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A Study of the Microstructure of Non-Standardised Alternative Piston Aluminium–Silicon Alloys Subjected to Various Modifications: The Influence of Modification Treatments on the Microstructure and Properties of These Alloys †

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Abstract

The present study examines the structure, properties and use of complex-alloyed hypereutectic aluminium-silicon alloys, emphasising the control of the morphology of primary silicon via treatment with various modifiers as well as their effects on its shape and distribution. Furthermore, this study reviews the experimental work related to the simultaneous modification of primary and eutectic silicon, which leads to the conclusion that favourable results can be obtained by complex modification treatment involving first- and second-type modifiers. After being cast, the AlSi18Cu3CrMn and AlSi18Cu5Mg non-standardised piston alloys are subjected to T6 heat treatment intended to enhance their mechanical performance, harnessing the full potential of the alloying elements. A microstructural analysis of the shape and distribution of both primary and eutectic silicon crystals following heat treatment was employed to determine their microhardness.

Keywords: hypereutectic aluminium-silicon alloys; microstructure; macro- and microhardness; modification treatment

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1. Introduction

Considered natural composites, hypereutectic aluminium-silicon alloys feature a soft and plastic aluminium matrix, with hard and wear-resistant silicon crystals being integrated into it. These properties, coupled with their relatively low weight, make them indispensable materials in various sectors of the machine industry. As a result of crystallisation, primary silicon typically has a rough and irregular shape, its dimensions being in the range of 80–150 μm, which leads to a strong notching effect on the eutectic matrix and worsens its mechanical properties [1–5]. As coarse, acicular eutectic silicon crystals produce the

same effect [6–8], these alloys are generally subjected to modification treatment, which is intended to affect the morphology of eutectic silicon, as well as reducing the size of the primary silicon and making its shape regular [9–14], thus improving their mechanical properties. In the treatment of primary silicon crystals in the structure of hypereutectic Al-Si alloys, second-type modifiers, such as phosphorus and sulphur, considered conventional for this group of alloys, are employed [15–21]. They form sparingly soluble compounds (AIP and AIS) with a crystal lattice, which is identical to that of silicon crystals in terms of type, but with regard to parameters, theirs are similar to those of silicon crystals [22–25]. Their distribution into the melt varies from a fine to colloidal dispersion, and they themselves become the centres of crystalline formation. The complex modification of the microstructure of hypereutectic aluminium–silicon alloys with the introduction of first- and second-type modifiers itself is a subject of special scientific interest. It has been proven that the modifying effect of phosphorus (P) [26–28] on primary silicon crystals is due not only to the AIP compound but also to the formation of solutions and their adsorption at the grain boundaries [29–33]. Considering that modifiers most often have a dual effect [34,35], phosphorus could also be adsorbed at the grain boundaries of the alpha phase, thus preventing them from growing, i.e., it affects the structure as a first-type modifier as well. With a residual phosphorus content of 0.05% in their composition, the alloys are found to have been overmodified, their structure appearing to be unmodified and their properties being degraded accordingly [36–39].

Iron is a detrimental impurity in Al-Si alloys for it forms intermetallic compounds that significantly and adversely impact their mechanical properties. Beryllium (Be), whose effect as a modifying element is associated with its interaction with iron-containing compounds, by a mechanism similar to that of manganese (Mn) [40,41], imparts more roundedness and compactness to the shape of the iron-containing phases and thus enhances mechanical performance [42,43].

The Al-Ti5-B1 modifier is also known to favourably influence the mechanical properties of hypereutectic aluminium-silicon alloys. A number of studies [44,45] reveal that the Al-Ti5-B1 ligature mainly modifies primary silicon. In addition to being able to improve the wear resistance of alloys, this treatment proves that combined modification contributes to a better effect in comparison with modification with a single modifier [46]. The mechanism of Al-Ti5-B1 modification involves the fact that Al3Ti and TiB2 belong to a heterogeneous core [47].

The aim of the present research is to investigate the influence of various modifiers (P, Be) as well as their combination (P, Be, Ti, B) on the microstructure and mechanical properties (microhardness of the α-phase) of non-standardised piston hypereutectic alloys.

2. Materials and Methods

The subjects of the present study are the AlSi18Cu3CrMn and AlSi18Cu5Mg hypereutectic aluminium-silicon alloys, with their chemical compositions being shown in Table 1. For the beryllium modification of the AlSi18Cu5Mg alloy, different beryllium bronze CuCo1Ni1Be concentrations (0.005, 0.007 and 0.01 wt%) were used. The alloys were also treated with a phosphorus concentration of 0.4 wt%, introduced by a CuP10 ligature, as well as with a titanium concentration of 0.015 wt% and a boron concentration of 0.003 wt%, introduced by an AlTi5B1 ligature.

Table 1. Chemical composition of studied alloys.

Alloys	Si	Cu	Mg	Mn	Ni	Al
AlSi18Cu3CrMn	18.5	3.12	0.01	0.76	0.01	rest
AlSi18Cu5Mg	19.2	5.1	1.5	0.02	0.02	rest

The AlSi18Cu3CrMn alloy was modified with phosphorus, as well as with a combination of P (0.04 wt%), Ti (0.015 wt%), B (0.003 wt%) and Be (0.005 and 0.007 wt%), introduced into the melt, as in the AlSi18Cu5Mg alloy.

The alloys under investigation were melted in a laboratory resistance furnace with a graphite crucible under a layer of covering-refining flux of 0.5 wt% of the charge amount. They were degassed by means of argon blowing for a 3 min duration at a temperature of 760 °C. In all experiments, phosphorus modification and specimen casting were conducted at alloy temperatures of 850 °C and 760 °C, respectively, with the temperature of the metal equipment being 210 °C. After being cast, the specimens were subjected to T6 heat treatment, conducted in a chamber furnace at a temperature of 510–515 °C and holding time of 6 h and 30 min, followed by quenching—at a temperature of 50 °C—and artificial ageing—at 330 °C for 8 h and at 210 °C for 16 h—and they were subsequently left to cool in still air.

Metallographic microsections were prepared for the purposes of microstructural analysis. After being wet-ground on sandpapers with the numbers 240, 320, 400, 600, 800 and 1000, the specimens were mechanically polished with diamond paste and lubricant. Their microstructures were developed with Keller's reagent (1 part HF, 1.5 part HCl, 2.5 part HNO_3, 95 part H_2O). This study was carried out on a Leica DM ILM microscope by means of software, a grain measurement module and phase analysis. The α-phase microhardness was measured with an HV-1000 Vickers Hardness Tester, with the load and holding time being 50 g and 10 s, respectively.

3. Results

As the first part of this study seeks to determine the optimal content of the alloying element beryllium, this element was introduced into the AlSi18Cu5Mg alloy at concentrations of 0.005, 0.007 and 0.01 wt%. After being cast and modified, the alloy was subjected to T6 heat treatment, with the artificial ageing parameters being 330 °C/8 h.

The microstructural analysis of the AlSi18Cu5Mg alloy modified with a Be concentration of 0.005% (Figure 1a) involves the measurement of the dimensions of both the primary and eutectic silicon crystals. The conditional mean diameter of the primary silicon crystals was measured and calculated to be in the range of 60–70 μm. A certain number of 100 μm irregularly shaped silicon crystals appear to have been unmodified. In addition, the beryllium modifier affected the shape of the α-phase in the eutectic composition of the alloy, transforming it into well-formed dendrites. The dimensions of the eutectic silicon crystals are in the range of 10–30 μm. The modification coefficient of the Be modifier at a concentration of 0.005% for this alloy is K = 67%. The microhardness of the α-phase was measured to be 90 $\mu HV_{50/10}$. The structure of the AlSi18Cu5Mg alloy modified with a Be concentration of 0.007% is shown in Figure 1b. The dimensions of the primary silicon crystals in the structure of the alloy thus modified are in the range of 50–70 μm. A small number of silicon crystals appear to have been unmodified, with their dimensions being in the range of 90–95 μm. The modification coefficient of the Be modifier at a concentration of 0.007% was calculated to be K = 80%. The α-phase in the eutectic composition has the same shape of well-formed dendrites, which, however, are more refined than the ones yielded by the 0.005% Be modification. This is the reason why refined silicon crystals whose dimensions are in the range of 4–23 μm are also present in the eutectic composition, but the ones that predominate are silicon crystals with dimensions of 4–10 μm. The α-phase microhardness was measured to be 90 $\mu HV_{50/10}$.

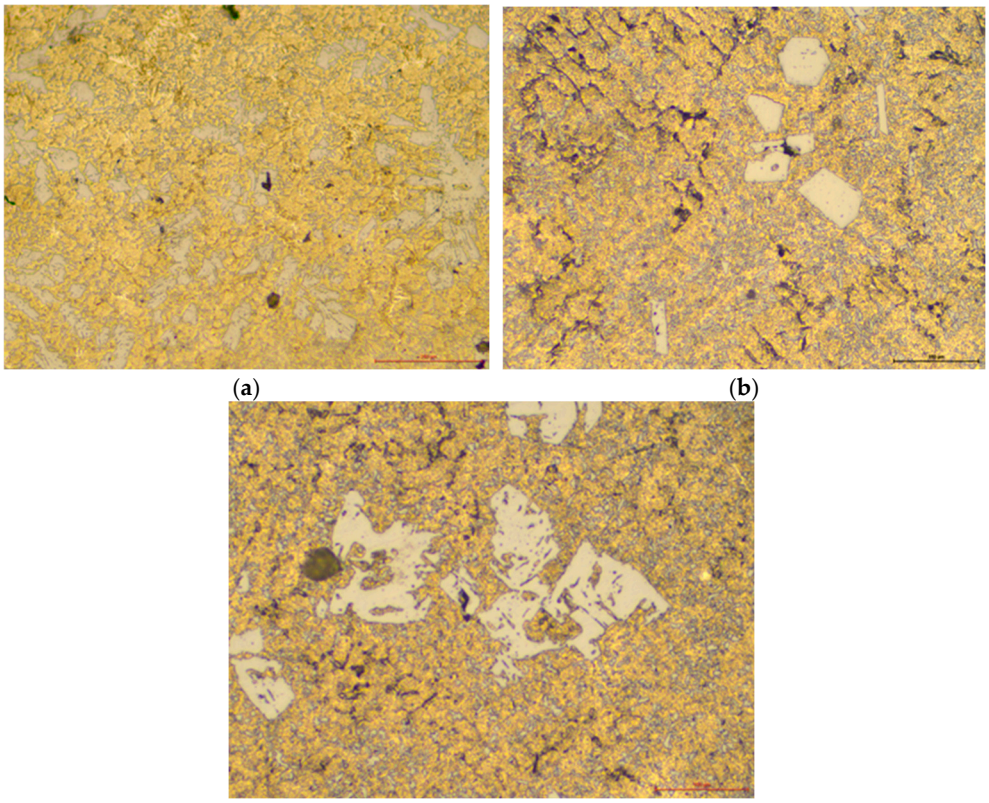


Figure 1. Microstructure of AlSi18Cu5Mg alloy modified with Be at concentrations of 0.005 (**a**), 0.007 (**b**) and 0.01 wt% (**c**) and subjected to T6 heat treatment with artificial ageing parameters of 330/8 h.

Following the treatment of the AlSi18Cu5Mg alloy at a beryllium concentration of 0.01%, a negligible number of primary silicon crystals appear to have been modified, the majority of them being coarse, irregularly shaped and of a large size. (Figure 1c). The conditional mean diameter was measured and calculated to be in the range of 95–110 µm. The most likely reason for the structure thus obtained is the overmodification of the alloy, which typically arises due to an increase in the amount of the respective modifier. The primary silicon crystals in the structure of overmodified alloys are larger in size than the ones in unmodified alloys. The modification coefficient of the beryllium modifier at a concentration of 0.01% was calculated to be K = 38%. The eutectic silicon crystals have dimensions in the range of 10–30 µm, as in all experiments that were carried out. The α-phase microhardness is 80.6 $\mu HV_{50/10}$.

The highest coefficient of the modifying effect is at a beryllium concentration of 0.007%, followed by the one at that of 0.005%. In the next stage of this study, phosphorus at a concentration of 0.004%, as well as titanium (0.015%) and boron (0.003%), was added to the modified alloy. The specimens were subjected to T6 heat treatment with artificial ageing parameters of 330 °C/8 h and 210 °C/16 h.

The microstructure of the AlSi18Cu5Mg alloy modified with 0.007% Be, 0.015% Ti, 0.003% B and 0.04% P and subjected to quenching and artificial ageing at a temperature of 330 °C for 8 h is shown in Figure 2a. The alloy structure consists of refined and evenly distributed primary silicon crystals, most of which are irregularly shaped, their dimensions varying in the range of 34.10–45.62 µm. The eutectic silicon crystals appear in the form of plates, arranged adjacently, with their dimensions being in the range of 1.5–7.46 µm, but Si grains with a rounded shape and dimensions below 1 µm are also present. The α-phase microhardness was measured and calculated to be 98 $\mu HV_{50/10}$.

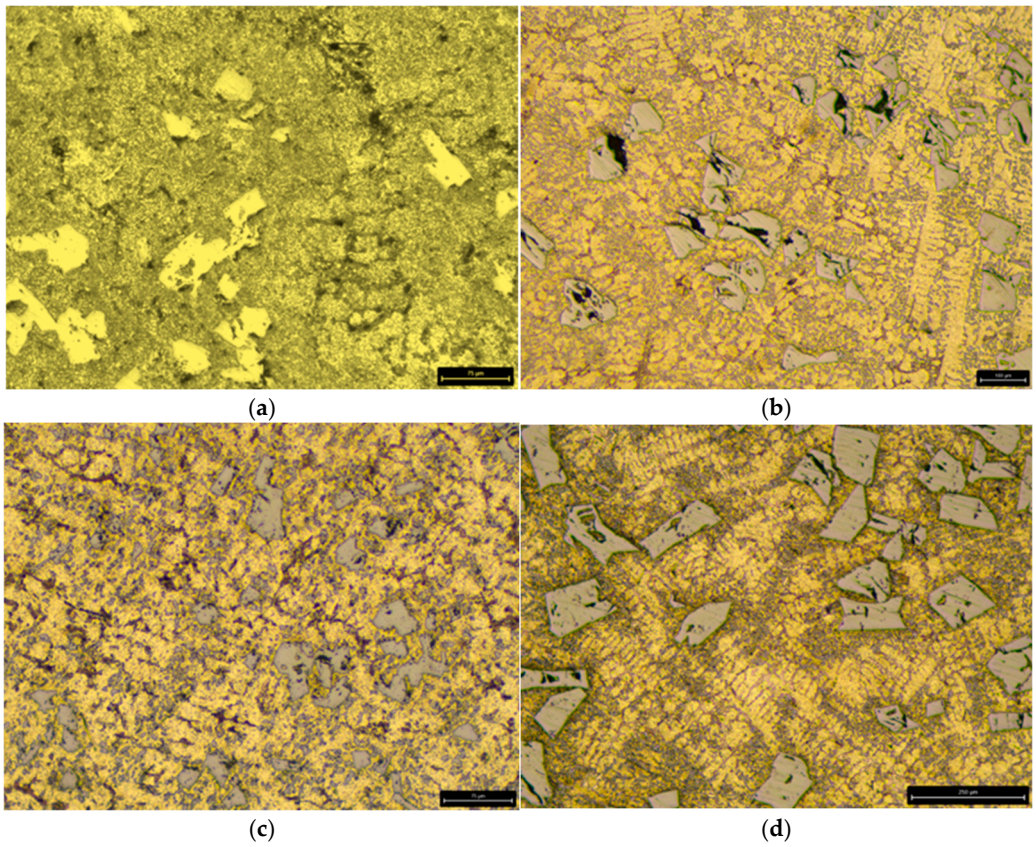


Figure 2. Microstructure of AlSi18Cu5Mg alloy modified with Be, Ti, B and P: (**a**) modified with Be concentration of 0.007 wt%, 0.015 wt% Ti, 0.003 wt% B and 0.04 wt% P and subjected to T6 heat treatment with artificial ageing parameters of 330 °C/8 h; (**b**) modified with Be concentration of 0.005 wt%, 0.015 wt% Ti, 0.003 wt% B and 0.04 wt% P and subjected to T6 heat treatment with artificial ageing parameters of 330 °C/8 h; (**c**) modified with Be concentration of 0.007 wt%, 0.015 wt% Ti, 0.003 wt% B and 0.04 wt% P and subjected to T6 heat treatment with artificial ageing parameters of 210 °C/16 h; (**d**) modified with Be concentration of 0.005 wt%, 0.015 wt% Ti, 0.003 wt% B and 0.04 wt% P and subjected to T6 heat treatment with artificial ageing parameters of 210 °C/16 h.

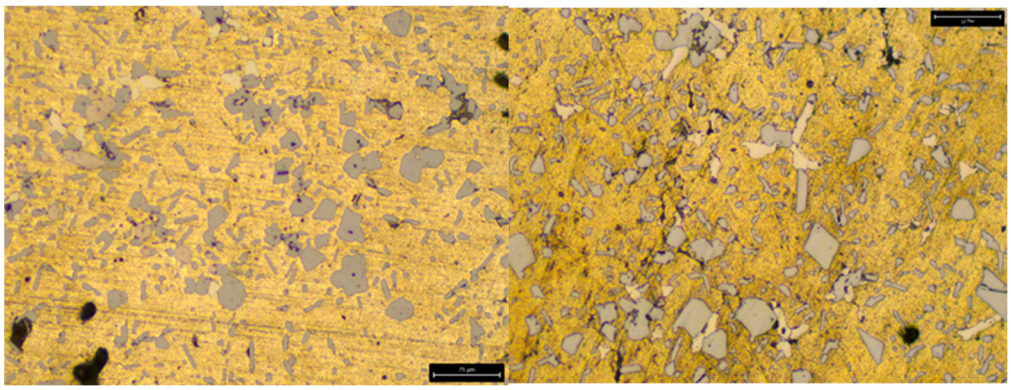
The structure of the AlSi18Cu5Mg alloy modified with a Be concentration of 0.005%, 0.015% Ti, 0.003% B and 0.04% P subjected to T6 heat treatment with artificial ageing parameters of 330 °C/8 h (Figure 2b) is made up of primary silicon crystals with dimensions in the range of 54–88 μm. An insignificant number of silicon crystals, whose dimensions are in the range of 96–115 μm, appear to have been unmodified. The majority of primary silicon crystals are plate-like, but those that are irregularly shaped are also present. The α-phase in the eutectic composition has the shape of well-formed dendrites, which are more refined and have dimensions in the range of 1–10 μm, but it is equiaxed silicon crystals of 1 μm that are predominant. The α-phase microhardness of the alloy thus modified was measured to be 90 $\mu HV_{50/10}$.

In the structure of the AlSi18Cu5Mg alloy modified with 0.007% Be, 0.015% Ti, 0.003% B and 0.04% P, quenched and artificially aged at 210 °C for 16 h (Figure 2c), the primary silicon crystals are highly refined, irregularly shaped and again evenly distributed in the alloy structure, with their dimensions varying in the range of 21.5—36 μm. Eutectic silicon, which is also highly refined, represents a string of small silicon crystals arranged adjacently, their length being in the range of 1–4.55 μm, but what predominates are silicon crystals with dimensions below 1 μm. The α-phase microhardness was measured to be 100 $\mu HV_{50/10}$.

The microstructure of the AlSi18Cu5Mg alloy modified with 0.005% Be, 0.015% Ti, 0.003% B and 0.04% P and quenched and artificially aged at 210 °C for 16 h (Figure 2c)

consists of uniformly distributed primary silicon crystals, the majority of which are plate-like or single, irregularly shaped. Their conditional mean diameter is larger than that measured after the previous treatment, varying in the range of 66–120 µm. The silicon crystals in the eutectic composition, which also has a dendritic structure, are plate-like, with their dimensions being in the range of 8–13 µm. The α-phase microhardness is 110 $\mu HV_{50/10}$.

The microstructure of the AlSi18Cu3CrMn alloy modified with 0.04% P, 0.015% Ti, 0.003% B and 0.007% Be subjected to T6 heat treatment with artificial ageing parameters of 210 °C/16 h consists of primary and eutectic silicon crystals. Being highly refined, the primary silicon crystals are 31 µm in size (Figure 3a), while the eutectic ones, which are needle-shaped in the observed field of the microsection, have linear dimensions of 3–7 µm. The α-phase microhardness is 147 $\mu HV_{50/10}$.

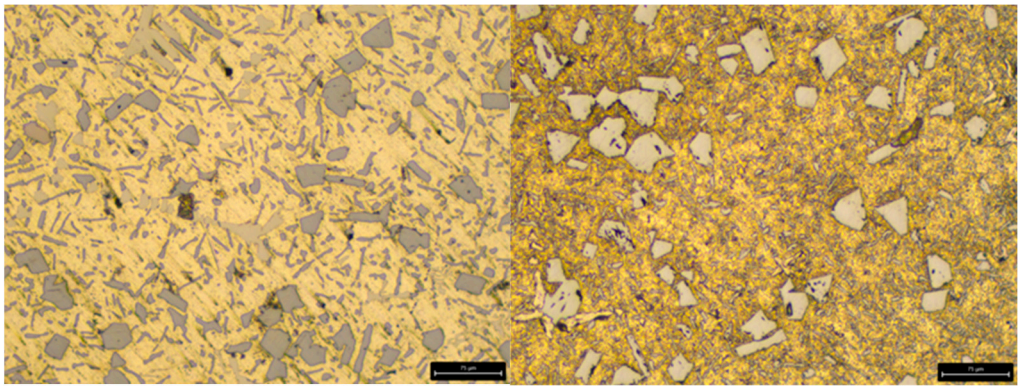


(**a**) (**b**)

Figure 3. Microstructure of AlSi18Cu3CrMn alloy modified with 0.007 wt% Be, 0.015 wt% Ti, 0.003 wt% B and 0.04 wt% P: (**a**) subjected to T6 heat treatment with artificial ageing parameters of 210 °C/16 h; (**b**) subjected to T6 heat treatment with artificial ageing parameters of 330 °C/8 h.

The microstructure of the specimens of the AlSi18Cu3CrMn alloy modified with 0.007% Be, 0.015% Ti, 0.003% B and 0.04% P and subjected to T6 heat treatment (artificial ageing parameters of 330 °C/8 h) consists of polygon-like primary silicon crystals located in a granular eutectic composition, with their conditional mean diameter being 25 µm. The eutectic silicon crystals, which are evenly distributed, have a strongly rounded shape, with their dimensions varying in the range of 7–13 µm. The α-phase microhardness of the alloy thus treated is 120,5 $\mu HV_{50/10}$.

A metallographic analysis of the AlSi18Cu3CrMn alloy modified only with phosphorus and subjected to T6 heat treatment with artificial ageing parameters of 210 °C/16 h and 330°/8h was also conducted. The microstructure of the AlSi18Cu3CrMn alloy subjected to quenching and artificial ageing at a temperature of 210 °C and a holding time of 16 h is shown in Figure 4a. The results of the microstructural analysis reveal that the majority of primary silicon crystals are polygon-like with straight walls, with their dimensions varying in the range of 27–40 µm. The majority of the eutectic silicon crystals are elongated and 'needle-shaped', but a certain number of them became rounded, with their dimensions being in the range of 7–26 µm. The α-phase macrohardness of the alloy thus treated is 140 $\mu HV_{50/10}$. In the alloy heat-treated by quenching and artificial ageing at a temperature of 330 °C and a holding time of 8 h, the primary silicon crystals are regularly shaped, with their dimensions being in the range of 24–28 µm. Eutectic silicon, whose dimensions are in the range of 15–18 µm, appears to be needle-like in the plane of the microsection, with numerous small crystals having adhered to each other. The α-phase microhardness of the alloy thus treated is 112 $\mu HV_{50/10.}$



(**a**) (**b**)

Figure 4. Microstructure of AlSi18Cu3CrMn alloy modified with 0.04 wt% P: (**a**) subjected to T6 heat treatment with artificial ageing parameters of 210 °C/12 h; (**b**) subjected to T6 heat treatment with artificial ageing parameters of 330 °C/8 h.

4. Discussion

The studies conducted on the two AlSi18Cu5Mg and AlSi18Cu3CrMn hypereutectic aluminium–silicon alloys found that heat treatment has a positive effect on both the primary and eutectic silicon crystals in their composition [48]. The measured microhardness values show that the alloys subjected to artificial ageing of a lower temperature and longer holding time exhibit a more supersaturated α-solid solution.

For both alloys modified with beryllium, phosphorus, titanium and boron at a concentration of 0.007% subjected to heat treatment, the lowest values of the primary and eutectic silicon crystals were measured in all experiments. The optimal amount of beryllium as a modifier in both hypereutectic piston alloys was established.

The macrohardness value of the AlSi18Cu5Mg alloy modified with a beryllium concentration of 0.01% subjected to heat treatment is commensurable to that of the other alloys, but the coefficient of the modifying effect is low, with the free silicon crystals being irregularly shaped and large-sized. This is typical of overmodified alloys, where the introduction of a larger amount of modifier results in the neutralisation of its modifying effect.

Apart from having the second most effective modification coefficient of primary silicon crystals at a relatively low concentration (K = 73% at a Be content of 0.005%) [49], beryllium does not affect the corrosion resistance of aluminium–silicon alloys. In order to alleviate the adverse effect caused by eutectic silicon, which is found between the branches of the α-phase in the eutectic composition, the α-phase needs to be modified so that the distances between its branches are reduced, thus preventing it from growing, i.e., dendrite crystallisation needs to be disrupted in order to yield small-sized, spheroidal eutectic silicon crystals. Titanium and boron were employed for the modification of the α-phase in the structure of aluminium–silicon alloys. The combination of minimal concentrations of Ti and Be was found to have a positive effect on the Silumin structure subjected to T6 heat treatment, increasing the concentration of point defects at the grain boundaries, thus accelerating the diffusion processes of alloying element atoms during ageing, which prompts earlier metastable and stable phase separation [50]. The positive outcomes serve as a starting point in the study of the complex modification treatment of hypereutectic aluminium–silicon alloys. The subject of interest is the study of alloy strengthening phases, given the fact that the AlSi18Cu3CrMn alloy modified with a smaller amount of copper, with magnesium (a highly diffusive mobile element) being excluded from its composition, has a much higher α-phase microhardness value.

5. Conclusions

The possibility of the complex modification of complex-alloyed hypereutectic aluminium–silicon alloys involving first- and second-type modifiers (P, Ti, B and Be) proves that the treatment has a favourable influence on both alloys investigated in the present study. The concentrations of the respective modifiers in the alloy composition were optimised.

The results obtained from the microstructural analysis (modified silicon crystals evenly distributed in the studied metallographic microsection) of the AlSi18Cu5Mg and AlSi18Cu3CrMn alloys that were complexly modified (with P, Ti, B and Be at a concentration of 0.007 wt%), as well as the α-phase microhardness, can be regarded as a prerequisite for improving their mechanical and operational properties.

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