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The phosphorus interaction on the process forming of primary structure of hypereutectic silumins

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Abstract

In this work the results of investigations concerning the hypereutectic silumins to be used as engine ports have been show. New idea on the interaction mechanism of phosphorus during modification of hypereutectic silumins has been shown. According to this hypothesis the influence of phosphorus is the result of local supercooling caused by evaporation and decompression of phosphorus steam. On the base to propose schematic diagram of the origin of local supercooling as a result of evaporation of phosphorus un microareas with a diversified concentration of silicon of the investigated Al-Si alloys.

Keywords: Theoretical basis for the crystallization process, Modification, Hypereutectic silumins

1. Introduction

Among the aluminium alloys used by foundry industry, silumins are certainly most popular. They owe this popularity to very good casting properties (high castability and low shrinkage). They are, moreover, characterised by low density, relatively low melting point, satisfactory thermal and electric conductivity, and dimensional stability [1-3]. Silumin castings also satisfy the requirements of their users in respect of the mechanical properties and corrosion resistance. These features make silumins particularly suitable for some specific applications and operating conditions, to mention as an example pistons and heads of I.C. engines [4].

2. Methods of investigation

Basing on a review of technical literature [5-7] and on the results of own investigations [8-10], a new approach to the

modifying effect of phosphorus in hypereutectic silumins has been proposed. The new approach takes into account the evaporation of phosphorus and expansion of thus formed vapour bubbles. The scope of the study includes:

- phosphorus effect on the primary crystallisation of hypereutectic silumins,
- metallographic examinations,
- examination of AIP particles distribution within the casting volume,
- X-ray microanalysis of AlP precipitates,
- evaluation of the phosphorus modifying ability after remelting of castings.

Studies were carried out on the silumins from a hypereutectic family containing from 16 to 20% Si with additions of 2% Cu, 1,5% Ni and 0,7% Mg.

The results of the analysis of the chemical composition of the examined silumins are given in Table 1.

Results of chemical analysis hypereutectic silumins								
	Sample	Content, in weight %						
		Al	Si	Cu	Ni	Mg	Fe	Ti
	AlSi16	79,023	16,647	1,780	1,105	0,548	0,679	0,009
	AlSi18	78,581	17,143	1,391	1,191	0,775	0,804	0,011
	AlSi20	75 824	19 265	2.061	1 307	0 488	1 0 3 5	0.016

 Table 1.

 Results of chemical analysis hypereutectic silumins

The modification with phosphorus added in an amount of 0,05% was carried out with a Cu-P master alloy (9,95%P). The refining treatment was done with "Rafglin-3" added in an amount of 0,3wt.%. The technology of hypereutectic silumins treatment with additions of Cu, Ni and Mg, and additionally with the additions of high-melting point elements, was discussed in detail in doctor's dissertation [9]. Metallographic examinations were carried out under a light microscope, model MeF-2 "Reichert". The X-ray microanalysis was carried out under a scanning microscope, model Hitachi S-4200, coupled with EDS Voyager X-ray spectrometer.

3. The results of investigation and their analysis

The bases of interpretation on the interaction mechanism phosphorus of phosphorus crystallisation process will be the results of thermal analysis. In this results show the influence of phosphorus on temperature of primary silicon crystals. This results are shown in Figure 1.



Fig. 1. ATD Thermal analysis diagram of silumin AlSi20 before (a) and after (b) modification phosphorus process (Cu-P)

The metallographic examinations aimed at a determination of the distribution of AIP particles within the entire casting volume, that are shown in Figure 2.



Fig. 2. The crystals of silumins witch the AIP particles.

The images of the metallographic structures indicate that the precipitates of AlP compound tend to gather in the upper part of casting forming large clusters of fine precipitates. In central areas of the casting, these clusters are absent. The primary silicon crystals have more or less the same shape and size as the crystals which do not contain AlP particles. The results of these investigations may prove that the aluminium phosphide has no ability to form the nuclei of crystallisation in the hypereutectic Si. The aim of the X-ray microanalysis was to confirm the presence of AIP particles near the casting surface and prove their high chemical activity. Linear distribution of Al, P and O along the analysing line in a sample taken from the casting surface after modification with 0,05% P. The results of these investigations confirm the presence in castings of aluminium phosphide (AlP) particles - Fig. 3. It is easy to note that in the areas where the reaction of AIP particles with H2O (during the operation of polishing) has already taken place, higher concentration of phosphorus is accompanied by higher concentration of oxygen. This proves the strong chemical activity of aluminium phosphide and difficulties in its identification in castings modified with P.



Fig. 3. The scanning image of specimen surface (a) and the linear distribution of P, Al and O

Technical literature [1-7] makes reference to the, so called, permanent modification of hypereutectic silumins with P. To check this statement, an experiment has been made. It consisted in melting a hypereutectic silumin (17% Si) without the alloying additions (Ni, Mg and Cu), and casting into ceramic samplers the silumin without modification and after modification with phosphorus added in an amount of 0,05%. The next step included cutting of test castings modified with phosphorus at 2/3 of their height. The lower part of castings was remelted and cast again in the ceramic samplers without modification treatment. Thermal analysis diagram this results are shown in Figure 4.



Fig. 4. Thermal analysis: a) not modified, b) modified with 0,05% P, c) not modified after remelting

From the studies of the thermal analysis it follows that for alloy without modification the temperature of hypereutectic silicon precipitation is 656°C. After the modification carried out with phosphorus, this temperature increased to a value of 665°C. After remelting of the lower casting part, in the non-modified silumin, a drop in the temperature of the hypereutectic silicon precipitation was observed. In the examined test castings, the crystallisation temperature of the α (Al)- β (Si) eutectic was almost the same and amounted to 575°C. The crystallisation temperature of a "ferrous" eutectic was similar and assumed the values from 543 to 548°C. This proves the same chemical composition of the examined castings.

From thus made castings, specimens were taken for the metallographic examinations; the results of the examinations are shown in Figure 5.



Fig. 5. The structure of hypereutectic silumin; a) not modification, b) after modification with 0,05% P, c) after remelting without modification

The structure of casting with an addition of phosphorus reveals some changes. The precipitates of silicon are now fine and evenly distributed in the matrix. The structure of the casting without modification and the structure of the casting from remelting clearly show the absence of modification effect. The silicon precipitates are large and of a non-uniform distribution in the matrix. This proves that once the areas rich in AIP precipitates are removed from casting, the latter has practically no possibility to pick up the phosphorus once again.

4. Summary and conclusions

Basing on the data stated in literature and on the results of the carried out experiments, the authors put forward for discussion a new idea regarding the effect of phosphorus and its role in the modification of hypereutectic silumins.

The proposed mechanism is illustrated in Figure 6.



Fig. 6. Schematic representation of the formation of undercooling as a result of phosphorus evaporation in areas with different silicon concentration

The studies done by other authors [1-5, 11] as well as own metallographic examinations have confirmed the segregation effect of silicon and other alloying elements in hypereutectic silumins. The segregation is due to the presence in liquid state of the areas of higher and lower silicon concentration (areas I and II). The analysis of phase equilibrium diagrams (Si, Cu, Ni, Mg) – P [12] indicates that various alloying additions have different effect on the phosphorus solubility in liquid silumin. Silicon reduces this solubility by promoting phosphorus precipitation from the liquid solution at an early stage of the process. The alloying additives like Cu, Ni, Mg improve phosphorus solubility in the solution, which retards its precipitation from the melt (lower temperature).

Phosphorus starts precipitating when the temperature of molten silumin after having been cast into a mould decreases to certain value (as a result of the combined effect of all the elements). At a temperature above 500°C phosphorus evaporates. The process of evaporation may cause in some microregions a severe undercooling ΔT . The forming bubbles (the phosphorus vapours have very high pressure) undergo sudden expansion. This effect may additionally increase the value of the undercooling ΔT . While moving towards the surface of the liquid silumin, the chemically active vapours of phosphorus are entering into reaction with aluminium, forming aluminium phosphides. And this is the reason why nearly all phosphorus gathers at the casting surface.

In the areas characterised by high silicon concentration, the temperature T_{liq} (from Al-Si phase equilibrium diagram) is so high that local temperature drop due to phosphorus evaporation (the expansion of bubbles) causes undercooling ΔTp . This undercooling is the driving force for the process of crystal nucleation and growth. In the areas of lower silicon concentration. the evaporation of phosphorus (the expansion of bubbles) is not strong enough to create for the undercooling ΔTp the conditions which would promote its drop below the equilibrium temperature T_{lio} . So, in these areas, the effect of modification does not occur. Structures of this type are often observed in castings modified with phosphorus. This also explains the refining effect of alloying additions on the silicon structure. By reducing the crystallisation temperature of the primary silicon crystals, they exert an effect similar to the modification with phosphorus. The said elements by increasing the phosphorus solubility in liquid phase reduce also the temperature of its precipitation and evaporation. Intense stirring of the melt during, for example, chlorination results in the compensation of chemical composition. Due to this, within the entire casting volume, similar conditions for the silicon nucleation are created, driven by the local undercooling due to evaporation and expansion of the phosphorus vapour bubbles.

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