Archives of Materials Science and Engineering

Volume 55
Issue 1
May 2012
Pages 29-36

International Scientific Journal
published monthly by the
World Academy of Materials
and Manufacturing Engineering

Light and electron microscope investigations of cast Zn-Al alloys

B. Krupińska [a],*, Z. Rdzawski [a,b], K. Labisz [a]

[a] Institute of Engineering Materials and Biomaterials, Silesian University of Technology,
ul. Konarskiego 18a, 44-100 Gliwice, Poland
[b] Institute of Non-Ferrous Metals, ul. Sowińskiego 5, 44-100 Gliwice, Poland
* Corresponding e-mail address: beata.krupinska@polsl.pl

Received 12.03.2012; published in revised form 01.05.2012

ABSTRACT

Purpose: The 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: approach The UMSA (Universal Metallurgical Simulator and Analyser) device allows it to determine the specific points of the solidifying alloy, including: Influence of the chemical concentrations of the modifiers, alloying additives, parameters of the 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 zinc cast alloys. For phase determination electron diffraction investigations were performed carried out on the transmission electron microscope.

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 pointwise 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; Thermo analysis; Zn-Al alloy; Microstructure

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

B. Krupińska, Z. Rdzawski, K. Labisz, Light and electron microscope investigations of cast Zn-Al alloys, Archives of Materials Science and Engineering 55/1 (2012) 29-36.

PROPERTIES

1. Introduction

The growing consumers demand concerning components produced from engineering materials with high mechanical properties, but also high corrosion resistance promotes research and development activities related on improving of existing and developing of new alloys, including Zn alloys, with improved functional properties, and competitive price [1-6].

Zn alloys are primarily used for manufacturing of fine, thin-walled casts, which require high precision. These alloys are also characterized by a higher casting speed, ensuring a 10 times more life time of the dies, which makes them very useful for mass production of small casts. Zinc alloys melted in cast iron crucibles heated electrically or by means of appropriate fuel gas and cast using pressure cast methods with heated chamber. Castings of this type are used for example in the automotive and electronic industry, as well in mechanical engineering [1,4,5].

Production of zinc alloy casts is at a level of about 11 000 tons (these are estimates data, because of the data lack from many small foundries).

For investigations there were selected aluminium and zinc - copper casts alloys, known as ZL8 according to the PN-EN 1774:2001 standard, used for production of casts with high precision, characterized by high castability and resistance to hot cracking. Improvements concerning the Zn-Al alloys is expected by microstructure modelling during addition of appropriate alloying additives, as well modification in most cases with cerium, lanthanum and strontium, but also titanium and boron [1,4-6].

The change of the crystallisation kinetics, caused by different cooling rates according to the equations of K. Jakson and J. Hunt, influences the degree of crystallization overcooling of the α solid solution and α + β eutectic, which is reflected in the occurred structure, and that fore influences also the properties of commercial cast Zn-Al alloys . In the literature there are no data available defining the interdependence between the crystallization overcooling level of the β solid solution and α + β eutectic in the cast Zn-Al alloys, and the applied cooling rate. The exact knowledge of the impact of the cooling rate of casts crystallised in dies on the structure and phase transformation temperature during non-equilibrium crystallization allows it to control optimal the production process [8-10].

In case of cast alloys the crystallization process takes place in a temperature range between the beginning and end of crystallization. The values of free energy for liquid and solid phases are dependent on the concentration of the second component (in binary alloys). A driving force in case of metal alloys is the difference between free energy and the energy of the liquid and solid phases in the concentration range of the second component for the liquid and solid phase [9-15].

Solidification itself can have both a directional and a volume nature, it is dependent on the phenomena occurring at the front of crystallization. Directional solidification is characterized by continuous change of the boundary between the liquid and solid, and the movement of the front from the outside to the inside of the casts (contrary to the direction of heat flow direction). Volume solidification is characterised by lacks of boundaries between liquid and the solid phase as well with a heat transfer from the crystallised phase, also through the liquid phase (a negative temperature gradient occurs). This solidification type can occur towards the casting direction, and can also occur in the entire volume of the casts [1,2,16-18].

Directional crystallization occurs at very specific conditions. One of them concerns the fact, that the crystallization front cannot reach too high values of undercooling - in terms of chemical concentration. Directional crystallization will occur , when the temperature increase on the casts cross-section is very high, what can be achieved through the appliance of metallic moulds, which are characterized by very high heat storage capacity[1,2].

Volume crystallization occurs in the sand dies, which have a low heat storage capacity. The occurred crystallization occurs in the entire cast volume and causes a grain structure with uniaxial grains. This is the most often occurred crystallization type for cast alloys [1,2].

Cooling rate has a significant influence on the structure and properties of cast zinc alloys. The effects of high cooling rates and consequently increasing solidification rates of the structure of the casting involves: avoiding of segregation (block- or dendritic segregation), a significant phase dispersion (including decreasing spacing between the eutectic plates).

Cooling rate has an big influence on dendritic segregation: slow cooling causes homogenization of the structure and decrease of dendrites; by a cooling rate - typical for a given alloy - instead of grain, there will be revealed a dendritic structure. Achievement of a certain temperature leads to a maximum of dendritic segregation, at very high cooling rates, a fine-grained structure will be achieved, by occurrence of chemical compositions differences in the grains [19-21].

The aim of rapid crystallization is to achieve materials with improved properties, which are obtained by: refinement of dendritic or eutectic structure, reduction or elimination of segregation, occurrence of solid phases with extended solubility of the alloying additives or new metastable phases, or with change of the phase morphology[19-21].

Functional properties of elements made of cast alloys depends on the primary structure of the alloy, which further depends on the crystallization kinetics. The crystallization kinetic is characterized by changing the following parameters: the metal temperature, cooling rate, the speed crystallization latent heat generation, grain density, which is equivalent with the density of the resulting nuclei. The crystallization kinetic is also characterized with the solid fraction of crystallized metal, the concentrations of the elements in the remaining liquid, characteristic distances, describing the size and shape of the structural components [1,21-25].

All these parameters are variables of the crystallisation time and the geometric coordinates [1,25-29].

Cooling of the liquid alloy proceeds from the liquid state - the liquidus line, this means from the beginning of the crystallization, followed by crystallization of eutectics and intermetallic phases until the alloy reaches a solid state - the solidus line, according to the equilibrium phase diagrams. Therefore, on the cooling curve there are present characteristic points (inflection points) - from the exothermic reaction or endothermic transformations of the crystallised phases or eutectics. It is difficult on the cooling curve, to determine the temperature of crystallization of the occurred phases. The determination of the temperature is possible by determination of the first derivative of the cooling curve as a function of time, ie. curve differential (ATD), also known as derivative curve derivation [26-28].

In order to improve the mechanical properties of cast alloys, in addition to the heat treatment there will be also applied modification operations, which causes changes in the morphology and decreases the interfacial distances of the $\alpha+\beta$ eutectic, as well microstructure refinement. For this reason, different modifiers are in use.

At present there are used modification with strontium and antimony, because these are modifiers of long-term operation. The effect of strontium persists also after many remelting processes of the alloy, which enables production of modified in the foundries. Increasingly, they are also widely used rare earth metals for modification of cast alloys .

Zn alloys, especially with high Al content, reveals susceptibility to cast shrinkage, which can be eliminate by the addition of alloying elements in form of: Sr, Ca, Li, Na, Be, - additions of Ti, Zr, Sb, B and rare earth metals are in this case irrelevant. Good castability and mould filling will be decrease by additions of rare earth metals, which also like Ti additions reveals the tendency of hot cracking.

Properly performed chemical modification as well application of a proper cooling of casts causes improvement of functional properties of the produced casts. Therefore it is very important to know how the structure of the casts changes compared to the cooling rate or compared to the chemical composition by addition of alloying additives or modifiers to the molten metal.

Among the methods for phase determination, the X-ray diffraction examinations (XRD), on the transmission electron microscope (TEM), were performed, which makes it possible to carried out the phase determination, which is essential for evaluation the crystalline structure and that fore also properties of the investigated alloys.

As a result of performed investigations concerning the effect of addition of rare earth metals it was found, that such addition causes deoxodation during the melting in the open furnace, as well fragmentation of the microstructure as a result of the occurrence of many crystallisation nuclei, and also precipitation strengthening. Addition of rare earth metals allows appliance of the material for production of elements working at elevated temperatures, because it improves mechanical properties at elevated temperatures (above 300°C).

2. Materials and experimental procedure

For statement of the interdependence between the chemical composition and the structure of the ZnAl8Cu1 (PN-EN:1774) zinc cast alloy (Tables 1, 2), cooled with different cooling speed investigation of the influence of lanthanum and cerium were performed using the UMSA device for simulation of crystallization processes on samples melted in a cylindrical graphite crucible (Fig. 1) [3,4].

Table 1.
Chemical composition of ZnAl8Cu1 zinc alloy (PN-EN:1774)

Mass concentration of the element, in wt.%, AA standard(?)				
Al	Cu	Mg	Pb	Cd
3.2-8.8	0.9-1.3	0.02-0.03	max. 0.005	max. 00.5
Sn	Fe	Ni	Si	Zn
max. 0.002	max. 0.035	max. 0.001	max. 0.035	rest

Table 2.
Chosen properties of the ZnAl8Cu1 alloy

Mass density	Strength	Elongation	Brinell hardness
6.7 kg/dm^3	196 MPa	1%	65HB

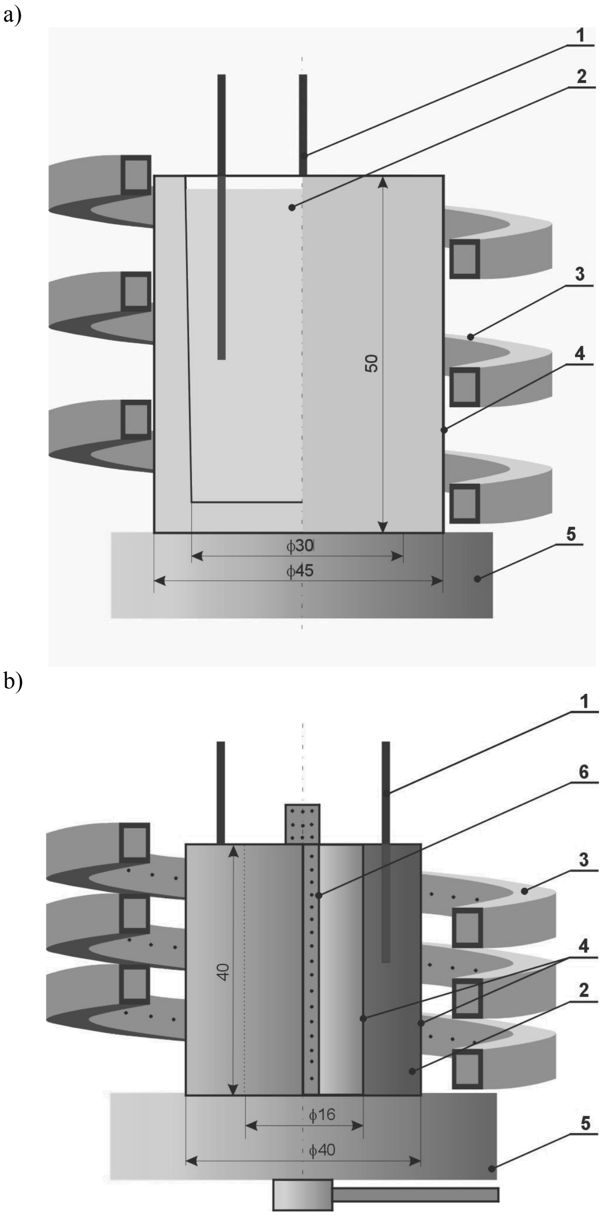

Fig. 1. Scheme of the heating and cooling of the UMSA device as well the placement of the thermoelements and size of samples used for thermoanalysis for: a) roll samples: 1 - thermocouple, 2 - sample, 3 - coil - cooling nozzles assemble, 4 - crucible, 5 - sampler isolation; b) cylindrical samples: 1 - thermocouple, 2 - sample, 3 - coil - cooling nozzles assemble, 4 - steel foil, 5 - sampler isolation, 6 -cooling lance for the inner wall of the sample

The examinations of thin foils microstructure and phase identification were carried out on the JEOL 3010 transmission electron microscope (TEM), at the accelerating voltage of 300 kV using selected area diffraction method (SAD) for phase investigations. The diffraction patterns from the TEM were solved using a special computer program "Eldyf" software supplied by the Institute of Material Science o the University of Silesia.

For temperature measurement a chromel-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 results

Preliminary investigations indicate a favourable effect of cooling rate and modification of the Zn-Al alloys with lanthanum and cerium.

Addition of La and 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. 2, 3).

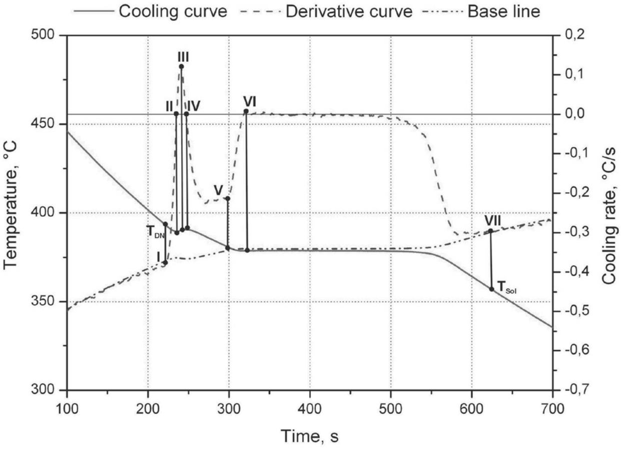

Fig. 2. Cooling curve, crystallisation curve and the calorimetric analysis of the ATD diagram for the ZL8 alloy, cooling rate ~0.1°C/s

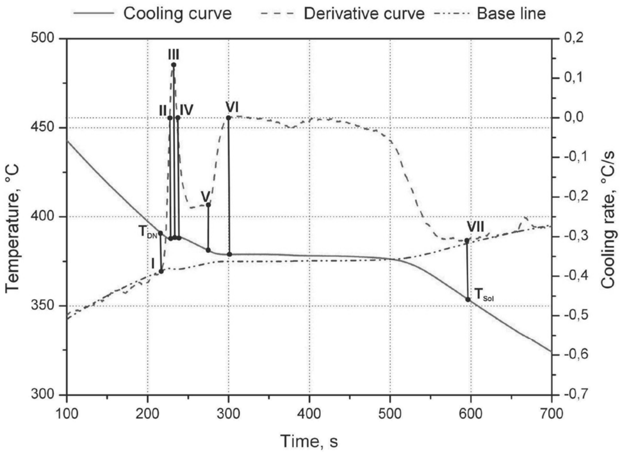

Fig. 3. Cooling curve, crystallisation curve and the calorimetric analysis of the ATD diagram for the ZL8 alloy, modified with La 0.5% mas. and Ce 0.5% mas., cooling rate 0.15°C/s

As a result of modification with La and 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 Figures 2 and 3, both for the nonmodified and modified zinc alloy are presented in Table 3.

Table. 3.
Description of the characteristic points on the cooling curve from Figs. 2 and 3

Point on the graph	Description
I	T_{DN} nucleation temperature
II	T temperature of the beginning of the crystal growth (α phase dendrites)
III	Dendrites of the α 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 α phase
V	Nucleation of the β+α eutectics
VI	A stable growth of the α + β 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 (Fig. 4), 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. 5).

It was found out, as a result of the microstructure investigations (Figs. 4, 5) 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.

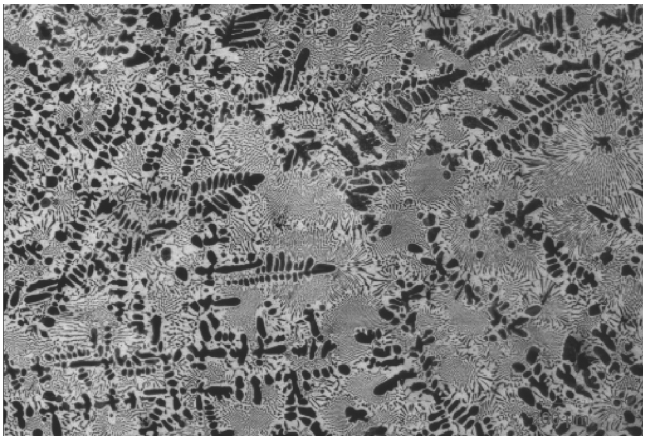

Fig. 4. Microstructure of the nonmodified cast ZL 8, etched in 10% HF

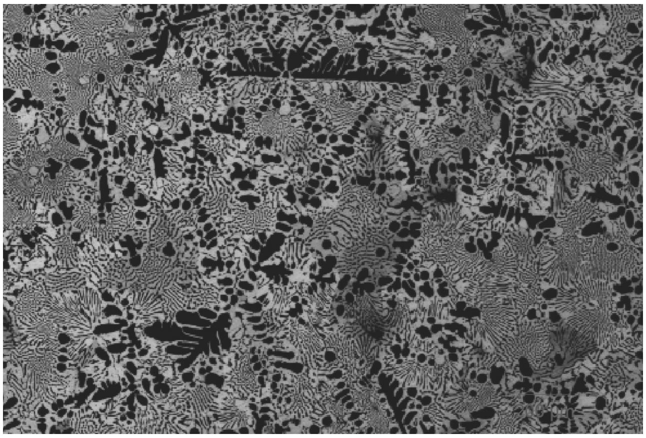

Fig. 5. Microstructure of the modified cast ZL 8, etched in 10% HF, modified with 0.5% mas. La and 0.5% mas. Ce,

TEM investigation results are presented in Figures 6-15. For the investigated zinc alloy a crystalline microstructure of the alloy after the controlled solidification process was detected. In Figures 6, 10 and 12 there are showed the microstructures of the alloy using the bright field technique the size of the subgrains or crystallites can be determined, as ca. 250 nm in diameter. 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 (Fig. 9) 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.

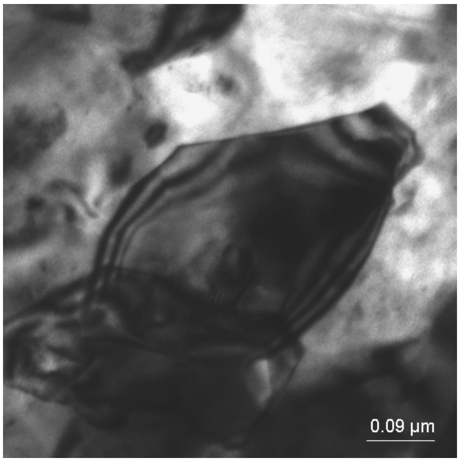

Fig. 6 .Microstructure of the ZL8 alloy modified with La and Ce, bright field, TEM

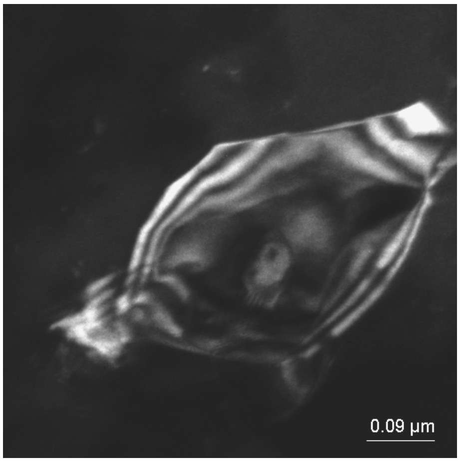

Fig. 7. Microstructure of the ZL8 alloy modified with La and Ce, dark field, TEM

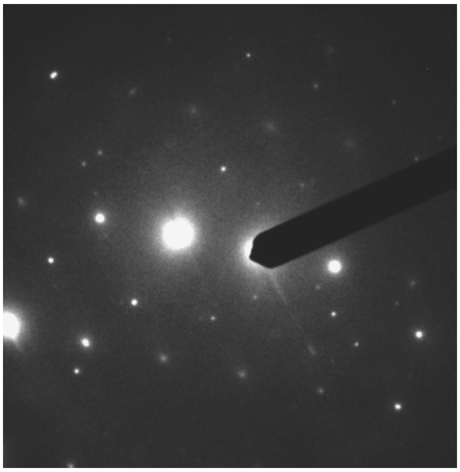

Fig. 8. Diffraction pattern of the area presented on Fig. 6

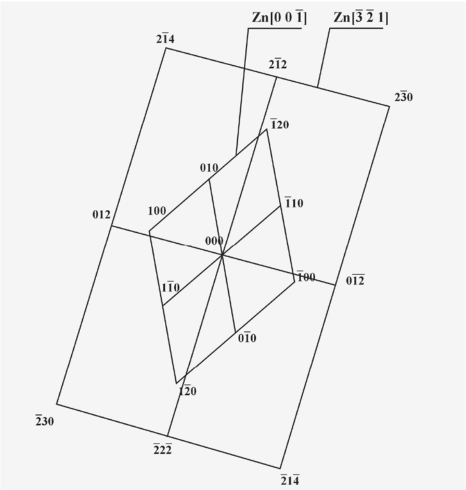

Fig. 9. Solution of the diffraction pattern presented in Fig. 8

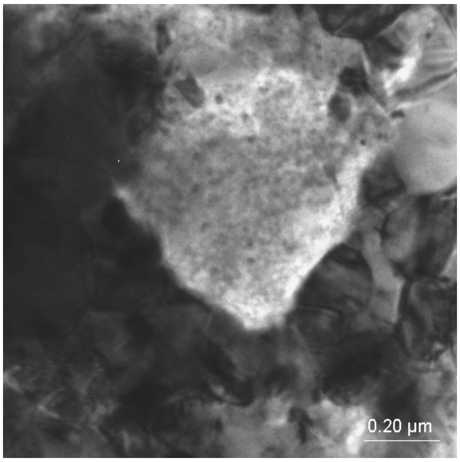

Fig. 10. Microstructure of the ZL8 alloy modified with La and Ce, bright field, TEM

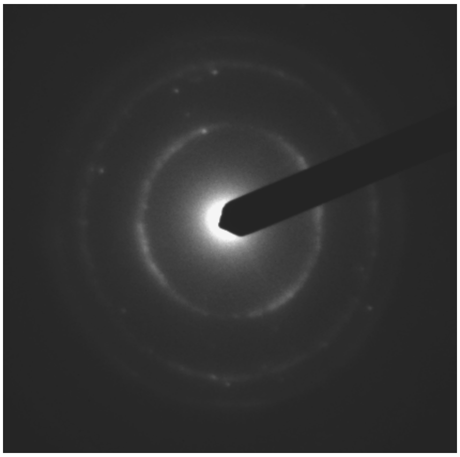

Fig. 11. Diffraction pattern of the area presented in Fig. 10

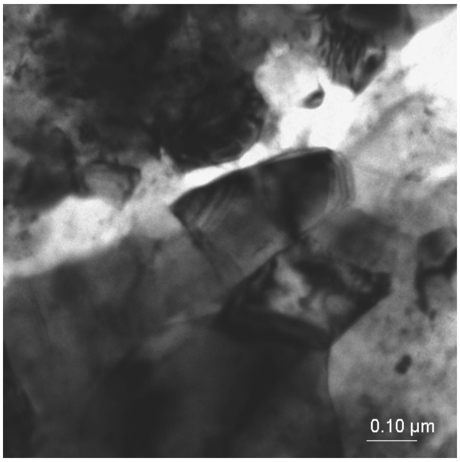

Fig. 12. Microstructure of the ZL8 alloy modified with La and Ce, bright field, TEM

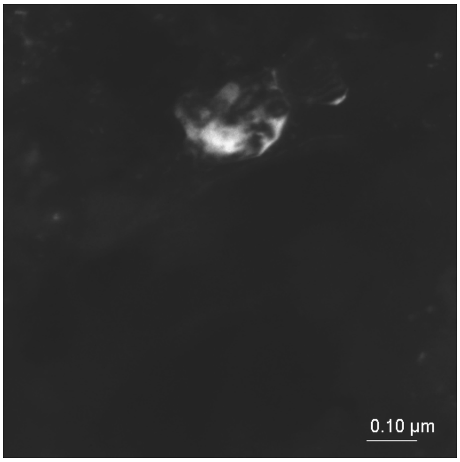

Fig. 13. Microstructure of the ZL8 alloy modified with La and Ce, dark field, TEM

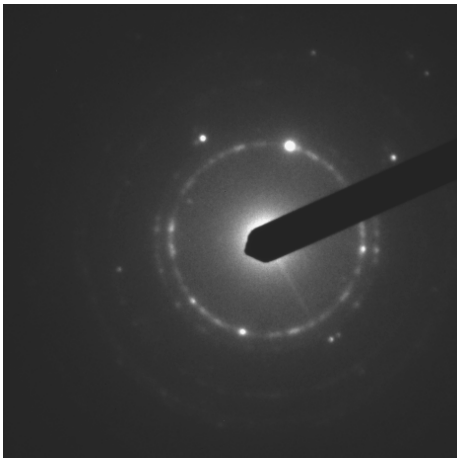

Fig. 14. Diffraction pattern of the area presented in Fig. 12

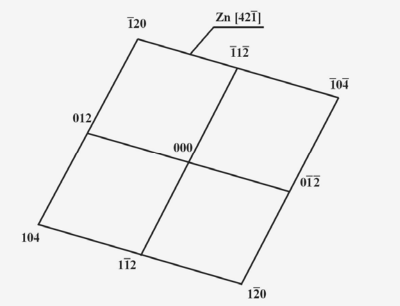

Fig. 15. Diffraction pattern of the area presented in Fig. 14

4. Conclusions

The investigated alloys were freely cooled, and as the cooling rate there was set the temperature change in time in the range of T_{DN} to T_{SOL}. The addition of modifiers will not significantly increase the costs, which is a clear advantage.

As a result of the performed investigations it was fund 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 in case of La and Ce increase of the alloy overcooling. Transmission electron microscope investigations have allow it to determine the Al_2Cu phase as a main phase in this alloy, responsible for mechanical properties enhancement.

Based on TEM investigations (Fig. 10) there was found carbon containing structures in form of bulk policrystailline particles with a diffraction pattern presented on Fig. 11, which could not be solved as the graphite phase. Further investigations should be performed to solve the crystallographic structure of this phase.

Acknowledgements

Research was financed partially within the framework of the Polish State Committee for Scientific Research Project No. N507 264 040 headed by Dr Beata Krupińska.

References

[1] E. Fraś, Alloy crystallisation, WNT, Warsaw, 2003.

[2] Z. Górny, J. Sobczak, Non-ferrous metals based materials in foundry practice, ZA-PIS, Cracow, 2005.

[3] B. Krupińska, K. Labisz, L.A. Dobrzański, Z. Rdzawski, Crystallization kinetics of Zn alloys modified with Ce, La, Sr, Ti, B, Journal of Achievements in Materials and Manufacturing Engineering 42 (2010) 50-57.

[4] B. Krupińska, L.A. Dobrzański, Z.M. Rdzawski, K. Labisz, Cooling rate influence on microstructure of the Zn-Al cast alloy, Journal of Achievements in Materials and Manufacturing Engineering 43/1 (2010) 13-20.

[5] M. Krupiński, K. Labisz, L.A. Dobrzański, Structure investigation of the Al-Si-Cu alloy using derivative thermo analysis, Journal of Achievements in Materials and Manufacturing Engineering 34/1 (2009) 47-54.

[6] M. Krupiński, K. Labisz, L.A. Dobrzański, Z.M. Rdzawski, Derivative thermo-analysis application to assess the cooling rate influence on the microstructure of Al-Si alloy cast, Journal of Achievements in Materials and Manufacturing Engineering 38/2 (2010) 115-122.

[7] L.J. Yang, The effect of casting temperature on the properties of squeeze cast aluminium and zinc alloys, Journal of Materials Processing Technology 140 (2003) 391-396.

[8] L.J. Yang, The effect of solidification time in squeeze casting of aluminium and zinc alloys, Journal of Materials Processing Technology 192-193 (2007) 114-120.

[9] W.R. Osorio, A. Garcia, Modeling dendritic structure and mechanical properties of Zn-Al alloys as a function of solidification conditions, Materials Science and Engineering A325 (2002) 103-111.

[10] A.E. Ares, L.M. Gassa, S.F. Gueijman, C.E. Schvezov, Correlation between thermal parameters, structures, dendritic spacing and corrosion behavior of Zn-Al alloys with columnar to equiaxed transition, Journal of Crystal Growth 310 (2008) 1355-1361.

[11] M. Durman, S. Murphy, An electronmetallographic study of pressure die-cast commercial zinc-aluminium-based alloy ZA27, Journal of Materials Science 32 (1997) 1603-1611.

[12] T.J. Chena, Y. Haoa, J. Sunb, Y.D. Lia, Effects of Mg and RE additions on the semi-solid microstructure of a zinc alloy ZA27, Science and Technology of Advanced Materials 4 (2003) 495-502.

[13] J. Szajnar, The impact of selected physical factors on the crystallization process and structure of castings, Archives of Foundry Engineering 9-1M, 2009.

[14] W. Kasprzak, J.H. Sokołowski, M. Sahoo, L.A. Dobrzański, Thermal and structural characteristics of the AM50 magnesium alloy, Journal of Achievements in Materials and Manufacturing Engineering 28/2 (2008) 131-138.

[15] L.A. Dobrzański, M. Kasprzak, W. Kasprzak, J.H. Sokołowski, A novel approach to the design and optimisation of aluminium cast component heat treatment processes using advanced UMSA physical simulations, Journal of Achievements in Materials and Manufacturing Engineering 24/2 (2007) 139-142.

[16] L.A. Dobrzański, M. Król, T. Tański, Thermal analysis, structure and mechanical properties of the MC MgAl3Zn1 cast alloy, Journal of Achievements in Materials and Manufacturing Engineering 40/2 (2010) 167-174.

[17] L.A. Dobrzański, T. Tański, L. Cížek, Heat treatment impact on the structure of die-cast magnesium alloys, Journal of Achievements in Materials and Manufacturing Engineering 20 (2007) 431-434.

[18] G. Moskal, Thermal barrier coatings: characteristics of microstructure and properties, generation and directions of development of bond, Journal of Achievements in Materials and Manufacturing Engineering 37/2 (2009) 323-331.

[19] L.A. Dobrzański, M. Król, T. Tański, Effect of cooling rate and aluminum contents on the Mg-Al-Zn alloys' structure and mechanical properties, Journal of Achievements in Materials and Manufacturing Engineering 43/2 (2010) 613-633.

[20] L.A. Dobrzański, R. Maniara, J. Sokołowski, W. Kasprzak, Effect of cooling rate on the solidification behavior of AC AlSi7Cu2 alloy, Journal of Materials Processing Technology 191 (2007) 317-320.

[21] L.A. Dobrzański, W. Borek, R. Maniara, Influence of the crystallization condition on Al-Si-Cu casting alloys structure, Journal of Achievements in Materials and Manufacturing Engineering 18 (2006) 211-214.

[22] J.H. Sokołowski, X-C. Sun, G. Byczyński, D.O. Northwood, D.E. Pentod, R. Thomas, The removal of copper phase segregation and the subsequent improvement in mechanical properties of cast 319 aluminium alloys by a two-stage solution heat treatment, Journal of Materials Processing Technology 53 (1995) 174-180.

[23] L.A. Dobrzański, R. Maniara, J.H. Sokołowski, The effect of cast Al-Si-Cu alloy solidification rate on alloy thermal characteristics, Journal of Achievements in Materials and Manufacturing Engineering 17 (2006) 217-220.

[24] L.A. Dobrzański, R. Maniara, J. Sokołowski, W. Kasprzak, M. Krupinski, Z. Brytan, Applications of the artificial intelligence methods for modeling of the ACAlSi7Cu alloy crystallization process, Journal of Materials Processing Technology 192-193 (2007) 582-587.

[25] L.A. Dobrzanski, W. Kasprzak, M. Kasprzak, J.H. Sokołowski, A novel approach to the design and optimization of aluminum cast component heat treatment processes using advanced UMSA physical simulations, Journal of Achievements in Materials and Manufacturing Engineering 24/2 (2007) 139-142.

[26] W. Kasprzak, J.H. Sokołowski, W. Sahoo, L.A. Dobrzański, Thermal and structural characteristics of the AZ50 magnesium alloy, Journal of Achievements in Materials and Manufacturing Engineering 29/2 (2008) 179-182.

[27] L.A. Dobrzański, M. Krupiński, J.H. Sokołowski, Computer aided classification of flaws occurred during casting of aluminum**,** Journal of Materials Processing Technology 167/2-3 (2005) 456-462.

[28] M. Krupiński, K. Labisz, L.A. Dobrzański, Z. Rdzawski, Derivative thermo analysis of the Al-Si cast alloy with addition of rare earths metals, Archives of Foundry Engineering 10/1 (2009) 79-82.

[29] M. Krupiński, K. Labisz, L.A. Dobrzański, Structure investigation of the Al-Si-Cu alloy using derivative thermo analysis, Journal of Achievements in Materials and Manufacturing Engineering 34/1 (2009) 47-54.