does not guarantee that the microstructure is correct in real parts which may solidify in a very various cooling rates [1, 2].

The solidification characteristics can be investigated through various thermal analysis techniques. There are standardized techniques such as differential thermal analysis (DTA), thermo gravimetric analysis (TGA), differential scanning calorimetry (DSC) and computer aided cooling curve analysis (CA-CCA) otherwise known as the thermal derivative analysis (TDA). Due to its ease of use and low-cost, TDA is much more appropriate for industrial applications compared to other techniques and TDA method has been successfully applied in investigations of solidification sequences of magnesium, aluminum and zinc alloys in recent years [2-5].

The aim of the present work is to promote thermal analysis of one centre cooling curve for the determination of the dendrite coherency characteristics such as temperature, time, instantaneous solidification rate and fraction solid. The first derivative of the cooling curve is plotted vs. the temperature and time and the thermal characteristics of all metallurgical reactions, including the DCP
are determined. The thermal analysis results of the present work will also provide data support for thermodynamic description of Mg-Al-Zn system.

2. Experimental procedure

2.1. Fabrication and materials preparation

The study was carried out on samples of MCMgAl6Zn1 and MCMgAl6Zn3 magnesium alloys. Chemical compositions of the tested materials are given in table 1. Experiments were carried out applying cylindrical samples with a diameter 18mm and a length 20mm. Samples were in the axis the hole to place a super sensitive K type thermocouple positioned at the centre of the test sample to gather the thermal information about the process and monitoring the processing temperatures.

Table 1. Chemical composition of examined magnesium alloys.

| Alloy         | Al  | Zn  | Mn  | Si  | Fe   | Mg   | Rest  |
|---------------|-----|-----|-----|-----|------|------|------|
| MCMgAl6Zn1    | 5.92| 0.49| 0.15| 0.037| 0.007| 93.33| 0.0613|
| MCMgAl6Zn3    | 5.7 | 2.5 | 0.22| -   | 0.0025| 91.5 | 0.0775|

2.2. Thermal analysis

The Thermal Derivative Analysis during the cycle of melting and solidification was performed using the Universal Metallurgical Simulator and Analyser (UMSA) [6]. Each thermal test was repeated at least three times. Cooling curves have been used to assess the behaviour of solidification process and to determine any specific temperatures. The temperature vs. time and first derivative vs. temperature were calculated and graphed. The test samples were heated to 700±2°C and isothermally maintained at that temperature for 90 seconds to stabilize the conditions of melt. Then the test samples were solidified to ambient temperature with three different cooling rates. Argon was used as a protective gas in order to enhance the cooling rate. The solid fraction was estimated by the calculating the area between the first derivative of the cooling curve and the so-called baseline (BL) [1-3].

2.3. Microstructure examinations

The observations of the examined cast magnesium alloys have been made on the light microscope LEICA MEF4A as well as on the electron scanning microscope Opton DSM-940. The X-ray qualitative and quantitative microanalysis and the analysis of a surface distribution of cast elements have been made on the Opton DSM-940 scanning microscope with the Oxford EDS LINK ISIS dispersive radiation spectrometer at the accelerating voltage of 15 kV.

3. Investigation results

3.1. Microstructure analysis

The representative microstructures presented in figure 1 and figure 2 confirms the results acquired by thermal derivative analysis presented in figure 3 and 4 represents a representative SEM structure of samples cut from the middle part of MCMgAl6Zn1 and MCMgAl6Zn3 alloy. It may be noted as a microstructure in which the divorced eutectic phase spread along primary magnesium dendrite and grain boundaries. The microstructures illustrated in figure 1 presents polygonal Mg₂Si particles built-in the edge of γ phase what is confirmed by EDS quantitative analysis. This state observed in entire microstructure of the MCMgAl6Zn1 cast sample. This means that Mg₂Si phase precipitated before eutectic transformation temperature. The SEM observation of MCMgAl6Zn1 magnesium alloy discloses the occurrence of white Al₈Mn₃ intermetallic in needle shapes mostly located at grain boundaries or in interdendritic areas. Detection this type of the intermetallic particle with this type of shape next to the γ phase can be indicated its simultaneous precipitation with Mg₂Si at lower
temperature. The XRD pattern is given in figure 1 confirm the coexistence of Al$_8$Mn$_5$ and Mg$_2$Si particles with the main phases of $\alpha$ and $\gamma$ in the microstructure of MCMgAl6Zn1. For MCMgAl6Zn3 alloy, SEM analysis presents a microstructure in which the divorced eutectic phase spread along primary magnesium dendrite and grain boundaries. The SEM observation of MCMgAl6Zn3 magnesium alloy reveals the presence of MgZn$_2$ intermetallic precipitation mainly situated at grain boundaries regions (figure 2). Detection this type of intermetallic particles next to the $\gamma$ phase can be indicated its simultaneous precipitation with Mg$_{17}$Al$_{12}$ at lower temperature. The XRD pattern given in figure 2 confirms the coexistence of Al$_8$Mn$_5$ and MgZn$_2$ particles with the main phases of $\alpha$ and $\gamma$ in the microstructure MCMgAl6Zn3 cast magnesium alloy. For both analysed cast magnesium alloys can be observed that the increase in cooling rate decreases the size and shape of precipitated particles.

![Figure 1](image1.png)

**Figure 1.** Representative SEM micrographs of an MCMgAl6Zn1 alloy solidify at 0.6°C/s cooling rate with EDS quantitative analysis results at marked points

![Figure 2](image2.png)

![Figure 3](image3.png)
3.2. Thermal derivative analysis
The solidification pathways of Mg-Al-Zn alloys have been investigated by cooling curve thermal analysis. Figure 3 and figure 4 shows typical cooling curves and its first derivatives which were used to determine some critical points during solidification. Thermal characteristics of analysed magnesium alloys obtained from the first derivative are summarised in table 2. The solidification of MCMgAl6Zn1 and MCMgAl6Zn3 alloys begins with nucleation of $\alpha$-Mg dendrites. After the formation of $\alpha$-Mg dendrites, for MCMgAl6Zn1 alloy phases contain Mg$_2$Si and phases contain Al and Mn occurs. For MCMgAl6Zn3, after the formation of $\alpha$-Mg dendrites, only MgZn$_2$ phase occurs. Last stage in the solidification process of investigated magnesium alloys is solidification of eutectic as divorced or partially divorced $\gamma$-$\text{Mg}_{17}\text{Al}_{12}$ in the interdendritic and grain boundary (figure 1, figure 2). It can be seen in figure 3 and figure 4 that the first derivative cooling curves consist three peaks.

Table 2. Thermal characterization of investigated cast magnesium alloys.

| Investigated alloy | Cooling rate, ($^\circ$C/s) | Characteristic points |
|--------------------|----------------------------|-----------------------|
|                   |                            | Liquidus, ($^\circ$C) | Mg$_2$Si+Al-Mn, ($^\circ$C) | MgZn$_2$, ($^\circ$C) | Eutectic, ($^\circ$C) | Solidus, ($^\circ$C) |
| MCMgAl6Zn1        | 0.6                        | 611.96                | 529.01                           | -                      | 430.36                  | 420.72                  |
| MCMgAl6Zn1        | 1.3                        | 619.6                 | 532                           | -                      | 432.7                   | 408.9                   |
| MCMgAl6Zn1        | 2.5                        | 619.58                | 535.35                           | -                      | 429.48                  | 404.76                  |
| MCMgAl6Zn3        | 0.6                        | 607.42                | -                                | 393.36                  | 355.68                  | 348.95                  |
| MCMgAl6Zn3        | 1.3                        | 612.38                | -                                | 388.45                  | 355.58                  | 344.46                  |
| MCMgAl6Zn3        | 2.5                        | 617.06                | -                                | 390.41                  | 354.97                  | 336.56                  |

Figure 2. Representative SEM micrographs of an MCMgAl6Zn3 alloy solidify at 2.5$^\circ$C/s cooling rate with EDS quantitative analysis results at marked points.
a) 

![Figure 3](image1.png)

**Figure 3.** Representative cooling and its first derivative curves and base line of the MCMgAl6Zn1 alloy solidify at a) 0.6°C/s; b) 2.5°C/s.

b) 

![Figure 4](image2.png)

**Figure 4.** Representative cooling and its first derivative curves and base line of the MCMgAl6Zn3 alloy solidify at a) 0.6°C/s; b) 2.5°C/s.

Taking into consideration the first derivative cooling curves, four observable temperature arrests including non-equilibrium nucleation temperature, crystallization of Mg$_2$Si and Al-Mn or MgZn$_2$ intermetallic, nucleation of the eutectic phase and solidus temperature can be determined. For MCMgAl6Zn1 magnesium alloy, for natural cooling rate, the nucleation temperature of primary magnesium dendrite was recorded at around 612°C. This phase grew on further cooling followed by Al-Mn and Mg$_2$Si intermetallic precipitation approximately as 530°C. Further cooling caused another sharp and clear positive peak manifested on the first derivative curve at 430°C due to the evolution of latent heat during eutectic transformation. Process finished at solidus temperature at around 420°C where remaining liquid completely transformed to the eutectic phase. It can be inferred that the increase in cooling rate increases the nucleation temperature and decreases the solidus temperature of investigated magnesium alloys. The intermetallic precipitation temperature slightly increases from 529°C to 535°C with increasing cooling rate. The increase in the cooling rate increased the solidification range from about 190°C to 215°C.

Accordingly for MCMgAl6Zn3 magnesium alloy, for natural cooling rate, the nucleation temperature of primary magnesium dendrite was recorded at around 607°C. This phase grew on further cooling followed by MgZn$_2$ intermetallic precipitation approximately as 493°C. Further cooling caused another sharp and clear positive peak manifested on the first derivative curve at 355°C due to the evolution of latent heat during eutectic transformation. Process finished at solidus
temperature at around 348°C. It can be concluded that the increase in cooling rate increases the nucleation temperature and decreases the solidus temperature of investigated magnesium alloys. Changing the cooling rate does not significantly effect on intermetallic precipitation temperature. The solidification range increases from about 260°C to 280°C with increasing cooling rate. Analysed series of cast magnesium alloys, thermal derivative analysis shows that the increase cooling rate does not effect on eutectic transformation temperature. Based on the results it can be concluded that the increase in Zn content decreases the nucleation temperature, eutectic temperature and solidus temperature of investigated magnesium alloys. In the solidification process dendrites begin to develop to the point where the collide with each other and continuous network become coherent. At this point, the dendrite coherency point, the system behaves less like a liquid and starts to resemble a solid behaviour. On the basis of thermal derivative analysis, the dendrite coherency point is present in the first minimum on the second derivative during formation of the primary magnesium. Figure 5 and figure 6 shows the characteristic points on the second derivative of the examined magnesium alloys.

![Figure 5](image1.png)

**Figure 5.** Representative cooling and second derivative curves and associated fraction solid curve of the MCMgAl6Zn1 alloy solidify at a) 0.6°C/s, b) 2.5°C/s.

![Figure 6](image2.png)

**Figure 6.** Representative cooling and second derivative curves and associated fraction solid curve of the MCMgAl6Zn3 alloy solidify at a) 0.6°C/s, b) 2.5°C/s.

For the one-thermocouple technique, one thermocouple located in the middle of the solidifying melt has been used to determine the dendrite coherency point (DCP). The minimum value of the second derivative of temperature versus time \( \left( \frac{d^2 T}{dt^2} \right) \) refers to a state that there is a considerable change in thermal conductivity of the alloy. A suitable temperature for the cooling curve \( (T_{DCP}) \) is the dendrite coherency temperature. Temperature changes at the dendrite coherency point and solid
fraction corresponding to the dendrite coherency ($f_{DCP}$) as a function of Zn content and cooling rate are presented in Table 3. It can be noticed that fraction solid of primary magnesium at the dendrite coherency point increases with the increase zinc content and with the increase in cooling rate. For examined series of magnesium alloys can be observed that increasing cooling rate does not influence on changes in temperature at the dendrite coherency point.

**Table 3.** Influence of cooling rate and Zn content on temperature at the dendrite coherency point and a fraction solid of investigated magnesium alloys.

| Cooling rate [°C/s] | DCP, °C | FS, % | DCP, °C | FS, % | DCP, °C | FS, % |
|---------------------|---------|-------|---------|-------|---------|-------|
| MCMgAl6Zn1          | 609.36  | 3.41  | 608.35  | 6.85  | 610.01  | 21.24 |
| MCMgAl6Zn3          | 603.84  | 9.11  | 602.8   | 15.17 | 601.97  | 21.81 |

4. Conclusions
The dendrite coherency point for magnesium alloys was studied using Thermal Derivative Analyse. It was found that the DCP could be determined by the second derivative curve (using the one thermocouple method). The one thermocouple method simplifies the platforms and lowers the costs of CA-CCA. The solidification pathways of Mg-Al-Zn alloys are obtained. The nucleation temperature of primary magnesium dendrite increases with increasing cooling rate and decreases with increasing of Zn content while solidus temperature decreases with increasing cooling rate and Zn content. For analysed series of magnesium alloys, the solidification range increases with increasing cooling rate. Knowing the microstructure in the thermal analysis sample, it is possible to have an idea of the microstructure that can be expected in the real part according to its thermal behave and to the mould type.

References
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