Cooling rate influence on microstructure of the Zn-Al cast alloy

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ABSTRACT

Purpose: In this work was presented the cooling rate influence on microstructure of the Zn-Al cast alloy. This research work presents also the investigation results of derivative thermoanalysis performed using the UMSA device. The material used for investigation was the ZnAl4Cu1 alloy.

Design/methodology/approach: Moreover the analysis of cooling rate influence on the derivative curve changes was performed as a result of the measured crystallisation kinetic changes. For the assessment of the cooling rate influence on the mechanical properties also hardness measurements were performed using the Rockwell hardness device.

Findings: The treated sample is without holes, cracks and defects as well as has a slightly higher hardness value compared to the as-cast material.

Research limitations/implications: The material was examined metallographically and analyzed 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: This work provides better understanding of the thermal characteristics and processes occurred in the new developed alloy. The achieved results can be used for liquid metal processing in science and industry and obtaining of a required alloy microstructure and properties influenced by a proper production conditions.

Keywords: Metallic alloys; Derivative thermo analysis; Zn-Al alloy; Microstructure

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MATERIALS

1. Introduction

Properties of cast zinc alloys are comparable to these of aluminium alloys. Differences are connected to a lower melting temperature and bigger density. Zinc has a density of 7.14g/cm^3,

melting temperature of 419.5ºC, and a boiling temperature of 906ºC. In the temperature range of 150 to 200ºC zinc is characterized by a good wrought susceptibility. It is also resistant against the influence of atmospheric factors (the carbide-oxide surface coating acts as a protective layer), but is not

resistant against acids. Main application of zinc alloys is placed in production of thin-walled castings, which need a high manufacturing precision. These alloys have found its application also for high pressure casts of bodies and covers for many devices, applied in the industry for precise elements manufacturing, in the electromechanically industry (computer panels, housings for writers, automobile industry, as well in the building industry (materials for building constructions, solar panels) [1-3].

Its application grows according to the process- and converting technology development. Very important advantage of zinc is its scrap recycling possibility, what is at present very important feature because of the shortage of natural resources

These alloys are characterized by a large cast rate, what increase about 10 times mould life.

For this reason zinc alloys are known as a material used for mass production of small elements. For casting of zinc alloys there is mostly used the mould high pressure casting [1-3].

The Zn-Al alloys contains usually 3.5-30% aluminium. Except aluminium they contains also Cu, with a content of ca 5% as well 0.05% Mg, that fore the zinc microstructures can be studied according to the Zn-Al and Zn-Cu equilibrium diagram [1,4,5].

Copper is one of the main alloying additive for zinc alloys, which influences the strength increase, hardness and corrosion resistance. Cu addition causes a shift of the eutectic point in the Zn-Al-Cu equilibrium diagram towards to the higher Al concentration. Cu increases also the Zn-Al alloy susceptibility to ageing and - connected with it - changes of dimensions. This is of only small impact to the eutectoid transformation of the β(β') phase as well to the solubility in the solid state in the low temperature range, but is has to do first of all with the phase transformations in the solid state with the hexagonal η phase, regular face centered β(β') phase, hexagonal ε (CuZn$_4$) phase as well the hexagonal τ phase (intermetallic CuZn$_3$ phase). This transformation of the main reason for the dimensions changes. A 0.6-0.7% Cu content in a zinc alloy is necessary for appearance of the τ phase [6-9].

Magnesium is added to the Zn-Al alloy for the reason of limiting of the impurities influence, particularly Pb and Sn as well for the reason of inter-crystalline corrosion limiting.

Addition above 0.1% Mg deteriorates castability, increases high temperature brittleness and leads to casting cracks. Variable Mg content and modification additives like Be, Cr or Ti causes in the ZnAl4Cu1 alloy basis differences changes in dimension during ageing.

Beryllium (Be) added to this alloy in a concentration of 0.005% increases fatigue strength of high pressure casts about 17-88%. Addition of Be protects the liquid alloy against oxidation. With a concentration of 0.004-0.0045% Be in the ZnAl4Cu1 alloy only a 25% natural slag will be obtained compared to the alloy without Be addition. Beryllium addition eliminates also Fe diffusion from the mould and other casting tools (made of steel or cast iron) [3,9,10].

In case of cast alloys the crystallization process occurs in the temperature range between the begin and end of crystallization. The free energy value for the liquid and solid phase depends from the concentration of the second additive (in case of binary alloys). The activating energy in case of alloys is the difference in free energy of liquid and the energy of the liquid and solid compound

in the concentration range of the second additive for the liquid and solid phase [1,11,13].

Crystallisation can have directional volume character, it is dependent on the phenomena occurred at the crystallisation front. Directional crystallisation is characterised by a change of the boundary between the liquid and solid phase, as well by a migration of the crystallisation front from inside to outside in the cast (contrary to the heat transfer direction). Volume crystallisation has typically a lack of a boundary between the liquid and solid phase as well is characterised by heat transfer from the solidified phase, also through the liquid phase (negative temperature gradient). Solidification occurs according to the cast direction, but it can be present also in the whole casting volume [11].

Directional crystallisation occurs by clearly determined conditions. One of the says, that on the crystallisation front there can not occur a too big value of (concentration-) overcooling.

Directional crystallisation favour big temperature decrease along the cast, what can be achieved by appliance of metal moulds, which have big ability for heat capacity.

Volume crystallisation occurs in sand moulds, which have lover ability for heat capacity

Crystallisation has generally a volume character and builds a microstructure consisting of equiaxial grains. This is the most frequently occurred crystallisation type among cast alloys.

Cooling rate has a big influence on microstructure and properties of the zinc cast alloys.

The effects of appliance of big cooling rates and in the consequence of increased solidification rates onto the cast micro-structure are: avoiding of segregation (block and dendritic), significant phase dispersion (also an decreasing distance between the eutectics plates). By cooling rates $dT/dt > 10^6$ to 10^8 °C/s appears in succession: unstable or metastable solid solutions, new meta-stable phases as well solidification in the amorphous state [11].

Cooling rate has a big influence on the dendritic segregation: low cooling causes microstructure homogenization and decay of dendrites, by a cooling rate typical for a given alloy, instead of dendritic microstructure a grained microstructure in present. Achieving of a certain temperature leads to maximal segregation of dendrites, by very high cooling rates a fine-grained microstructure will be achieved by very high differences of the chemical composition of individual grains [14-18].

The aim of fast crystallization is to obtain materials with better properties, which are achieved by dendritic or eutectic microstructure refinement, lowering or avoiding of segregation occurrence, generating of stable phases with extended solubility of compounds or new metastable phases, as well morphology change of phases occurred [19-21].

In this work the derivative thermo-analysis was performed using the UMSA device (Universal Metallurgical Simulator and Analyzer). The UMSA Platform is used extensively for the following applications [22-25]:

- for physical simulation of metal casting technologies (i.e. sand, permanent and high pressure die casting), including melting, melt treatment (chemical and thermal), efficiency of master alloys, solidification and heat treatment operations (including continuous ones) that involve solution treatment, quenching and artificial aging,
- for development of new materials and processes as well as Quality Control,

- for analysis of phase nucleation, growth and transformations during melting, solidification and heat treatment under different environmental conditions,
- for analysis of structural and related physical changes of the test sample(s) subjected to quenching at predetermined temperatures (during heating and cooling cycles).

2. Material and experimental procedure

Investigations were performer using the Zn-Al alloy according to the (PN-EN 12844 (IX2001)) standard with a chemical composition given in Table 1. Table 2 presents some chosen mechanical and physical properties of the investigated Zn-Al alloy.

Table 1.
Chemical composition of ZnAl4Cu1 zinc alloy

Mass concentration of the element, in wt. %, AA standard			
Al	Cu	Mg	Pb
4.16	0.8	0.039	0.0007
Cd	Sn	Fe	Ni
0.0009	0.0004	0.0041	0.001

Table 2.
Chosen mechanical and physical properties of the investigated ZnAl-4Cu1 alloy

Properties of the ZnAl4Cu1 alloy			
Density	Strength	Elongation	Rockwell Hardness in the B scale
677 kg/dcm^3	196 MPa	1%	65 HRB

Samples for investigation were cut off in the horizontal axis as well in the vertical axis in the high of ~15 mm. This place represents the end the thermocouples for temperature change registration during the heating and cooling process (Fig. 1).
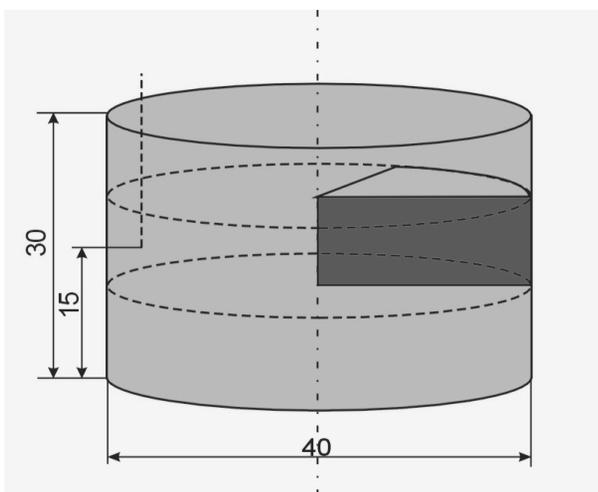
Fig. 1. Geometric size of the samples with the marked planes for microstructure investigations

For investigations the chromium-nickel thermocouples were used of the K type. The samples were mounted in a rolled steel foil with a thickness of ca. 0.025mm and coated with BN powder emulsion, as shown on Fig. 2.
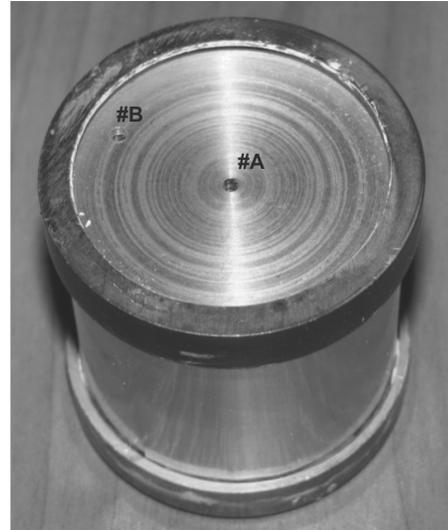
Fig. 2. Model of the sample of the investigated ZnAl4Cu1 alloy. With #A and #B are marked the places where the thermocouples were mounted

The investigated alloy was carried out with different cooling rates applied. The low cooled samples were cooled with the furnace without any additional cooling system, were the cooling rate was measured and set on 0.08 ºC/s. Where for the cooled sample (gas flow cooling) the achieved cooling rate was achieved of ca. 0.68 ºC/s for samples with a geometry as shown on Fig. 1.

Within a framework of investigations of the Zn-Al alloy following tests were performed:

- Microstructure and chemical composition investigations using EDS microanalysis on the scanning electron microscope Zeiss Supra 25;
- Thermo-derivative analysis using the UMSA device equipped with a computer-controlled cooling system, which allows it to set flexible the cooling rate applied. This is necessary for précising simulation of the cooling conditions like temperature and time during the crystallization of the investigated alloy. This device makes it also possible to perform very accurate measurements by mind of the computer aided induction heating system by simultaneously low thermal inertia of the samples;
- Hardness measurement with the Rockwell method using the Zwick ZHR 4150 model in the B scale.

In Fig. 3. there is present the working chamber, where the temperature and time measurement takes place. The samples were heated and cooled in an argon atmosphere, as the inert gas.

The cooling rate was determined as the temperature change during time between beginning of the crystallisation of the matrix Zn (T_{DN}) and end this crystallization (T_S).

Fig. 3. Working chamber of the UMSA device: 1 – thermocouple, 2 – tested sample, 3 – induction coil, 4 – ceramic isolation

3. Research results and discussion

Increase of the cooling rate of the Zn alloy samples causes as a result of the forced cooling by compressed gas injection, a grain size refinement (Figs. 5-12).

There are also some differences visible in form of micro-structure morphology changes of the phases and precipitations occurred in the investigated alloy. The changes are depending on the place in the whole sample where the planes for microscopic investigations were cut off, in the X-axis as well in the Y axis, where the thermocouples were present. The places are marked as #A and #B on Figure 2. The changes are mainly concerning the Zn-Al eutectic refinement.

The microstructure refinement has influence also the mechanical properties change, was compared by hardness measurements of the samples cooled with different cooling rates.

An increase of the cooling rate about 0.6ºC/s has caused a hardness increase of ca 24.9% (Fig. 4). The average hardness values were calculated using particular measurement values of the investigated samples. They are characterised by a smaller statistical dispersion in case of the samples cooled with a higher cooling rate, what is in visible also on the calculated standard deviation on Figure 4.

As a result of the quantitative EDS microanalysis, performed by the Electron Dispersive X-Ray Spectroscopy method, some information were achieved about the mass and atomic concentration of the particular elements (Table 3) on the investigated precipitations of the Zn alloy (Figs. 13, 14). Investigation performed using the SEM microscope has revealed, that the Zn alloy is composed of the (α) matrix (#1 in Fig. 12) as well of the Zn-Al eutectic (#2 in Fig.12), whereby the alloy matrix contains also some copper dissolved (Fig. 14).
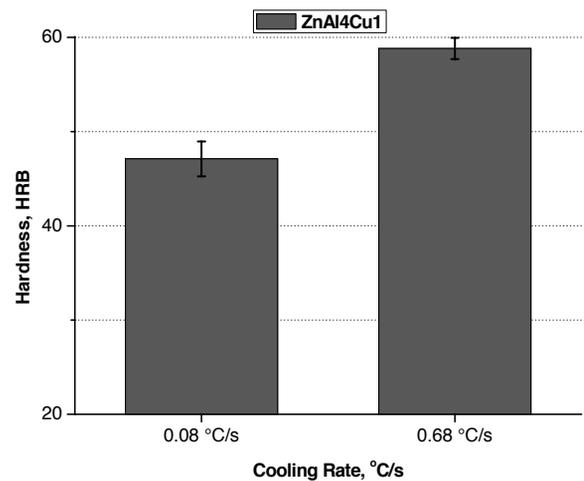
Fig. 4. Average hardness with standard variation values vs. calculated cooling rate of the Zn alloy samples

Table 3.
Mass and atomic concentration of the elements

Element	Wt%	At%
AlK	09.12	19.54
CuK	01.30	01.19
ZnK	89.58	79.27
Matrix	Correction	ZAF

In Figure 16 there are presented the cooling curves for the ZnAl4Cu1 alloy cooled with a cooling rate of 0.08ºC/s and 0.68ºC/s. The forced cooling process with compressed air on a range of 15 litre/hour has caused a change in the cooling curves of the alloy. Cooling with furnace of a sample with a similar mass and in similar heating conditions (heating time, heating temperature) causes a six times increase of elongation of the cooling time until the temperature of 50°C is achieved.

In Figs. 17 and 18 there are presented the derivative curves dT/dt for the ZnAl4Cu1 alloy, heated to the temperature of 450ºC and cooled with a cooling rate of 0.08ºC/s as well 0.68ºC/s. In Table 4 there are presented the characteristic points of the curve marked in Figures 17 and 18.

Table 4.
Description of the points marked in the diagrams in Figs. 17 and18

Number	Note the main metallurgical reaction
# 1	Start of alloy malting process
# 2	Dissolution of Zn-Al eutectic
# 3	Dissolution of Zn dendrite network
# 4	Nucleation of Zn dendrite network (Liquidus Temperature T_{DN})
# 5	Nucleation of solidification of the multi-component eutectic
# 6	Finish of the alloy solidification (Solidus Temperature T_S)

Figure 19 shows the cooling curves, derivative curves as well the baseline with marked points, were crystallisation of the α phase has started (T_{DN} – temperature of the beginning of the alloy solidification) and where the crystallisation has been finished - T_S. During the cooling rate increase about 0.6 ºC/s an overcooling of the alloy has occurred as well a shift of the characteristic points as the liquidus and solidus point into an other temperature range, what is presented in Table 5.

Table 5.
Temperature of the beginning and the end of the crystallisation of the investigated alloy compared to the cooling rate

	Colling rate	
	0.08 ºC/s	0.68ºC/s
T_{DN}	388.90	395.35
T_S	339.41	335.45
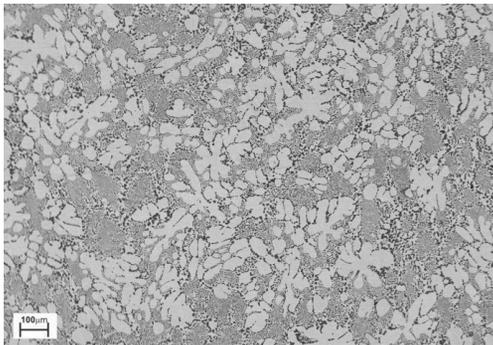
Fig. 5. Microstructure of the ZnAl4Cu1 alloy in place of the thermocouple #B, cooling rate of 0.68°C/s
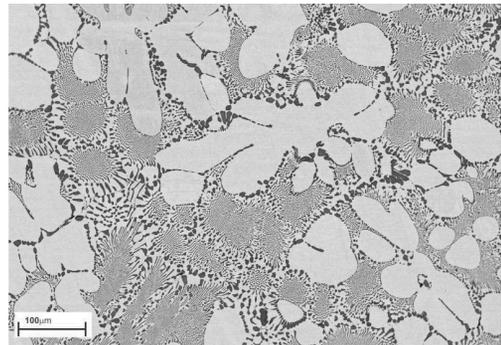
Fig. 8. Microstructure of the ZnAl4Cu1 alloy in place of the thermocouple #A, cooling rate of 0.68°C/s
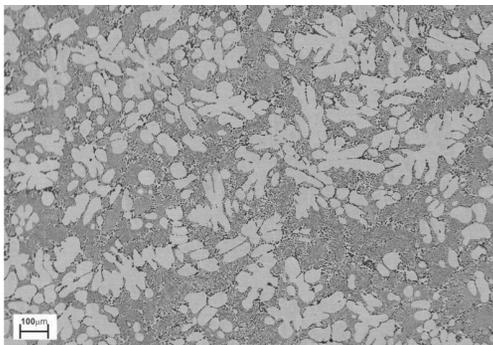
Fig. 6. Microstructure of the ZnAl4Cu1 alloy in place of the thermocouple #A, cooling rate of 0.68°C/s
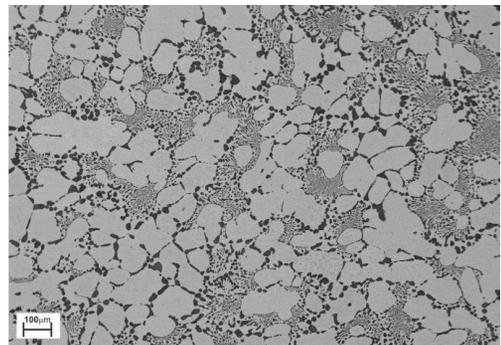
Fig. 9. Microstructure of the ZnAl4Cu1 alloy in place of the thermocouple #B, cooling rate of 0.08°C/s
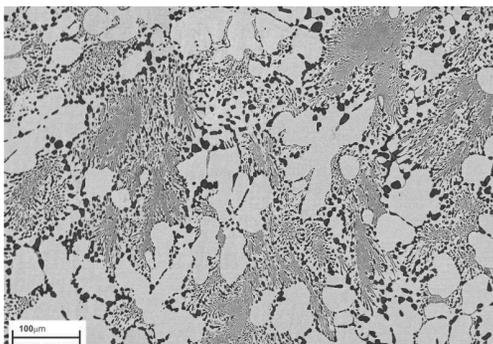
Fig. 7. Microstructure of the ZnAl4Cu1 alloy in place of the thermocouple #B, cooling rate of 0.68°C/s
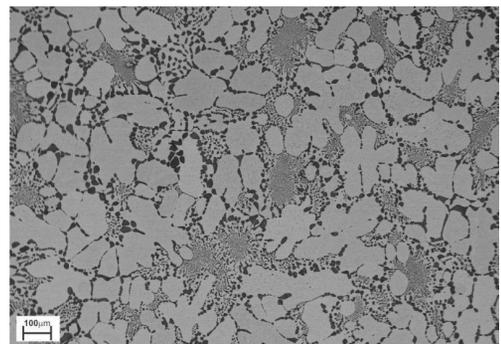
Fig. 10. Microstructure of the ZnAl4Cu1 alloy in place of the thermocouple #A, cooling rate of 0.08°C/s
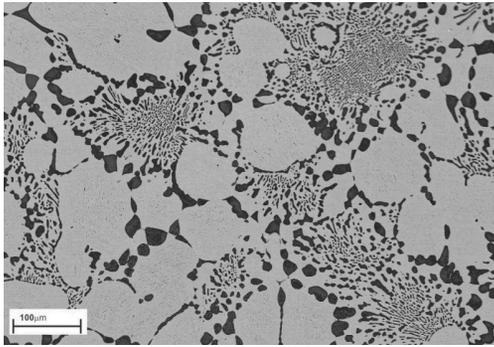
Fig. 11. Microstructure of the ZnAl4Cu1 alloy in place of the thermocouple #B, cooling rate of 0.08°C/s
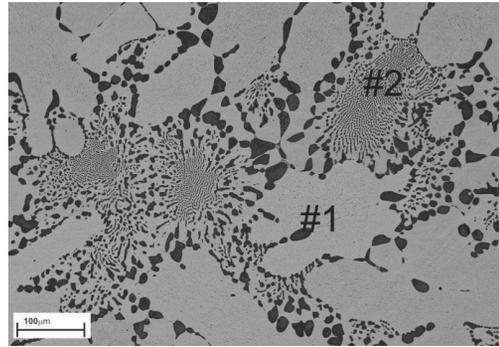
Fig. 12. Microstructure of the ZnAl4Cu1 alloy in place of the thermocouple #A, cooling rate of 0.08°C/s
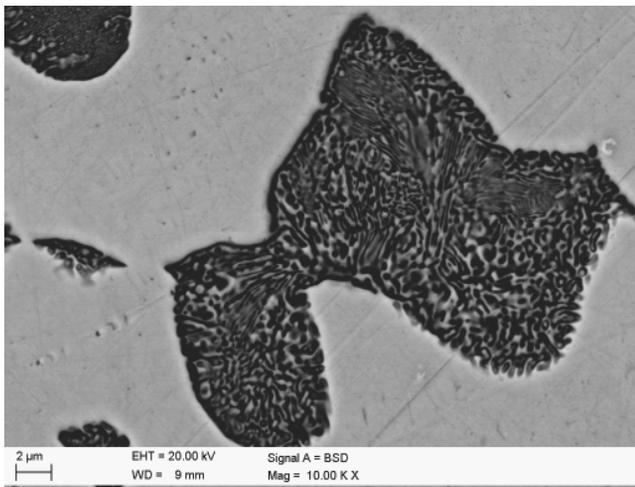
Fig. 13. SEM micrograph of the investigated ZnAl4Cu1 alloy

a)
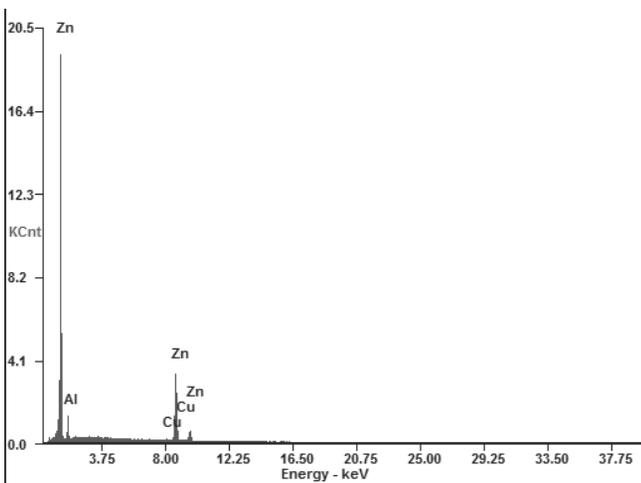
Fig. 14. EDS point wise analysis of the investigated zinc cast alloy, in Figure 13

b)
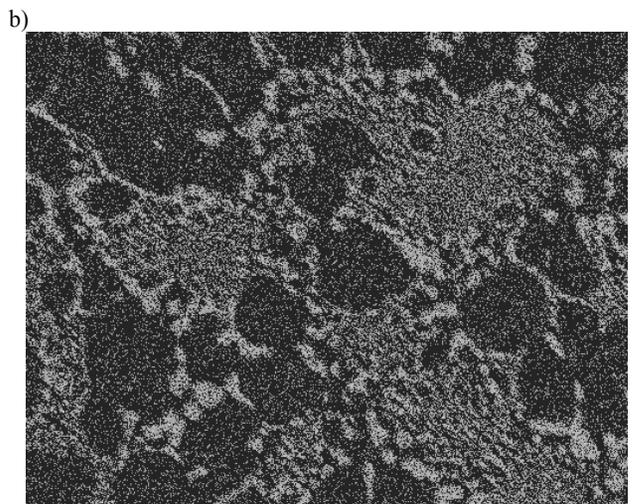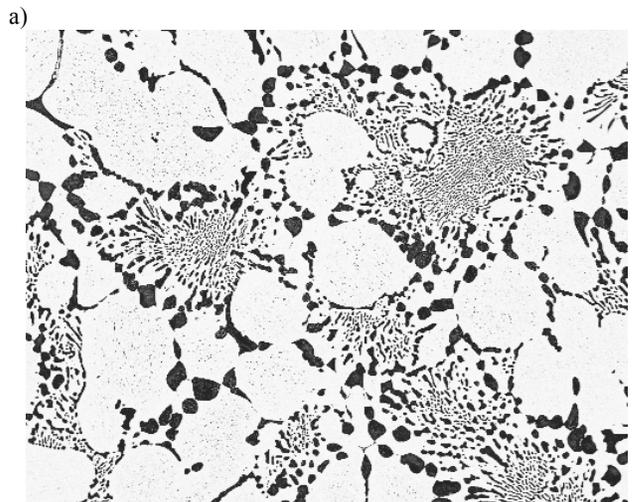
Fig. 15. EDS area analysis of the element concentration in the Zn-Al alloy: a) SE, b) Al
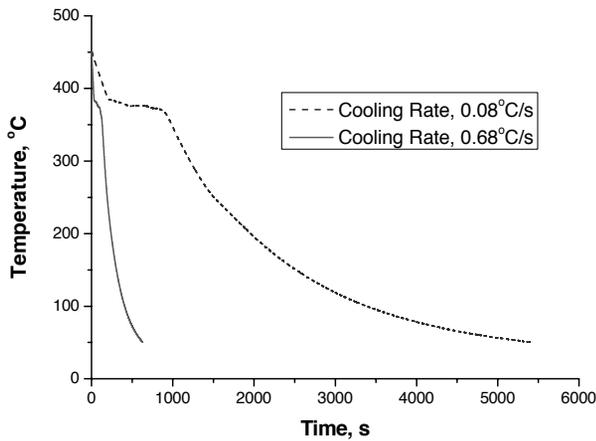
Fig. 16. Cooling curves of the Zn alloy of the low cooling - with furnace - (0.08°C/s) as well with the forced cooling (0.68°C/s)
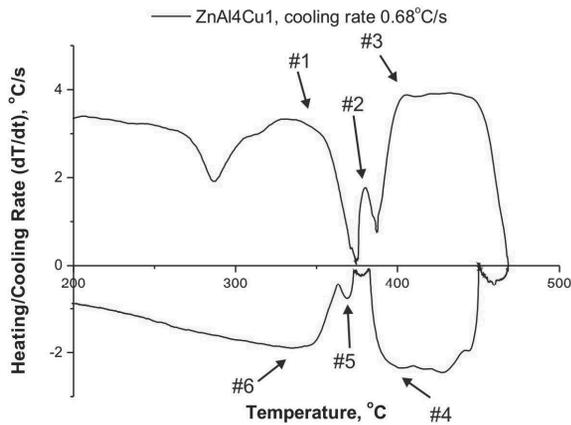
Fig. 17. Processed first derivative curves of the Zn alloy with hight speed cooling
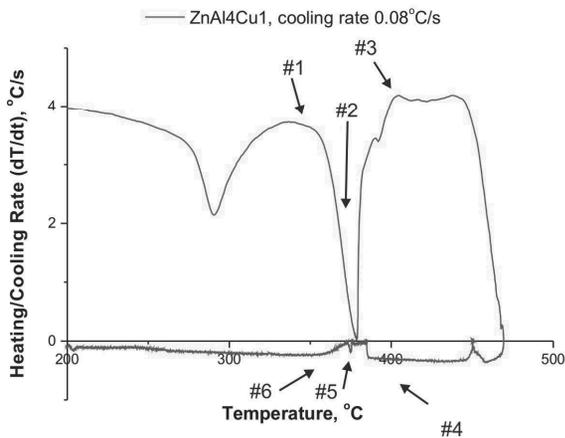
Fig. 18. Processed first derivative curves of the Zn alloy
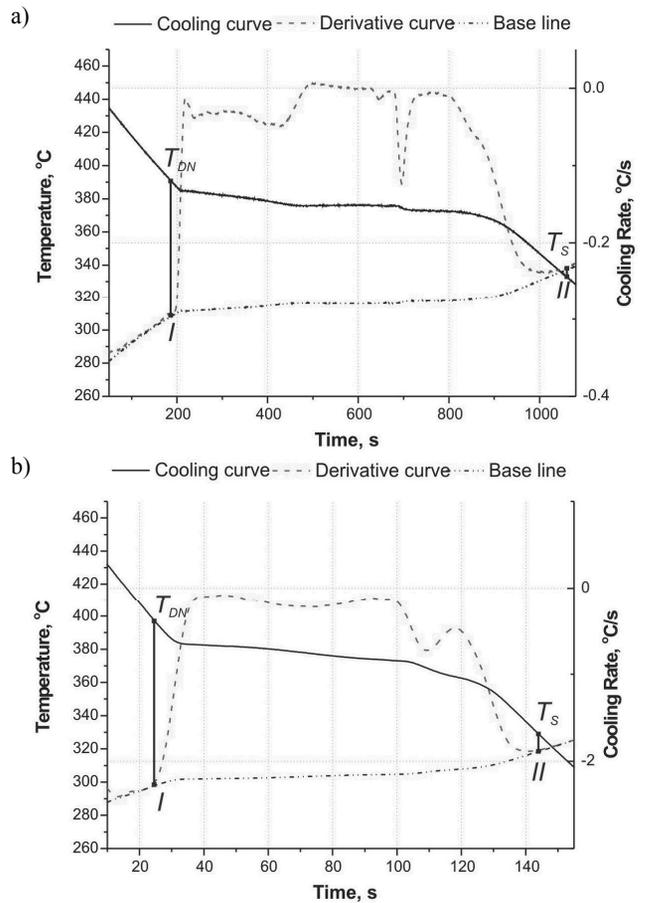
Fig. 19. Cooling curve, crystallisation curve and baseline of the ZnAl4Cu1 alloy cooled with different cooling rate: a) 0.08 C/s, b) 0.68°C/s

4. Conclusions

Conclusions can be summarised in the following points:

- The knowledge of the processes occurred on the crystallisation process of the alloys allows it to change in a reasonable way the microstructure and that for also the mechanical properties of these materials;
- In the investigated alloy the change of the cooling rate about 0.6°C/s causes an microstructure refinement as well an increase of the alloy hardness about 24.9%. Increase of the cooling rate causes mainly changes in the morphology of the Zn-Al eutectics;
- Copper present in the chemical composition of the ZnAl4Cu1 alloy is dissolved in the Zn matrix;
- Increase of the cooling rate causes an global overcooling of the alloy as well a change in the temperature of the beginning T_{DN} as well the end T_S of the crystallisation.

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