Microstructure investigations of cast Zn-Al alloys

B. Krupińska*, Z. Rdzawski, M. Krupiński, K. Labisz
Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland
* Corresponding e-mail address: beata.krupinska@polsl.pl
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Properties

ABSTRACT

**Purpose:** The goal of he presented investigations was to evaluate to possibility of application of popular modifiers for chosen types of zinc alloys. The special aim of this work is to determine the influence of alloy modification on the crystallisation kinetics and microstructure of the cast zinc alloy. This research work presents also the investigation results of derivative thermoanalysis performed using the UMSA device. The material used for investigation was the ZnAl8Cu1 alloy.

**Design/methodology/approach:** For phase determination there were used electron microscope techniques like SAD diffraction investigations which were carried out on the 200 kV transmission electron microscope. The UMSA (Universal Metallurgical Simulator and Analyser) device allows it to determine the specific melting process, influence of the cooling rate on the crystallization of phases and eutectics of the investigated alloys. Cooling rate influences the microstructure and properties of the investigated cast alloys.

**Findings:** Change of the crystallization kinetics allows it to produce materials with improved properties, which are obtained by: microstructure refinement, reduction or elimination of segregation.

**Research limitations/implications:** The material was examined metallographically and analysed qualitatively using light and scanning electron microscope as well as the area mapping and point-wise EDS microanalysis. The performed investigation are discussed for the reason of an possible improvement of thermal and structural properties of the alloy.

**Practical implications:** The investigated material can find its use in the foundry industry; an improvement of component quality depends mainly on better control over the production parameters.

**Originality/value:** Investigations concerning the development of optimal chemical composition and production method of zinc-aluminium alloys with selected rare earth metals with improved properties compared to elements made of alloys with appliance of traditional methods, will contribute to a better understanding of the mechanisms influencing the improvement of functional properties of the new.

**Keywords:** Metallic Alloys; Electron diffraction investigations; Thermo Analysis; Zn-Al Alloy; Microstructure

Reference to this paper should be given in the following way:

1. Introduction

Zinc-aluminium alloys are alloys with very good technological and mechanical properties. One of the main problems in the casting technology of cast zinc alloys is their high susceptibility for gassing and oxidation. Moreover they have also a predisposition to the development of coarse structures during solidification with low cooling rate. All of these issues affect the need for innovation, increasing the quality of casting technology, which after cast into the mould will eliminate metal precipitates
and gas bubbles. In addition, it will help to obtain structure, which will ensure high and stable mechanical properties. Such assuming are realised in case of other alloys mainly by implemented refining and modification of the molten metal before casting operation as well as optimal heat treatment processes [1-7].

At the moment, the lack of sufficient knowledge and the lack of data, which allows to determine the effect of modifications, the cooling rate and crystallization kinetics on the alloys microstructure and properties, as well as the relationship between the properties of the Zn alloys, and the obtained results from the thermo-derivative analysis. [3,4]

In order to improve the mechanical properties of cast alloys, in addition to the applied heat treatment there is used structure modification which changes the morphology and interfacial α-β eutectic distance, as well as fragmentation of the microstructure. Currently there is used strontium and antimony for modification, because this are long-term modifiers. Increasingly, there are also widely used rare earth metals to modify the casting alloys [1,2,5-7].

The addition of alloying elements such as Sr, Ca, Li, Na, Be, Zn alloys especially with high Al content can mitigate their tendency to shrinkage of castings. The rare earth metals, which similary like Ti - also cause hot cracking, but allow to obtain good castability and filling of the mould.

Grain refinement in the dendritically crystallised a solid solution by addition of Ti, which causes forming of heterogeneous TiZn3 and Al3Ti nuclei creating the triple phase Ti(Al,Zn)3 with a high nucleation coefficient [5-7].

Properly carried out chemical modification and the use of proper cooling of castings leads to improved functional properties of the produced castings. Therefore it is very important to know how changes in the structure of casts with according to the changing cooling rate or changing of the chemical composition by addition of modifiers to the liquid metal.

Functional properties of elements produced of cast metal alloys depend on the primary structure of the alloy, which is dependent on the crystallization kinetics. The crystallization kinetics is characterized by changes of the following parameters: temperature of the metal, cooling rate, the rate of latent crystallization heat generation, particle density, which is equivalent to the density of the formed nuclei, fraction solid of the crystallized metal, the concentration of components in the remaining liquid, the size of the characteristic distance and values describing the shape and size of structural components. [1,5,8].

All these parameters are variables of crystallization time and geometric coordinates of the casting. A full characterization of crystallization kinetics obtained after crystallization equations connected with the equations of heat transfer and crystallization exothermal is a factor connecting these equations and depends on the amount of crystallized structural components [1].

Cooling of the liquid metal goes from the molten state from 

\[ \frac{dT}{dt} - \left( \frac{dT}{dt} \right)_b = 0 \]  

(1)

If the crystallisation heat is emitted, and the crystallization proceeds, the temporary heating effect is described by the relationship [1,2,8]:

\[ \frac{dQ}{dt} = c_p \cdot m \left[ \frac{dT}{dt} - \left( \frac{dT}{dt} \right)_b \right] \]  

(2)

where:
- \( Q \) - crystallisation heat,
- \( c_p \) - heat capacity,
- \( m \) - mass of the crystallised metal.

Calculating the thermal crystallization effect in time \( t \) there should be taken into account also the capacity, which depends on the proportion of the solidified metal and the remaining liquid.

The total heat of crystallization is obtained by integral calculation based on the equation: \( \frac{dQ}{dt} \):

\[ Q = c_p \cdot m \left[ \int_{t_0}^{t} \frac{dT}{dt} dt - \left( \frac{dT}{dt} \right)_b \right] \]  

(3)

At a time when there are no phase changes, and therefore there is no additional heat source present, a differential curve corresponds to the cooling curve, a the crystallization function is composed of two parts - of derivative curve and cooling curve, where the first term is described on the basis of the Fourier heat transfer [9], while the second term shows the general form of the crystallization function describing the nucleation function of one phase.

Considering the cell - dendritic crystallization model which extends uniformly from the surface to the centre of the mould in the same direction as the heat transport directions, but in the opposite run, the mass of the solidified crystals can be determined according to the Chvorinov theory, where after the differentiating
over time, is known as the rate of the growing of the crystallised layer [1,2,8):

\[
d\sigma = \frac{G}{2\pi t}
\]

(4)

where:

G - constant thickness of the crystallised layer in a time unit

Changes in temperature, cooling rate and the fraction solid is determined experimentally using thermal analysis and thermo-derivative analysis. Currently there are used in industrial practice following thermal analysis methods: simplified thermal analysis, which allows to determine the temperature of the physical and chemical changes in the continuous heating or cooling on the basis of the recorded data changes as a function of time, temperature, derivative thermo-analysis DTA (Differential Thermal Analysis), which is measuring the temperature difference between the test sample and reference sample in which there exist no thermal changes during heating or cooling. The samples are heated or cooled at the same time under identical conditions. This measurement allows the detection of thermal effects occurring during the physical or chemical transformation [1,2,10,11]

The casting temperature has a significant influence on the mechanical properties of cast zinc alloy. Best tensile strength values are achieved for Zn-Al alloys containing 4.6% Al, at a melting temperature of 460°C [12,13]. Influence of variation of the gradient and solidification rate on the structure of the reinforcing elements has a different character depending if the considered particle is a local heat source with the highest temperature, or if it is a resistance for the heat flow. The measured changes in the temperature gradient and, above all, the gradient change itself as a function of time and location of the investigated area relative to the particle is only caused by differences in thermal properties of components. Variation of derivatives of the temperature may cause variability, which may involve changes in both amplitude and duration of the process [1,2,12-17].

Microstructure and phase transformations occurring in the Zn-Al alloys containing additions of Cu and Si. Based on the research there are identified two metastable phase \( \eta \) and \( \eta \). The dissolution of Cu and Al in the Zn-rich \( \eta \) phase results in a change of the unit cell of the crystal structure, which affect the physical and mechanical properties, in particular the dimensional stability of the alloy.\[12-18]\]

Dependent on the conditions of the casting process, the material is prepared in a variety of structures, due to solidification of liquid metal. They have impact on the microstructure, grain size, interdendritic distance and thermal conditions [19-20].

Zinc and zinc alloys have good corrosion resistance in atmosphere, salts and many chemical environments. Corrosion is more intense when the pH has a value less than 6 and more than 11.5. By increase of the Al content in the alloy the corrosion rate is Zn-Al alloy increases and for the ZA27 alloy achieves one third of the corrosion rate compared to Zn-Al alloys with a lower content of Al.

Solidification of the ZA27 alloy starts with the \( \alpha \) phase dendrites, and then by peritectic reaction of the Zn-\( \beta \) reach phases around the edge of the \( \alpha \) phase. The increase in the cooling rate during solidification reduces the range of occurrence of peritectic reaction in order to enrich the liquid with Zn and stop the solidification of the eutectic \( \beta \) and phase \( \eta \). The rapid cooling causes - through the \( \beta \) phase transition in eutectoid temperature some irregular particles \( \alpha \) and \( \eta \). Most of the \( \alpha \) phase generally consist of a mixture of Zn-rich phase and Al matrix. These structures are formed by the rapid super cooling of the alloy [13].

The disintegration of the metastable phase is limited by the addition of Cu during the eutectic transformation. After solidification the copper-rich phase forms with the Zn-\( \eta \) the CuZn4 phase in interdendritic areas, most of the remaining copper is dissolved in the \( \eta \) phase with a size of 70-120nm and a thickness of 2-3nm, \( \alpha \) phase with parameters a=0.274 nm, c=0.428 nm and c/a=1.566 nm [1,2,13].

Addition of rare earth metals causes the reduction of coalescence of particle, because it inhibits diffusion of carbon. This prevents the coalescence of the particles to provide homogeneity of the microstructure [15].

Investigations concerning the development of an optimal chemical composition and methods for preparing of modified aluminum alloys with selected rare earth metals, and boron helps to achieve improved properties in comparison with components made of alloys produced by conventional methods. It will contribute to a better understanding of the mechanisms underlying the improvement of functional properties of newly developed alloy. Constantly reduction of the costs of components and simultaneously increase of their mechanical properties, particularly low weight and high wear and corrosion resistance, increase the range and multiplication of projects concerning the improvement of these properties through a combination of newly developed materials design and manufacturing conditions.

Current knowledge indicates that aluminium alloys with the addition of boron and rare earth metals are not fully recognised research area. Also appearing technical difficulties, economic factors in the production of aluminium alloys with very high mechanical properties are of high interest in this group of materials. At the end of last decade there is present an increasing grow of application of these materials, but the production and processing cost as well as the difficulties associated with the manufacturing conditions limit the range of applications to more specialized elements [12,13,19-26]. As a result of the performed investigations concerning the effect of the rare earth metals addition there were found redox reactions during the melting process, as well as fragmentation of the microstructure due to the introduction of many nucleation and precipitation strengthening additives like rare earth elements allowing working of the components at elevated temperatures, resulting also in improved properties at elevated temperatures (above 300°C) [27-29,31-34].

Technical difficulties associated with conventional casting process, where occurs strengthening of the material related to segregation and emergence of clusters, interfacial reactions, increasing occurrence of porosity and low interfacial coherence largely limited capabilities and application of conventional methods of materials producing allowing an increase of commercial properties. The use of inductive and mechanical blending methods causes low segregation and very good mechanical properties, but there occur difficulty of obtaining reproducible properties, completely elimination of the occurrence of blowholes and porosity, as well as the presence of homogeneous structure, what is largely causes a reduction in the use of conventional production methods of metal alloy castings [1,2,18-21].
2. Materials and experimental procedure

Using the UMSA device to simulate crystallization processes there were determined interrelationships between chemical composition and structure of the ZnAl8Cu1 alloy (EN: 1774) modified with lanthanum and cerium, cooled at different cooling rates [3,4].

Investigation of cerium addition influence using the device for crystallisation process simulation UMSA was performed on cylindrical samples melted in graphite crucible [3,4].

The alloys were cooled in air with a non-forced cooling, as well cooled with a set cooling rate there was set as 0.1 and 0.15°C/min. for determination of the temperature change in time in the range of $T_{DN}$ to $T_{SOL}$. The addition of modifiers was set as 0.5% and 1% mass percent.

Thin foils microstructure investigations and phase identification were carried out on the JEOL 3010 transmission electron microscope (TEM), at the accelerating voltage of 200 kV using SAD diffraction method as a tool for phase investigations. The diffraction patterns from the TEM were solved using a computer program “Eldiff” software supplied by the Institute of Material Science o the University of Silesia.

For temperature measurement a chronometer-alumel thermocouple of the K type was applied with a reaction time of 250 ms.

In order to determine the relationship between the crystallization kinetics of the investigated alloy, and the chemical composition, microstructure and mechanical properties of zinc cast alloys modified with rare earth metals additions, cooled with various cooling rates, following investigations were carried out: thermo-derivative analysis of the investigated Zn alloys, macro- and microstructure of the alloys using light microscopy as well scanning and transmission electron microscopy with EDS microanalysis, electron diffraction investigation carried out using transmission electron microscope, which allow it to determine the structure as well phases occurred in the investigated alloy.

3. Description of achieved result

Addition of Ce to the ZL8 alloy modifies the microstructure (by mind of refinement resulting from the modification of grain and subgrains - according literature data), but does not significantly change the derivative curve and also does not cause the formation of new phases and eutectics during the solidification process of the melt (Figs. 1, 2).

As a result of modification with Ce there occurs an increase of undercooling of the ZL8 alloy, which can be recognised especially on the fraction solid diagram calculated on the basis of the obtained thermal analysis results.

The phases and eutectics crystallization sequence marked in Fig. 1, both for the nonmodified and modified zinc alloy are: I - $T_{DN}$ nucleation temperature, II - $T$ temperature of the beginning of the crystal growth ($\alpha$ phase dendrites), III - Dendrites of the $\alpha$ phase occurred in the liquid alloy become coherent, and the second derivative of the cooling curve reaches the value zero, IV - Stable growth of dendrite $\alpha$ phase, V - Nucleation of the $\beta+\alpha$ eutectics, VI - A stable growth of the $\alpha + \beta$ eutectic. This process occurs at a constant temperature, so there is achieved thermal equilibrium between the crystallised phases. In this point, the derivative of the cooling curve reaches again the value zero, VII - $T_{SOL}$ end of eutectics nucleation, entire alloy crystallised.

There is visible also a change in the morphology of Al dendrites, which have extended secondary arms prior to the modification, whereas after the modification there occurs a limited amount of secondary dendrite arms, and in their place there are present precipitations with a globular shape.

Fig. 1. Cooling curve, crystallisation curve and the calorimetric analysis of the ATD diagram for the ZL8 alloy, cooling rate ~0.1°C/s

Fig. 2. Cooling curve, crystallisation curve and the calorimetric analysis of the ATD diagram for the ZL8 alloy, modified with Ce 1% mass., cooling rate 0.15°C/s

It was found out, as a result of the microstructure investigations (Figs. 3-9) on light microscope, that there are no pores or cracks in the produced material and any defects and failures occurring spontaneously are not of significant importance for the properties of the whole sample.
Fig. 3. Microstructure of the nonmodified cast ZL 8, etched in 10% HF

Fig. 4. Microstructure of the modified cast ZL 8, etched in 10% HF, modified with 0.1% mas. Ce

Fig. 5. Microstructure of the modified cast ZL 8, etched in 10% HF, modified with 0.1% mas. Ce

Transmission electron microscope investigation results are presented on Figs. 10 to 17. For the investigated zinc alloy a crystalline microstructure of the alloy after the controlled solidification process was detected.

Microstructures of the alloy using the bright field technique are showed on Figs. 10 and 14. The size of the subgrains or crystallites can be determined, as ca. 0.3 μm in size. For the reason of smaller crystalline structure could have also better mechanical properties. For phase determination of the structure of the surface layer diffraction pattern analysis of the investigated areas has allow to identify the Zn α phase (α) as a hexagonal phase of the P63/mmc space group with the d-spacing of a=b=0.26648 nm and c=0.49467 nm.

Fig. 6. Microstructure of the modified cast ZL 8, etched in 10% HF, modified with 0.5% mas. Ce

Fig. 7. Microstructure of the modified cast ZL 8, etched in 10% HF, modified with 1% mas. Ce

Fig. 8. Microstructure of the modified cast ZL 8, etched in 10% HF, modified with 1% mas. Ce
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Fig. 3. Microstructure of the nonmodified cast ZL 8, etched in 10% HF

Fig. 4. Microstructure of the modified cast ZL 8, etched in 10% HF, modified with 0.1% mas. Ce

Fig. 5. Microstructure of the modified cast ZL 8, etched in 10% HF, modified with 0.5% mas. Ce

Fig. 6. Microstructure of the modified cast ZL 8, etched in 10% HF, modified with 1% mas. Ce

Fig. 7. Microstructure of the modified cast ZL 8, etched in 10% HF, modified with 1% mas. Ce

Transmission electron microscope investigation results are presented on Figs. 10 to 17. For the investigated zinc alloy a crystalline microstructure of the alloy after the controlled solidification process was detected. Microstructures of the alloy using the bright field technique are showed on Figs. 10 and 14. The size of the subgrains or crystallites can be determined, as ca. 0.3 - 0.4 μm in size. For the reason of smaller crystalline structure could have also better mechanical properties. For phase determination of the structure of the surface layer diffraction pattern analysis of the investigated areas has allowed to identify the Zn₁ phase as a hexagonal phase of the P6₃/mmc space group with the d-spacing of a=b=0.26648 nm and c=0.49467 nm.

Fig. 9. The X-ray diffraction-graph of ZL8 with Ce phases composition

Fig. 10. Microstructure of the ZL8 alloy modified with Ce, bright field, TEM

Fig. 11. Microstructure of the ZL8 alloy modified with Ce, dark field, TEM

Fig. 12. Diffraction pattern of the area presented on Fig. 10

Fig. 13. Solution of the diffraction pattern presented on Fig. 12

Fig. 14. Microstructure of the ZL8 alloy modified with Ce, bright field, TEM
4. Conclusions

As a result of the performed investigations it was found that: there occurs morphology changes of the α phase dendrites as well microstructure refinement, alloy modification causes a shift of the characteristic points of the phases and eutectics crystallisation as well solidus/liquidus points, and increase of the alloy overcooling. Transmission electron microscope investigations have allow it to determine the Zn phases as a main phase in this alloy, responsible for mechanical properties enhancement, with the possibility to determine to size of the crystallites, reaching up to 300 nm.

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References

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