Crystallization of AlSi17Cu5Mg Alloy after Time-thermal Treatment

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Abstract

In the dissertation it has been shown, that so called "time-thermal treatment" (TTT) of the alloy in liquid state as overheating the metal with around 250°C above $T_{liq.}$ and detailing it in temperature for 30 to 40 minutes has the influence on changing the crystallization parameters ($T_{liq.}$, $T_{Emin.}$, $T_{Emax.}$, $T_{E(Me)}$, $T_{Sol.}$). It was ascertained, that overheating the AlSi17Cu5Mg alloy substantially above $T_{liq.}$ results with microcrystalline structure. Evenly distributed in the eutectic warp primeval silicon crystals and supersaturated with alloying additives of base content (Cu, Mg, Fe) of α(Al) solution, ensures not only increase durability in ambient temperature, but also at elevated temperature (250°C), what due to it's use in car industry is an advantage.

Keywords: Hypereutectic Al-Si alloys, Overheating, Thermal analysis, Crystallization process

1. Introduction

The technology of melting and casting, and especially the overheating and casting temperature and the intensity of cooling the casts down decides of the alloy structure, its properties and possible use. In result of solidification in hypereutectic silumines the structure of irregular, big, primeval crystals of Si is being created, the eutectic of α(Al)+β(Si) and multicomponent eutectics and dendrites Al [1, 2]. Such type of structure has disadvantageous influence on the use properties and machine processing capacity of the casts. Therefore the key issue, of increasing the field of using the Al-Si alloys, is to decrease the dimensions and even distribution of primeval crystals of Si in the α+β [3÷5] eutectic warp. It can be done for example with modification [6÷8], fast cooling [9÷11] and as it has been shown in [12÷14] with so called "time-thermal treatment", that is an overheating of liquids alloy with around 250°C above T_{liq}, detaining in temperature for around 30 to 40 minutes and casting. It does happen, thanks to creation of much higher volume of bases for heterogenic nucleation of silicon crystals [15].

2. Scope and purpose of research

The aim of the study was the analysis of the AlSi17Cu5Mg alloy crystallization process after overheating it to the temperature of around 920°C, holding at that temperature for around 30 minutes and casting it to the ATD sampler. The evaluation of solidifying was conducted with ATD thermo derivation method. The scope of research included:
- development of time-thermal treatment of the alloy,
- setting-up the research stand for ATD thermo analysis,
- registering the crystallization curve and characteristic temperatures: $T_{liq.}$, $T_{E(\alpha+\beta)}$, $T_{E(Cu)}$, $T_{E(Mg)}$, T_{sol},
- development of theoretical model of alloy crystallization after substantial overheating above $T_{liq.}$ temperature.
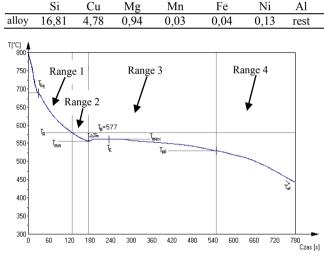
3. Research methods and materials

The AlSi17Cu5Mg alloy was chosen for the research, it is used for heavy loaded casts of combustion engines pistons and heads, cylinders blocks and corpses. The overheating parameters were selected on the basis of literature [13, 14] and own research [16÷19]. The ATD thermo analysis was conducted on a stand equipped with multichannel temperature recorder Crystaldigraph NT3-8K, with the use of Mlab2 software. The converter meets the requirement of EN61010 and EN60584 standards for industrial measurements with thermo elements. Four technological variants were chosen.

4. The results of investigations

The result of the chemical content analysis of AlSi17Cu5Mg cast alloy is given in table 1. Exemplary crystallization curve with division to ranges is given on the figure 1.

Table 1.
Chemical composition of AlSi17Cu5Mg cast alloy (wt.%)

	Si	Cu	Mg	Mn	Fe	Ni	Al
alloy	16,81	4,78	0,94	0,03	0,04	0,13	rest

Range 1 – crystallization from casting temperature $T_{zal.}$ equilibrated crystallization temperature T_R Al-Si (577°C), Range 2 – crystallization from equilibrated temperature to lowest temperature of eutectic crystallization α+β $T_{Emin.}$, Range 3 – crystallization for eutectic crystallization lowest temperature α+β $T_{Emin.}$, to the solidus temperature $T_{sol.}$, Range 4 – crystallization from $T_{sol.}$ to ambient temperature.
Fig. 1. Crystallization curve with characteristic parameters

Individual fragments of the curve informs about:
- The beginning of the TA curve refers to the analysis of the nucleation of the alloy, it can be used for the evaluation of modification process,
- Middle range of the dT/dt curve allow the quantified analysis of solidification heat and prediction of structural content,
- Last section gives the information about the purity of the alloy, presence of impurities, inclusions and gases, which

cause the creation of fusible eutectics that influence the solidifying time substantially increasing it.

For the implementation of assumed methodological concept and examine the overheating level influence on the parameters of the crystallization process of solid solution of α(Al), α(Al)+β(Si) eutectics and primeval silicon crystals, during the first stage of the research the ATD thermo analysis has been conducted. With the use of Analdta software the curves were drawn: temperature in real time (TA) and first derivative (DTA), determining T_{start}, $T_{liq.}$, T_X, $T_{E.min}$, T_E, $T_{E(Cu)}$, $T_{E(Mg)}$ and T_{sol}. In order to show the modifying effect of phosphorus, the crystallization curve of AlSi17Cu5Mg alloy had been done after modification of 0,05wt.% phosphorus (as a CuP10 master alloy). The result of ATD thermal analysis od not modified alloy and after modification process with phosphorus has been shown on figure 2.
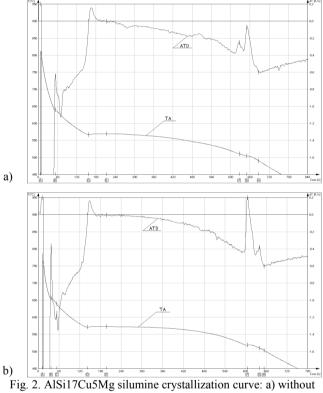

Fig. 2. AlSi17Cu5Mg silumine crystallization curve: a) without modification, b) after modification with 0,05 wt.% P

Characteristic parameters values of the crystallization process of AlSi17Cu5Mg cast alloy had been shown in table 2.
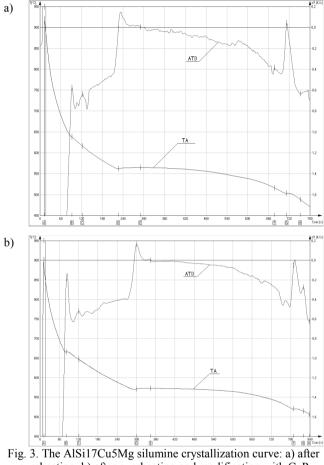
Table 2.
Characteristic temperature crystallization values of AlSi17Cu5Mg alloy before and after modification process

Points on fig. 2	A	B	C	D	E	F	G	H
Alloy symbol	T_{max}	$T_{liq.}$	T_x	$T_{Emin.}$	T_E	$T_{E(Cu)}$	$T_{E(Fe)}$	$T_{sol.}$
SW	810	640	–	568	570	511	504	492
SM	790	656	639	571	573	519	508	503

On the later stage thermo analysis of AlSi17Cu5Mg alloy subjected to substantial overheating over the $T_{liq.}$. In order to confirm assumed concept, the silumine was overheated to the temperature of 920°C, held at that temperature for 30 minutes and casted with registration of crystallization curve. The other portion of the cast alloy, overheated with the same parameters TTT, additionally was subjected to phosphorus modification. The results of selected alloy, overheated without modification and after added phosphorus has been shown on figure 3 and table 3.

Fig. 3. The AlSi17Cu5Mg silumine crystallization curve: a) after overheating, b) after overheating and modification with CuP

Table 3.
Characteristic temperature crystallization values of AlSi17Cu5Mg alloy before and after modification

Points on fig. 3	A	B	C	D	E	F	G	H
Alloy symbol	T_{max}	$T_{liq.}$	T_x	$T_{Emin.}$	T_E	$T_{E(Cu)}$	$T_{E(Fe)}$	$T_{sol.}$
SP	920	638	616	562	565	516	503	488
SPM	916	665	646	570	572	520	508	503

5. Summary of the results

From the theory of thermo analysis comes, that the derivation curve shows the change of internal source of solidifying alloy's heat, and the value is directly proportional to heat effects. As it comes from referred research, the ATD thermo analysis allows fast and quite accurate evaluation of the modifier impact and/or other factor on the crystallization process.

Using Analdta software, the temperature curves were drawn in real time (TA) and the first derivative (ATD), determining in order of appearance: T_{max}, $T_{liq.}$, T_X, $T_{E.min}$, $T_{E.max.}$, $T_{E(Cu)}$, $T_{E(Mg)}$ and $T_{sol.}$. In a first stage of the research, thermo analysis of the AlSi17Cu5Mg cast alloy had been done in not modified state (designation SW) and after modification 0,05wt.% P (designation SM). As it comes from the data shown on the figure 2 and in table 2, the casting temperature in both cases was close to assumed, and it was around 800°C. From the thermo analysis comes also, that the temperature of primeval silicon crystals creation for base alloy is 640°C, what is being confirmed in the phase equilibrium graph of Al-Si [7] and chemical content (table 1). After modification with Phosphorus the T_{liq} is being increased to around 650°C. It was confirmed, that phosphorus as master alloy CuP10 caused the increase of crystallization temperature of primeval silicon crystals of around 16°C. It is in line with so-far notion about double-stage crystallization process of Al-Si-Me alloys, as per which in T_{liq} the primeval silicon crystals are being created, and after reaching the eutectic temperature double eutectic α(Al)+β(Si) and multi component fusible eutectics crystalizes. However from the research results it comes, that before solidifying of the α+β eutectic, on the derivation curve of the alloy after modification with phosphorus, additional heat effect is being observed at a temperature of around 639°C (T_x). Then the α(Al)+β(Si) eutectics starts the crystallization in the temperature range of 570÷573°C. This process lasts until another passage on the ATD curve in temperature of 511°C, what is the crystallization of triple eutectic of α+AlCuSi+β, the includes intermetallic phase Al_2Cu with equilibrated crystallization temperature of 525°C in Al-Si-Cu alloys. The secretion of this phase lasts until the temperature will reach 504°C, when the α+AlMgSi+β, which consists of intermetallic compound Mg_2Si, eutectic starts to crystallize. Crystallization of this eutectic lasts until temperature of 492°C, what is an end of solidification process of the alloy. The phosphorus modification of AlSi17Cu5 alloy increases these temperatures by few degrees so respective temperatures are: 519°C for "copper" eutectic and 508 for "magnesium" eutectic. End of solidification is at 503°C.

Then, the thermo analysis of the AlSi17Cu5Mg alloy, after overheating it to the temperature of 920°C and holding at that temperature for around 30 minutes (SW), had been conducted. Second part of the overheated alloy was modified with 0,05wt.%P (SPM). As it comes from ATD curves (figure 3), the casting temperature (T_{max}) is around 920°C, what confirms, that assumed research methodology allows to achieve the melting and casting conditions on similar level. It is quite important, especially in newly developed alloys, in order to eliminate the influence of external factors. The primeval Si crystals crystallization temperature in the alloy (SP) is 638°C and it is 2°C lower than T_{liq} for base alloy (SW). The phosphorus modification process caused

increase of this temperature to 665°C. In case of modified alloy, the exothermal heat effect is being observed in temperature of 616°C – for SP alloy, and 646°C – for overheated and modified alloy (SPM). Since this effect occurs for the samples subjected to phosphorus modification, substantial overheating and modification with overheating, it is probably combined with pre-eutectic nucleation and α(Al, Me) dendrites solidification.

The modification and/or substantial overheating, of the alloy, above T_{liq} causes the appearance in the liquid state the micro areas of different concentration of Si atoms. In case of modification it is caused by the introduction to the alloy the crystallization nucleuses (AlP), while substantial overheating causes complete dissolving of solid silicon particles in the liquid. As an effect the areas of close arrangement and relatively short fluctuation time and micro areas depleted of close arrangement states appears. With decreasing liquid temperature, the Si-Si clusters are being formed locally and with increased concentration, what is the effect of certain overcooling of liquid alloy. It is caused by increased volume of over-critical radius clusters and hypereutectic Si crystals. In result of Si depletion of crystallization front (during fast cooling), these areas are solidifying with creation of α(Al, Me) dendrites, which crystalizes in the temperature range from 616 to 646°C, what is probably the result of diversified Si content in these areas. It is dynamic enough process, that as a result of local overcooling, the heat is being emitted, and it shows on ATD curves as a visible exothermic effect.

In the alloys which were only overheated, the crystallization of hypereutectic silicon takes place in lower temperature (around 638°C), due to required overcooling (creation of Si-Si clusters). Therefore the secretion of Al dendrites takes place later on (in the temperature of 616°C – table 3). In case of the alloys subjected to substantial overheating above T_{liq} and phosphorus modification, in result of additional effect of AlP nucleus, the crystallization of hypereutectic silicon takes place "earlier" (in temperature of 665°C), therefore the α(Al, Me) dendrites secretion takes place in higher temperature (around 646°C – table 3). The chart of such process is shown on figure 4.
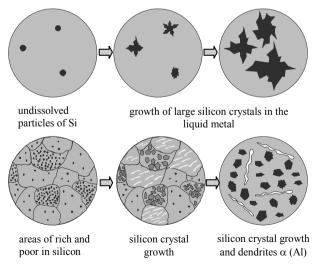

Fig. 4. Theoretical crystallization model for AlSi17Cu5Mg alloy after: a) in the initial state, b) after overheating

6. Conclusion

On the basis of the research it comes, that, with overheating the AlSi17Cu5Mg cast alloy with around 250°C above T_{liq} the primeval silicon crystals are being almost completely dissolved. In result in the metallic liquid appears the areas of diversified dissolved silicon content. And they are:
- Multiple areas enriched with dissolved silicon, where, as a result of substantial overheating, the partial creation of homogeneous silicon crystals nucleus takes place. Strong overcooling during fast cooling of the alloy facilitates creation of such concentrations. These clusters, after achieving hypercritical size, can stand for the nucleus for hypereutectic Si crystals solidification. It had been determined, that this process is additionally facilitated by introduction of the modifier (phosphorus) and then in he metallic liquid the additional "bases" (AlP) are being created for heterogeneous nucleation of hypereutectic silicon crystals.
- In the close surrounding of these areas in metallic liquid, the areas depleted of silicon are also created, where may happen pre-eutectic α(Al, Me) dendrites crystallization.

So in the micro-areas rich with silicon, there are the conditions for both homogeneous and heterogeneous nucleation, whereas in places of silicon depletion the aluminum dendrites are crystallizing. It confirms the ATD thermo analysis graphs, where additional exothermal effect is visible (T_x), after nucleation and crystallization of primeval Si crystals, and before solidification of double eutectic of α(Al)+β(Si).

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