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AlSi21CuNi silumin modification with phosphor and strontium micro additions

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Abstract. The paper presents the results of investigation of the influence of AlFeP and AlSr modifiers on the structure of the hypereutectoid silumin, AlSi21CuNi. The silumin has been modified in two stages. The first stage was melt with the addition of phosphor in the quantity of 120ppm. The second stage was combined application of phosphor and strontium. The strontium addition amounted 150, 250 and 350 ppm. At each melt, the metal has been cast after 10, 30, and 60 minutes from the introduction of the modifiers. The effectiveness of the modification has been assessed basing on qualitative and quantitative analysis of the microstructure of castings. It has been determined that the applied addition of phosphor causes significant comminution of the primary silicon secretions. Maximum comminution of primary silicon has been obtained after the longest time of the modified alloy soaking. The most advantageous effects of combined modification have been obtained with the application of 120ppm addition of P and 350ppm addition of Sr after 60 minutes from the introduction of the modifiers to the metal bath.

1 Introduction

The AlSi21CuNi alloy belongs to the group of piston hypereutectoid silumins. The structure of the alloy consists of hard primary secretions of phase â (Si) and relatively soft eutectic mixture (á +â) and intermetallic phases. In addition to many advantages, the hypereutectoid silumins have a negative feature related to their tendency to form coarse grained structure directly influencing deterioration of mechanical properties. Phase â in the form of very big brittle crystals creating clusters appears on the background of coarse-grained lamellar eutectic mixture. The proved features of such material prevent meeting the requirements concerning surface smoothness and dimensional accuracy of the processed castings, mostly pistons, and significantly deteriorate their tribological properties [1, 2].

In order to eliminate the indicated drawbacks of the structure, hypereutectoid silumins atrre subjected (at the stage of casting) to the process of modification with theμ use of phosphor addition. After modification, the structure of the obtained castings consists of significantly comminuted (down to the sizes below 50 μm) primary silicon secretions with compact wall structure, evenly distributed in the matrix of the irregular lamellar eutectic mixture (α +β) [3].

The up-to-date development of the production technology forces engineers to improve the quality of the materials used constantly [4,5]. This concerns, among others, pistons which are subjected to more and more severe thermal and mechanical loads and longer time of exploitation in the automotive industry. A survey of literature [6-8] shows that, in the case of hypereutectoid silumins, there is a possibility of further structure improvement and, consequently, obtaining better mechanical properties of the castings. This is to be achieved due to the change of the morphology of the irregular lamellar eutectic mixture into one with fibrous structure while maintaining the adequate degree of comminution and even distribution of the primary silicon secretions. Unlike lamellar eutectic mixture, fibrous one has minimum interfacial distance, ë, and rounding of the eutectic silicon crystal contours, which is of much importance for the improvement of impact strength and wear resistance [7]. That is why more and more researchers working on improvement of the hypereutectoid silumin properties think that it is purposeful to elaborate complex modifiers containing, in addition to phosphor, other additives aiming at modification of the eutectic mixture. The change of irregular lamellar eutectic mixture into fibrous one is achieved due to the modification of silumin with sodium or strontium. An important feature of strontium as a modifier is its resistance to oxidation. The mechanism of phosphor acting in modification of hypereutectoid silumins is different from that of strontium acting in the process of eutectic mixture modification in hypoeutectic alloys. That is why combined modification of hypereutectoid silumins with the addition of phosphor and strontium is problematic and its effectiveness depends mainly on the application of adequately selected technological parameters of the modification. In the foundry practice, manufacturing a casting with the desired structure and, consequently, desired properties, depends on many factors, such as: the temperature and

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time of the liquid alloy heating, kind and quantity of the applied modifier, modification temperature, time of maintaining liquid alloy after modification, casting temperature, solidification rate.

Although the technology of combined (phosphor and silicon) modification of hypereutectoid silumins is widely described in literature, the results of those investigations concern mostly alloys with less content of silicon. As far as high silicon alloys are concerned, there is shortage of information about the influence of specific parameters; this is particularly related to the influence of: the quality of the modifying agents, quantity of the applied modifiers, time of the liquid alloy maintenance after modification on the effectiveness of the performed modification. Complex treatment of the process of modification of hypereutectoid silumins is, therefore to be understood as creation of such conditions of the alloy crystallization in which the above partial elements are summed and make it possible to obtain advantageous structure and, consequently, advantageous properties of castings.

In recent years, investigations aiming at comminution of the structure of castings by the application of magnetic field or advanced casting techniques are also performed [9, 10]. The use of those techniques, however, is complicated and, therefore, limited.

2 Investigation methodology

The tests have been performed with the use of the popular hypereutectoid piston silumin, AlSi21CuNi with the chemical composition to be found in Table 1.

Table 1. Chemical composition of the tested AlSi21CuNi alloy

Percentage [%]					
Si	**Cu**	**Ni**	**Mg**	**Mn**	**Fe**
21.170	1.200	0.870	0.680	0.170	0.450
Ti	**Zn**	**Pb**	**Sn**	**Al**	
0.020	0.200	0.020	0.007	residual	

The melts have been performed at the temperature of the metal bath soaking, 850ºC for a period of 30 minutes. The operation of single modification has been performed with the use the initial alloy, AlFeP, with the chemical composition shown in Table 2. The quantity of the modifying agent has been selected so as to ensure phosphor addition at the level of 120ppm.

Table 2. Chemical composition of the modifying agent, AlFeP.

AlFeP- percentage [%]						
Fe	**P**	**Si**	**Mn**	**Ti**	**C**	**Al**
14.36	4.69	0.49	0.30	0.15	0.05	residual

Complex modification of silumin has been performed by combining agent AlFeP with the modifying agent AlSr10 (10% of Sr, Al – the rest). Maintaining the quantity of the first agent (120ppm of P), three quantities of strontium addition have been applied: 150, 250, 350ppm referred to the mass of the alloy being tested. In order to determine the influence of the time of modified alloy soaking on the effectiveness and durability of the modification results, the alloy has been cast after 10, 30 and 60 minutes from the moment of the modifier introduction to the metal bath. In order to obtain samples of unmodified alloy, a trial of melting has been performed applying the procedure as in the case of modified alloy with the omission of the operation of modification.

The silumin has been melted in a resistance furnace with type use of a chamotte – graphite crucible. Maintenance of the desired metal temperature has been ensured by a microprocessor temperature control device type TC6 made by METROL company coupled to a thermocouple installed in the cylindrical chamber of the furnace. The liquid metal temperature has been monitored by dipping in it the measurement end of the thermocouple type K (NiCr-NiAl), entering it through a hole made in the insulation cover of the furnace. The mass of the metal charge was 1.2 kg for each melt. After the predetermined temperature of (850ºC) has been reached, the liquid metal was soaked for 30 minutes. Next, at 750ºC, a soaked graphite sinker was used to introduce the modifier to the metal bath. The tests have been performed with the use of a cylindrical split gravity die (with the inner diameter of 27 mm, wall thickness of 17 mm and the height of 45 mm), located on a steel base. In order to obtain samples for metallographic examination, when the casting cooled down a part of it was cut off at the level one third of the height from the mould bottom (in the direction perpendicular to the casting axis). Microsections have been made on the sample cutting surface by means of an automatic grinding and polishing machine made by "STRUERS" company. Polished samples have been subjected to etching for 10 seconds with reagent 0.5% HF with the composition of (0.5 ml HF + 99.5 ml H_2O).

Metallographic examination has been performed with the use of a scanning microscope, JSM-5600LV made by JEOL company, coupled to an x-ray microanalyzer, EDS. Qualitative analysis of the samples has been performed basing on the image obtained with the use of a detector of backscattered electrons (BEI). For a more full description of the structure of castings, a quantitative analysis of the primary silicon secretions and eutectic silicon secretions has been performed. Those tests have been performed with the use of quantitative metallographic methods basing on computer analysis of image. The analyses have been performed with the use of the "Particle Analysis" module of the EDS 2000 microanalyzer software. Metallographic examinations (qualitative and quantitative) of all samples have been performed in micro-areas located at the middle of the microsection radius. In the quantitative description of the microstructure, the following parameters have been used: N_A – relative amount of secretions (number of primary or eutectic silicon crystals in a unit of the microsection surface, mm^{-2}), D_2 - average diameter of

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primary silicon secretions (calculated as the diameter of a circle with the same area as the particle, μm) and ë- average interfacial distance (formula 1).

$$\lambda = 1/N_A^{1/2} \quad (1)$$

The results of quantitative metallography, in the form of the values of stereological parameters of the primary silicon crystals, have been statistically elaborated. For each sample, the values of N_A, D_2, being arithmetical average ones of those parameters from N analysed micro areas of the microsection and then, for each stereological parameter, standard deviation (S) has been calculated, as well as the width of the confidence interval (δ) [10]. Since the number of the analysed micro images has always met the condition of $N < 30$, t-Student distribution has been adopted for the calculations; the $t_{\alpha,n-1}$ value for ut has been taken from tables, for the adopted level of confidence, P= 0.95.

3 Test results

Analysis of the structure of unmodified alloy has shown that the crystals of primary silicon have big dimensions and irregular shapers. The crystals often form clusters (Fig. 1a, b), which indicates uneven distribution of those secretions in the volume of the casting. another negative feature of those secretions is their not compact structure as evidenced by "voids" visible in the crystal cross sections. In an analysis of the quality of the eutectic silicon structure, occurrence of micro areas with secretions in the small lamellar and fibrous form has been found (Fig. 1a, b). This is due to the quick cooling of the casting (application of the gravity die) and the cluster character of the primary silicon secretions. Those observations prove the results of quantitative metallography shown in Table 3. Basing on those results, one can also state that, as the time of the bath soaking flows, more comminution of the primary silicon secretions is obtained. The average diameter of the silicon crystals after the first casting time (10 minutes) was about 65.7 μm; in a casting obtained after 60 minutes it was only about 50.5 μm. When comparing the N_A parameter, i.e. relative amount of primary silicon crystals, small value of it has been found for all castings, however, for the subsequent casting times, the value increases from N_A = 33.6 mm^{-2} to 52.5 mm^{-2} in a casting obtained after 60 minutes. In the case of eutectic silicon, it has been found that the degree of its comminution decreases with the extension of the metal bath soaking time (Table 3) while the interfacial distance increases.

Table 3. The results of measurements of stereological parameters of primary and eutectic silicon of silumin in the unmodified state, after modification with the AlFeP agent and after complex modification with AlFeP and AlSr.

Melt designation	**Casting time, min.**	**PRIMARY SILICON**									**EUTECTIC SILICON**	
		Stereological parameters										
		D_2	**S**	**δ**	**N_A**	**S**	**δ**	**λ**	**S**	**δ**	**N_A**	**λ**
		μm			mm^{-2}			μm			mm^{-2}	μm
Unmodified alloy	10	65.7	5.5	± 3.1	33.6	9.9	± 5.7	178.4	28.9	± 16.5	235873.2	2.1
	30	63.8	6.4	± 4.0	34.8	7.6	± 4.7	172.5	20.2	± 12.6	220126.7	2.1
	60	50.5	4.2	± 2.8	52.5	10.1	± 6.0	140.0	15.1	± 9.0	145260.9	2.6
AlFeP 120ppm P	10	28.4	2.1	± 1.6	184.8	43.0	± 31.9	75.1	9.5	± 7.1	60885.2	4.1
	30	21.0	1.0	± 0.7	317.3	58.7	± 43.6	56.8	5.1	± 3.8	17961.7	7.5
	60	17.7	0.8	± 0.5	411.9	19.1	± 55.0	49.9	5.0	± 3.5	21323.8	6.8
AlFeP 120ppmP **AlSr** 150ppm Sr	10	70.6	9.0	± 5.1	28.8	9.2	± 5.3	193.3	31.7	± 18.0	167662.9	2.4
	30	43.4	1.9	± 1.2	70.2	10.6	± 7.0	120.3	8.7	± 5.7	98347.5	3.2
	60	25.0	1.8	± 1.3	227.5	23.2	± 17.2	66.5	3.4	± 2.5	99954.8	3.2
AlFeP 120ppmP **AlSr** 250ppm Sr	10	65.1	6.1	± 4.0	27.9	5.5	± 3.6	192.7	23.6	± 15.5	367606.5	1.6
	30	47.3	2.7	± 1.9	59.8	12.2	± 8.5	131.4	15.2	±10.6	136119.3	2.7
	60	32.0	2.4	± 1.8	135.4	25.8	± 19.2	87.0	8.5	± 6.3	119644.4	2.9
AlFeP 120ppmP **AlSr** 350ppm Sr	10	42.5	4.5	± 3.6	87.6	12.6	± 10.1	107.6	7.8	± 6.2	540217.8	1.4
	30	31.4	4.1	± 3.0	153.2	39.3	± 29.2	82.6	10.5	± 7.8	100457.1	3.2
	60	28.2	2.5	± 1.9	160.9	35.3	± 26.2	80.1	8.4	± 6.2	107589.5	3.0

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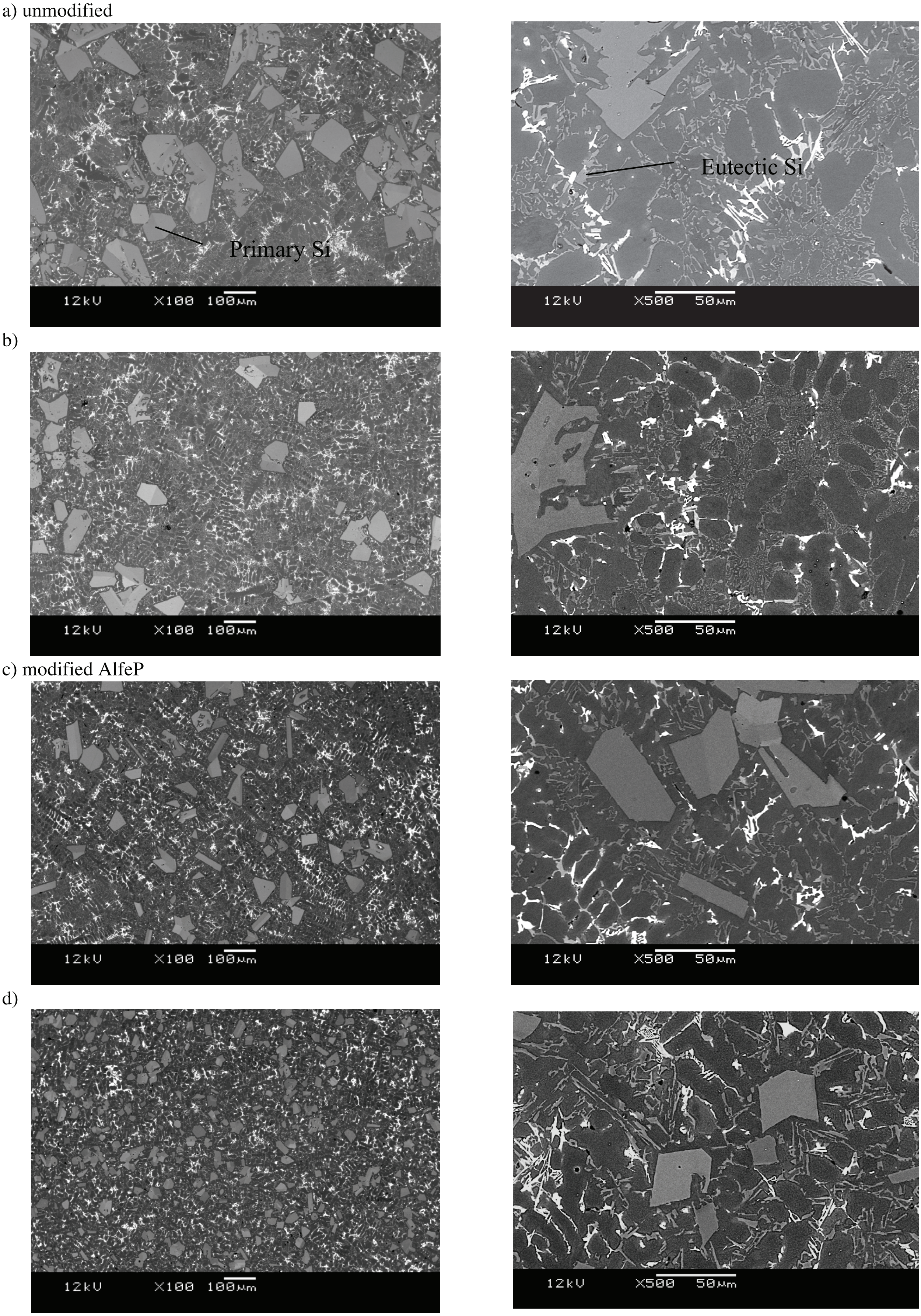

Fig. 1. Microstructure of AlSi21CuNi silumin: unmodified, time to casting: a) 10 minutes, b) 60 minutes; modified with phosphor, time to casting: c) 10 minutes, d) 60 minutes. Soaking temperature 850°C, magnification 100x and 500 x.

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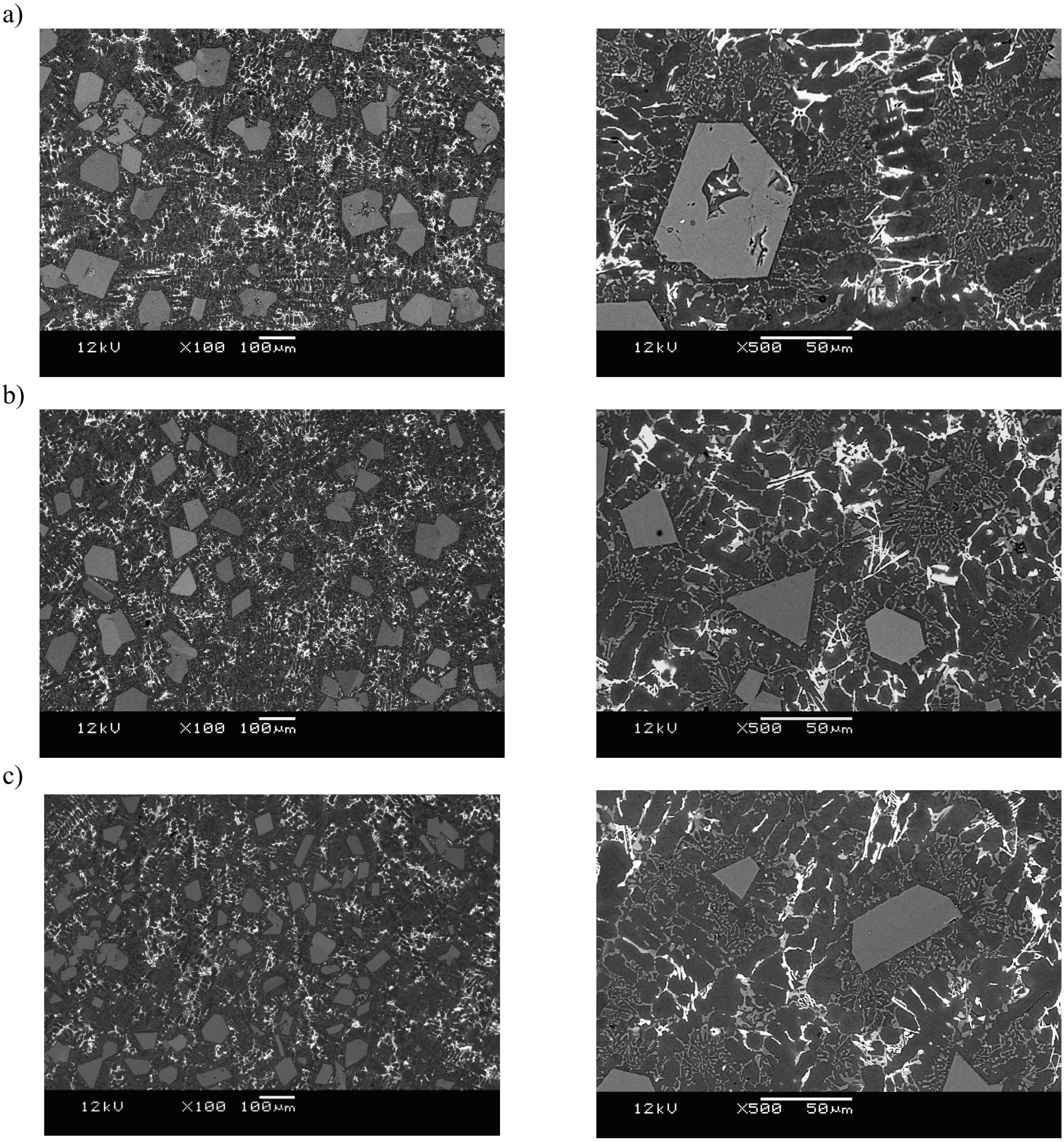

Fig. 2. Microstructure of AK20 silumin after combined modification with AlFeP agent in the phosphor quantity of 120 ppm and AlSr agent in the strontium quantity of 350 ppm., time to casting: a) 10 minutes, b) 30 minutes, c) 60 minutes. Magnification 100x and 500x.

Modification with the use of phosphor has resulted in advantageous changes in the silumin structure (fig.1c, d) as compared to unmodified alloy. In the sample cast after 10 minutes (fig.1c) from the moment of modifier introduction, primary silicon had fine and compact structure. The structure analysis shows that the effect of comminution of the primary secretions of silicon increases with the extension of the time of the modifier contact with the metal bath. As regards comminution of the primary silicon, the most advantageous structure has been obtained in the sample cast after 60 minutes (fig.1d). However, longer time of the modified metal soaking deteriorates the structure of eutectic silicon. From fine crystal structure (magnification 500x, fig. 1c), eutectic silicon changes to lamellar (magnification 500x, fig. 1d). These observations are proved by the results of quantitative metallography (table 3). With the comminution of the primary secretions of silicon, their amount grows significantly. The N_A value in the sample cast after 60 minutes from the introduction of phosphor to the bath is 411.9 mm^{-2} and is more than twice as high as that recorded in a sample cast after 10 minutes. opposite effect has been observed for eutectic silicon. In the sample cast after 10 minutes, the N_A value was 60885.2 mm^{-2}; in a sample cast after 60 minutes, the relative amount of eutectic silicon crystals has decreased by about three times.

The examination results of complex modification

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(with phosphor and strontium) of AlSi21CuNi silumin have been shown in the form of examples of microstructure photographs (fig. 2) and table 3 in which the values stereological parameters of all melts of the investigation cycle under discussion are presented. The structure analysis shows that combined modification with the addition of phosphor and strontium, regardless of the addition quantity applied (150, 250, 350 ppm) has brought the most advantageous effects of the primary silicon comminution after casting time of 60 minutes (fig. 2c). It has also been proved by the results of quantitative metallography.

The smallest average diameter of the primary silicon crystals, D_2 = 25.0 μm, has been found after casting time of 60 minutes with the presence of the smallest applied quantities of strontium (together with phosphor). Increase of the addition of strontium has resulted in an increase of that value, i.e. deterioration of the effectiveness of the primary silicon modification. In an analysis of the results of the melts under discussion in relation to the modification of eutectic mixture, the effect of strong refinement of it has been observed. T his has been proved not only by microstructure photographs but also by the obtained values of N_A and λ. In this aspect, the most advantageous effects have been obtained in the casting modified with the additions of 120 ppm of P and 350 ppm of Sr, cast after10 minutes where N_A = 540217.8 mm^{-2} and λ= 1.4 μm. The analyses presented above show that, with extension of the modified alloy soaking time, the degree of comminution of the primary silicon secretions increases, but the effect of eutectic mixture refinement gets weaker. In connection with that, obtaining of complex modified structure of the AlSi21CuNi silumin structure can depend on reaching a "compromise" between satisfactory comminution of the primary silicon and adequate quality of the eutectic mixture. Such assumption indicates that the most advantageous effects of complex modification have been obtained with the addition of 120 ppm of phosphor and each of the applied quantities of strontium, in castings obtained after 60 minutes from the introduction modifiers to the metal bath.

4 Conclusions

Basing on the investigation of AlSi21CuNi silumin modification, it has been stated that the obtained structure of the castings has been influenced not only by the kind and quantity of the added modifiers but also by the time of the modified alloy soaking.

The performed tests are a basis to formulate the following conclusions:

- the structure of unmodified alloy castings consists of big secretions of primary silicon and fine crystal eutectic silicon forming clusters. As the soaking time of the liquid alloy is extended, the primary secretions get slightly smaller with the simultaneous deterioration of the effect of the eutectic mixture comminution;
- maximum comminution of primary silicon has been found in a sample cast after 60 minutes from the introduction of the AlFeP agent (120 ppm of P) to the metal bath. It has been determined that the longer time of soaking the alloy modified with phosphor, the more disadvantageous (thick lamellar) structure has the eutectic silicon;
- complex modification of AlSi21CulNi silumin (with phosphor and strontium) is a "compromise" between a satisfactory effect of primary silicon comminution and adequate quality of the eutectic mixture. From such point of view, the most advantageous effects of modification have been obtained in the sample cast after 60 minutes from the introduction of 120 ppm of P and 350 ppm of Sr.

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