Investigation of the Influence of the Modifiers P, Sr, Ti and Combinations of them on the Structure and Mechanical Properties of AlSi25 Alloy

Ivan Panov  
Technical University - Sofia, Plovdiv  
Branch  
Plovdiv, Bulgaria  
specialista57@abv.bg

Boyan Dochev  
Technical University - Sofia, Plovdiv  
Branch  
Plovdiv, Bulgaria  
boyan.dochev@gmail.com

Desislava Dimova  
Technical University - Sofia, Plovdiv  
Branch  
Plovdiv, Bulgaria  
desislava608738@gmail.com

Abstract - The most commonly used elements to modify primary silicon crystals in the structure of hypereutectic aluminum-silicon alloys are phosphorus and sulfur. Phosphorus has been shown to have the highest coefficient of modification with respect to the primary silicon and is therefore a preferred modifier. There are also data on the positive effect of the modifiers Sb, Sr, Ti, and B on the silicon crystals in the structure of this type of alloys. The influence of the modifiers phosphorus, strontium, titanium and combinations of them on the size and shape of both the primary silicon crystals and the silicon crystals in the composition of the eutectic of the AlSi25 alloy has been studied in this work. Mechanical tests have been performed to determine both the strength and the plastic parameters of the investigated alloy (in unmodified and modified state). The classic for this type of alloys modifier - phosphorus - has been introduced into the melt by the ligature CuP10. Strontium has been introduced by the ligature AlSr10, and titanium - by the ligature AlTi5B1, the two ligatures in the form of rods. The investigated alloy has also been modified by combinations of the used modifiers: phosphorus and strontium, phosphorus and titanium.  The influence of the used modifiers on the structure and mechanical properties of AlSi25 alloy has been discussed.

Keywords - hypereutectic aluminum-silicon alloy, modification, structure, mechanical properties

I. INTRODUCTION

Modification is a process of metallurgical processing of the melt, in which by introducing small amounts of special additives - modifiers [1], the structure of the aluminum-silicon alloys changes unnaturally.

According to the generally accepted classification of P.A. Rehbinder [2], the modifiers are divided into two groups. Type I modifiers are surfactants, adsorbed on the crystalline germs and reducing the growth rate of the solid phase. Type II modifiers are usually refractory substances with a crystal lattice, identical in appearance and with parameters close to those of the crystallizing alloy. For higher efficiency it is desirable that the particles have a maximum size of less than 5 µm. [3]. Distributed in the melt in a finely dispersed to colloidal-dispersed state, they become independent centers of crystallization or form such centers as a result of the interaction with the melt.

The modification of aluminum-silicon alloys is a two-stage process in which two main types of treatment are required – refinement of the grains of the α-solid solution using Al-Ti-B agents and modifying the eutectic (αAl + Si) by Na (classic example of a type I modifier) or sodium salts (NaF, NaCl, Na3AlF6), Sr or Sb. The modification of the eutectic silicon in the structure of the hypoeutectic aluminum-silicon alloys is performed with Na (0.005-0.01 wt%), Sr (0.01 -0.04 wt%) or Sb (up to 0.2 wt%). In unmodified alloys, the eutectic silicon is separated in the form of coarse needles or plates, which, under certain conditions, serve as stress concentrators. In modified alloys, the silicon crystallizes in the form of small particles with a spherical or thread-like (filamentous) shape. The disadvantages of the modification with Na [4], [5] are that the tendency of gas saturation of the alloys increases, the thinness decreases, the modifier burns quickly, which leads to the need to introduce it every 30-40 minutes in the form of chlorine- or fluorine-containing salts, which is not environmentally friendly. Strontium (Sr) and antimony (Sb) have a long-lasting modifying effect (up to 4 hours). However, contamination of the melt with traces of chlorine and sodium can eliminate their action. The methods used in modern casting practice for refining the α-grains and
modifying the eutectic of Al-Si alloys are considered the literature [6], [7], [8], [9], [10], [11], [12], [13]. Most often, the melt is treated with ligatures in the form of rods with a diameter of 10-15 mm, obtained by pressing or rolling cast workpieces of aluminum ligatures. During the deformation treatment, the non-metallic elements, present in the ligatures, get crushed, their quantity increases and the modifying effect intensifies [6]. To modify the eutectic, Al-Sr ligatures are added at a dosage of 0.04 wt. % Sr max, while for refining the α-grains - double Al-Ti ligatures with a dosage of 0.2% Ti max and triple Al-Ti-B with a dosage of 0.006% B max are introduced. Triple Al-Ti-C ligatures are also used, as their advantage over the Al-Ti-B ligatures consist in the relative simplicity of preparation and the comparable effect. Compositions with different ratios of Ti, B and C [8], [12], [13] are experimented to optimize the treatment with Al-Ti-B and Al-Ti-C ligatures.

The modification of the primary Si coarse crystals in the hypereutectic silumins is performed with phosphorus or sulfur, and the formed AlP or AlS, respectively, serve as crystallization germs [45], [51]. It is known that the mechanical properties of the piston aluminum-silicon alloys depend both on the size, quantity and distribution of the eutectic silicon, and on the quantity, size and shape of the primary silicon crystals [14].

II. MATERIALS AND METHODS

The object of this study was a two-component hypereutectic aluminum-silicon alloy AlSi25 with a chemical composition shown in Table 1.

<table>
<thead>
<tr>
<th>Si</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Cr</th>
<th>Fe</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.7</td>
<td>0.084</td>
<td>0.01</td>
<td>0.006</td>
<td>0.0012</td>
<td>0.17</td>
<td>rest</td>
</tr>
</tbody>
</table>

Phosphorus (P) in the amount of 0.04 wt%, strontium (Sr) - 0.05 wt% and titanium (Ti) - 0.2 wt% were used to modify the studied alloy. A combined modification treatment was performed both with the combination of phosphorus and strontium, and with phosphorus and titanium. Phosphorus is a classic modifier for refining the primary silicon crystals in the structure of hypereutectic aluminum-silicon alloys. Ti is most often used to modify the α-grains in the structure of hypoeutectic aluminum-silicon alloys. Sr is used to modify the eutectic silicon in the structure of hypoeutectic and eutectic aluminum-silicon alloys. There are data on the positive effect of both titanium (Ti) and strontium (Sr) at certain concentrations on the primary silicon crystals in the structure of hypereutectic aluminum-silicon alloys [4].

All experiments were performed under the same conditions. Test samples were cast from all studied compositions, from which sections were prepared for microstructural analysis and standard test specimens were made for conducting mechanical tests.

III. RESULTS AND DISCUSSION

The main amount of primary silicon crystals in the structure of the unmodified AlSi25 alloy are irregular in shape and large in size - 190μm. The eutectic silicon crystals in the alloy structure are in the form of plates with a length of 10 to 40μm (Fig. 1).

After modification of the alloy with phosphorus in the amount of 0.04 wt%, refinement of the primary silicon crystals in the structure of the alloy is observed, they are regular in shape, evenly distributed in the structure of the studied alloy and measure in the range of 25-55μm. Phosphorus also modifies the eutectic silicon crystals and they are in the form of plates with a maximum length of 7μm (Fig. 2). The microstructural analysis proves the claim that phosphorus has a complex modifying effect on the structure of hypereutectic aluminum-silicon alloys, i.e. it works as a modifier of both types - I and II - at the same time.
The results of the microstructural analysis show that the primary silicon crystals in the structure of the AlSi25 alloy, modified by titanium in an amount of 0.2 wt%, have an irregular shape and size of 150µm. The silicon crystals in the eutectic composition have a rounded shape and dimensions of the order of 4-5 µm (Fig. 3). The size of the primary silicon crystals in the structure of the alloy, modified with the help of Ti - 0.2 wt% is refined by 21%, compared to the unmodified alloy. This confirms the opinion that this modifier affects the size of the primary silicon crystals, but does not change their shape and does not favor their uniform distribution in the structure of the alloy. Due to the used amount of the modifier titanium (Ti), the eutectic silicon crystals become highly refined and have a rounded shape.

![Fig. 3. Structure of AlSi25 alloy, modified by 0.2% Ti x200](image)

The primary silicon crystals in the structure of the studied AlSi25 alloy, when modified by strontium (Sr) in the amount of 0.05 wt%, have an irregular (star-like) shape and measure 110µm. The silicon crystals in the composition of the eutectic are also highly refined and have dimension of the order of 4-5µm (Fig. 4). The primary silicon crystals in the structure of the alloy, modified by Sr - 0.05 wt%, are refined by about 42%, in comparison with the unmodified alloy. This confirms the opinion that this modifier affects the size of the primary silicon crystals, but does not change their shape, nor does it affect their distribution in the structure of the alloy. Due to the used amount of the modifier strontium (Sr), the eutectic silicon crystals become highly refined and get a rounded shape.

![Fig. 4. Structure of AlSi25 alloy, modified by 0.05% Sr x200](image)

After carrying out a combined modifying treatment of the studied AlSi25 alloy with phosphorus 0.04 wt% and titanium 0.2 wt%, the primary silicon crystals take the form of straight-walled polygons with dimensions of the order of 10-30µm, evenly distributed in the structure of the alloy. The silicon crystals in the eutectic composition of the modified alloy are refined, with a filamentous shape and dimensions of the order of 4-5 µm (Fig. 5).

![Fig. 5. Structure of the AlSi25 alloy, modified by 0.04% P and 0.2% Ti x200](image)

The results of the microstructural analysis of the studied alloy AlSi25, when modified by the combination, consisting of phosphorus 0.04 wt% and strontium 0.05 wt%, show that the primary silicon crystals are in the form of straight-walled polygons with dimensions of the order of 20-35µm and are evenly distributed in the structure of the alloy. The silicon crystals in the eutectic composition of the modified alloy are refined and have the form of plates with dimensions in the range of 4-5 µm (Fig. 6).

![Fig. 6. Structure of the AlSi25 alloy, modified by 0.04% P and 0.05% Sr x200](image)

The results of the performed microstructural analyses of the hypereutectic aluminum-silicon alloy AlSi25 - unmodified, modified by phosphorus, titanium, or strontium and by the combinations phosphorus plus titanium and phosphorus plus strontium are shown in Table 2.

Table 3 shows the results of the mechanical tests of all studied compositions.

**TABLE 2 RESULTS OF MICROSTRUCTURAL ANALYSIS**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Modifier</th>
<th>Si, µm</th>
<th>Siα, µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlSi25</td>
<td>Unmodified</td>
<td>190</td>
<td>10-40</td>
</tr>
<tr>
<td>AlSi25</td>
<td>0.04% P</td>
<td>25-55</td>
<td>7</td>
</tr>
<tr>
<td>AlSi25</td>
<td>0.2% Ti</td>
<td>150</td>
<td>4-5</td>
</tr>
<tr>
<td>AlSi25</td>
<td>0.05% Sr</td>
<td>110</td>
<td>4-5</td>
</tr>
<tr>
<td>AlSi25</td>
<td>0.04% P+0.2% Ti</td>
<td>10-30</td>
<td>4-5</td>
</tr>
<tr>
<td>AlSi25</td>
<td>0.04% P+0.05% Sr</td>
<td>20-35</td>
<td>4-5</td>
</tr>
</tbody>
</table>

**TABLE 3 RESULTS OF MECHANICAL TESTS**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Modifier</th>
<th>Rm, MPa</th>
<th>A5, %</th>
<th>HB</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlSi25</td>
<td>Unmodified</td>
<td>58.8</td>
<td>1.8</td>
<td>61.1</td>
</tr>
<tr>
<td>AlSi25</td>
<td>0.04% P</td>
<td>78</td>
<td>-</td>
<td>64.3</td>
</tr>
<tr>
<td>AlSi25</td>
<td>0.2% Ti</td>
<td>55.3</td>
<td>0.8</td>
<td>65.4</td>
</tr>
<tr>
<td>AlSi25</td>
<td>0.05% Sr</td>
<td>41.1</td>
<td>-</td>
<td>62.8</td>
</tr>
<tr>
<td>AlSi25</td>
<td>0.04%P</td>
<td>84</td>
<td>-</td>
<td>73</td>
</tr>
<tr>
<td>AlSi25</td>
<td>0.05%Sr</td>
<td>73.8</td>
<td>-</td>
<td>70.4</td>
</tr>
</tbody>
</table>

**IV. CONCLUSIONS**

The classical modifier phosphorus (P) in the used concentration of 0.04 wt% has a complex modifying effect on the structure of the studied AlSi25 alloy. The primary silicon crystals get refined (25-55µm), have a more compact shape and are evenly distributed in the structure of the alloy. The eutectic silicon is in the form of plates and threads up to 7 µm long. Both the tensile strength and the hardness of the investigated alloy increase, compared to the unmodified one.

When modifying the alloy by titanium (Ti), the size of the primary silicon crystals reduces by about 21%, but their shape is not affected by this modifier in the used concentration of 0.2 wt%. In contrast, the silicon crystals in the eutectic are highly refined and rounded. This leads to a decrease in the level of hardness and an increase in ductility (A5-0.8%) compared to the phosphorus-modified alloy, while the strength decreases by about 30%.

The strontium (Sr)-modified alloy has the lowest values of hardness and mechanical strength of all studied modified compositions. The eutectic silicon in it is highly refined - 4-5µm, while the shape and the distribution of the primary silicon crystals are not affected by this modifier in the used concentration of Sr - 0.05%.

The alloy, modified by the combination of phosphorus and titanium has the best strength parameters. Not only the primary silicon crystals become refined here (10-30µm), but also the silicon crystals in the composition of the eutectic - 4-5µm.

The alloy, modified by the combination of phosphorus and strontium, has lower but comparable strength parameters with the alloy, modified by phosphorus and titanium combined. It is noteworthy that the complex modification (P + Ti; P + Sr) leads to greater refinement of the primary silicon crystals compared to the modification by phosphorus alone. In addition, the eutectic silicon crystals in the case of complex modification are significantly smaller and compact in shape.

The structures, obtained after complex modification, suggest an increase in abrasion resistance. This assumption, however, needs to be proven by additional tribological tests.

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**REFERENCES**


