Effect of iron and silicon on structure and properties of the Al – Ca – Cu – Mn casting alloys

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In this work, the effect of Fe and Si impurities on the structure and properties of alloys of the Al4Ca0.5CuMn system was studied. To determine the optimal concentration ranges of alloying and impurity elements, the phase composition was simulated in the Thermo-Calc software. The simulation results showed that the concentration of Mn is 0.8 wt.% can be considered as optimal in terms of forming a favorable structure and phase composition of the alloy with an increased content of Fe and Si up to 0.4 wt.% of each element. Smelting of model alloys of the Al4Ca0.5CuMnFeSi system with a Mn content of 0.7–0.8% and varying Fe content in the range up to 0.6 wt.% and Si up to 0.2 wt.%. with subsequent analysis of the cast structure by optical and scanning electron microscopy, it was possible to confirm the simulation results. The structure of the optimal composition of Al4Ca0.5Cu0.8Mn0.4Fe0.2Si alloy, adapted for smelting with the involvement of secondary raw materials, has a fine morphology with a size of eutectic intermetallic of ~ 4 microns. An increase in the proportion of Fe in the alloy of more than 0.4 wt.% leads to the appearance of coarse primary crystals of the Al6(Fe, Mn) phase. The alloy under study demonstrates a balanced set of casting and mechanical properties at the level of traditional silumins of type A356.0. The tensile strength is 180 MPa, the yield strength is 125 MPa, the elongation is 5.2%. The general appearance of the fracture structure is fibrous, which corresponds to the characteristics of favorable ductile fracture.

Key words: Al – Ca alloys, casting alloys, structure, phase composition, mechanical properties.
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Introduction

The development of the electric vehicle market has become one of the points of possible aluminum consumption growth. It is expected that part of the overall share of consumption in the automotive industry, namely increasing the share of aluminum castings, in particular large-size castings, will become one of the priority areas, thus ensuring a reduction in the labor intensity of assembly operations and a reduction in production costs, while reducing the weight characteristics of vehicles [1–7]. The weight characteristics, in turn, are decisive for the costs attributable to the batteries of an electric vehicle, regulating its range and charging speed, significantly determining the competitiveness of the vehicle [6, 7].

However, the full concept of affordability and eco-friendliness of an electric vehicle in terms of minimizing life-cycle CO_2 emissions needs to be ensured at the production stage. In the case of aluminum alloys, it is possible to achieve similar characteristics by involving a higher share of secondary raw materials in production and reducing the production cycle of the products [6–8]. Certain results in this direction are achieved in modernization of traditional casting alloys (silumines). One example of this approach is the UniCast alloy, which was developed to provide a closed cycle of recycled material involvement in production due to the alloy's resistance to Fe impurities. [9]. However, new alloys based on alternative alloying systems can compete with traditional alloys in solving these issues.

An actual solution of the last decade is the development of alloys based on new alloying systems, in particular on the basis of Al – Ca eutectics [10–26]. Alloys of this system are characterized simultaneously by high processability [10, 11], strength properties at room and elevated temperatures [13–14], corrosion resistance [15–17], which is primarily due to the fine structure and phase composition of the alloys. An important feature of these alloys is the formation of iron- and silicon-containing phases ($Al_{10}CaFe_2$, Al_2CaSi_2) of favorable morphology in the process of solidification [18–21], which makes it possible to perform smelting on the technical purity aluminum basis or to involve an increased share of secondary raw materials in production, significantly increasing the margin of finished products. However, the content of basic elements in secondary raw materials is characterized by a variety of concentrations of Fe, Si, Mn, Cu, Mg, Zn, which is significantly capable of both complicating the phase composition of alloys [22] and changing

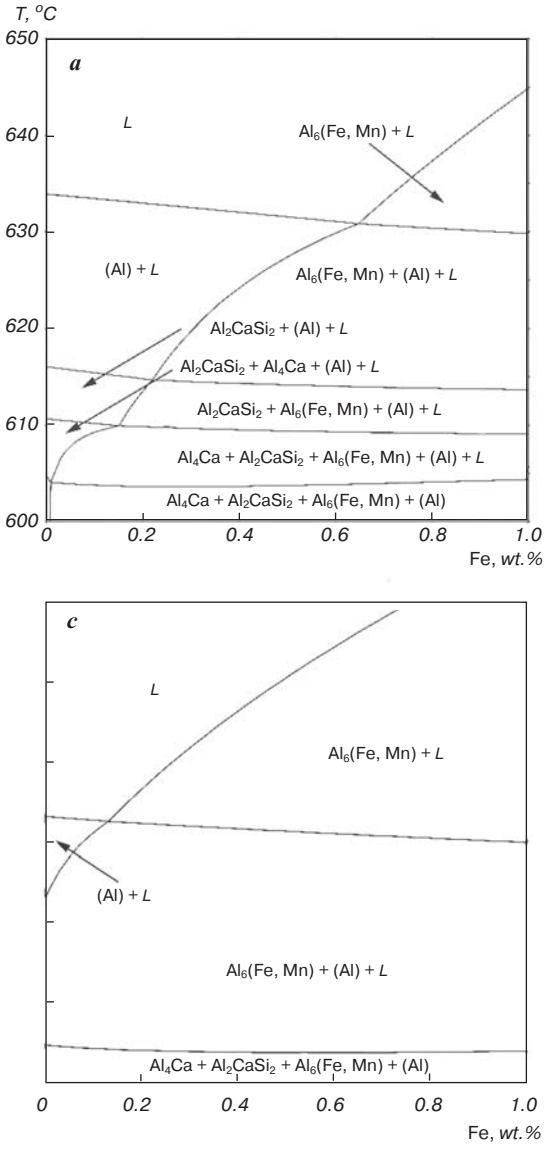

Fig. 1. Polythermal section of the Al4Ca0.5CuMnFeSi system: 0.5Mn0.2Si (*a*), 0.8Mn0.2Si (*b*), 1.0Mn0.2Si (*c*)

the admissible concentration ranges of the content of impurity elements.

The most representative examples of aluminocalcium alloys, on which processability and properties have been sufficiently studied, are alloys of Al – Ca – Cu – Mn system [12, 14, 23]. The phase composition of the base alloy Al3Ca0.5Cu1.5Mn includes the eutectic phase (Al, Cu)$_4$Ca, formed as a result of the characteristic dissolution of Cu in the aluminocalcium intermetallides Al_4Ca [12, 23], the phase $Al_{10}CaMn_2$ [24, 25], as well as the manganese-doped solid solution. Such phase composition at varying the volume fraction of second phases allows to achieve properties comparable to those of traditional silumin in the as-cast state, or to the level of 6xxx series alloys in the deformed state (without homogenization and hardening) [12, 14]. However, to develop the potential of these alloys for industrial applications, it is necessary to evaluate the influence of Fe and Si on the structure, phase composition and properties of the alloys.

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Methodology of the experiment

Preparation of model alloys of Al4Ca0.5CuMnFeSi system was carried out in Plavka.Pro PP-10 resistance furnace in graphite chamotte crucible. As charge materials were used: aluminum A99 (GOST 11069–2019), metallic calcium 98.5% (TU 083.5.314–94), copper M1 99.9% Cu (GOST 859–2014), silicon Kr00 (GOST 2169–69), ligatures Al–20%Mn (GOST 53777–2010), Al – 10%Fe (GOST P 53777–2010). The actual chemical composition of the experimental alloys is given in **Table 1**.

The preliminary phase analysis of the system and the choice of composition of the experimental alloys were carried out on the basis of thermodynamic calculations made with the help of Thermo-Calc software and TTAL 5 database.

The microstructure of the samples was investigated by optical microscopy (OM, Olympus GX41) and scanning electron microscopy (SEM, TESCAN VEGA 3) methods.

Qualitative assessment of the propensity of alloys to form hot cracks was carried out by determining the minimum diameter of a successfully cast pencil sample

Table 1
Chemical composition of experimental alloys

Alloy	Element content in the alloy, wt. %					
	Ca	Cu	Mn	Fe	Si	Al
Al4Ca0.5Cu0.8Mn	3.9	0.6	0.9	–	–	Base
Al4Ca0.5Cu0.8Mn0.2Fe0.2Si	4.0	0.5	0.8	0.2	0.2	Base
Al4Ca0.5Cu0.8Mn0.4Fe0.2Si	3.9	0.5	0.7	0.35	0.2	Base
Al4Ca0.5Cu0.8Mn0.6Fe0.2Si	3.9	0.5	0.8	0.6	0.3	Base

determined by visual inspection of the integrity (presence of cracks) of the sample after casting and removal from the metal mould.

The mechanical properties of the samples in the as-cast state were determined by measuring Vickers hardness on a DUROLINE MH-6 machine (load 1 H, dwell time 10 s), as well as by performing uniaxial tensile tests on a Zwick/Roll Z250 testing machine.

Data visualization and analysis were performed in the Anaconda IDE using the libraries pandas, searborn, matplotlib.

Results and disscission

To establish the permissible concentration ranges of the considered alloying and impurity elements, calculations were performed in Thermo-Calc (TTAL 5 database). The results showed **(Fig. 1)** that the presence of Fe and Si in Al4Ca0.5CuMn alloys significantly regulates the allowable Mn content. The previously considered Mn concentrations in the range of 1–1.5 wt.% for model alloys Al4Ca0.5CuMn [12, 14], smelted on pure components without impurity elements, are irrelevant, and lead in the presence of Fe to the formation of primary crystals of Al_6(Fe, Mn) phase in the process of solidification. Calculations show that an increase in manganese content in the concentration range of 0.5-1 wt.% leads to a decrease in the admissible Fe content from 0.6 to 0.1 wt.%. Moreover, the presence of Si in the amount of 0.2–0.4 wt.% does not significantly affect the pattern of phase transformations, which is also confirmed by the data [16]. Thus, it can be assumed that the concentration of Mn 0.8 wt.% can be considered as the maximum in the formation of favorable structure and phase composition of the alloy at the content of Fe and Si up to 0.4 wt.% of each element.

To confirm the calculated data, a number of laboratory experiments were carried out, consisting in melting alloys of the Al4Ca0.5CuMnFeSi system at the Mn content of 0.7–0.8 wt.% and varying the Fe content in the range up to 0.6 wt. % and Si content up to 0.2 wt.%.

Microstructural analysis (MA) of multicomponent alloys **(Fig. 2)** revealed that the alloys in the as-cast state have a typical pre-eutectic structure. However, an increase in Fe concentration above 0.4 wt.% leads to the appearance of crystals of unfavorable morphology during the solidification process.

More detailed SEM analysis **(Fig. 3)** showed that the structure of the alloy of optimal composition Al4Ca0.5Cu0.8Mn0.4Fe0.2Si, adapted for smelting with the involvement of secondary raw materials, has a thin morphology with the size of eutectic intermetallides not more than 4 microns. The pre-eutectic structure is formed by dendrites of aluminum solid solution and aluminocalcium

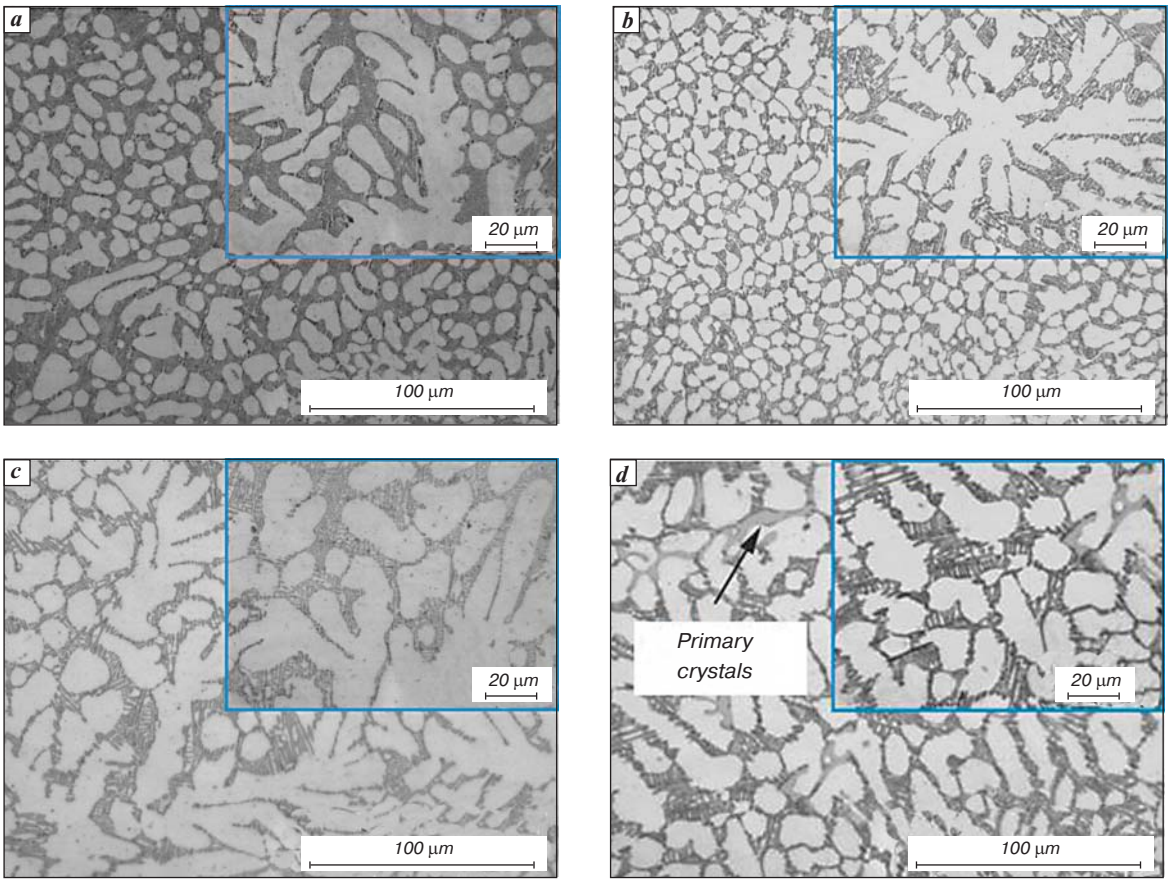

Fig. 2. Microstructures of alloys of the Al3Ca0.5Cu0.8MnFeSi system in the as-cast state: 0Fe0Si (*a*), 0.2Fe0.2Si (*b*), 0.4Fe0.2Si (*c*), 0.6Fe0.2Si (*d*)

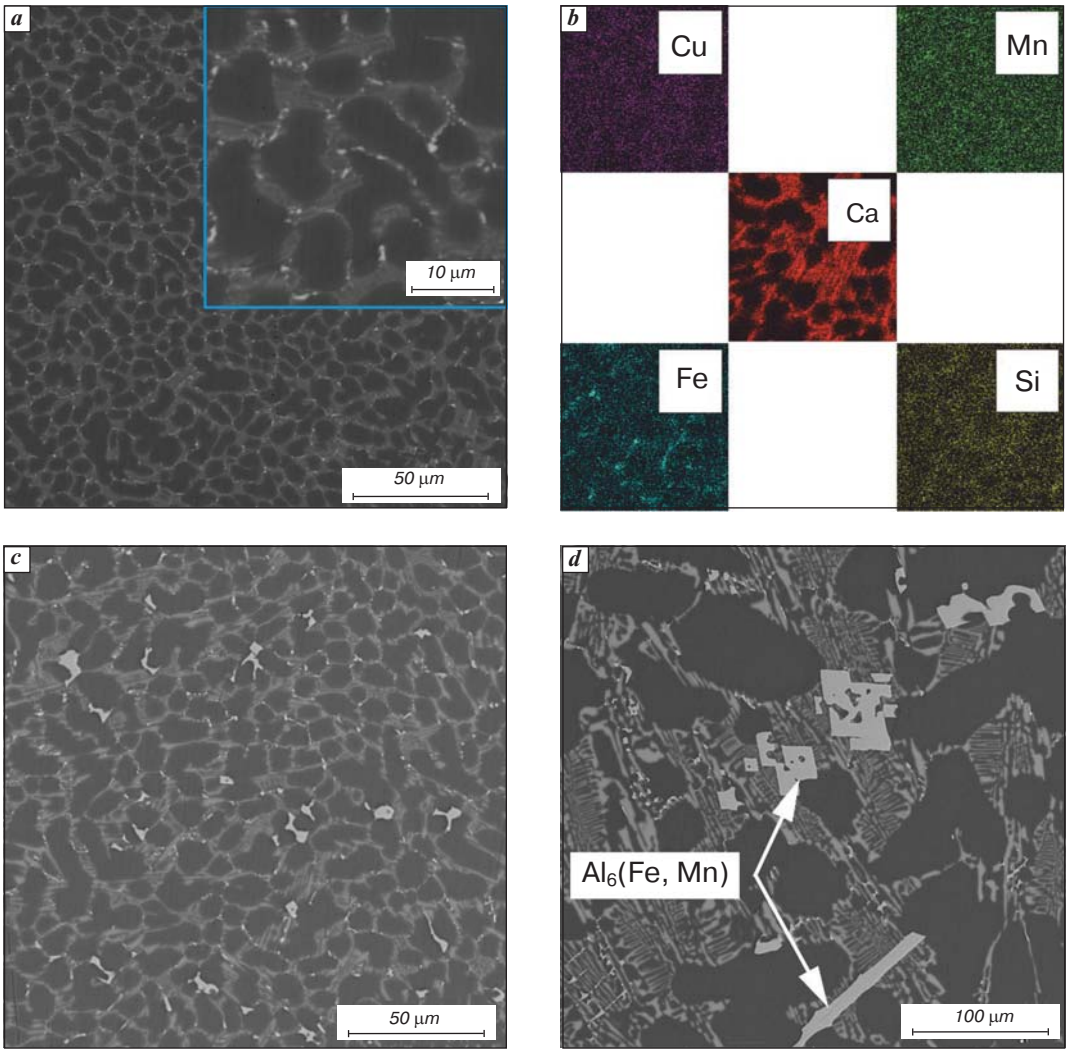

Fig. 3. Microstructure of Al3Ca0.5Cu0.8Mn0.4Fe0.2Si alloy in the as-cast state (*a*) and element distribution map (*b*); microstructure of Al3Ca0.5Cu0.8Mn0.6Fe0.2Si alloy in the as-cast (*c*) and slowly cooled state (*d*)

eutectic ((Al) + (Al, Cu)$_4$Ca). Manganese, according to the MRSA results, up to 0.4 wt.% is included in the aluminum solid solution, while the remainder is distributed in the eutectic [12, 14]. The coarse crystals observed with increasing iron content are identified as Al$_6$(Fe,Mn) phase (according to the MRSA results 6.8 at.% Fe, 6.8 at.% Mn, 86.2 at.% Al), which is consistent with the calculated data.

The propensity of the alloys of the Al4Ca0.5Cu0.8××MnFeSi system to hot crack was evaluated using pencil test samples. The experimental alloys showed a slight increase in hot cracking propensity **(Table 2)** compared to the grade A356 alloy.

During uniaxial tensile testing **(Table 3, Fig. 5)**, it was found that the mechanical properties of the Al4Ca0.5Cu0.8Mn0.4Fe0.2Si alloy were balanced and comparable to the properties of the base alloy without the impurity elements Fe and Si. Tensile strength is 180 MPa, yield strength — 125 MPa, relative elongation — 5.2 %.

The general appearance of the structure **(Fig. 4, *b*)** of the specimen fracture is fibrous. Twisted dimpled fracture, with traces of plastic deformation of the structure in the process of loading of the specimen corresponds to the characteristics of favorable ductile fracture.

Table 2
Comparative evaluation of casting properties of experimental alloys and traditional silomine

Alloy	Indicator of the tendency of alloys to hot cracks
Al4Ca0.5Cu0.8Mn	4
Al4Ca0.5Cu0.8Mn0.4Fe0.2Si	4
A356	3

Table 3
Mechanical properties of alloys of Al4Ca0.5Cu0.8MnFeSi system

Alloy	Hardness, HV	σ_T, MPa	$\sigma_{0.2}$, MPa	δ, %
Al4Ca0.5Cu0.8Mn	54	188 ± 3	132 ± 6	5.7 ± 0.4
Al4Ca0.5Cu0.8Mn0.4Fe0.2Si	55	180 ± 5	125 ± 3	5.2 ± 0.3

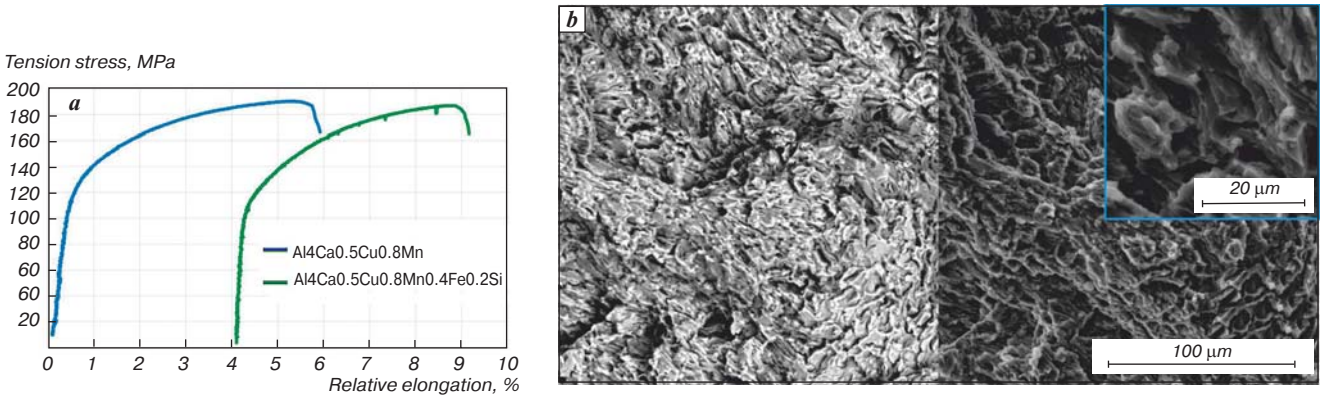

Fig. 4. Tensile diagram of alloys in the as-cast state (*a*) and fracture structure of Al4Ca0.5Cu0.8Mn0.4Fe0.2Si (*b*)

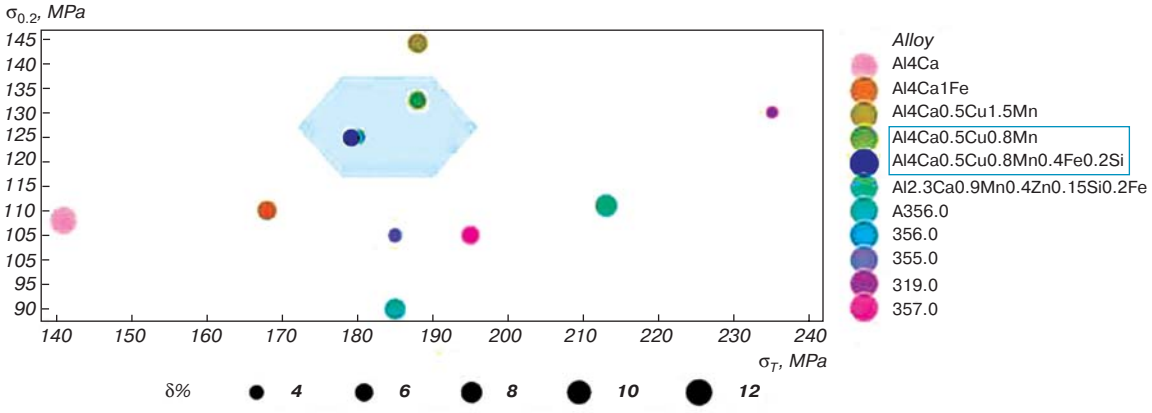

Fig. 5. Comparative analysis of mechanical properties of alumina-calcium alloys and traditional silumin in the as-cast state [12, 16, 21, 27]

The data of comparative analysis of properties **(Fig. 5)** show that alloying of model alloy Al_4Ca with elements contained in secondary raw materials (Cu, Mn, Fe, Si) allows to achieve a significant increase in the indices of mechanical properties. The tensile strength increases on average by 27 %, yield strength — by 15 %. At the same time, the ductile properties of the alloys are significantly reduced, which is accompanied by a decrease in relative elongation from 13 to 5.2 %. In the case of the studied alloy Al4Ca0.5Cu0.8Mn0.4Fe0.2Si, it can be stated that the decrease in Mn content due to the presence of Fe and Si, as well as the presence of additional impurity elements (Fe, Si) leads to a noticeable decrease in yield strength by an average of 13 % compared to the previously studied alloy Al4Ca0.5Ca1.5Mn [12] and a decrease in relative elongation by ~ 20 %.

However, the demonstrated range of mechanical properties of the new alloy allows it to compete with commercial alloys such as A356.0, 357.0, 355.0, 319.0 in the as-cast state, the properties of which are shown in **Fig. 5**.

Conclusion

Calculation and experimental analysis of phase composition, structure and properties of alloys of Al4Ca0.5Cu0.8MnFeSi system at Fe content up to 0.6 wt. % and Si content up to 0.2 wt. % in the as-cast state have been carried out. It is shown that the content of Fe up to 0.4 wt. % and Si up to 0.2 wt. % ensures the formation of a fine eutectic structure. The increase of Fe fraction in the alloy leads to the appearance of primary crystals of Al_6(Fe, Mn) phase of rough morphology.

The hot brittleness of Al4Ca0.5Cu1Mn0.4Fe0.2Si alloy is at the level of traditional silumines (A356).

Al4Ca0.5Cu1Mn0.4Fe0.2Si alloy demonstrates mechanical properties at the level of traditional silumines in the as-cast state. The tensile strength is 180 MPa, yield strength is 125 MPa, and relative elongation is 5.2 %. The general appearance of the fracture structure is fibrous, which corresponds to the characteristics of favorable ductile fracture.

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