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# Influence of modifying elements on the structure and mechanical properties of casting Al−Si alloys

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The state of scientific research on the modification of aluminum-silicon (Al−Si) alloy with strontium, sodium, phosphorus, which are widely employed in industrial alloys, and the modification of Al−Si alloy with intensively studied rare-earth elements (cerium, europium, samarium and others) was analyzed. Scientific articles related to the study of the effect of modifiers on the mechanical properties, mainly on the strength and ductility of hypoeutectic, eutectic and hypereutectic alloys was considered. On the basis of a literary data analysis, ways of improving the mechanical properties have been proposed by jointly modifying several elements, the possibility of forming the solely eutectic structure in the hypereutectic composition alloy 0.01 wt% strontium (Sr) modified and directionally crystallized at a rate that provides paired growth of the eutectic components is noted. This composition of Al−Si alloy has superfine-grained eutectic structure, its strength and ductility exceed the mechanical properties of Al−Si alloys obtained by other techniques.

**Keywords:** rare-earth elements, eutectic, microstructure, elongation, tensile strength.

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## Introduction

Despite significant progress in the field of creating new alloys and composites that have superior physical and mechanical characteristics compared to alloys based on a mixture of aluminum and silicon (silumins), materials based on the Al−Si alloy, both hypoeutectic and hypereutectic, have so far time, they occupy leading positions in a number of industries, for example, in the automotive industry. This is due to the relatively low cost of silumins, the possibility of using secondary raw materials, a low melting point, and the absence of the need for a protective atmosphere. At the same time, modern requirements for technology are becoming more stringent, and even a slight improvement in the quality of silumin-based alloys is justified, given the large volumes of production. The most important characteristics of silumins are casting and mechanical properties, which are determined by the structure and phase composition, which, in turn, depend on the chemical composition, crystallization conditions and subsequent heat treatment.

According to the equilibrium state diagram of the aluminum−silicon system presented in [1,2] (Fig. 1), the eutectic point at which the alloy consists only of a eutectic — a mixture of crystals $\alpha$-Al and Si, is observed at 12.6% silicon (hereinafter weight percent) (Fig. 1, dot *b* on the abscissa). In hypoeutectic compositions, upon cooling from the beginning of solidification to the crystallization temperature of the eutectic, primary $\alpha$-Al crystal-dendrites appear (Fig. 1, dot *a*), in hypereutectic – - primary lamellar silicon crystals (Fig. 1, dot *c*). At the same time, it was found that in the case of an increase in the melt solidification rates, the eutectic point shifts in the diagrams of the Al−Si system towards higher silicon concentrations due to a decrease in the solidification temperature. At the same time, it is shown that in directional crystallization [3,4] the physical and mechanical properties at the displaced eutectic point are extreme in relation to other silumin compositions.

Industrial grades of Al−Si-alloys [5–10] contain dopants in addition to aluminum and silicon, which requires the analysis of a more complex phase composition. On the other hand, just such an analysis can ensure the

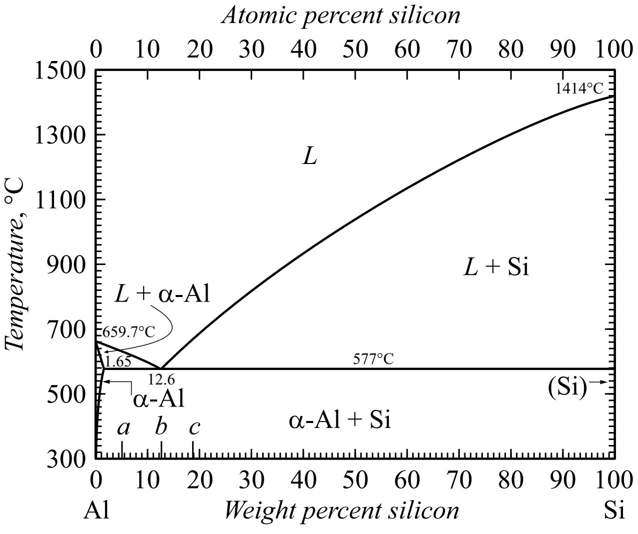

**Figure 1.** Equilibrium state diagram of the aluminum−silicon system [2].

quality of new alloys based on silumins. The structure and properties of both two-component and more complex industrial silumins are quite widely represented in the scientific literature [1–18], but to a small extent they are tied to diagrams of multicomponent systems. Therefore, the study of the influence of modifiers and alloying elements on the structure and properties of silumins is still relevant. The purpose of this paper is to systematize and analyze the available data in articles on the selected review topic, to identify new promising areas and recommendations for improving the casting and physical and mechanical properties of aluminum-based alloys based on the results of the analysis of scientific results.

## 1. Alloying elements in Al–Si-alloys

The main alloying metals in silumins are magnesium and copper. Less common as alloying elements in industrial silumins are manganese, zinc, and nickel. The above alloying elements form double or triple compounds with the main components of the alloy, which primarily increase the strength of the alloy [2,11–16].

Magnesium introduced into the melt forms an intermetallic compound with silicon (Fig. 2) [13], which has high hardness. During aging of the Al–Mg–Si [11,15,16] ternary alloy, $Mg_2Si$ particles precipitate in a finely dispersed form from the solid solution. Magnesium additions lead not only to hardening of the alloy, but also improve the machinability, increase the creep and hot brittleness characteristics of silumins [11]. Additions of copper to silumins also lead to dispersion strengthening of the alloy. The increase in strength upon hardening in this case is noticeably higher than upon alloying with magnesium. As a result, fatigue resistance and casting properties of silumin [11] are increased. At the same time, according to literature sources [12,16], magnesium and copper in aluminum-based alloys, on the contrary, increase the tendency to form hot cracks and reduce the casting characteristics of the alloy. Manganese eliminates the harmful effect of iron on strength and causes an increase in fatigue resistance, improves creep and heat resistance characteristics [16]. Zinc additives are introduced within 3% to increase strength and to improve machinability. A feature of zinc silumins is the ability to self-hardening during crystallization [17]. The introduction of up to 3% nickel, molybdenum, cobalt increases the heat resistance and strength of the alloy. In alloys, the strengthening of which during heat treatment depends on the concentration of copper, it is partially bound by nickel, the formed compound Al–Cu–Ni reduces the strength [11]. The joint introduction of iron and nickel makes it possible to leave most of the copper in the aluminum matrix, while maintaining the strength properties of the alloy [12].

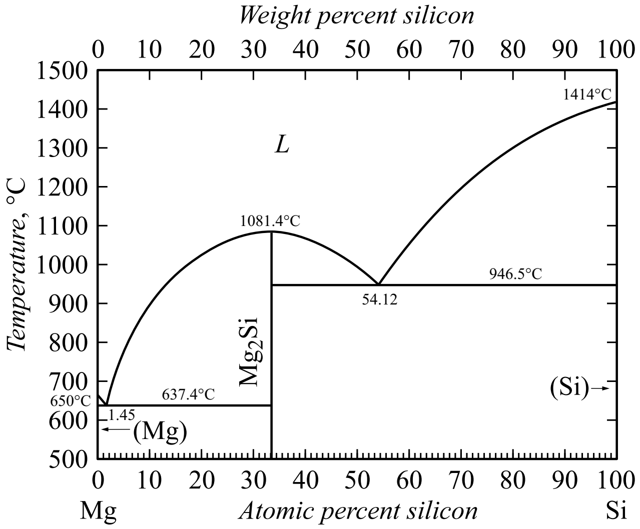

**Figure 2.** Equilibrium state diagram of magnesium–silicon [13].

## 2. Modifiers in industrial Al–Si-alloys (Na, Sr, P)

Modifiers — elements that are introduced into the alloy in small quantities that do not affect the main phase composition of silumin. Up to now, modification has been one of the main methods for improving the structure. Small additions of a number of elements grind grains of eutectic and primary silicon or strengthen aluminum dendrites. The most well-known elements at present as modifiers for industrial Al–Si-alloys — sodium, strontium and phosphorus [7,8,10,18–28]. The last modifier effectively grinds primary silicon crystals in hypereutectic silumin, thereby increasing strength and relative elongation.

Sodium is introduced into hypoeutectic and eutectic alloys of the aluminum–silicon system to prevent the formation of a coarse structure containing large lamellar silicon crystals and the formation of a fine eutectic structure. To modify industrial silumins, metallic sodium, sodium fluoride, or sodium compounds are used to reduce the size of eutectic silicon crystals in these alloys.

One of the variants of the mechanism of modification upon the introduction of sodium into the alloy, presented in [28], can be the following: at the moment of nucleation of eutectic colonies, sodium, being adsorbed on the surface of silicon nuclei, hinders their development and lowers the eutectic formation temperature, increasing the amount of Si nuclei due to supercooling. The aluminum dendrite, developing under conditions of strong supercooling and the restraining influence of the modifier, acquires the ability to grow in the form of highly branched crystal dendrites with axes that divide the liquid into a number of microvolumes closed in the interaxal spaces of the dendrites. Crystallization of silicon under such conditions leads to its strong grinding and transformation of the grain shape from lamellar to fibrous. At the same time, there is still no

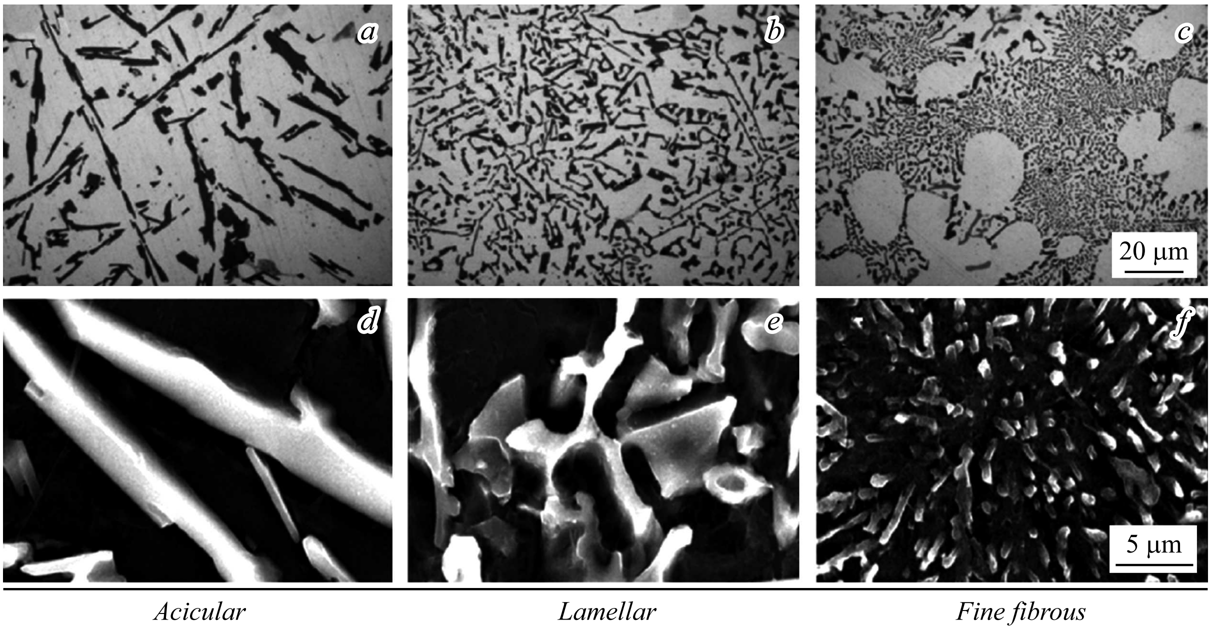

**Figure 3.** Photograph of the microstructure obtained using an optical microscope and scanning electron microscopy (SEM) of Al$-$10.5% Si$-$2.0% Cu alloy with different Sr contents: *a, d* — 0.0%; *b, e* — 0.02% Sr; *c,f* — 0.03% Sr [30].

unambiguous opinion about the mechanism of modification of silumin [27,29,30].

The modification of silumins with sodium and its salts has certain disadvantages: a decrease in the fluidity of the melt, an increased tendency to gas absorption. But the main one — is the limited time of allowable holding of the melt after the introduction of the modifier (usually up to 30 min) [29]. Longer exposure of the melt leads to the evaporation of fusible sodium and a decrease in strength properties.

Strontium is currently the most widely used modifier of aluminum$-$silicon alloys and an element [10,22,24,29–41] that attracts the attention of researchers. Strontium, like sodium, causes the refinement of the aluminum-silicon eutectic, a change in the coarse lamellar shape of silicon to a fine fibrous one (Fig. 3) [30], but at the same time provides a stable effect of melt modification. The effect is preserved during long exposure (up to 6 h) and repeated remelting of the modified alloy [29]. The refinement of the alloy structure leads to an improvement in its mechanical properties. In the paper [30] it is shown that the strength characteristics with the introduction of strontium in an amount of up to 0.05% increase relative to the initial composition of the alloy Al$-$10.5%Si$-$2.0%Cu, reaching the maximum values: tensile strength 237 MPa and elongation to failure 4.1% (Fig. 4). In addition, as noted in the paper [40], modification with strontium promotes an increase in the conductivity of the alloy due to a change in the structure of the eutectic.

A similar increase in the tensile strength and elongation to failure is also noted in the paper [32]. In addition, when strontium is introduced into the alloy, a change in the amount, morphology, and size of $\alpha$-Al primary dendrites from - was found due to a decrease in the eutectic transformation start temperature and a shift of the eutectic point in the transformation diagram in the direction higher concentrations Si. Dendrites — $\alpha$-Al become less branched and shrink in size [10,32]. A more detailed study of the distribution of Sr in modified silumin allowed the authors [33,34] to detect clusters of the Al$-$Si$-$Sr compound, which bind to Si atoms, thus deactivate the formation of eutectic nuclei and cause supercooling of the melt.

In the paper [41], the effect of modifying with strontium a hypereutectic alloy of the composition Al$-$15%Si, the samples of which were formed by the method of directional crystallization (the Stepanov method) at two solidification rates, $10^3$ $\mu$m/s and $10^2$ $\mu$m/s, on its structure and strength characteristics. Samples in the form of rods were obtained by drawing the melt at a constant speed through a forming device, followed by crystallization under air cooling conditions. Under these experimental conditions, the shape and size of the cross section of the sample do not change, and the temperature gradient near the boundary between the liquid and solid phases is constant. This ensures the consistency of the structure along the entire length. As a result of the application of the method of directed crystallization, optimal conditions were obtained for the formation of the structure of samples modified with strontium from an alloy of aluminum with silicon, which have high strength characteristics.

It is noted that the combination of a high solidification rate ($10^3$ $\mu$m/s), leading to the pairwise growth of the components and the formation of only eutectics in the Al$-$15%Si alloy, without the formation of primary Si

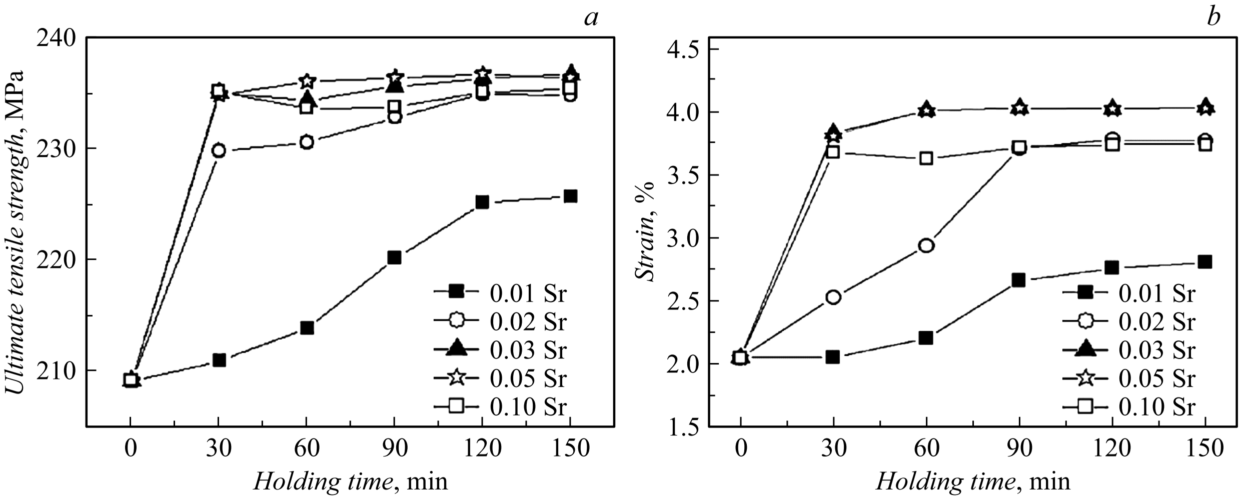

**Figure 4.** Tensile strength (*a*) and elongation (*b*) of Al−10.5% Si−2.0% Cu alloy samples depending on the content of Sr and melt holding time [30].

crystals and $\alpha$-Al dendrites, modified with strontium makes it possible to obtain a submicrograined (60−90 nm [3]) eutectic structure even when 0.01% Sr is added to the alloy. As a result, a sharp increase in the elongation to fracture of samples containing 0.01% Sr from 14 to 33% was obtained with a simultaneous increase in the tensile strength from 22 to 280 MPa.

In the industrial alloy A319 (Al–7% Si–3% Cu—0.2% Mg), a change in the method of eutectic nucleation depending on the concentration of strontium in the melt [35]. In the unmodified A319 alloy, the eutectic is nucleated at the ends of the primary $\alpha$-Al dendrites, as well as in the case of the overmodified (Sr = 0.05%) alloy. At Sr = 0.007 and 0.011%, the nucleation of the eutectic occurs in the interdendritic volume, regardless of the morphology of the primary $\alpha$-Al crystals. In the paper [39] the effect of strontium modification on such a physical characteristic of the alloy as the heat of fusion of the eutectic in a wide range of cooling rates (from 0.033 to $10^5$ K/s) was studied. The effect of melt modification was found only for relatively low velocities. For an unmodified alloy, as the cooling rate increases, the heat of fusion decreases, while the introduction of strontium into the composition of the alloy leads to an accelerated decrease in this value compared to the unmodified alloy to rates of the order of $10^2$ K/s. Such a change in the heat of fusion with an increase in the cooling rate in [39] is explained by an increase in free energy due to the - formation of defects in the sample. It is assumed that at low rates, strontium contributes to the accelerated formation of defects in the crystal lattice.

In the paper [36], studies were carried out on the effect of modification with strontium on the corrosion resistance of the industrial alloy A356 (Al–6.45% Si–0.34% Mn–0.24% Mg). Alloy samples were cast into metal or sand molds to obtain different cooling rates. The highest corrosion resistance was obtained at 0.017% Sr for the sample when casting into a sand mold and 0.012% Sr when casting into a metal mold. In comparison with samples without strontium, the corrosion resistance increased by 7 and 35 times, respectively.

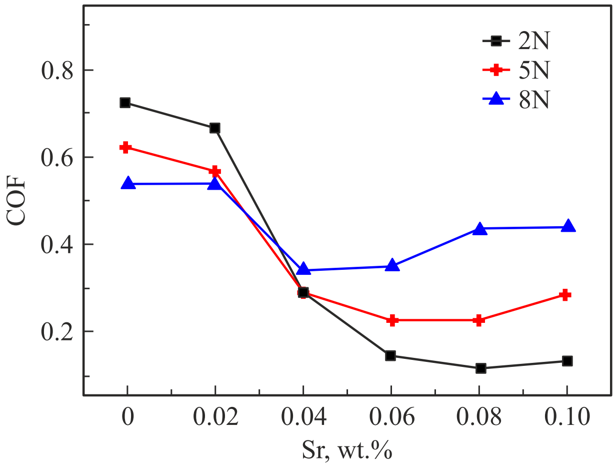

**Figure 5.** Dependence of the friction coefficient on the content of Sr at various (2N, 5N, 8N) loads on the sample [37].

The modification of an alloy of hypereutectic composition with strontium led, as found in [23,37,38], to a change in such important characteristics for hypereutectic piston silumins as the coefficient of friction and wear resistance of the alloy. The coefficient of friction when strontium was added to the Al−20% Si melt in an amount of 0.04% decreased by about a factor of two, the wear resistance increased by an average of 1.5 times compared to the values of the unmodified alloy in [37] (Fig. 5). Directionally crystallized alloy of hypereutectic composition (15% Si), modified with strontium (0.01%), obtained at an increased solidification rate ($10^3$ $\mu$m/s), without primary Al crystals and Si, with only a eutectic structure, has a lower coefficient of friction and lower wear parameters than the industrial alloy A390 with 16% Si, used for the manufacture of liners and pistons of internal combustion engines, under similar test conditions [38].

At the same time, modification with strontium leads to an increase in the porosity of the alloy and, accordingly, products from it [20]. When an excess amount of strontium is introduced into the melt, intermetallic compounds of the $Al_2Si_2Sr$ phase are formed, which can be initiators of the nucleation of pores on complex oxide films [24,31].

The introduction of antimony into silumins, as well as strontium, provides the effect of long-term modification, reduces the size of silicon crystals in the eutectic, increases the strength and wear resistance of the alloy [8,15,42,43]. But due to - toxicity and the formation of harmful compounds, antimony is used much less frequently to modify industrial Al−Si-alloys.

In hypoeutectic silumins, refractory elements are often used to improve strength characteristics — titanium, boron, vanadium, zirconium, — which have a significant effect on the microstructural parameters of primary crystals and eutectics, are often used to improve strength characteristics in hypoeutectic silumins: sizes of dendrites of primary $\alpha$-Al, distance between branches of second-order dendrites (SDAS), shape of silicon crystals in eutectic [44,45]. According to the data [17,45–48], when these elements are introduced into the melt, the nuclei of complex chemical compounds are formed, which are the crystallization centers of $\alpha$-Al. In practice, modifiers are used in the form of appropriate salts or ligatures, since the elements have a high melting point. The use of salts provides a modifying and refining effect on the melt. In addition, the compounds formed in the melt are in this case in an ultrafine state.

The main modifier for hypereutectic silumin is phosphorus, which reduces the size of primary silumin crystals and changes their shape, reducing the stress concentration in the structure [18,21,49–53]. Phosphorus is introduced into the Al−Si melt in various ways to enhance the efficiency of modification, mainly in combination with other elements, using cast master alloys based on Al, Si, Cu [18,21,49–53]. At the same time, the formation of such master alloys is associated with hazardous production pollution and, therefore, other promising directions for the creation of modifiers with phosphorus are being explored. One of these options may be the use of complex compounds AlFeP, AlSrP containing phosphorus in the form of a fine powder. Powder finely dispersed ligatures are less harmful in production, allow reducing the modification time and improving the microstructural characteristics of the alloy [54,55].

The main tasks of modifying hypereutectic silumins with phosphorus are to reduce the growth rate of primary silicon crystals, as well as to increase the number of crystallization centers.

In the paper [49], the effect of phosphorus modification on the physical characteristics of hypereutectic silumin was studied using a differential scanning calorimeter (DSC), which makes it possible to observe the kinetics of crystallization and melting, and a microanalyzer (EPMA). From the calculation results, it was concluded that the values of the activation energy and the work of formation of nuclei of the eutectic structure decrease and, at the same time, the frequency of formation of nuclei increases in comparison with the composition without phosphorus. The authors associated these changes with the appearance in the melt of particles of the AlP compound (aluminum phosphide), which serve as sites for the nucleation of primary silicon crystals and eutectic, which, in addition, can also form on primary crystals. In the paper [50], where silumin of the initial composition A1−14.6% Si was modified with the Cu−P master alloy, it was found that only primary silicon is intensely heterogeneous nucleation on AlP particles and as a consequence, there is an increase in the values of tensile strength and relative elongation.

The authors [51] observed the kinetics of the development of primary crystals in an Al−22% Si−18.8% Cu alloy in the course of its solidification using the methods of microfocus X-ray diffraction (microfocus X-ray radiography). It was found that the introduction of phosphorus into the alloy significantly reduces the growth rate and branching of primary silicon formations, their shape approaches a block one, consisting of small crystals. The time required for the formation of adsorption layers in the modified alloy is longer and the structure of these layers is more complex. It is assumed that the development of such a block form is controlled by diffusion processes, and a model is proposed for such development of primary crystals upon the incorporation of phosphorus. Similar changes in the shape of crystals upon modification of a hypereutectic alloy with phosphorus were observed in [21,23]. As a result of the modification, an increase in strength and resistance to the formation of surface cracks during wear resistance tests is noted.

Hypereutectic silumins are characterized by high casting properties: good fluidity, low shrinkage and minimal tendency to hot cracking. The dependence of the coefficient of thermal expansion of alloys of the Al−Si system in the range of operating temperatures is inversely proportional to the content of silicon in them, which is important for piston silumins [53]. The increase in the fluidity of Al−Si melts of hypereutectic composition is explained, first of all, by the relatively high thermal effects of crystallization of primary silicon, which has the highest heat of crystallization among metals — 327 cal/g, more than three times the heat of crystallization of aluminum. Therefore, the presence of even a small amount of primary silicon crystals, formed during the solidification of hypereutectic silumins, helps to maintain the alloy in a liquid state [17]. The main areas of application of hypereutectic silumins are heat-resistant wear-resistant piston alloys with a maximum operating temperature of about 350°C, having in their composition 16−25% Si along with alloying additives: copper, titanium, cobalt or chromium [53].

Phosphorus has a negative effect on the structure when it is introduced into the alloy — along with the grinding of primary silicon crystals, silicon particles in the eutectic are coarsened. Therefore, a certain number of papers were devoted to the study of the effect of a combination of such eutectic modifiers as sodium and strontium together with phosphorus on the microstructure of hypereutectic silumins [11,18,23,56,57]. It has been shown in the papers [23,56] that primary silicon crystals are formed on dispersed particles of the AlP compound, which has a crystal lattice close to that of Si in terms of parameters and structure. The chemical compound AlP appears in the melt at a higher temperature than primary silicon. The nucleation sites for eutectic silicon are dispersed SrP formations, which also appear in the melt at temperatures above the eutectic formation temperature and partially replace AlP. At the same time, it was noted in the paper [57] that the joint introduction of phosphorus and strontium into the alloy causes a decrease in the eutectic formation start temperature. In addition, the authors [57] found that strontium reduces the number of primary silicon crystals even in the presence of phosphorus and lowers the temperature at which they begin to form in the melt.

Aluminum and silicon of technical purity always contain iron impurities, therefore, fine particles of the $\beta$-(Al, Si, Fe) phase may form in the alloy at high temperatures [29], which can be initiators of the nucleation of silicon crystals and thereby contribute to the refinement of the eutectic structure. On the other hand, the $\beta$- phase has a thin flat shape and is a crack initiator when the sample is loaded. To change the morphology of $\beta$-(Al, Si, Fe) particles in alloys, rare earth elements are used, in particular, scandium (Sc) [58]. As a result, dispersed particles of the $Al_{12}Si_6Fe_2(Mg,Sc)_5$ compound are formed in the alloy, having a larger shape.

## 3. Rare earth elements as silumin modifiers

There is a significant number of papers related to the research of rare earth elements or rare earth metals (REM) with the aim of using them as modifiers, simultaneously improving the structure and eutectics and primary crystals of silumins, as well as optimizing the morphology of refractory phases of alloying elements and, thus, improving strength properties of multicomponent industrial alloys based on aluminum.

The rare earth element scandium (Sc) as a modifier was used in hypoeutectic and hypereutectic alloys in [59–61]. In the papers [59,60] the microstructure of the eutectic of the alloy with the addition of scandium was studied using reflected electron diffraction (EBSD) and X-ray spectral microanalysis. It was found that scandium is in a solid solution of the $\alpha$-Al phase, primary and eutectic, and modification leads to an increase in plasticity (by 60%) and strength (by 70%). The form of silicon crystals in the eutectic becomes fibrous only with the simultaneous introduction of Sc equal to 0.8% and Sr (0.04%). At the same time, the tensile strength during joint modification is higher than in the case of modification separately with Sc or Sr [59] (Fig. 6). In hypereutectic alloys, the addition of Sc to their composition does not lead to a significant change in the morphology of primary silicon and strength properties [60]. At the same time, when studying the structure and strength properties of the hypoeutectic industrial alloy A357 (Al–Si–Mg–Ti) modified only with Sc, a decrease in the size of primary dendrites $\alpha$-Al, increase in tensile strength and hardness by 28% and 19% respectively, elongation to failure increased by 165% [61]. The authors [61] associated this behavior of the alloy with the appearance of $Al_3(Sc_{1-x}Ti_x)$ phase particles in it, which become additional centers of crystallization and obstacles to the movement of dislocations.

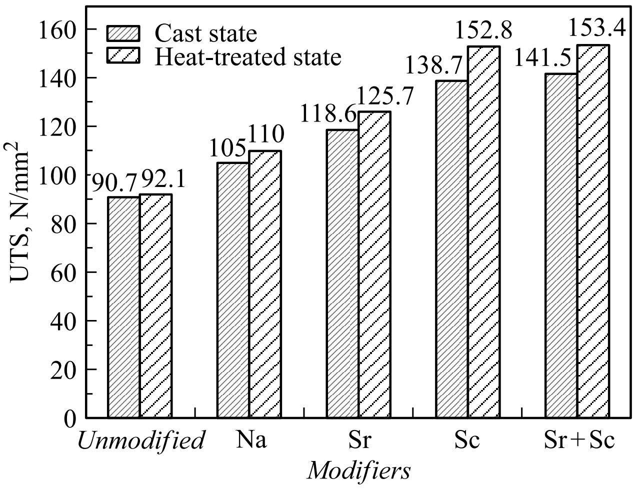

**Figure 6.** Tensile strength of Al–8.5% Si alloy with Na, Sc, Sr modification and combination of elements Sc and Sr [59].

Lanthanides, which are part of the REM group, have recently been used as potential modifiers to improve the performance properties of silumins (both eutectic and hypereutectic compositions) in a number of studies. The structure and properties of silumins modified with europium (Eu) [25,62,63], erbium (Er) [6,64–66], lanthanum (La) [9,67], cerium (Ce) [68] and their combination, La/Ce [69–74], ytterbium (Yb) [75–78], yttrium (Y) [79–81] and a number of other rare earth lanthanides [82–85].

The addition of europium in an amount of 0.05% to the hypoeutectic silumin Al–5% Si leads to a refinement of the structure, the appearance of a fibrous form of eutectic silicon crystals (Fig. 7) and ternary chemical compounds $Al_2Si_2Eu$ [62]. In the case of a hypoeutectic industrial grade A356 alloy additionally alloyed with magnesium, the introduction of europium revealed intermetallic compounds of a more complex shape [63]. At the same time, the tensile strength (UTS) increased at the optimum content of 0.1% Eu from 250 to 265 MPa, elongation to failure from 7.4 to 14.7% compared with the unmodified composition.

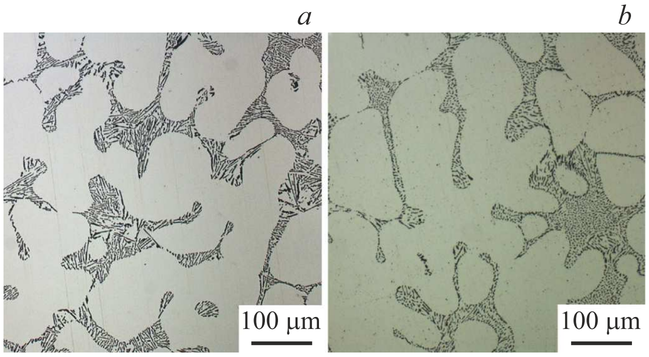

**Figure 7.** Microstructure of silumin Al–5% Si: *a* — without Eu, *b* — added 0.05% Eu [62].

Only modification with europium, according to the results of studies of the effect of various rare earth elements on the structure and strength properties of the Al–10% Si alloy in the paper [82], makes it possible to completely change the shape of silicon crystals in the eutectic from coarse lamellar to fine fibrous.

The effect of modifying the hypoeutectic alloy A356 with erbium (Er) was studied in the paper [65]. The obtained cast samples without subsequent heat treatment showed a decrease in strength and ductility, despite the fact that the sizes of primary aluminum dendrites and eutectic crystals became smaller with Er modification. The authors associated this behavior of the alloy with the appearance of $Al_3Er$ and $\beta$-$Al_5FeSi$ compounds, which have an acicular shape. Only after solid solution annealing (mode T6) did the strength and elongation to failure of the alloy increase by about a factor of 2 at the optimum content of 0.3% Er compared to the initial composition without the modifier. In addition, modification with erbium in an amount of 0.3% of eutectic silumin, as was also found in the paper [66], promotes a decrease in the friction coefficient and an increase in the wear resistance of the alloy. In Er-modified hypereutectic cast alloy Al–20% Si obtained by the authors [64], the shape of primary silicon changed from lamellar to bulk, while the eutectic crystals became smaller. As a result, at the optimum content of 0.5% Er, an increase in ultimate strength by 72.5% and elongation to failure by 72% was obtained in comparison with alloy samples without a modifier. A similar effect was also observed in [76] upon modifying 0.5% Yb of the Al–20% Si hypereutectic alloy. In this case, the increase in tensile strength was 64.5%, and the elongation to failure was 73.6%.

When introduced into the composition of commercial alloys A357 [69], A356 [70.71], A413 [74] and into the composition of Al–8% Si [68] lanthanum and cerium change the form of silicon in the eutectic from coarse lamellar to partially fibrous. As a result of mechanical tests carried out on [70,71] specimens of A356 alloy modified with La/Ce (0.2%) [70] or La (1.0%) [71], only an increase in the value of elongation to failure by about 1.5 times and a small increase, by 15%, in the values of hardness and tensile strength after annealing for aging (T6) were found. In the paper [69] in the industrial hypoeutectic alloy A357 (Si — 6.75%, Mg — 0.63%, Ti — 0.14%, the rest Al), modified complex La/Ce (0.2%), a decrease in the size of primary $\alpha$-aluminum dendrites and silicon crystals from - was observed due to the formation of dispersed particles of Al(La/Ce) intermetallic compounds, which retain component growth. As a result, the increase in tensile strength was 11.2%, elongation — 34.2% after additional heat treatment (T6).

In hypereutectic silumins, the effect of Ce on the silicon structure is more effective [72,73]. The mechanical properties of hypereutectic silumins are largely determined by the morphology and size of primary silicon and silicon in the eutectic. Modification with cerium in an amount of 0.5% leads to the refinement of primary silicon and the most significant increase in strength and ductility. In [72] the tensile strength of an industrial alloy of hypereutectic composition with 17% Si, modified by Ce, was 195 MPa (the original alloy had a tensile strength value of 170 MPa). According to the authors [73], who studied the structure and properties of the Al–20% Si alloy, when Ce (1.0%) was added to the composition, the ultimate strength increased

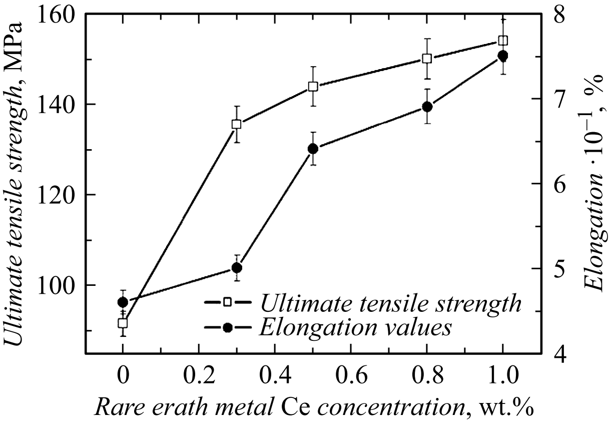

**Figure 8.** Strength properties of Al–20% Si depending on the Ce content in the alloy [73].

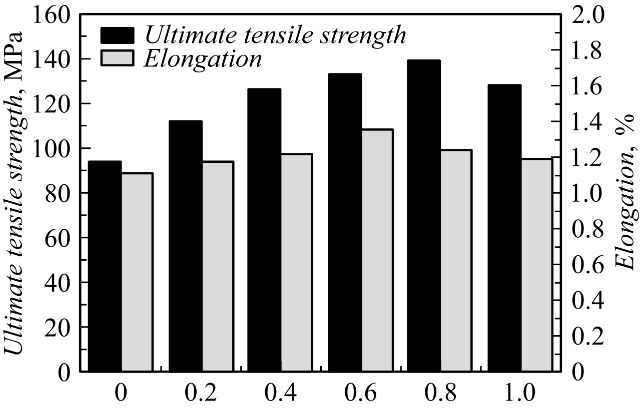

**Figure 9.** Tensile strength and elongation depending on the content Y in the alloy Al–20% Si [81].

Influence of modifiers on the strength properties of silumins

| Composition, wt.% | Modifier, wt.% | Strength properties | Crystallization method | Literature |
|---|---|---|---|---|
| Al−15.0 Si | 0.01 Sr | $\varepsilon = 32.0\%$, UTS = 270 MPa | Directional crystallization | [41] |
| Al−10.5 Si−2.0 Cu | 0.03 Sr | $\varepsilon = 4.0\%$, UTS = 235 MPa | In graphite molding shape | [30] |
| Al−11.6 Si−0.2 Fe | Without Sr | $\varepsilon = 1.57\%$, UTS = 163 MPa | In graphite molding shape | [32] |
| Al−11.6 Si−0.2 Fe | 0.04 Sr | $\varepsilon = 12.8\%$, UTS = 218 MPa | In graphite molding shape | [32] |
| A1−14.6 Si | Without P | $\varepsilon = 0.9\%$, UTS = 133 MPa | To crucible from $A1_2O_3$ | [50] |
| A1−14.6 Si | 0.05 P | $\varepsilon = 3.3\%$, UTS = 165 MPa | To crucible from $A1_2O_3$ | [50] |
| Al−8.5 Si | Without Sc | UTS = 91 MPa | In graphite molding shape | [59] |
| Al−8.5 Si | 0.40 Sc | UTS = 139 MPa | In graphite molding shape | [59] |
| Al−6.9 Si−0.6 Mg−0.1 Ti (A357) | Without Sc | $\varepsilon = 3.2\%$, UTS = 320 MPa | In steel molding shape+t/t (aging) | [61] |
| Al−6.9 Si−0.6 Mg−0.1 Ti (A357) | 0.40 Sc | $\varepsilon = 7.0\%$, UTS = 410 MPa | In steel molding shape+t/t (aging) | [61] |
| Al−6.9 Si−0.4 Mg (A356) | Without Eu | $\varepsilon = 9.6\%$, UTS = 250 MPa | In steel molding shape+t/t (aging) | [63] |
| Al−6.9 Si−0.4 Mg (A356) | 0.10 Eu | $\varepsilon = 14.7\%$, UTS = 265 MPa | In steel molding shape+t/t (aging) | [63] |
| Al−20 Si | Without Er | $\varepsilon = 0.5\%$, UTS = 90 MPa | In steel molding shape | [64] |
| Al−20 Si | 0.50 Er | $\varepsilon = 1.8\%$, UTS = 160 MPa | In steel molding shape | [64] |
| Al−7.0 Si−0.4 Mg (A356) | Without Er | $\varepsilon = 4.5\%$, UTS = 235 MPa | In steel molding shape+t/t (aging) | [65] |
| Al−7.0 Si−0.4 Mg (A356) | 0.30 Er | $\varepsilon = 8.5\%$, UTS = 310 MPa | In steel molding shape+t/t (aging) | [65] |
| Al−6.8 Si−0.6 Mg−0.1 Ti (A357) | Without Ce/La | $\varepsilon = 2.6\%$, UTS = 310 MPa | In steel molding shape+t/t (aging) | [69] |
| Al−6.8 Si−0.6 Mg−0.1 Ti (A357) | 0.20 Ce/La | $\varepsilon = 3.9\%$, UTS = 350 MPa | In steel molding shape+t/t (aging) | [69] |
| Al−20 Si | Without Ce | $\varepsilon = 0.5\%$, UTS = 92 MPa | In steel molding shape | [73] |
| Al−20 Si | 1.0 Ce | $\varepsilon = 0.8\%$, UTS = 154 MPa | In steel molding shape | [73] |
| Al−20 Si | Without Yb | $\varepsilon = 0.4\%$, UTS = 93 MPa | In steel molding shape | [76] |
| Al−20 Si | 0.60 Yb | $\varepsilon = 0.8\%$, UTS = 153 MPa | In steel molding shape | [76] |
| Al−20 Si | Without Y | $\varepsilon = 1.1\%$, UTS = 93 MPa | In steel molding shape | [81] |
| Al−20 Si | 0.80 Y | $\varepsilon = 1.2\%$, UTS = 140 MPa | In steel molding shape | [81] |
| Al−20 Si | Without Sm | $\varepsilon = 0.5\%$, UTS = 102 MPa | In steel molding shape | [85] |
| Al−20 Si | 0.60 Sm | $\varepsilon = 0.8\%$, UTS = 151 MPa | In steel molding shape | [85] |
| Al−7.0 Si−0.7Mg−0.1 Ti (A357) | Without Sm | $\varepsilon = 1.6\%$, UTS = 190 MPa | In graphite molding shape | [84] |
| Al−7.0Si−0.7Mg−0.1 Ti (A357) | 0.60 Sm | $\varepsilon = 3.3\%$, UTS = 215 MPa | In graphite molding shape | [84] |

by 68.2%, from 91.5 to 153.9 MPa, elongation to failure by 53.1%, from 0.49 to 0.75% (Fig. 8) [73]. At the same time, the size of primary silicon crystals decreased from 94 to 33 $\mu$m, and the form of lamellar associations was transformed into a three-dimensional faceted form. The silicon in the eutectic also changed from a coarse flake to a finer one. It can be noted from the results of studies that Ce, in terms of its effect on the structure of silicon, combines the effects of modification with strontium, which changes the structure of the eutectic, and modification with phosphorus, which affects the shape and size of primary crystals.

Similarly [69], where the influence of the combination of elements Ce and La on the hypoeutectic industrial alloy A357 was studied and dispersed particles of intermetallic compounds were found, when ytterbium was added to the hypoeutectic alloy Al–Si, the chemical compound $Al_2Si_2Yb$ [75] in the form of dispersed particles, but ytterbium did not affect the lamellar shape of silicon and $\alpha$-aluminum dendrites [75,77].

The influence of yttrium (Y) on the structure of eutectic silicon in the industrial alloy A357 depends, as it is believed in the paper [80], on the mechanism of crystal modification, which varies depending on the cooling rate of the alloy. At low cooling rates (0.16°C/s), modification with yttrium causes an increase in the number of silicon nuclei in the melt and lowers the crystallization onset temperature. In the case of high speeds (3.2°C/s), yttrium promotes the accelerated growth of silicon crystals in the eutectic, facilitating the appearance of twins in growing crystals (twinning mechanism). In addition, yttrium in the A357 alloy lowers the nucleation temperature of primary $\alpha$-Al crystals, which leads to a decrease in the size of the dendrites of this phase [79]. In hypereutectic silumins, modification with yttrium promotes, as in the case of addition of Ce to the alloy, an improvement in the structure of primary and eutectic silicon and an increase in strength characteristics [81] (Fig. 9).

Modification of A356 alloy with gadolinium (Gd) affected the structure of both $\alpha$-Al primary dendrites and Si crystals in the eutectic. The authors [83] showed that the optimal content of Gd (0.2%) in combination with heat treatment causes the formation of intermetallic dispersed phases $GdAl_2Si_2$ and $\alpha$-$Al_5FeSi$ distributed in the Al-matrix and an increase in the hardness of the alloy.

The most significant effect of samarium (Sm) modification of an alloy with the composition Al–7% Si–0.7% Mg (357) is observed at 0.6% [84]. At such a concentration of samarium, the shape of some silicon crystals in the eutectic changes from lamellar to fibrous and the number of primary dendrites of the $\alpha$-Al- phase increases. A similar effect of samarium on the eutectic was also found in [85], where a study was made of the hypereutectic alloy Al–20% Si. In addition, the authors [85] found that the morphology of the primary silicon crystals changed from a rough lamellar form to a form in the shape of fine faceted crystals. In both papers, an increase in tensile strength and elongation to failure was noted when modifying Sm with an optimal amount of 0.6%. In the case of alloy 357, tensile strength changed from 180 to 215 MPa, and relative elongation from 1.7 to 3.3% with the addition of Sm. For silumin Al–20% Si, an increase in tensile strength from 103 to 153 MPa and elongation from 0.45 to 0.76% was observed.

The table presents the results of strength tests obtained in the papers considered in this review. In general, according to the results of modifying aluminum-based cast alloys with rare earth elements, it can be concluded that the modification of REM to some extent increases the strength of silumins with a simultaneous increase in plasticity and expands the possibilities of using such alloys in industry.

## Conclusion

The literature on the modification of hypoeutectic, eutectic and hypereutectic silumins with both conventional modifiers (strontium, phosphorus) and rare earth elements was analyzed, and a comparison was made of the structures and strength properties of modified Al–Si- alloys. Based on the results of the scientific research conducted in the literature, the following conclusions can be drawn.

Strontium and phosphorus are currently the most common silumin modifiers, including industrial ones. Strontium causes the grinding of eutectic silicon, the transformation of the eutectic structure into fine-fibered and improves the strength properties of products. At the same time, the addition of strontium to the alloy can lead to the formation of particles of the $Al_2Si_2Sr$ compound, which initiate the nucleation of pores. When phosphorus is introduced into the melt, an intermetallic compound AlP is formed, which initiates the intensive nucleation of primary silicon crystals. There is an increase in tensile strength and relative elongation. At the same time, phosphorus causes coarsening of silicon particles in the eutectic.

Rare earth elements form refractory chemical compounds (intermetallic compounds) with aluminum, silicon and alloying additives. Dispersed formations are formed, which contribute to a decrease in the temperature of the massive formation of eutectic nuclei or primary crystals. When silumin is modified with elements from the REM group, only europium makes it possible to completely change the shape of silicon crystals in the eutectic from coarse lamellar to thin rod.

In the review, based on the results of the analysis of literature data, methods are proposed for improving the mechanical properties of alloys modified with strontium and phosphorus by heat treatment and additional modification with other elements, including rare earths.

The modification of the Al–Si melt has a significant potential for improving the functional properties of silumin. Thanks to the use of the considered modifiers based on REM elements, the possibilities of using industrial Al–Si- alloys in more severe operating conditions in machine units and mechanisms are expanded. Possessing an increased level of plasticity compared to standard alloys, casting blanks of modified silumins can be subjected to further thermomechanical processing to improve their properties and ensure the accuracy of the product shape.

For hypereutectic alloys with a eutectic structure obtained by directional solidification with a rate corresponding to the pairwise growth of the alloy components, modification with strontium makes it possible to obtain a submicrograin eutectic and can provide higher requirements for the quality of the alloys.

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## Conflict of interest

The author declares that he has no conflict of interest.

## References

[1] N.A. Belov, S.V. Savchenko, V.D. Belov. *Atlas mikrostruktur promyshlennykh siluminov: spravochnik* (MISiS, Moskva, 2009) (in Russian)

[2] M. Warmuzek. *Aluminum-Silicon Casting Alloys: an Atlas of Microfractographs* (ASM Intern., Novelty, OH, 2004)

[3] S.P. Nikanorov, V.N. Osipov, L.I. Regel. J. Mater. Engin. Perform. (JMEPEG), **28** (12), 7302 (2019). https://doi.org/10.1007/s11665-019-04414-3

[4] S.P. Nikanorov, L.I. Derkachenko, B.K. Kardashev, B.N. Korchunov, V.N. Osipov, V.V. Shpeizman. Phys. Solid State, **55** (6), 1207 (2013). https://doi.org/10.1134/S1063783413060255

[5] M.H. Abdelaziz, A.M. Samuel, H.W. Doty, S. Valtierra, F.H. Samuel. J. Mater. Res. Technol., **8** (2), 2255 (2019). https://doi.org/10.1016/j.jmrt.2019.03.003

[6] M. Colombo, E. Gariboldi, A. Morri. J. Alloys Compounds, **708**, 1234 (2017). https://doi.org/10.1016/j.jallcom.2017.03.076

[7] R. Haghayeghi, G. Timelli. Mater. Lett., **283**, 128779 (2021). https://doi.org/10.1016/j.matlet.2020.128779

[8] Ching-Yi Yang, Sheng-Long Lee, Cheng-Kuo Lee, Jing-Chie Lin. Wear, **261**, 1348 (2006). https://doi.org/10.1016/j.wear.2006.03.051

[9] S.A. Bagaber, T. Abdullahi, Z. Harun, N. Daib, M.H.D. Othman. Arab. J. Sci Eng., **42**, 4559 (2017). https://doi.org/10.1007/s13369-017-2553-8

[10] L. Liu, A.M. Samuel, F.H. Samuel, H.W. Doty, S. Valtierra. J. Mater. Sci., **39**, 215 (2004). https://doi.org/10.1023/B:JMSC.0000007747.43275.34

[11] L.F. Mondolfo. *Aluminium Alloys: Structure and Properties* (London, Butterworths Ltd., 1976)

[12] V.S. Zolotorevskiy, N.A. Belov. *Metallovedeniye liteynykh alyuminiyevykh splavov* (MISIS, M., 2005) (in Russian)

[13] H. Okamoto. J. Phase Equil. Diff., **28**, 229 (2007). https://doi.org/10.1007/s11669-007-9038-5

[14] N.P. Lyakishev. *Diagrammy sostoyaniya dvoynykh metallicheskikh sistem.* Spravochnik v 3 t. Pod obshchey red. N.P. Lyakishev. (Mashinostroyeniye, M., 2001), v. 3, p. 1 (in Russian)

[15] A.I. Belyayev, O.A. Romanova, O.S. Bochvar, K.S. Pokhodayev, N.N. Buynov, N.A. Loktionova, I.N. Frilyander. *Alyuminiyevyye splavy. Metallovedeniye alyuminiya i yego splavov.* Spravochnoye rukovodstvo. (Metallurgiya, M., 1971) (in Russian)

[16] N.A. Belov, S.V. Savchenko, A.V. Khvan. Fazovyy sostav i struktura siluminov (MISIS, M, 2007) (in Russian)

[17] M. V. Mal'tsev. *Metallografiya promyshlennykh tsvetnykh metallov i splavov* (Metallurgiya, M., 1970) (in Russian)

[18] Song-Mao Liang, R. Schmid-Fetzer. Acta Mater., 72, 41 (2014). https://doi.org/10.1016/j.actamat.2014.02.042

[19] S. Wang, M. Fu, X. Li, J. Wang, X. Su. J. Mater. Proc. Technol., **255**, 105 (2018). https://doi.org/10.1016/j.jmatprotec.2017.12.008

[20] H. Liao, W. Huang, Q. Wang, F. Jia. J. Mater. Sci. Technol., **30** (2), 146 (2014). https://doi.org/10.1016/j.jmst.2013.05.003

[21] F. Cao, Y. Jia, K.G. Prashanth, P. Ma, J. Liu, S. Scudino, F. Huang, J. Eckert, J. Sun. Mater. Design, **74**, 150 (2015). https://doi.org/10.1016/j.matdes.2015.03.008

[22] Y.C. Lin, Shun-Cun Luo, J. Huang, Liang-Xing Yin, Xing-You Jiang. Mater. Sci. Engin. A, **725**, 530 (2018). https://doi.org/10.1016/j.msea.2018.04.049

[23] V. Vijeesh, K. Narayan Prabhu. Trans. Indian Inst. Met., **67** (1), 1 (2014). https://doi.org/10.1007/s12666-013-0327-x

[24] S.M. Miresmaeili, J. Campbell, S.G. Shabestari, S.M.A. Boutorabi. Metall. Mater. Trans. A, **36**, 2341 (2005). https://doi.org/10.1007/s11661-005-0106-3

[25] K. Gammer, E. Ogris, P.J. Uggowitzer, H. Hutter. Microchim. Acta, **141**, 23 (2003). https://doi.org/10.1007/s00604-002-0908-6

[26] S.D. Mc Donald, K. Nogita, A.K. Dahle. J. Alloys and Compounds **422**, 184 (2006). https://doi.org/10.1016/j.jallcom.2005.11.070

[27] K.F. Kobayashi, L.M. Hogan. J. Mater. Sci., **20** (6), 1961 (1985). https://doi.org/10.1007/BF01112278

[28] E.A. Boom. *Priroda modifitsirovaniya splavov tipa silumin.* (Metallurgiya, M.,1972) (in Russian)

[29] S. Moniri, A.J. Shahani. J. Mater. Res., **34** (1), 20 (2019). https://doi.org/10.1557/jmr.2018.361

[30] Sang-Soo Shin, Eok-Soo Kim, Gil-Yong Yeom, Jae-Chul Lee. Mater. Sci. Engin. A, **532**, 151 (2012). https://doi.org/10.1016/j.msea.2011.10.076

[31] M. De Giovanni, J.M. Warnett, M.A. Williams, P. Srirangam. J. Alloys and Compounds. **727** (12), 353 (2017). https://doi.org/10.1016/j.jallcom.2017.08.146

[32] H. Liao, Yu Sun, G. Sun. Mater. Sci. Engin. A, **335**, 62 (2002). https://doi.org/10.1016/S0921-5093(01)01949-9

[33] P. Srirangam, S. Chattopadhyay, A. Bhattacharya, S. Nag, J. Kaduk, S. Shankar, R. Banerjee, T. Shibata. Acta Materialia, **65**, 185 (2014). https://doi.org/10.1016/j.actamat.2013.10.060

[34] M. Timpel, N. Wanderka, R. Schlesiger, T. Yamamoto, N. Lazarev, D. Isheim, G. Schmitz, S. Matsumura, J. Banhart. Acta Materialia, **60** (9), 3920 (2012). https://doi.org/10.1016/j.actamat.2012.03.031

[35] A.K. Dahle, K. Nogita, J.W. Zindel, S.D. Mc Donald, L.M. Hogan. Metallurg. Mater. Transact. A, **32** (4), 949 (2000). https://doi.org/10.1007/s11661-001-0352-y

[36] İ. Öztürk, G.H. Ağaoğlu, E. Erzi, D. Dışpınar, G. Orhan. J. Alloys and Compounds, **763**, 384 (2018). https://doi.org/10.1016/j.jallcom.2018.05.341

[37] G. Liu, G. Li, A. Cai, Z. Chen. Materials and Design, **32** (1), 121 (2011). https://doi.org/10.1016/j.matdes.2010.06.027

[38] V.N. Osipov, Yu.A. Fadin, S.P. Nikanorov. Technical Physics, **65** (12), 1981 (2020). https://doi.org/10.1134/S1063784220120191

[39] El-Benawy Talaat, F. Hasse. Mat. Trans., JIM, **41** (4), 507 (2000). https://doi.org/10.2320/matertrans1989.41.507

[40] M.H. Mulazimoglu, R.A.L. Drew, J.E. Gruzleski. Metallurgical Transactions: A, **20A** (3), 383 (1989). https://doi.org/10.1007/BF02653917

[41] A.I. Averkin, B.N. Korchunov, S.P. Nikanorov, V.N. Osipov. Tech. Phys. Lett., **42** (2), 201 (2016). https://doi.org/10.1134/S106378501602019X

[42] R. Haghayeghi, G. Timelli. Mater. Lett., **283** (3–4), 128779 (2021). https://doi.org/10.1016/j.matlet.2020.128779

[43] H. Yan, C. Zhu, Z. Wu, W. Gao. Mat. Trans., JIM, **61** (1), 181 (2020). https://doi.org/10.2320/matertrans.MT-M2019225

[44] L. Ceschini, A. Morri, A. Morri, A. Gamberini, S. Messieri. Mater. Design, **30** (10) 4525 (2009). https://doi.org/10.1016/j.matdes.2009.05.012

[45] R.Yu. Barkov, A.S. Prosviryakov, M.G. Khomutov, A.V. Pozdniakov. Phys. Metals Metallography, **122** (6), 614 (2021). https://doi.org/10.1134/S0031918X210 60028

[46] M. Zamania, L. Morini, L. Ceschini, S. Seifeddine. Mater. Sci. Engin. A, **693**, 42 (2017). https://doi.org/10.1016/j.msea.2017.03.084

[47] Z. Chen, H. Kang, G. Fan, J. Li, Y. Lu, J. Jie, Y. Zhang, T. Li, X. Jian, T. Wang. Acta Materialia, **120** (11), 168 (2016). https://doi.org/10.1016/j.actamat.2016.08.045

[48] R.Yu. Barkov, A.G. Mochugovskiy, M.G. Khomutov, A.V. Pozdniakov. Phys. Metals Metallography, **122** (2), 161 (2021). https://doi.org/10.1134/S0031918X21020022

[49] Wu Yuying, Liu Xiangfa, Jang Binggang, Huang Chuanzhen. Rare Metals, **29** (1), 62 (2010). https://doi.org/10.1007/s12598-010-0011-9

[50] H. Zhang, H. Duan, G. Shao, L. Xu. Rare Metals, **27** (1), 59 (2008). https://doi.org/10.1016/S1001-0521(08)60031-5

[51] Min Zuo, Xiangfa Liu, Qianqian Sun. J. Mater. Sci., **44**, 1952 (2009). https://doi.org/10.1007/s10853-009-3287-0

[52] Min Zuo, Kun Jiang, Xiangfa Liu. J. Alloys Compounds, **503** (2), L26 (2010). https://doi.org/10.1016/j.jallcom.2010.05.017

[53] V.K. Afanas'yev, S.A. Gladyshev, B.S. Yefimenko, S.M. Nikitenko, M.V. Popova, A.N. Prudnikov, A.A. Ruzhilo, M.N. Churik, A.V. Gorshenin. Porshnevyye siluminy. (Poligraf, Kemerovo, 2005) (in Russian)

[54] M.V. Glavatskikh, A.V. Pozdniakov, S.V. Makhov, V.I. Napalkov. Russ. J. Non-Ferrous Metals, **55** (5) 450 (2014) https://doi.org/10.3103/S1067821214050095

[55] A.V. Pozdniakov, M.V. Glavatskikh, S.V. Makhov, V.I. Napalkov. Mater. Lett., **128**, 325 (2014). http://dx.doi.org/10.1016/j.matlet.2014.04.068

[56] Min Zuo, D. Zhao, X. Teng, H. Geng, Z. Zhang. Mater. Design, **47** (5), 857 (2013). https://doi.org/10.1016/j.matdes.2012.12.054

[57] M. Faraji, I. Todd, H. Jones. Metall. Mater. Transactions A, **40** (7), 1710 (2009). https://doi.org/10.1007/s11661-009-9842-0

[58] Yu-Chih Tzeng, Chih-Ting Wu, Hui-Yun Bor, Jain-Long Horng, Mu-Lin Tsai, Sheng-Long Lee. Mater. Sci. Engin. A, **593**, 103 (2014). https://doi.org/10.1016/j.msea.2013.11.039

[59] M. Kim, Y. Hong, H. Cho. Met. Mater. Intern., **10** (6), 513 (2004). https://doi.org/10.1007/BF03027412

[60] M. Kim. Met. Mater. Intern., **13** (2), 103 (2007). https://doi.org/10.1007/BF03027559

[61] A. Muhammad, C. Xu, W. Xuejiao, S. Hanada, H. Yamagata, Li R. Hao, Ma Chaoli. Mater. Sci. Engin. A, **604**, 122 (2014). https://doi.org/10.1016/j.msea.2014.03.005

[62] J.H. Li, X.D. Wang, T.H. Ludwig, Y. Tsunekawa, L. Arnberg, J.Z. Jiang, P. Schumacher. Acta Mater., **85**, 153 (2015). https://doi.org/10.1016/j.actamat.2014.10.064

[63] F. Mao, G. Yan, Z. Xuan, Z. Cao, T. Wang. J. Alloys Compounds, **650**, 896 (2015). https://doi.org/10.1016/j.jallcom.2015.06.266

[64] Q. Li, T. Xia, Y. Lan, P. Li, L. Fan. Mater. Sci. Eng. A, **588**, 97 (2013). https://doi.org/10.1016/j.msea.2013.09.017

[65] Z.M. Shi, Q. Wang, G. Zhao, R.Y. Zhang. Mater. Sci. Eng. A, **626**, 102 (2015). https://doi.org/10.1016/j.msea.2014.12.062

[66] Xing Pengfei, Gao Bo, Zhuang Yanxin, Liu Kaihua, Tu Ganfeng. J. Rare Earths, **28** (6), 927 (2010). https://doi.org/10.1016/S1002-0721(09)60222-2

[67] Q. Zheng, L. Zhang, H. Jiang, J. Zhao, J. He. J. Mater. Sci. Technol., **47**, 142 (2020). https://doi.org/10.1016/j.jmst.2019.12.021

[68] V. Vijeesh, K. Narayan Prabhu. *Light Metals 2015*, ed. by M. Hyland (Springer, Cham, Switzerland, 2016), p. 403. https://doi.org/10.1007/978-3-319-48248-4_67

[69] W. Jiang, Z. Fan, Y. Dai, C. Li. Mater. Sci. Engin. A, **597**, 237 (2014). https://doi.org/10.1016/j.msea.2014.01.009

[70] E. Aguirre-Dela Torre, R. Pérez-Bustamante, J. Camarillo-Cisneros, C.D. Gómez-Esparza, H.M. Medrano-Prieto, R. Martínez-Sánchez. J. Rare Earths., **31** (8), 811 (2013). https://doi.org/10.1016/S1002-0721(12)60363-9

[71] Yu-Chou Tsai, Cheng-Yu Chou, Sheng-Long Lee, Chih-Kuang Lin, Jing-Chie Lin, S.W. Lim. J. Alloys Compounds, **487**, 157 (2009). https://doi.org/10.1016/j.jallcom.2009.07.183

[72] S. Kores, M. Vonchina, B. Kosec, P. Mrvar, J. Medved. Mater. Technol., **44** (3), 137 (2010).

[73] Q. Li, T. Xia,Y. Lan, W. Zhao, L. Fan, P. Li. J. Alloys Compounds, **562**, 25 (2013). https://doi.org/10.1016/j.jallcom.2013.02.016

[74] E.M. Elgallad, M.F. Ibrahim, H.W. Doty, F.H. Samuel. Philos. Magaz., **98**, 1337 (2018). https://doi.org/10.1080/14786435.2018.1435917

[75] J.H. Li, S. Suetsugu, Y. Tsunekawa, P. Schumacher. Metallurg. Mater. Trans., A, **44** (2), 669 (2013). https://doi.org/10.1007/s11661-012-1410-3

[76] Q. Li, J. Li, B. Li, Y. Zhu, D. Liu, Y. Lan, S. Wang. J. Mater. Engin. Perform., **27** (7), 3498 (2018). https://doi.org/10.1007/s11665-018-3456-x

[77] B. Li, H. Wang, J. Jie, Z. Wei. J. Alloys Compounds, **509**, 3387 (2011). https://doi.org/10.1016/j.jallcom.2010.12.081

[78] Z. Hu, Z. Dong, Z. Yin, H. Yan, J. Tian, H. Xie. J. Rare Earths, **36**, 662 (2018). https://doi.org/10.1016/j.jre.2017.12.007

[79] G. Mao, S. Liu, Z. Wu, C. Zhu, W. Gao. Mater. Lett., **271**, 127795 (2020). https://doi.org/10.1016/j.matlet.2020.127795

[80] G. Mao, H. Yan, C. Zhu, Z. Wu, W. Gao. J. Alloys Compounds, **806**, 909 (2019). https://doi.org/10.1016/j.jallcom.2019.07.107

[81] Q. Li, B. Li, J. Li, Y. Zhu, T. Xia. Mater. Sci. Engin. A, **722**, 47 (2018). https://doi.org/10.1016/j.msea.2018.03.015

[82] K. Nogita, S. D. McDonald, A. K. Dahle. Mater. Transact., **45** (2), 323 (2004). https://doi.org/10.2320/matertrans.45.323

[83] Shi Zhiming, Wang Qiang, Shi Yuting, Zhao Ge, Zhang Ruiying. J. Rare Earth, **33**, 1004 (2015). https://doi.org/10.1016/S1002-0721(14)60518-4

[84] Qiu Hongxu, Yan Hong, Hu Zhi. J. Alloys Compounds, **567**, 77 (2013). https://doi.org/10.1016/j.jallcom.2013.03.050

[85] Q. Li, J. Li, B. Li, Y. Lan, T. Xia. Intern. J. Metalcast., **12**, 554 (2017). https://doi.org/10.1007/s40962-017-0193-0