Effect of P modifiers, SiC nanomodifiers and combinations them on the structure of a hypereutectic aluminum-silicon AlSi18 alloy

Iv Panov¹, B Dochev², V Manolov³, A Velikov⁴, V Dyakova⁵, P Kuzmanov⁶

¹ Head Assistant, PhD - TU Sofia, Plovdiv Branch
² Assistant - TU Sofia, Plovdiv Branch
³ Associate Professor, PhD - IMSETHC-BAS
⁴ Head Assistant - IMSETHC-BAS
⁵ Head Assistant, PhD - IMSETHC-BAS
⁶ Head Assistant, PhD - IMSETHC-BAS

¹ specialista57@abv.bg
² boyan.dochev@gmail.com
³ v.manolov@ims.bas.bg
⁴ anmabg@abv.bg
⁵ v_dyakova@ims.bas.bg
⁶ pawel_71@abv.bg

Introduction. Studies have been carried out with the following types of an aluminum-silicon AlSi18 alloy: unmodified, modified by a standard P modifier, modified by a SiC nanomodifier, and modified by a combination of both types if modifiers. The paper discusses the influence of the different types of modifiers and the combination of them on the shape and size of the primary Si crystals and their distribution in the structure of the alloy, as well as on the shape and size of the Si crystals in the eutectic composition.

Keywords: aluminum alloy, modification, nanomodifier, primary Si crystals, Si crystals in the eutectic composition

Exposition. The primary silicon crystals in hypereutectic aluminum-silicon alloys are large in size - from 80 to 100 µm - and have an irregular shape. This is the reason why they have a considerable notching action on the structure of the hypereutectic aluminum-silicon alloys and worsen their mechanical and operational properties. In order to improve the properties of the alloys, the primary silicon crystals need to be refined, their uniform distribution in the structure of the alloy ensured and a compact shape given, thereby reducing their notching action. It is believed that this can be achieved by strengthening the eutectic matrix and refining it by modifying the primary silicon crystals [12]. Strengthening of the eutectic matrix can be achieved by alloying and/or grinding the silicon and alpha crystals in the eutectic composition. This is the aim of the recent experiments with novel types of modifiers - nanomodifiers. Nanomodifiers are ultra-fine nanosized powders with a particle size of 4-100 nm and a high melting point. The problem with their use is their difficult absorption by the melt and their homogeneous distribution in it. In order to obtain wettability and to facilitate the homogeneous distribution of the nanoscale particles as they are introduced into the molten metal, they need to be pre-coated with different metals [1,2,3,4,5]. Due to their small size and large specific surface area, the nanoparticles are characterized by extremely high sediment resistance and high surface stress; they are in constant motion and do not precipitate or float under the action of the gravitational forces [6]. By acquiring wettability (after cladding) and because of having high sediment resistance, these particles can serve as crystallization centers in heterogeneous crystallization when the melt solidifies.
Experiments with hypoeutectic and eutectic aluminum-silicon alloys and some grades of cast iron and steel only predominate in the literature [7, 8, 9, 10, 11].

**Aim:** The present work aims at investigating the influence of a standard modifier - P, a nanomodifier - SiC and their combinations, on the shape and size of the crystals of primary Si and their distribution in the melt, as well as on the shape and size of the Si crystals in the composition of the aluminum-silicon AlSi18 alloy eutectics.

1. **Tested alloy and used modifiers**
   The object of the present study was a two-component hypereutectic aluminum-silicon AlSi18 alloy with a chemical composition shown in Table 1.

   **Table 1. Chemical composition of the alloy AlSi18, wt.**
   |   |   |   |   |   |   |   |   |   |
   |---|---|---|---|---|---|---|---|---|
   | Si | Fe | Cu | Mn | Mg | Cr | Ni | Zn | Pb |
   | 17,55 | 0,120 | 0,025 | 0,047 | 0,001 | 0,001 | 0,005 | 0,102 | 0,01 |

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

   **Table 2. Parameters of the 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 aluminium-silicon alloy consisted in conducting experiments with unmodified, modified by a P modifier, modified by a SiC nanomodifier, and simultaneously modified by both a P modifier and a SiC nanomodifier alloy.
   Metallographic sections were prepared to study the microstructure of samples from the hypereutectic aluminum-silicon AlSi18 alloy (unmodified, modified by P, modified by SiC nanomodifier, and modified by P plus a nanomodifier at the same time). The size of the primary silicon crystals, their roundness, as well as the size and roundness of the silicon crystals in the eutectics were determined.
   The influence of the different modifiers (the standard one, the nanomodifier, and the combination of them) on the structure of the investigated aluminum-silicon alloy AlSi18 was established.

3. **Results**
   The results from the conducted microstructural studies of the hypereutectic aluminum-silicon alloy AlSi18 - unmodified, modified by phosphorus, modified by a SiC nanomodifier and modified by the combination of both the standard modifier and the nanomodifier - are shown in Table 3.
Table 3. Results from the microstructural studies of AlSi18 alloy

| Alloy   | Modifier | Arbitrary average diameter of the primary Si crystals D [µm] | Refinement % | Size of the Si crystals in the eutectic composition [µm] | Refinement % |
|---------|----------|-----------------------------------------------------------|--------------|--------------------------------------------------------|--------------|
| AlSi18  | -        | 92.4                                                      |              | 250-260                                               |              |
| AlSi18  | SiC      | Not measured *                                           |              | 4-5                                                   | 98           |
| AlSi18  | P        | 55.7                                                      | 40.8         | 115-135                                               | 54           |
| AlSi18  | SiC + P  | 45.18                                                     | 51.1         | 57-59                                                 | 85           |

The microstructure of the unmodified AlSi18 alloy samples is composed of eutectics and individual primary silicon crystals (Figure 1). The shape of the primary silicon crystals is different: straight-walled polygons, well-formed plates, which in the plane of the microscopic observation resemble needles or irregularly shaped plate-type crystals (Figure 2). The average diameter of the primary silicon crystals in the unmodified AlSi18 alloy is in the range 87.2-97.6 µm.

Several types of zones are observed in the eutectics of an unmodified AlSi18 alloy. The first type has well-shaped, oblong-looking needle-like plates, measuring up to 250-260 µm in length (Figure 3). In the second type zone, small silicon crystals of several microns in size are formed, which group together or remain adjacent to each other, and under small microscopic magnification resemble a broken needle. In the third type zone, fine silicon crystals resembling a "fish bone" are observed (Figure 4).
In the AlSi18 alloy modified by the SiC nanomodifier (Fig. 5, Fig. 6), almost all primary silicon crystals have an irregular-star shape. Therefore, the arbitrary average diameter of the primary silicon crystals is not measured or calculated.

* The longest dimension of the primary Si crystals is measured about 250 µm.

In the AlSi18 alloy, modified by the SiC nanomodifier, the eutectics is highly refined, whole needles rarely occur - they are a series of stacked small silicon crystals not longer than 4-5 µm in length (Fig. 7, Fig. 8).
The microstructure of the samples made of modified by phosphorus hypereutectic aluminum-silicon alloy AlSi18 consists of plate-like eutectics and primary silicon crystals, but the crystals differ in shape and size from those in the unmodified alloy (Fig.9, Fig.10). The arbitrary average diameter of the primary silicon crystals ranges from 52.1-59.2µm. Crystals in the form of straight-walled polygons predominate and no primary silicon crystals in the form of plates are observed.

The eutectics in the modified by phosphorus hypereutectic aluminum-silicon AlSi18 alloy is refined. The silicon needles in it reach sizes of 115-135µm (Fig.11, Fig.12). Small round silicon crystals, which look like clumps or resemble broken needles, are observed here.
The microstructure of the modified by both a standard modifier (P) and a nanomodifier (SiC) hypereutectic aluminum-silicon AlSi18 alloy is composed of eutectics and individual primary silicon crystals (Fig. 11). The amount of primary silicon crystals having an irregular shape in the alloy structure is insignificant, and the primary silicon crystals in the form of polygons predominate (Figure 12). The arbitrary average diameter of the primary silicon crystals in the AlSi18 alloy, modified by both the nanomodifier (SiC) and the standard phosphorus modifier (P) in combination is 45.18 µm.

The eutectics of the hypereutectic aluminum-silicon alloy AlSi18 modified by the combination of a standard modifier (P) plus a nanomodifier (SiC), is made of well-formed wafers of eutectic silicon (having a needle-like shape in the plane of the section) around which small silicon crystals adhere (Fig. 13, 14). The average maximum length of the "needles" in this structure is in the range 57-59µm.
4. Conclusions

- The SiC nanomodifier (in the concentrations we used) has a modifying effect on the size of the silicon crystals in the AlSi18 eutectic composition. However, it has no modifying effect on the deposited Si crystals of primary silicon.
- Since SiC has a positive effect on the structure of the hypoeutectic and eutectic aluminum-silicon alloys, but does not have a modifying effect on the primary silicon crystals in the hypereutectic aluminum-silicon alloy AlSi18, it cannot be recommended as a single and stand-alone modifier for this type of an alloy.
- The results from the microstructural analysis of the AlSi18 alloy, simultaneously modified by a standard phosphorus (P) modifier and a nanomodifier SiC show refinement of both the primary silicon crystals and the silicon crystals in the eutectic composition. Thence, it can be assumed that, with the use of a combination of a first-order modifier (SiC) and a second-order modifier (P), the formation of the AlSi18 alloy proceeds simultaneously according to both the adsorption and the overcooling theories.

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

References:

[1] Kalinin N.E., Kalinin V.T., Nanomaterials and nanotechnologies: production, structure, application. Monography. Dnepropetrovsk: Makovetskij, Y.V, Publishing House, 188

[2] Cherepanov A.N., managing editor Fomin V.M., 1995, Plasma-chemical synthesis of ultradisperse powders and their application in metal and alloy modification, Low-temperature plasma, volume 12, Novosibirsk, Science, Syberian Publishing Company RAN, 344

[3] Manolov V., Cherepanov A., Lazarova R., and Konstantinova S., March, 22-25, 2011, Properties of the aluminium alloy AlSi7Mg, modified by refractory nanopowders, Interaction of highly concentrated energy flows with materials in promising technologies and medicine, IVth all-Russian conference, Novosibirsk, 186-190, ISBN 9785-93089-034-1

[4] Kalinina A.P., Cherepanov A.N., and Borisov O.V., 1999, The effect of linear tension on the rate of heterogeneous nucleation on dispersed particles, Metals, №5, 40-43

[5] Popov S., Manolov V., and Cherepanov A., Mathematical modelling of metal alloys crystallization, http://www.nanomodifiers-ims.com/botl.htm

[6] Krushenko, G.G, M.N. Filkov, Крушenko Г. Г., Фильков М. Н. Application of titanium nitride
nanopowder to obtain complex loaded aluminum-silicon alloys with the required mechanical properties, Nanotechniques, 2008, №3, 77-70 (in Russian);

[7] Lazarova R, Bojanova N, Dimitrova R, Panov I and Manolov V, Influence of Nanoparticles Introducing in the Melt of Aluminum Alloys on Castings Microstructure and Properties, https://link.springer.com/article/10.1007/s40962-016-0033-7

[8] Lazarova R, Dimitrova R, Bojanova N, Stanev S, Velikov A and Manolov V, Modifying of aluminium alloys using nanosized powders, Project TK 01/076 funded by the National Fund “Scientific Researches”, published on http://www.nanomodifiers-ims.com/

[9] Manolov V., Cherepanov A., Lazarova R., and Konstantinova S., Influence of nanopowder inoculants on the structure and the properties of the AlSi7Mg alloy, Foundry, M., № 11, 11-14, ISSN: 0024-449X, IF 0,088

[10] Stanev S., Lazarova R., Konstantinova S., and Manolov V., September, 2010, Study of the effect of nanopowder modification of AlSi7Mg alloy by thermal and metallographic analyses, Proceedings of the XXVIth international scientific conference “65 years Mechanical and technological Faculty at TU – Sofia (Sozopol, Bulgaria), 277-282.

[11] Kuzmanov P, Dimitrova R, Lazarova R, Cherepanov A and Manolov V, March 2014, Investigations of the structure and mechanical properties of castings of alloy AlSi7Mg, cast iron GG15 and GG25 and steel GX120Mn12, modified by nanosized powders, Journal of Nanoengineering and Nanosystems, vol. 228 no. 1, pp. 11-18

[12] Stroganov, G.B., V.A Rotenberg, G.B Gershman, Aluminum alloys with silicon. M., Metallurgy, 1977,(in Russian).