Influence of a P modifier, a nanosized SiC modifier, and a combination of them on the mechanical properties of a hypereutectic aluminium-silicon alloy AlSi18

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Introduction. The hypereutectic aluminium-silicon alloy AlSi18 has been modified by: a standard P modifier, introduced into the melt by means of the ligature CuP 0.4 wt.%; a nanomodifier SiC 0.1 wt.%; and a combination of these two. The influence of the different types of modifiers and their combination on the mechanical properties of the alloy has been discussed. The mechanical properties of an unmodified AlSi18 alloy have been used as basic data to compare the obtained results with.

Key words: aluminium alloy, modification, nanomodifier, mechanical properties.

Exposition. In recent years, experiments have been carried out to modify aluminum alloys by new types of modifiers, namely, by nanomodifiers. Nanomodifiers are ultra-fine nanopowders with a particle size of 4-100 nm, and a high melting point. The main problem preventing the use of the nanoscale powders is that the nanoscale insoluble particles are difficult to get wet (or they do not get wet at all) by liquid metals and alloys. Therefore, their homogeneous distribution when introduced into the molten metal is a very difficult task [1]. The decision to pre-coat the nanoparticles has brought the resolution of this problem. One way to obtain active and melt-wetted nanomodifiers is by the method of their mechanical-chemical treatment, consisting in using cladding metals in centrifugal planetary mills [2]. When the modifiers are introduced into the melt, the coating layer dissolves and facilitates the process of wetting - thus the activated surface of the nanoparticles serves as a crystallization center upon which crystallites grow [5]. Another way to prepare and activate the surface of the nanoparticles is to chemically coat them in order to obtain a suitable metal cladding by various metals [6, 7].

Most of the existing studies have been performed with only hypo-eutectic and eutectic aluminum-silicon alloys, as well as with some grades of cast iron and steel [8, 9, 10, 11, 12].

Aim: The present work aims at studying the effect of a standard modifier - P, a nanomodifier - SiC and a combination of these, on the mechanical properties of a hypereutectic aluminium-silicon alloy AlSi18.
1. Tested alloy and used modifiers

The subject of this study was a two-component AlSi18 aluminum-silicon alloy. Its chemical composition is shown in Table 1.

| Si   | Fe  | Cu  | Mn | Mg | Cr | Ni | Zn | Pb | Al   |
|------|-----|-----|----|----|----|----|----|----|------|
| 17.55| 0.120| 0.025| 0.047| 0.001| 0.005| 0.102| 0.01| rest |

A nanomodifier SiC 0.1 wt.%, passivated with oleic acid for protection against weathering was used. Cu served as a metal protector of the nanomodifier, and the nanomodifier was applied by a currentless method to the surface of the nanomodifier. Table 2 shows the parameters of the coated SiC nanomodifier.

| Composition of the nanomodifier | Specific Surface, m²/g | Average Particle Size, nm | Particle Shape | Crystallographic phases |
|---------------------------------|-------------------------|---------------------------|----------------|-------------------------|
| SiC + Cu (SiC:Cu-1:0.1)         | 35 ± 5                  | 50 ± 5                    | cubic          | β SiC                   |

The used standard modifier P 0.4 wt.% was introduced into the melt by the ligature CuP10.

2. Methodology of the study

The study of the hypereutectic aluminum-silicon alloy AlSi18 consisted in conducting experiments with unmodified, modified by P, modified by a nanomodifier SiC, and simultaneously modified by both P and SiC modifiers alloy.

The melting of the alloy was carried out in an electrical resistance laboratory furnace using pre-cleaned and dry stock materials. The melting process takes place under a layer of refining flux in the amount of 0.5 wt.% from the charge material amount. After melting, the melt is vigorously stirred for removal of non-metallic inclusions out of it, then the slag is removed and degassing of the alloy is started. The degassing is carried out at 760 °C by purging with argon for 3min, cleaning the melt surface and casting samples.

When working with a P-modified alloy, the modification is carried out at 760 °C before degassing. It is typical for treating the hypereutectic aluminum-silicon AlSi18 alloy by a SiC nanomodifier, that the process of modification is performed after refining and degassing, at 760 °C again. The calculated amount of the SiC nanomodifier is mounted on the blade of a titanium stirrer, which is part of the stirring device. The nanomodifier is introduced near the bottom of the crucible. Mechanical stirring is then started for 3 min a lower number of revolutions per minute at 120 - 130 min-1, aiming at a uniform dispersion of the nanomodifier particles throughout the melt volume.

In order to produce from the tested alloy types (unmodified, modified with phosphorus and nanomodified) test specimens for carrying out mechanical tests and workpieces for metallographic microsections, samples were cast – see the “wedge castings” in Fig. 1. Metal die casting equipment (steel mould) with vertical dividing surface was used. Prior to casting, the metal mould was heated, coated with mould coating, and heated until it reached the temperature for pouring, e.g., 200°C. The temperature of the form is measured by a contact thermocouple, and all the experiments were performed at the same temperature of the metal form used.
To determine the mechanical parameters of the AlSi18 aluminum-silicon alloy under study, short test samples were made from the marked by the number 1 places in the wedge casting. The samples were tested on a “Zwick/Roell Z 250” tensile test machine and both their tensile strength Rm and relative elongation A5 were established. The values of the mechanical characteristics were averaged over the test results from 3 ÷ 4 samples. The macro-hardness of the tested samples was also measured.

3. Results and discussion

The results from the mechanical tests of the different aluminum-silicon AlSi18 alloys – unmodified, modified by phosphorus, modified by a SiC nanomodifier, and modified by a combination of a standard P modifier and a nanomodifier SiC - are shown in Table 3.

Table 3. Results from the mechanical tests of the AlSi18 alloy

| Alloy   | Modifier | Rm/Mpa | A5 /% | HB2,5/62,5/30 |
|---------|----------|--------|-------|---------------|
| AlSi18  | -        | 108    | 1,4   | 65            |
| AlSi18  | SiC      | 82     | 0,8   | 65            |
| AlSi18  | P        | 128    | 1,6   | 64            |
| AlSi18  | SiC + P  | 133    | 1,2   | 69            |

Figures 2, 3 and 4 present the recorded tensile strength, relative elongation and macro-hardness of the test samples in the form of diagrams.
The results from the mechanical tests of the unmodified aluminum-silicon alloy AlSi18 are the following: tensile strength (Rm) 108 MPa, relative elongation (A5) 1.4% and hardness 65 HB (HB2.5 62.5/30). During the conducted microstructural analysis, the dimensions of the primary silicon crystals (92.4 µm) and the silicon crystals in the eutectic composition (250-260 µm) were measured.

The results from the mechanical tests of the modified by a standard modifier (P) AlSi18 alloy show an increase in its tensile strength (Rm) by 18.5% and also an increase in its relative elongation (A5) by 14.3%. The hardness decreased by 1.6%. The mechanical properties of the alloy, as well as its structure have changed in result of the modifying treatment. The microstructural analysis reveals that the primary silicon crystals in modified by a standard modifier (P) test samples have been refined by 39.7%, and the silicon crystals in the eutectics have been refined by 48.1% to 54% compared to the unmodified alloy. It has been proved that the modifying effect of phosphorus (P) on the primary silicon crystals comes not only from the AlP compound, but also from the formation of solutions and their adsorption at the boundaries of the grains [11]. Considering the fact that the modifiers most often have double effects [12], we assume that (P) could also be adsorbed along the grain boundaries of the alpha phase, thus preventing the alpha phase grains from growing, i.e. it influences the structure the way it does a first-order modifier as well. By preventing the growth of the alpha phase grains, the distances between the branches of the dendrites remain small, and this is where the separated silicon crystals distribute when the eutectics is formed. In our view, this is a prerequisite for the effect of phosphorus (P) on the size of the silicon crystals in the composition of the eutectics of the alloy. The modification of the primary silicon crystals and the silicon crystals in the eutectic composition leads to an increase in the hardness and plasticity of the alloy under investigation.

The microstructural analysis of the AlSi18 alloy modified by a nanomodifier (SiC) reveals that the silicon crystals in the eutectic composition refine by 98.1% to 98.4%, compared to the unmodified alloy. This modifier in the concentrations we use does not affect the shape or the size of the primary silicon crystals. The notchching action of the primary silicon crystals on the structure of the alloy results in reduction of its tensile strength (Rm) by 24.1% and decrease in the relative elongation (A5) by 43%. The hardness of the tested sample stays the same, as in the unmodified alloy, despite the significant refinement of the silicon crystals in the eutectic composition. The nanomodifier (SiC) has been shown to have a modifying effect on the hypoeutectic aluminum-silicon alloys [6, 7], though, in the used concentrations, it does not affect the shape or the size of the primary silicon crystals in the hypereutectic aluminum-silicon alloy. This fact confirms the view that in the pointed concentrations, the SiC nanomodifier acts only as a first-order modifier. It can be assumed that it is adsorbed along the grain boundaries of the alpha phase, thus inhibiting the growth of the alpha crystals, and many silicon crystals are formed on the branches of the dendrites as a result of the concentration fluctuations, which

![Figure 4. HB change](image-url)
also do not have the potential to increase significantly in dimensions. This is the most likely reason for the considerable refinement of the silicon crystals in the eutectic composition, which is confirmed by the results from the microstructural analysis of the alloy.

The mechanical tests results from for a hypereutectic aluminum-silicon alloy modified simultaneously by both a standard modifier P and a nanomodifier SiC, are as follows: increase in the tensile strength (Rm) by 23.2%, relative elongation (A5) by 14.3%, and increase in hardness by 6.2%. The increase in the mechanical properties of the alloy (tensile strength and macro-hardness) is due to a change in its structure. In this modification, the primary alloy crystals refine by 51.1% and the silicon crystals in the eutectic composition - by 77.2%-77.3%, compared to the unmodified alloy. The measured arbitrary average diameter of the primary silicon crystals is 45.18 μm, and the sizes of the silicon crystals in the eutectic composition are in the order of 57-59 μm. From the results of all conducted experiments with a hypereutectic aluminum-silicon AlSi18 alloy it becomes clear that when the alloy is modified by the combination of a standard modifier (P) and a nanomodifier (SiC), the refinement of the crystals of primary silicon is the most significant and the highest values of tensile strength and hardness of the alloy are measured.

The microstructural analysis of the AlSi18 alloy, simultaneously modified by a standard phosphorus (P) modifier and a nanomodifier SiC shows refinement of both the primary silicon crystals and the silicon crystals in the eutectic composition. We can assume that, with the use of one first-order modifier (SiC) and one second-order modifier (P), the structure formation of the AlSi18 alloy proceeds in accordance with the adsorption theory and the overcooling theory at the same time. The successful two-stage modification treatment (P + SiC) proves the assumption that the modification of the eutectic silicon, as well as of the silicon crystals in the eutectic composition will have a positive effect on the properties of the hypereutectic aluminum-silicon AlSi18 alloy.

4. Conclusions

- The use of the SiC nanomodifier as a stand-alone and sole modifier for the AlSi18 aluminum-silicon alloy degrades its mechanical properties and is not recommended in this concentration.
- Due to the inability of the SiC nanomodifier to etch and change the shape of the primary Si crystals (i.e., to avoid their notching action on the structure of the alloy), its application does not lead to increasing the hardness characteristics of the AlSi18 alloy, despite the considerable refinement of the eutectics of the alloy.
- The complex modification of the AlSi18 alloy melt by both a standard P modifier and a SiC nanomodifier results in the highest values of the hardness parameters (Rm, HB), compared to the other compositions tested and could be recommended for practical application.

Acknowledgements: The authors would like to thank the Research and Development Sector at the Technical University of Sofia for the financial support.

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