Journal
of Achievements in Materials
and Manufacturing Engineering

VOLUME 42
ISSUES 1-2
September-October
2010

Crystallization kinetics of Zn alloys modified with Ce, La, Sr, Ti, B

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Received 18.05.2010; published in revised form 01.09.2010

Materials

ABSTRACT

Purpose: This paper presents the investigation results of cooling rate influence on microstructure of the Zn-Al cast alloy. Thermo-derivative analysis of the investigated alloys was performed using the UMSA device (Universal Metallurgical Simulator and Analyzer). This device makes it possible to characterise the important points of the crystallised alloy diagram including: phase and eutectics crystallisation, as well liquidus/solidus points. The material used for investigation was the ZL8 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: Microstructure and mechanical properties investigations of the investigated alloy was performed for the reason of alloying additives influence on alloy microstructure and properties change, the microstructure was 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; DTA; Kinetic crystallisation; Zn-Al

Reference to this paper should be given in the following way:
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 42/1-2 (2010) 50-57.

1. Introduction

In case of the zinc cast alloys, the crystallisation process occurs after casting of the metal into the mould. The parameters of this process decide about the microstructure of the obtained casts, on which depends also the achieved physical and mechanical properties [1-4]. The crystallisation kinetics is characterised by changes of the following parameters: liquid metal temperature, cooling rate, generating hidden crystallisation heat rate, density of the nuclei, solid fraction of the crystllised metal, concentration of the alloying elements in the remaining liquid, characteristic distances as well parameters describing shape and size of the structure components [5, 6]. All these parameters are variables of the crystallisation time and geometric coordinates of the cast. A full characteristic of the crystallisation kinetics can be achieved after unification of the crystallisation equations together with the heat transfer equations, where the emitted crystallisation heat acts as a connecting factor for these equations and depends on the fraction of the crystllised structure components [7].

The solidification process of the liquid metal goes from the liquid state – from the liquidus line, as the beginning of the crystallisation, after that begins the crystallisation of the eutectics and intermetallic phases until the point, where the alloy will achieve the stable state – the solidus line, according to the phase equilibrium diagrams. For this reason, on the cooling curve there occurs some characteristic points (inflexion points) from the exothermic or endothermic reactions of the crystallizing phase and eutectics transformations. The crystallized metal causes a heat flow into the surroundings in a continuous way, a lack of temperature change or a instantaneous temperature increment testifies about a additional crystallization heat inside the crystallized metal, and the derivative curve describes the kinetic process of the heat transport [8-14].

Solidification of the hypereutectic Zn-Al-Cu alloy begins with the α' phase dendrite grow, followed by Zn-β rich phases around α' phase boundaries as a result of peritectic reaction. Increase of the cooling rate during solidification decreases the range of occurrence of the peritectic reaction, in order to enrich the liquid with Zn and finish solidification of the β eutectic and the η phase. However the majority of the α' phase consists of a solution of Zn rich phases and Al matrix. Structures of this type coming into existence as a result of fast overcooling of the alloy. Decomposition of the metastable phases is limited by Cu addition as a result of the eutectic transformation. Copper is recognized as the main alloying additive for the zinc alloys, which influences the increase of strength, hardness and corrosion resistance. Cu addition causes also a shift of the eutectic point inthe Zn-Al-Cu system toward to a higher Al content. Cu increases also the susceptibility of the Zn-Al alloys to ageing and connected with this volume changes. This has a small influence onto the eutectoid transformation of the $\beta(\beta')$ phase as well onto the changes of solubility in the stable state in a low temperature range, but first of all it influences phases transformation in the stable stated with the hexagonal η phase, regular face centered $\beta(\beta')$ phase, hexagonal ε (CuZn4) phase as well hexagonal τ (intermetallic phase CuZn3) phase. This transformation is the main reason of volume change. For occurrence of the τ phase there is necessary a 0.6-0.7% Cu concentration in the alloy. The microstructure has a big significance, because it determines the mechanical properties of the alloy, and the chemical composition changes these properties, for example rare earths addition causes an decrease of the phenomenon of particle coagulation, because it decreases atom diffusion. This helps to avoid coalescence of the particles and ensures that fore homogeneity of the microstructure 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. 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 [7, 15-19].

In Fig. 1. there is present the working chamber, where thetemperature 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 (TDN) and end this crystallization (TS).

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

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 $\beta(\beta')$ 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.

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.

Field of application for the Universal Metallurgical Simulator and Analyzer (UMSA) device can be describing as following:

- Develop recipe for annealing, vacuum carburizing, and tempering of heavy duty axle gears;
- Qualify heat treatment furnace for Low Pressure Carburizing/High Pressure Gas Quench;
- Review and approve material specification for suppliers of steel bars, and gear forgings;
- Coordinate metallurgical and failure analysis of prototype axles after dynamometer testing;
- Establish quote requests to purchase metallurgical laboratory equipment, and fixture tray conveyor;
- Develop using DOE the process settings for stud welding equipment used in axle manufacturing;
- Revise control limits for material specifications of supplied alloy ingots;
- Develop and test cooling curve analysis software as a quality control tool for foundry application;
- Develop and test chemical analysis software as a quality control tool for foundry application;
- Design a novel melt sampling device for conducting cooling curve analysis (patent pending);
- Optimize melting and heat treat process using;
- Perform heat treatment experiments to evaluate effect of alloying elements specially on light alloys, like aluminium and magnesium;
- Perform microstructure and micro hardness analysis.

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.

Crystallisation can have directional o 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 faze, 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.

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 microstructure 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 ºC/s appears in succession: unstable or metastable solid solutions, new meta-stable phases as well solidification in the amorphous state.

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.

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.

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:

- 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

The aim of the investigation was to investigate the influence of the alloying additives: La, Ce, Sr as well Ti and B on the crystallisation kinetics of the Zn-Al cast zinc alloy with the elements concentration given in Table 1, freely cooled.

The investigations involve the analysis of the alloying additives influence on the characteristic points placed on the cooling curve, as a result of the derivative curve analysis as well the calorimetric curve and the influence of these additives on the solid fraction during the alloy crystallisation and the microstructure analysis and alloy hardness. The investigations were performed on specially performed samples melted in graphite mould in a Ar protective atmosphere.

Table 1.
Chemical composition of ZL8 zinc alloy

Mass concentration of the element, in wt. %, AA standard		
Al	Cu	Mg
8.2-8.8	0.9-1.3	0.02-0.03
Pb	Cd	Sn
max 0.005	max 0.005	max 0.002
Fe	Ni	Si
max 0.035	max 0.001	max 0.035

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.

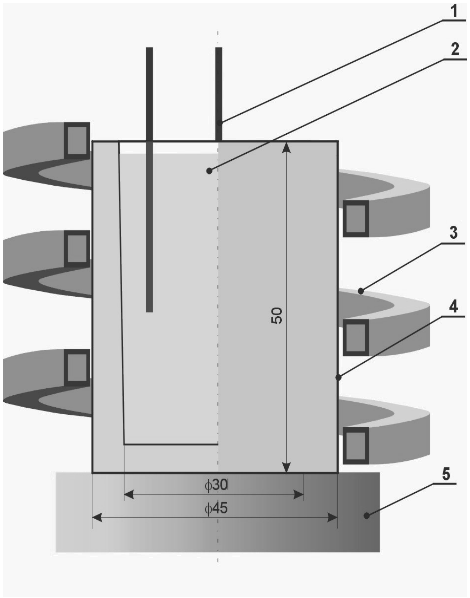

Fig. 2. Heating and cooling system scheme of the UMSA device, thermocouples placement and samples dimensions: 1 – thermocouple, 2 – sample, 3 – induction coil, 4 – crucible, 5 – sample isolation

For statement of the interdependence between the chemical composition, crystallisation kinetic, and microstructure of the freely cooled ZL8 alloy, following investigations were performed:

- derivative thermo analysis using the UMSA thermo simulator, 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;
- Alloy structure using Zeiss LSM 5 Exciter confocal microscope. The samples for optical microscope investigations were etched using 10% HF solution;
- Hardness measurement with the Rockwell method using the Zwick ZHR 4150 model in the B scale.

For measurement and recording of the temperature changes a K-type (chromo–alumel) thermocouples was used. The samples were mounted in a rolled steel foil with a thickness of ca. 0.025 mm and coated with BN powder emulsion. The heating system scheme is presented in Fig. 2 [9].

The investigated alloy was carried out with a constant cooling rates applied. The samples were cooled with the furnace without any additional cooling system, were the cooling rate was measured and set on 0.1 ºC/s.

3. Research results and discussion

As a result of the alloy modification there occurs microstructure refinement of the ZL8 cast alloy, what is presented in Figures 3 to 6.

Addition of alloying elements causes a change of the dendrite morphology of the α` phase. La and Ce addition causes changes in dendrite arm length (Fig. 5), whereas the addition of Ti and B causes change of the dendrite shape to a globular one (Fig. 6). There can be found also a refinement of the dendritic structure as well a decrease of the secondary dendrite arms and increase of the primary dendrite arms (Figs. 3 and 4)

Modification of the investigated ZL8 alloy causes hardness increase. In Fig. 7 there is presented the hardness change for the nonmodified as well for the modified alloy, which was freely cooled.

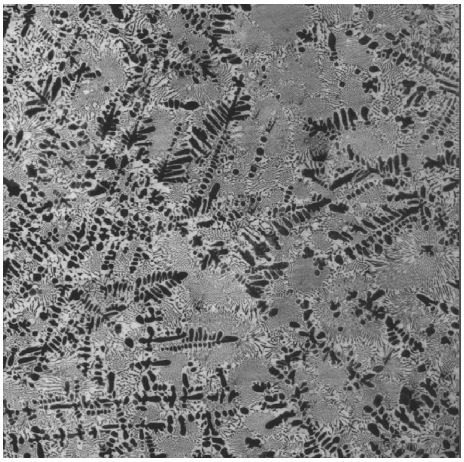

Fig. 3. Microstructure of the cast ZL8 alloy, etched with 10%HF

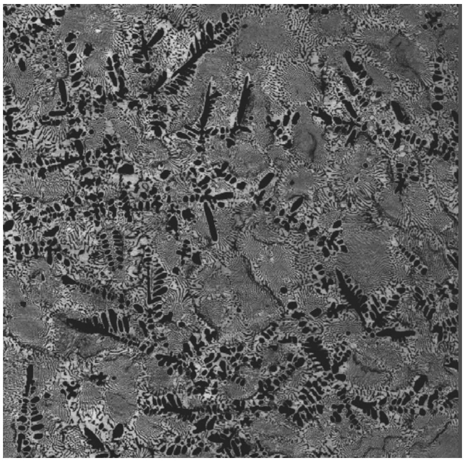

Fig. 4. Microstructure of the cast ZL8 alloy with Sr addition, etched with 10%HF

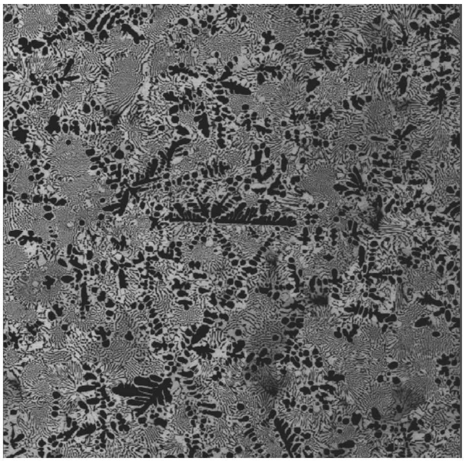

Fig. 5. Microstructure of the cast ZL8 alloy with La and Ce addition, etched with 10%HF

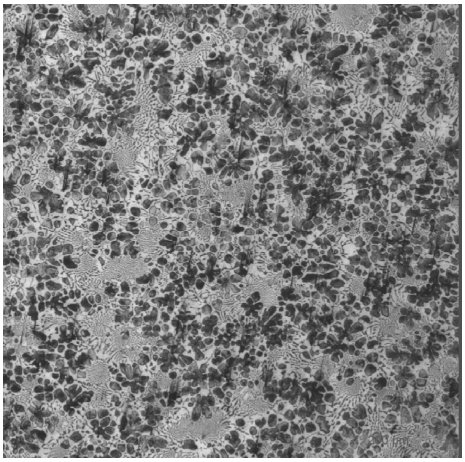

Fig. 6. Microstructure of the cast ZL8 alloy with Ti and B addition, etched with 10%HF

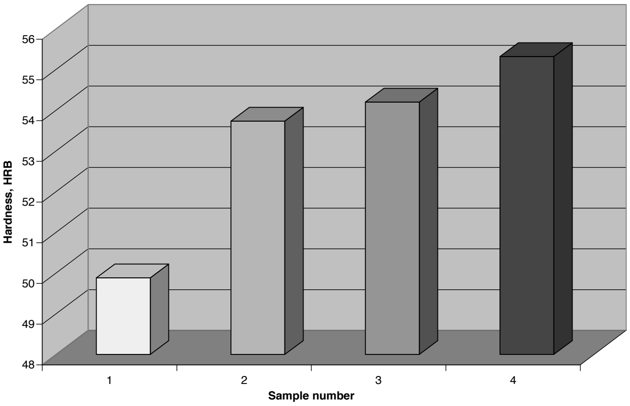

Fig. 7. Hardness results of the ZL8 alloy: 1 – nonmodified, 2 – with La and Ce addition, 3 – with Sr addition, 4 – with Ti and B addition

Alloying additives cause an increase of the alloy overcooling mainly as a result of La and Ce addition (Fig. 8). The temperature of beginning of $\beta + \alpha$ eutectic crystallisation doesn't change, however it is achieved earlier and shifted to a lower time values. La and Ce addition causes an increase of the α phase amount, whereas Sr addition causes a decrease of the crystallised α phase as well increase of the $\beta + \alpha$ eutectic content.

There are also some differences of the microstructure morphology and 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 areas using for investigations are taken always from the same place.

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

In Figure 8 there are presented the cooling curves for the ZL8 alloy cooled with a cooling rate of 0.1ºC/s and 0.68ºC/s. The freely cooling process with furnace 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 ca. six times decrease of elongation of the cooling time until the temperature of 50°C is achieved.

In Fig 8 there is presented the derivative curves dT/dt for the ZL8 alloy, heated to the temperature of 450ºC and cooled with a cooling rate of 0,1ºC/s. In Table 2 there are presented the characteristic points of the curve marked in Figure 8.

Fig. 8 shows also 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 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 2. As a result of the La and Ce modification there occurs an overcooling of the ZL8 alloy, what is visible also on the fraction solid diagram (Fig. 9) calculated on the basis of the performed thermo-derivative analysis. La and Ce addition causes decrease of the temperature of the α phase dendrite crystallisation beginning. Alloying additives cause also changes of the end of the β+α eutectic crystallisation (Fig. 9).

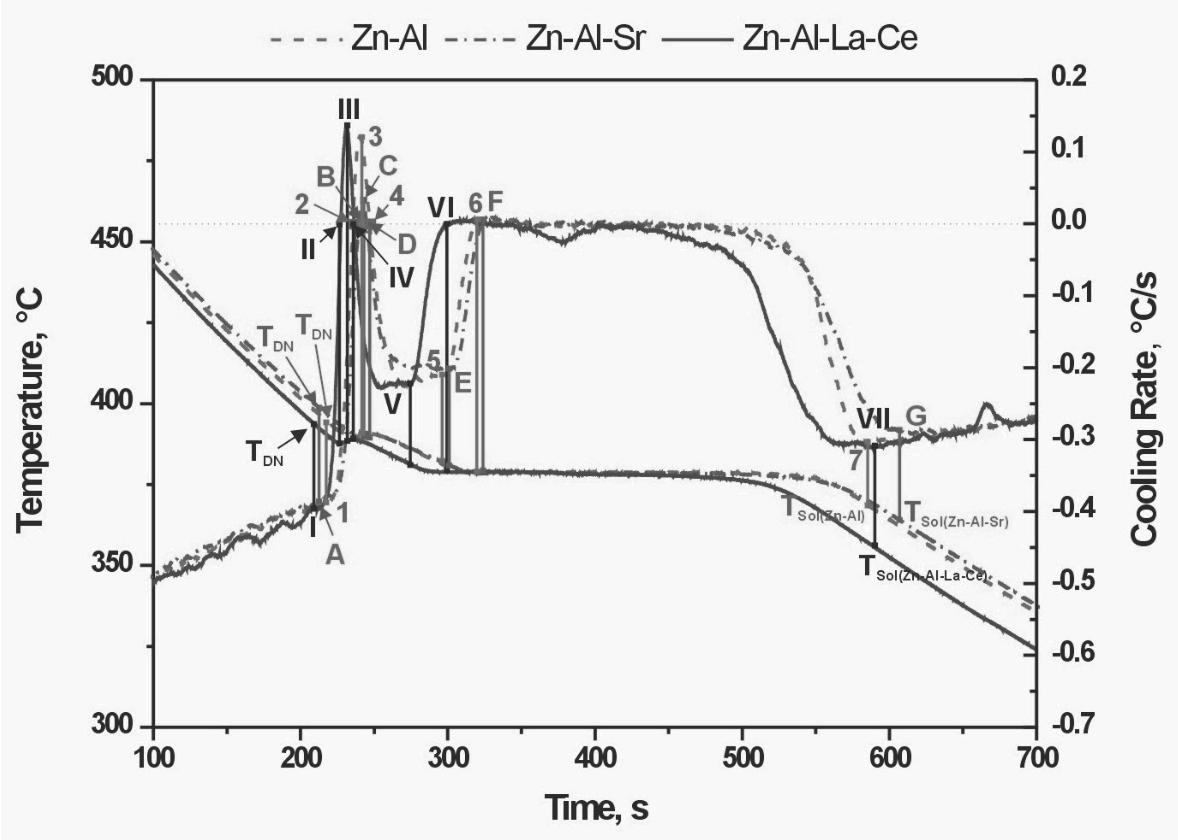

Fig. 8. Cooling curve and crystallisation curve of the ATD diagram for the ZL8 alloy and ZL8 alloy with Sr, La and Ce addition, cooling rate ~ 0.1°C/s

Table 2.
Description of the characteristic crystallisation points of the investigated alloy

Point on the diagram	Description of the characteristic points of the thermal processes (Fig. 8) occurred during alloy crystallisation
I, 1, a	T_{DN} - α phase dendrite nucleation
II, 2, b	α – phase dendrite crystallisation
III, 3, c	α – phase dendrites growing in the liquid alloy are getting coherent, the second derivative of the cooling curie takes the value zero
IV, 4, d	Stable growth of the dendritic α – phase
V, 5, e	Nucleation of the β+α eutectic
VI, 6, f	Stable β+α eutectic growth. This process occurs in a constant temperature, that fore there exists an heat equilibrium of the crystallizing phases. In this point the cooling curve gets one more time the value zero.
VII, 7, g	T_{Sol} – end of the eutectic crystallisation, until the alloy is wholly crystllised

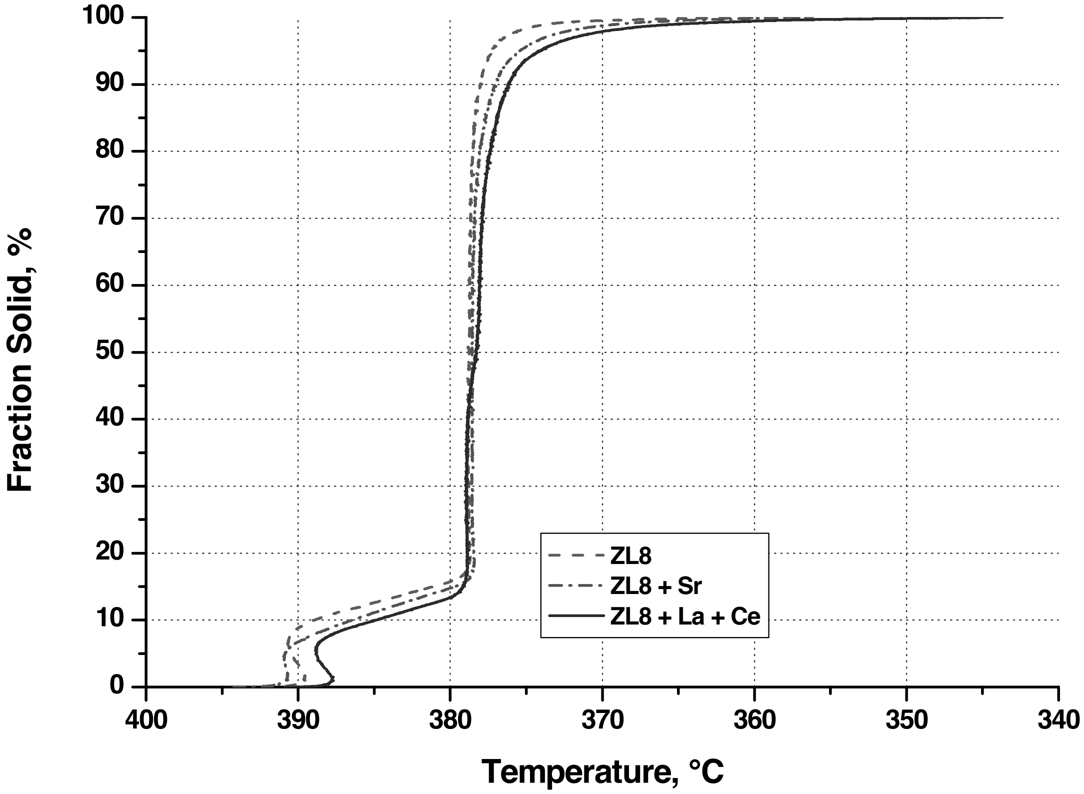

Fig. 9. Fraction solid diagram of the investigated alloy

4. Conclusions

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,
- microstructure changes as result of chemical composition change causes hardness increase for freely cooled samples compared to samples without alloying additives.

Additional information

Selected issues related to this paper are planned to be presented at the 16th International Scientific Conference on Contemporary Achievements in Mechanics, Manufacturing and Materials Science CAM3S'2010 celebrating 65 years of the tradition of Materials Engineering in Silesia, Poland and the 13th International Symposium Materials IMSP'2010, Denizli, Turkey.

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