Effect of Mg addition on the crystallization kinetics of Zn-Al-Cu alloys

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Abstract
In this work, the main aim was to determine the effect of Mg addition on the crystallization kinetics and microstructure of Zn-10Al-1Cu alloy. The effectiveness of magnesium addition was detected on the basis of microstructure morphology investigations and changes occurring in the cooling curves of the investigated alloys. To describe the phenomena that occur in the material during solidification under various conditions caused by a change in the chemical composition as a result of the appliance of modifiers, it was decided to use methods of thermal derivative analysis, allowing to effectively and accurately describe the crystallization kinetics of the tested materials. The scientific goal of the presented work was examination of the impact of magnesium addition, affecting the crystallization kinetics of the examined alloys. Determining the relationship between the changes in the derivative curve and the related microstructure the influence of modifiers addition was analysed.

The addition of Mg has caused a shift of the solidification temperature values of phases and eutectics and monotectoid transformation (α→α’) to lower temperature values, as well as has changed the morphology of the occurring eutectic α’+η.

Introduction

The contemporary technological development involves increasing demands in developing new materials for modern design solutions and increases the application potential of materials for parts used under hard environmental conditions. It becomes possible, inter alia, by modification of the chemical composition of metal alloys, resulting in creation of a more stable
microstructure and thus achieving more favorable functional properties. This type of treatments is also used for zinc alloys, which are used mainly for production of small, thin-walled castings requiring high precision of manufacturing [1].

The phase composition of the material is determined by the chemical composition and crystallization kinetics. In order to improve the mechanical properties of cast zinc alloys, a modification procedure is used. After modification there are changes occurring in the morphology of the structural compounds of the alloy by reducing the interfacial distance of the \( \alpha' + \eta \), eutectic, refining of the microstructure and reducing the distance between the dendrite arms [2, 3].

Modifying alloys with titanium, strontium and antimony is a common procedure, because Ti, Sr and Sb are modifiers of long-term action [2, 4, 5]. The strontium effect is persistent also after many remelting stages of the alloys [4]. Recently, rare earth metals have been increasingly used to modify cast alloys [6, 7]. The modifiers may constitute a substrate for heterogeneous nucleation and may occur as primary or secondary (depending on the tempering temperature of the liquid state) [8]. However, the modification brings the expected results when the components of the alloying additives solidify last in the form of multi-component eutectics [3]. In Zn-Al alloys, Zn\(_{11}\)Mg\(_2\) phases may be formed already at low Mg mass concentration and together with decreased concentration of the remaining alloying compounds in the alloy also the phases ZnMg\(_2\), Zn\(_3\)Mg\(_2\) phases can be formed (Fig. 1) [9].

![Figure 1](image1.png)

**Fig. 1.** Liquidus projection of the Mg-Al-Zn system [9]
The addition of extra copper promoted the formation of significant quantities of the copper-rich phase \((\text{CuZn}_4 \text{ precipitate})\) in the interdendritic region, while the addition of extra magnesium promoted the formation of the magnesium-rich phase and changed not only the morphology of the primary dendrites but also its relative content in the microstructure. Besides, an increase of the relative amount of primary eutectic structure and a decrease of the quantity of the lamellar eutectoid structure were observed. Additionally, the secondary lamellar eutectic became more refined in case of the presence of higher magnesium content \([10]\).

Copper increases strength and causes a shift of the eutectic point in the Zn-Al-Cu system towards higher aluminium concentration. Copper also increases the susceptibility of Zn-Al alloys to aging and that fore also dimensional changes, because of a precipitation process that occurs during ageing. However, this has only a little impact on the transformation of the \(\alpha \rightarrow \alpha'\) phase as well as on the changes in solubility in the solid state in low temperature range, but primarily influences phase changes in the solid state \([11, 12]\). The increased copper mass concentration causes crystallization \(\text{CuZn}_4 (\varepsilon)\) phases in the form of broken quasi–regular lamellas. This structure change is observed for all used and applied solidification parameters \([13]\).

Demands for highly corrosion resistant coated steel are growing. As a result, Zn-Al-Mg coatings were developed. The possibilities of these coatings were investigated and the thermodynamics of the Zn-rich corner/part of the Zn-Al-Mg system were modelled \([14]\).

**Material and methodology**

The casts were made in a resistance furnace in chamotte-graphite crucibles. The performed alloys were cast into properly prepared metal dies. Preliminary investigation of mass concentration of the Al, Cu and Mg alloying additions were carried out in accordance with the ICP/OES \([15]\) test procedure on the ULTIMA 2 Jobin-YVON device (sequential spectrometer with 1 m optics, equipped with a vertical plasma source). The chemical composition is presented in Table 1.
Table 1. Chemical composition of the analysed zinc alloys

<table>
<thead>
<tr>
<th>Alloy number</th>
<th>Alloy description</th>
<th>Mass concentration of alloying elements in the investigated alloys, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>1</td>
<td>ZnAlCu</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>ZnAlCu0,1Mg</td>
<td>8,5</td>
</tr>
</tbody>
</table>

In particular, the range of performed research involves the following issues:

- Thermal-derivative analysis (TDA) with the use of the UMSA MT5 (Patent Serial No. PCT/CA02/01903) metallurgical platform of the tested free-cooled alloys for the reason to investigate the temperature of the begin (T<b>L</b>) and end (T<b>SOL</b>) of solidification of the alloy both before and after modification. As well as temperature of solid phase transformation. The test samples have dimensions Ø 30 x 35 mm. K-type thermocouples were placed at the heat centre.
- Microstructure investigations using scanning electron microscopy methods, stereological research. For investigations the scanning electron microscope Zeiss Supra 25 was used,
- Chemical and phase composition investigations of the alloy microstructure, thin foil microstructure and crystallographic phase identification studies were carried out using a Joel 3010CX high resolution transmission electron microscope (HRTEM) at 300 kV acceleration voltage using selected area diffraction (SAD) to identify crystallographic phases occurring in the alloy microstructure. The bright field image technique as well as HAADF method was used for high resolution images.

**Investigation Results**

The important factor leading to improvement of quality of the cast products involves appropriate use of knowledge on crystallization and its mechanisms, which allows creating castings with optimum microstructure and properties. In the case of the cast alloys, the crystallization process runs in the temperature range specified by its value for the begin and end of crystallization, i.e. between the liquidus and solidus temperature, which depend primarily on
the composition of the alloy, the cooling rate and the thermodynamic conditions change. The values for the free energy of the liquid phase and constant depend on concentration of the second component (two-competitive alloys). The difference in the free energy of liquid and the energy of mixture of liquid phase and the constant in the range of concentration of the second component for the liquid phase and constant is the driving force for crystallization of alloys [4, 16].

By registering the temperature change over time, derivative calculations were made at the point, where no function of temperature change over time occurs and a base curve was determined using Newtonian 3 grade polynomial [17].

Structural studies show that the Zn-Al-Cu alloy is characterized by a microstructure formed in the crystallization process, in which there are grains of a solid solution of aluminium (α) in zinc and α + η eutectics in which the α' phase is formed as a result of the monotectoid transformation (α → α').

Analysing the crystallization process based on the obtained curves, it was found that the process of nucleation of the α begins at $T_L$ (point I). The chemical composition of the remaining liquid changes according to the liquidus line of the Zn-Al diagram. The liquid is enriched more and more with zinc and after reaching the temperature $T_{E(α+η)}$ the nucleation of eutectic $α + η$ occurs (point II). As a result of further cooling, the remaining liquid is supercooled and the growth of $α + η$ eutectic begins. Crystallization ends when the alloy reaches the solidus $T_{SOL}$ temperature (point IV, Fig. 3). In the alloy with the addition of Mg occurs a shift of the temperature values of the crystallization beginning of the α phase and the eutectics $α + η$ (Table 2). Whereas in point III crystallization of multi-component eutectics $α + η + Mg$ takes place (Fig. 2). As a result of the modification of the chemical composition with magnesium, there is also visible a change in the course of the solid fraction curve (Figs. 2, 3).

In Table 2 was presented the temperature values of crystallisation of the discovered phases.
The modification of the chemical composition has also caused a shift in the temperature of the beginning of the monotectoid transformation ($\text{TS}_{\alpha + \text{E}(\alpha' + \eta)} \rightarrow \alpha' + \text{E}(\alpha' + \eta)$) and the end temperature ($\text{TF}_{\alpha + \text{E}(\alpha + \eta)} \rightarrow \alpha' + \text{E}(\alpha' + \eta)$) to lower temperature values (Table 2).
Table 2. Reaction and reaction temperature during solidification and cooling of alloys

<table>
<thead>
<tr>
<th>Markings on the figs. 2, 3</th>
<th>Reaction</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZnAlCu0.1Mg</td>
<td>ZnAlCu</td>
</tr>
<tr>
<td>I</td>
<td>L → α</td>
<td>L → α</td>
</tr>
<tr>
<td>II</td>
<td>L → α + η</td>
<td>L → α + η</td>
</tr>
<tr>
<td>III</td>
<td>L → α + η + Mg</td>
<td>-</td>
</tr>
<tr>
<td>IV</td>
<td>L → Sol</td>
<td>L → Sol</td>
</tr>
<tr>
<td>V</td>
<td>S_{α+(α+η)}→α'+E(α'+η)</td>
<td>S_{α+(α+η)}→α'+E(α'+η)</td>
</tr>
<tr>
<td>VI</td>
<td>F_{α+(α+η)}→α'+E(α'+η)</td>
<td>F_{α+(α+η)}→α'+E(α'+η)</td>
</tr>
</tbody>
</table>

The investigated alloys are characterized by a microstructure in which aluminium precipitations and α’+η eutectics were observed (Figs. 4, 5) as a result of the transformation α→α’. The derivative curve also shows that the α+η eutectics morphology has changed. Also visible on derivative curves (Figs. 2, 3). Change of the derivative curve from point II (temperature $T_{E(α+η)}$).

Fig. 4. Microstructure of Zn-8Al-0.8Cu alloy with addition of 0.1% wt. Mg: #1 – phase α’, #2 – phase η, #3 – eutectic with Mg

Fig. 5. Microstructure of Zn-10Al-1Cu alloy: #1 – phase α’, #2 – eutectic α’+η

Fig. 6. Microstructure of Zn-8Al-0.8Cu-0.1Mg, mass concentration of elements in the marked area: Mg – 1.84 % wt.; Al – 23.9 % wt.; Zn – ballance
In figs. 7 to 11 there are presented the investigation results of the microstructure by transmission electron microscope. The revealed microstructure consists of Zn polycrystalline structure with a subgrains size of ca 0.1-0.5 μm (Fig. 7). The electron diffraction pattern presented in Fig. 8 confirms the polycrystalline nature of the microstructure. Zinc crystallises in a hexagonal lattice with d-spacing parameters of the cell a =0.266nm, c =0.494 nm, (c/a=1.856). After addition of Mg the microstructure changes in a way, that the micrograins are more irregular with larger size range between 0.02-0.2 μm Fig. 9. Also the eutectic area showed in Fig. 10 is more irregular compared to the material without Mg addition, however no magnesium addition was found, but only zinc and aluminium with low amount of copper (Fig. 11).

Fig. 7 Microstructure of ZnAlCu0.1Mg alloy, micrograins Zn, TEM bright field
Fig. 8 Electron diffraction of the area in fig. 7, polycrystalline Zn phase structure
Fig. 9 Microstructure of ZnAlCu0.1Mg alloy, micrograins Zn, HAADF
Fig. 10 Microstructure of ZnAlCu0.1Mg alloy, Zn eutectics, HAADF
Conclusions

The driving force for crystallization in the case of alloys is the difference in free energy of liquid and energy of the mixture of liquid and solid phases in the concentration range of the second component for the liquid and solid phases. The tested alloys are characterized by a microstructure in which aluminium precipitation and $\alpha' + \eta$ eutectics were observed as a result of the monotectoid transformation $\alpha \rightarrow \alpha'$. However, as a result of the modification of the chemical composition of magnesium alloys Zn-Al-Cu it was found that:

1. Magnesium modification causes a decrease in the temperature of the begin of the phase transformation during solidification as well as the monotectoid transformation temperature in the solid state. The modification also reduces the temperature value of the solidification point.
2. The visible change in the derivative curve indicates a change in the morphology of the eutectics $\alpha' + \eta$.
3. Phases of the $\varepsilon$ type (CuZn$_4$) containing Cu were not found in the investigated alloy and Cu was only dissolved in eutectics. However, literature studies [18] show that as a result of long-term spontaneous aging, the $\varepsilon$ phase is precipitated during long term ageing.
4. The occurred Zn-Al eutectic after Mg addition is of irregular shape compared to the material without magnesium, where the eutectics are more uniform and regular.
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References