



# Influence of silver addition on crystallisation kinetics of the AlSi12CuNiMg alloy

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## ABSTRACT

**Purpose:** The aim of investigation was to found out the influence of silver addition, as an alloying element on microstructure and crystallisation kinetics of the cast AC-AlSi12CuNiMg alloy.

**Design/methodology/approach:** In this work there was applied the thermo-derivative analysis for the reason to investigate the changes occurred in the structure of the aluminium alloys with silver addition. The microstructure was investigated using light and scanning electron microscope.

**Findings:** Change of chemical composition and cooling rate causes microstructure change of aluminium alloys. Alloying additives and modifiers causes change in the crystallisation kinetics as a result of different conditions of homogeneity nucleation of phases and eutectics in the investigated alloys.

**Practical implications:** The performed investigations are designed to assess the impact of precious metal additives for modification of the microstructure and properties of cast light alloy, as well as for evaluation of the impact of the modification of the chemical composition and cooling rate in order to obtain a material with stable microstructure and high properties.

**Originality/value:** The cooling rate as well as the chemical composition influences the crystallization of eutectic and phases, and determines also the microstructure and properties of alloys. Determination of technological process parameters and chemical composition will make possible to predict the properties of materials.

**Keywords:** Aluminium alloys; Thermo analysis; Structure; UMSA

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## MATERIALS

### 1. Introduction

Casting properties of the alloys depend on many factors, the most important is the chemical composition, wherein each of the elements affects individually or the components increase (eventually decrease) their mutual influence on structure and properties. A significant influence on the properties of cast alloys

have external conditions, such as centrifugal force, metallostatic pressure as well as carried out modifications. The prevalence of the use of cast components makes, that it becomes necessary to increase the research activities concerning not only on the selection of an appropriate balance of alloying elements affecting the improvement of mechanical properties by modifying the structure, but also the production technology of elements with the highest mechanical properties, wear and corrosion resistance as

well as the development and verification of manufacturing technology based on industry conditions [1-3].

Functional properties of elements made of cast metal alloys depend on the primary structure of the alloy, which is dependent on the kinetics of crystallization. The crystallization kinetics is characterized by changes of the following parameters: temperature of the treated metal, cooling rate, the rate of generation of latent crystallization heat, particle density, which is equivalent to the density of the formed nuclei, fraction solid of crystallized metal, concentration of components in the remaining liquid, size of the characteristic distance and values describing the shape and size of structure components. The morphology of eutectic crystallization depends on the cooling conditions and modification of the alloy, determining mechanical and technological properties of aluminium alloys. For this reason there was created a classification of different types of the  $\alpha + \beta$  eutectic structure. According to traditional classification linked crystallization conditions, the  $\alpha + \beta$  eutectic structure was divided into three basic types of hypoeutectic and eutectic structures, which include: pre-eutectic silicon and  $\alpha$  phase crystals or  $\alpha$  phase only and irregular plate-like eutectic, pre-eutectic silicon crystals and phase  $\alpha$  as well as irregular plate-like eutectic, characterized by a smaller interphase distance, pre-eutectic silicon crystal and phases  $\alpha$  and fibre-like eutectic [4-7].

Properly carried out chemical modification as well as the application of properly performed cooling of the castings leads to improvement of functional properties of the produced castings. Therefore it is very important to know how changes the structure of the cast according to the change of cooling rate or chemical composition by adding modifiers to the liquid metal [6,7].

Silver addition causes modification of the microstructure and properties of alloys. Addition of silver to aluminium affects the strengthening of aluminium alloy, what predisposes their use in the transport and aviation industry. Studied by means of optical metallography, transmission electron microscopy and X-ray diffraction. In the high Li, low Cu/Mg ratio alloys the main phases found were  $\delta'$ ,  $\beta'$ ,  $S'$  and  $T_1$ , while fewer  $T_2$  and Al<sub>7</sub>Cu<sub>2</sub>Fe precipitates were also observed. The addition of up to 0.5 wt% Ag diminishes the  $\delta'$  and  $T_1$  precipitates size [8].

The DTA curves were obtained for annealed and quenched samples. The results indicated that the presence of silver introduces new thermal events, associated to the formation of a silver-rich phase, to the shift of the equilibrium concentration to higher Al contents and to the decomposition of the silver-rich phase in the same temperature range of the  $\beta_1$  phase decomposition [9].

The results showed that the presence of silver causes (Cu)- $\alpha + (\alpha + \gamma_1) \rightarrow$  (Cu)- $\alpha + \beta$  transformation to occur in two stages. In the first one, part of the produced  $\beta$  phase combines with the precipitated Ag to give a silver-rich phase and in the second one the transformation is completed. The formation of this silver-rich phase seems to be enhanced at very low cooling rates [10].

Exact knowledge of the impact of the cooling rate applied for die castings on the structure and phase transition temperature during non-equilibrium crystallization allows optimal control of the production process.

The separation of the differential curve defines to basic functions allows accurate calculation of latent crystallization heat

of various phases crystallising during solidification. Assuming that the latent crystallization heat is proportional to the share of the various phases in the alloy, the thermo-derivative analysis also allows the calculation of the amount crystallized phases. Calculation of the above-mentioned properties is based on the characteristic points determined in a differential curve. These points are usually reflecting the thermal effects occurring in the melt during crystallization, and are dependent on the alloy composition, cooling rate, heat generation rate, and crystallization temperature of the molten metal, and so the parameters affecting the final structure of the resulting alloy. These parameters characterize also the crystallization kinetics of the alloys [11-14].

The general equation, describing (Table 1) the crystallisation function as a derivative of the crystallisation, is given as:

$$\frac{dT}{dt} = \frac{A}{m \cdot c_p} \cdot \alpha(\dot{t}) \cdot (T - T_0) + \frac{K_K}{m \cdot c_p} \cdot \left( m \frac{dz}{dt} + z \frac{dm}{dt} \right) \quad (1)$$

Table 1.  
Description of the equation factors

Symbol	Descriptions
$cp$	Heat capacity
$m$	Mass of the crystallised metal
$T$	Temperature at time $dt$
$T_0$	Environment temperature
$A$	Sampler surface
$K_K$	Crystallisation constant
$z$	Nucleus number

Investigation of crystallization kinetics of phases or eutectics can be carried out using devices for recording of time and temperature changes. For this purpose, there can be used the Universal Metallurgical Simulator and Analyzer UMSA for investigation of metallurgical processes, this is a device used to simulate the physical processes of melting and crystallization. This device uses also a computer controlled induction heating system, which provides precise control of heating rate while low thermal inertia of the sample. The UMSA system is equipped with a suitable computer program to control the simulation process, it allows also in flexible way to program the simulation including heating rate, cooling and isothermal hold time, etc. The system is also provided with the module for interpretation of the results on the basis of thermal analysis, allowing to investigate the characteristic of phase transformation temperature occurring during the melting or solidification processes. Representative test samples can be taken from real elements or semi products such as bars or ingots, etc. The dimensions and geometry of the samples allows it to analyze the structure and selected mechanical properties. Simulations may be performed in an inert or active atmosphere. The system is equipped with dual cooling system, that can be used to simulate non-equilibrium solidification processes including directional solidification. The computer-controlled cooling system allows also a flexible control of the cooling rate, which enables accurate simulations of a wide combination of solidification processes of metals and alloys [15,16].

## 2. Materials and experimental procedure

For investigation of the silver addition on crystallisation kinetics and microstructure of the cast AC- AlSi12CuNiMg alloys named according to the EN 1706:2001 standard, freely cooled with a cooling rate of  $\sim 0.2^\circ\text{C/s}$ , there were performed following investigations:

- Alloy structure using MEF4A optical microscope supplied by Leica together with the image analysis software as well electron scanning microscope using Zeiss Supra 25 device within high resolution mode. The samples for optical microscope investigations were electro etched using 30%  $\text{HBF}_4$  solution,
- For investigations of the crystallisation kinetics and determination of the phase transition temperature of the begin and end of the crystallisation  $T_{\text{DN}}$  and  $T_{\text{Sol}}$ , there were applied the Universal Metallurgical Simulator and Analyzer (UMSA) equipped with a two ay cooling system, allowing cooling in the range from  $0,11^\circ\text{C/s}$  to  $1^\circ\text{C/s}$ . The appliance of the UMSA simulator has allow it to determine to temperature od characteristic points od phase transitions occurred during the crystallisation process.

Chemical composition of the investigated alloy is presented in Table 2. As alloying additive there was used silver alloy with 0.65 % (mass concentration).

Table 2.

Chemical composition of AC-AlSi12CuNiMg aluminum alloy

Mass fraction of the element, %							
Si	Cu	Mg	Mn	Fe	Ti	Zn	Ni
11.8	1.05	1	0.14	0.5	0.1	0.13	0.95

For thermo-derivative analysis there were used cylindrical samples with a diameter of 30 mm, high ok 35 mm and whole cylindrical with the inner diameter of 16 mm. The samples were melted in a graphite crucible and a steel foil having a thickness of 0.025 mm. The samples were freely cooled as well as with forced cooling using compressed argon. The cylindrical samples were cooled through holes in the induction coil, whereas the whole cylindrical samples through holes in the induction coil as well as through the lance positioned within the sample. The gas flow system is presented in Fig. 1

For measurement and recording of the temperature changes a K-type thermocouples in steel cover used, with a length of 15 cm and diameter of 1 mm and reaction time of 250 ms. Tests were performed several times for each cooling speed for statistical estimation of the investigation results. The thermocouples were placed in a distance of 5 mm from the generating line of the cylinder and in the geometric axes of the sample in a depth, where the highest temperature occurs (thermal centre).

## 3. Results and discussion

The present in this work investigation results reveals an influence of silver addition (0,65% mass percent) on the microstructure of the investigated aluminium (Figs. 2 and 3). There occurs refinement of the phases present in the alloy, on Fig. 4 there

is present the microstructure revealing the morphology of Si as well as phases containing Fe and Mn, where the Si phase shape changes from dendritic to a plate-like form (Fig. 5).

The microstructures of the AlSi12CuNiMg alloy before and after silver modification feely cooled with a cooling rate of  $0.11^\circ\text{C/s}$  is presented on Figs. 2 to 4. SEM structures of the investigated alloys are presented on Figs. 6 and 7.

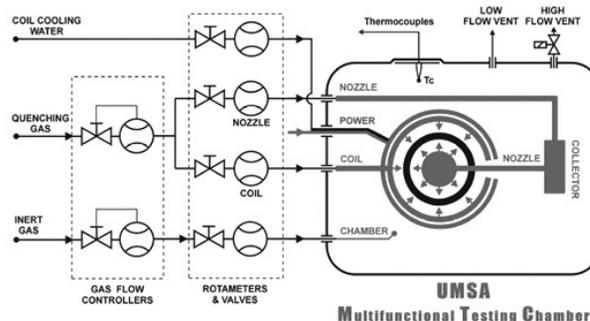


Fig. 1. Cooling system with the cooling gas flow



Fig. 2. Microstructure of the AC-AlSi12CuNiMg cooled with  $0.11^\circ\text{C/s}$



Fig. 3. Microstructure of the AC-AlSi12CuNiMg cooled with  $0.18^\circ\text{C/s}$ , with addition of Ag

Change of the cooling rate causes structure refinement of the investigated alloy. Ag addition of 0.65% mas percent causes also change of the morphology of the Si precipitation (#1 on Fig. 9) and of the phases containing Fe and Mn (#2 on Fig. 9).

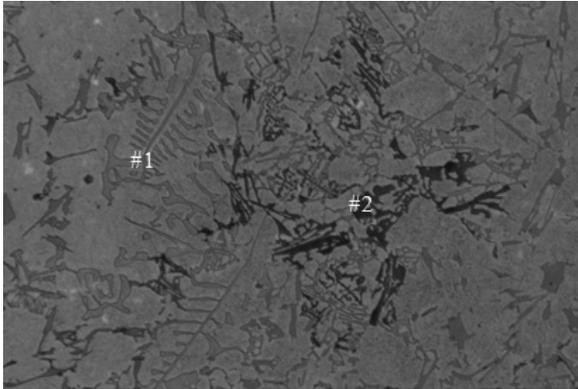


Fig. 4. Microstructure of the AC-AlSi12CuNiMg cooled with 0.11°C/s

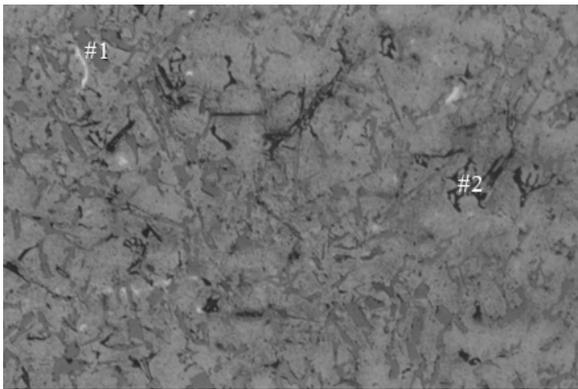


Fig. 5. Microstructure of the AlSi12CuNiMg cooled with 0.18°C/s, with addition of Ag

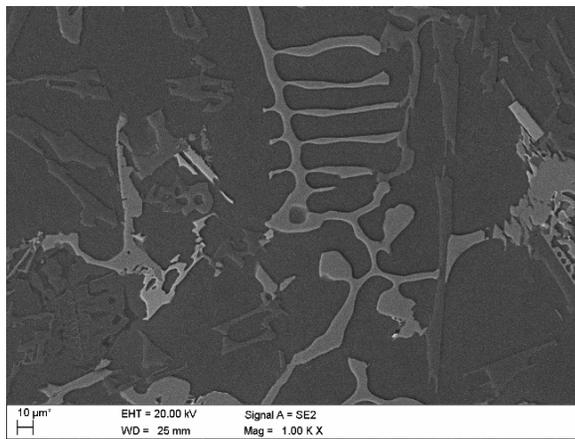


Fig. 6. SEM microstructure of the AlSi12CuNiMg cooled with 0.11°C/s

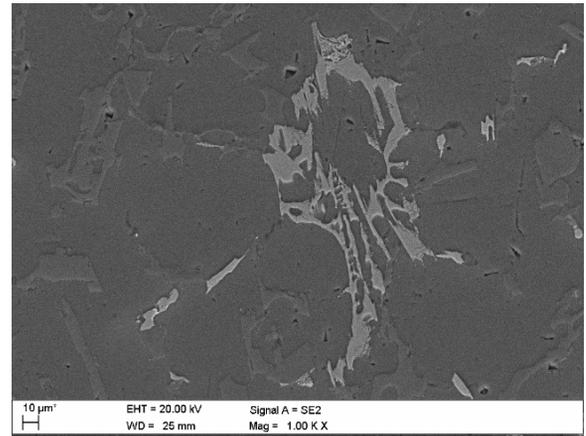


Fig. 7. SEM microstructure of the AlSi12CuNiMg cooled with 0.18°C/s, with addition of Ag

Silver addition causes in the investigated alloys material overcooling. The temperature values of crystallisation begin  $T_{DN}$  and end  $T_{Sol}$  were are presented in Table 2.

Table 2.  
 $T_{DN}$  and  $T_{Sol}$  solidification temperature

	AC-AlSi12CuNiMg+Ag	AC-AlSi12CuNiMg	
	~0.18°C/s	~0.11°C/s	~1°C/s
$T_{DN}$	562	566	570
$T_{Sol}$	468	484	469

$T_{DN}$  - Temperature start of the crystallisation  
 $T_{Sol}$  - Solid Temperature

On Fig. 8 there is presented the calorimetric curve, cooling curve and derivative curve of the investigated AlSi12CuNiMg alloys. On the diagram there were marked the characteristic points of the begin and end of crystallisation of the alloys as well as of the multi-compound eutectics and phases. On Fig. 9 there is presented derivative curve of the investigated alloys with silver addition.

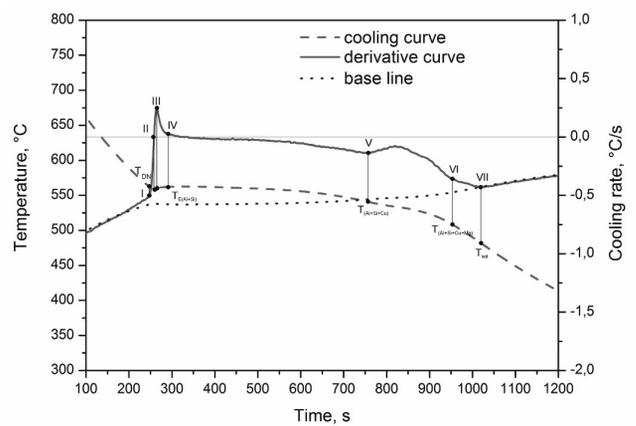


Fig. 8. Calorimetric curve, cooling curve and derivative curve of the investigated AlSi12CuNiMg alloys

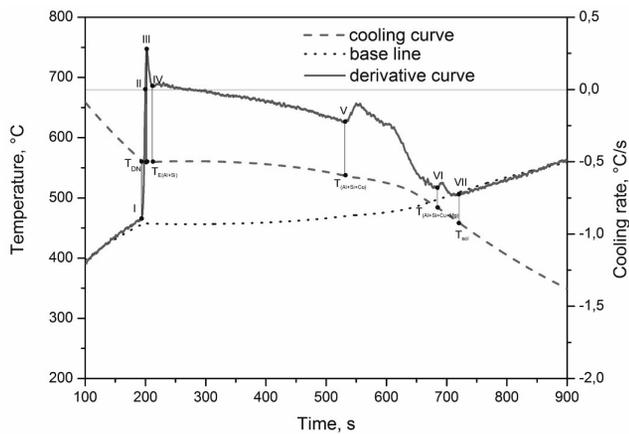


Fig. 9. Calorimetric curve, cooling curve and derivative curve of the investigated AlSi12CuNiMg alloys with silver addition

#### 4. Conclusions

Addition of 0.65% mas. Ag to the AlSi12CuNiMg alloy causes microstructure change as a result of morphology changers of phases present in the alloy before and after modification. Morphology changes of phases visible based on light and scanning electron microscope were found also as characteristic points on the thermo-derivative analysis diagrams  $T_{Sol}$ . Addition of Ag causes also alloy overcooling and change of the values of crystallisation end.

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