



## The Influence of Manganese on Phase Formation in the Al-Fe-Si System

<sup>1</sup>\***ANDREYACHSHENKO Violetta**, PhD, Head of TLEP, Vi-ta.z@mail.ru,

<sup>1</sup>**TOLEUOVA Ainagul**, PhD, Docent, rymkul.ainagul@mail.ru,

<sup>1</sup>**ALINA Arailym**, PhD, Senior Lecturer, altynbekovna\_21@mail.ru,

<sup>1</sup>NPJSC «Abylkas Saginov Karaganda Technical University», N. Nazarbayev Avenue, 56, Karaganda, Kazakhstan,

\*corresponding author.

**Abstract.** Using the Thermo-Calc software package (version TCW8, TTAL 8.2 database), the Al-Fe-Si phase diagram was analyzed. A polythermal section of the Al-Fe-Si system with the addition of manganese as an alloying component was constructed and analyzed. Using composition curves, the optimal manganese concentration required for the formation of the  $\alpha$  ( $Al_8Fe_2Si$ ) and  $\alpha_{Mn}$  ( $Al_{15}Si_2Mn_4$ ) phases was determined. Also, using cooling curves, the boundaries of the appearance of primary crystals of Fe-containing phases were determined. Based on the results obtained, the possibility of assessing the efficiency of alloying the Al-Fe-Si system alloy with manganese is shown. Simulation results in the Thermo-Calc software package (version TCW8, database TTAL8.2) make it possible to predict phase transformation temperatures with great accuracy and thereby prescribe the optimal heat treatment regime. From a practical point of view, the complex of proposed studies will make it possible to scientifically substantiate and develop new technologies for the production and processing of semi-finished and finished products from aluminum-based alloys and functional materials with a given structure.

**Keywords:** aluminum alloy, phase, crystallization, polythermal cut, alloying element.

### Introduction

Today, the Republic of Kazakhstan has a high potential for the development of production, processing and production of finished

products from aluminum alloys of local content, subject to the updating of the modernization of current production or the creation of a new group of aluminum alloys. For this, all the

necessary resources are available, namely: the availability of raw materials, fairly cheap electricity, rising prices for metal.

One solution to this problem is the use of modern technological solutions to create a group of aluminum alloys from domestic raw materials.

The manufacture of products from aluminum alloys with improved performance characteristics is one of the current areas of modern materials science. One of the promising technologies for producing such alloys is additive technologies (layer-by-layer synthesis technology). This technology makes it possible to significantly speed up the solution of problems of technological preparation for the production of finished products, namely, it allows the use of deformable aluminum alloys to produce complex-profile products.

The Al-Fe-Si system has been widely studied for a long time [1-3]. This system is of considerable interest, since iron and silicon are the most common impurities in aluminum alloys. In aluminum alloys, these elements usually form hard and brittle ternary phases. This affects the chemical and mechanical properties [4]. Aluminum alloy is improved by changing the chemical composition and processing method [5]. Iron is the most common and harmful impurity element in aluminum alloys due to the formation of iron-containing intermetallic compounds, which negatively affect the mechanical properties of aluminum alloy components [6]. The most harmful intermetallic compound in Al-Si-Fe alloys is the  $\beta$ -phase ( $\beta$ -Al<sub>5</sub>SiFe) [7].  $\beta$ -Al<sub>5</sub>SiFe has a negative effect on the mechanical properties of the aluminum alloy, since it forms hard and brittle needles. To change the morphology of  $\beta$ -particles, transition metal additives (Mn, Cr, Zr, Ni, Be, V, Co, Ti) are used. Mn is most often used, since it is the most effective [8]. The addition of manganese affects the microstructural morphology, hardness, mechanical properties and fracture behavior [9]. Microchemistry has a significant effect on the recrystallization grain structure and texture after isothermal annealing of Al-Mn-Fe-Si alloys [10]. The addition of manganese stabilizes  $\alpha$ -particles due to the exchange of manganese atoms for iron atoms. This leads to a transition of the  $\beta$ -phase to a cubic morphology [11]. Increasing the Mn content improves the mechanical properties [12, 13]. Small additions of Mn prevent the formation of the  $\beta$ -phase, causing the formation of less harmful intermetallics. The Mn:Fe ratio up to 0.5 changes the morphology of  $\beta$ -particles from needle-shaped to polygonal in Al-Si alloys [14]. It is of interest to consider the influence of manganese on the phase composition of intermetallic alloys of the system. The aim of this

study is to determine the effect of manganese at different Mn:Fe ratios on phase formation in the Al-Fe-Si system with high content of both silicon and iron.

### Material and research methodology

At the initial stage, when choosing an aluminum alloy, it was decided to consider an Al-Fe-Si alloy with the addition of manganese as an alloying element. For this purpose, fundamental research was carried out on the optimal choice of manganese concentration and its effect on the formation of iron-containing phases responsible for high mechanical properties. Using Thermo-Calc (version TCW8, database TTAL 8.2) program a system based on aluminum was analyzed in order to determine the concentration limits for the appearance of primary crystals of Mn-containing phases.

### The results obtained and their discussion

The Al-Fe-Si-Mn diagram has a very complex structure and includes five Fe-containing phases. Conventionally, the section was divided into 3 concentration regions at which the maximum transition of phase  $\alpha$  (Al<sub>8</sub>Fe<sub>2</sub>Si) to phases  $\beta$  (Al<sub>9</sub>Fe<sub>2</sub>Si<sub>2</sub>) and  $\alpha_{Mn}$  (Al<sub>15</sub>Si<sub>2</sub>Mn<sub>4</sub>).

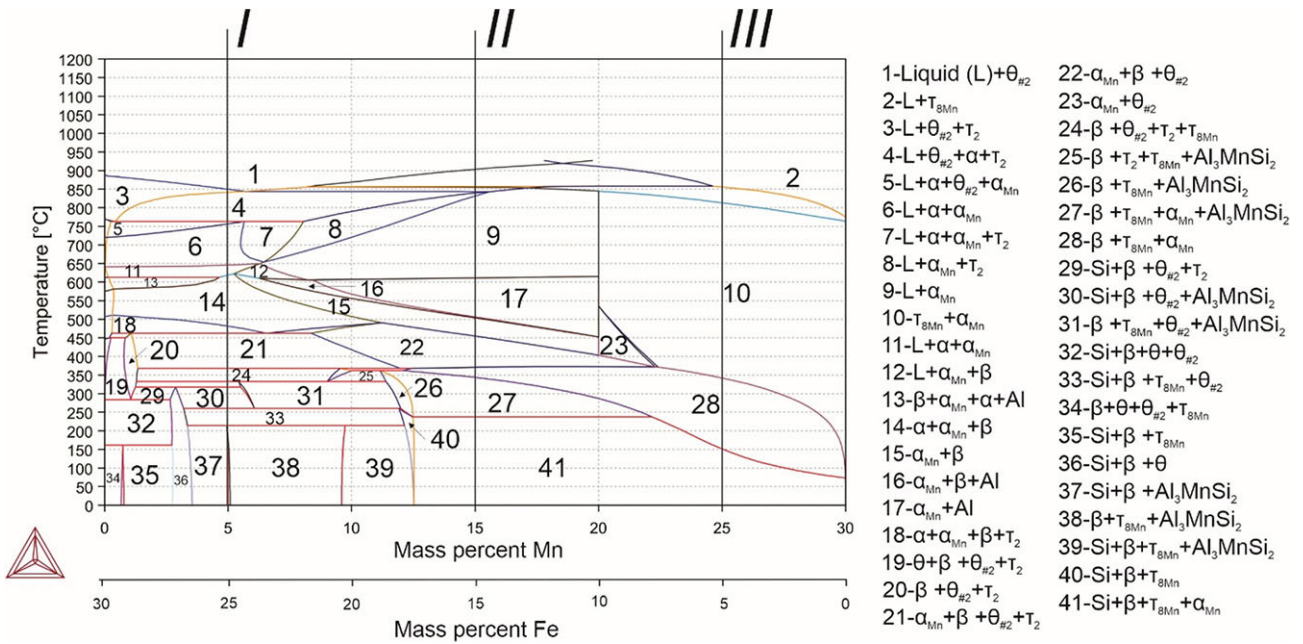
Crystallization of the alloy begins with the formation of the  $\theta_{\#2}$  (compound, %: 59,51Al, 39,6Fe, 0,82Si) phase and  $\tau_{8Mn}$  (compound, %: 51,05Al, 33,89Fe, 15,05Si).

Next, at a temperature of approximately 780°C, crystallization of phase begins  $\alpha$  (composition, %: 57,11Al, 32,55Fe, 10,33Si). Phase  $\alpha$  has a fairly narrow crystallization interval and its formation is suppressed by the formation of phase  $\beta$ , which is an extremely undesirable process, since the presence of this phase in the alloy significantly worsens the mechanical characteristics of the future alloy.

Phase  $\beta$  (Al<sub>9</sub>Fe<sub>2</sub>Si<sub>2</sub>) is the most harmful, reducing the mechanical properties of aluminum alloys. In particular, platelet or needle-shaped Al<sub>9</sub>Fe<sub>2</sub>Si<sub>2</sub> phases not only decompose the matrix, but also promote the formation of casting defects such as pores and shrinkage porosity.

These phases easily cause stress concentration and crack propagation, thereby becoming the weakest areas in Al-Si alloys. As can be seen from the section, it is impossible to completely get rid of the  $\beta$  phase (13-16, 19-22, 24-41 areas); moreover, this phase suppresses the  $\alpha$  phase, which is a very undesirable process.

At the same time, the formation of a phase is observed throughout the entire cross section of the section  $\alpha_{Mn}$  (5-18, 21-28 region). Phase Al<sub>15</sub>Mn<sub>3</sub>Si<sub>2</sub> (26,3%Mn, 8,9%Si), denoted in the same way as Al<sub>10</sub>Mn<sub>2</sub>Si, Al<sub>12</sub>Mn<sub>3</sub>Si, Al<sub>9</sub>Mn<sub>2</sub>Si<sub>1,8</sub>,  $\alpha$  (MnSi) or  $\alpha_m$ , exists in the region



**Figure 1 – Polythermal section of the Al-Fe-Si-Mn system with variable manganese and iron content**

of homogeneity 25-29%Mn, 8-13%Si. Phase  $\alpha_{Mn}$  has a skeletal shape and has a less harmful effect on the mechanical properties of the alloy compared to other phases. Primary crystals of this phase have the shape of equiaxed polyhedra; they often form clusters. This phase has a cubic lattice (the most favorable for further deformation of the alloy) (space group Pm3, 138 atoms in a unit cell) with parameter  $a = 1,265-1,268$  nm or 1,260 nm. The phase density is 3,55 g/cm<sup>3</sup>, and the microhardness at room temperature is 8,8 GPa. The solubility of manganese in the  $Al_{15}Mn_3Si_2$  phase is 0,7-0,8% [15].

It is also necessary to note the brittle phase  $\tau_{8Mn}$ , which precipitates throughout almost the entire region of the alloy, but in small quantities (within 1-2% with a manganese content of approximately 25%). It can be assumed that at such low concentrations this phase can precipitate either along the grain boundaries, or will precipitate in the form of individual dispersed particles and thereby have a positive effect as a strengthening additive.

Phase diagrams do not fully give us an idea of the relationship between the phases included in each area of the diagram, i.e. one region may consist of several phases, but the ratio of each individual phase in this region is unknown. Therefore, further composition curves for the Al-Fe-Si-Mn alloy with variable manganese and iron content were constructed. The construction of such composition curves makes it possible to predict the amount of a particular

phase at a certain temperature. Such curves are necessary in the future when developing heat treatment regimes.

Composition curves were constructed for manganese contents of 5, 15, 25%, respectively (Figure 2).

With a manganese content of 5% at a temperature of 780°C, the maximum content of the  $\alpha$  phase is formed within 38%, then decreases to 28% at a temperature of 480°C, further this phase is not observed. Those the region of existence of the  $\alpha$  phase is the temperature range within these limits. At manganese contents of 15% and 25%, no evolution of the  $\alpha$  phase is observed.

With a manganese content of 5%  $\beta$  ( $Al_9Fe-2Si_2$ ), the phase is formed at a temperature of 620°C and the transformation proceeds up to room temperature and its content reaches 82%. With a manganese content of 15%, phase separation occurs in the temperature range of 500°C and up to room temperature, the maximum content is approximately 58% at 200°C. With a manganese content of 25%, this phase has a fairly narrow crystallization range (400-50°C) with a maximum content of 18% at room temperature.

With a manganese content of 5%  $\alpha_{Mn}$  ( $Al_{15}Si_2Mn_4$ ), the phase is formed at a temperature of 820°C and the separation ends at a temperature of 380°C, the maximum content of this phase is observed at a temperature of 620°C, approximately 92%. With a manganese content of 15%, phase separation occurs in the

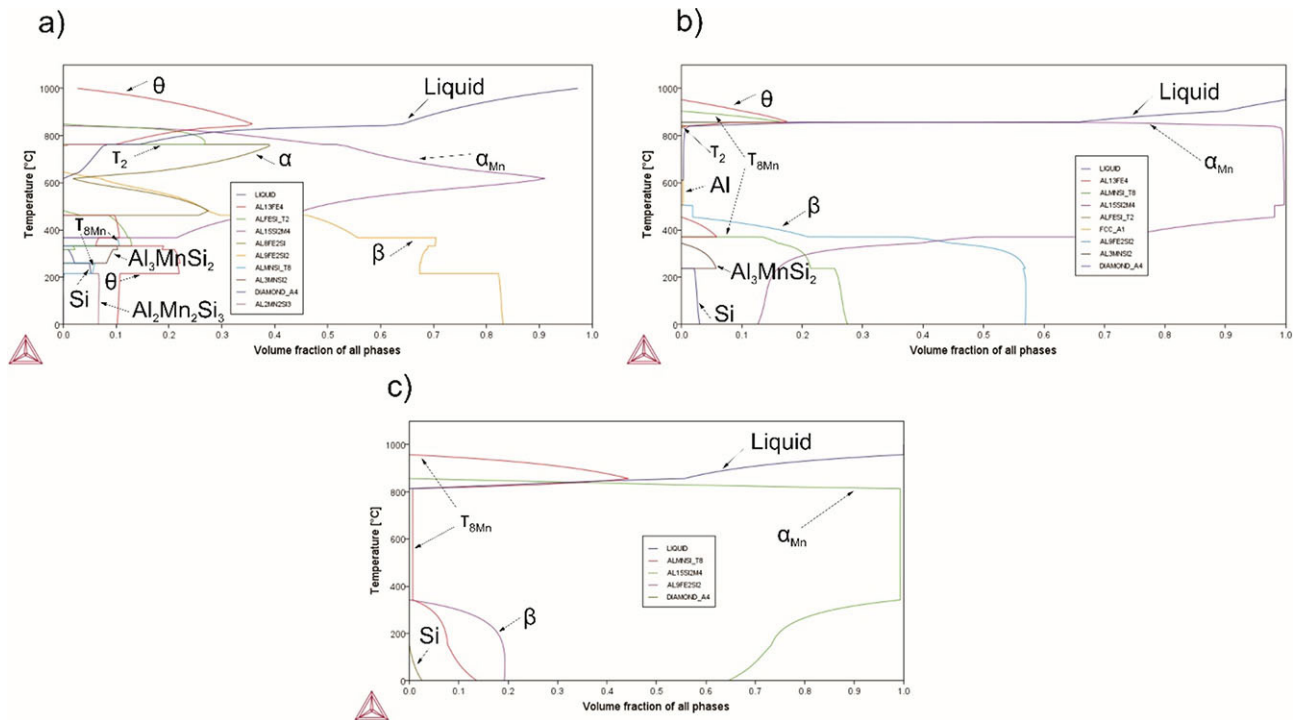


Figure 2 – Composition curves of the Al-Fe-Si-Mn alloy: a) with a manganese content of 5%; b) with a manganese content of 15%; c) with a manganese content of 25%

temperature range of 810°C and up to room temperature. Moreover, the maximum content of almost 100% is observed in the temperature range of 810-500°C; a further decrease in temperature reduces the concentration of this phase to 12%.

With a manganese content of 25%, this phase, on the contrary, has a fairly wide crystallization range (810-50°C), the maximum content of 98% is formed in the temperature range 790-380°C. A further decrease in temperature entails a decrease in the concentration of this phase to 64% at room temperature.

Thus, we can conclude that the  $\alpha$  phase is transformed into the  $\beta$  and  $\alpha_{Mn}$  phases in areas of elevated temperatures (810-380°C) with an optimal manganese content of 5%. A further increase in the manganese concentration is impractical, since it does not affect the formation of the  $\alpha$  phase.

Next, we plotted the dependence of the mass fraction of solid phases on temperature during crystallization of the Al-Fe-Si-Mn alloy, calculated using the Thermo-Calc program (version TCW8, TTAL8.2 database), shown in Figure 3. The dotted lines show nonequilibrium crystallization.

At a manganese content of 5 and 15%, crystallization of the  $\theta_{\#2}$  ( $Al_{13}Fe_4$ ) phase begins primarily from the liquid phase (Figure 3a, b). This phase is one of the most complex structures of intermetallic compounds, having a

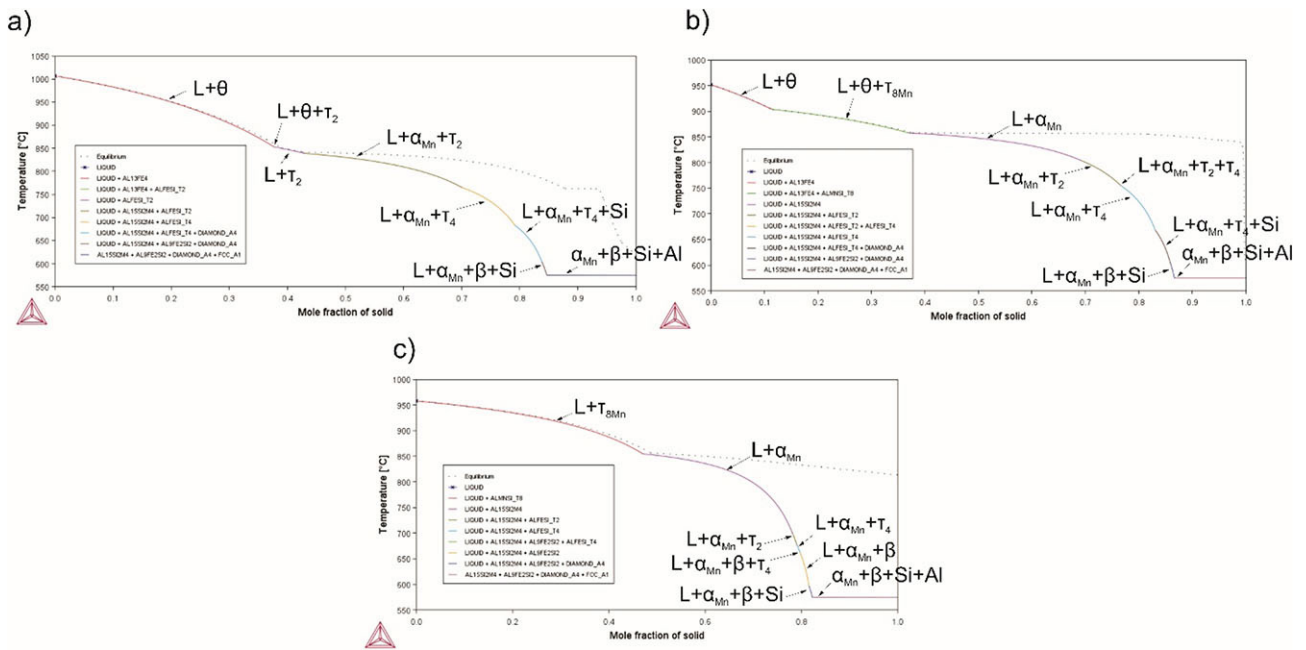
monoclinic unit cell. Silicon is added to prevent the formation of  $\theta_{\#2}$  phase particles and to ensure precipitation of the  $Al_8Fe_2Si$  phase into the alloy. Next comes the separation of the  $\alpha_{Mn}$  phase in parallel with the phases of the  $\tau$  composition. And just from this cooling curve it can be assumed that the  $\tau$  phases will precipitate in small quantities along the grain boundaries of the  $\alpha_{Mn}$  phase, thereby increasing the technological properties of the alloy with further plastic deformation.

At a manganese content of 25%, the  $\tau_{8Mn}$  phase (composition, %: 51.05Al, 33.89Fe, 15.05Si) primarily crystallizes, presumably in the form of dispersoids. Next comes the precipitation of the  $\alpha_{Mn}$  phase up to 550°C, and the crystallization of the  $\beta$  phase is minimal, which is most likely explained by the wide range of crystallization of the  $\alpha_{Mn}$  phase. Also in the structure there is the presence of structurally free silicon (crystallization range 600-550°C).

## Conclusions

Using the Thermo-Calc software package (version TCW8, TTAL8.2 database), an experimental calculation was carried out to determine the optimal concentration of manganese as an alloying element when producing an aluminum-based alloy.

The  $\alpha$  phase we are interested in has a fairly narrow crystallization range and its transformation is suppressed by the undesirable



**Figure 3 – Cooling curves of the Al-Fe-Si-Mn alloy: a) with a manganese content of 5%; b) with a manganese content of 15%; c) with a manganese content of 25%**

$\beta$  phase. Accordingly, it was decided to add manganese as an alloying additive in order to suppress the formation of the  $\beta$  phase. With a variable manganese content of up to 5%, the  $\alpha$  phase is completely transformed into the

$\alpha_{Mn}$  phase; it has a fairly wide crystallization range and helps suppress the formation of the  $\beta$  phase. A further increase in manganese concentration does not entail significant changes.

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### **Марганецтің Al-Fe-Si жүйесіндегі фаза түзілуіне әсері**

<sup>1</sup>\*АНДРЕЯЩЕНКО Виолетта Александровна, PhD, ИБСЗ меңгерушісі, Vi-ta.z@mail.ru,  
<sup>1</sup>ТОЛЕУОВА Айнагуль Рымкуловна, PhD, доцент, rymkul.ainagul@mail.ru,  
<sup>1</sup>АЛИНА Арайлым Алтынбековна, PhD, аға оқытушы, altynbekovna\_21@mail.ru,  
<sup>1</sup>«Әбілқас Сағынов атындағы Қарағанды техникалық университеті» КеАҚ, Н. Назарбаев даңғылы, 56, Қарағанды, Қазақстан,  
\*автор-корреспондент.

**Аңдатпа.** Thermo-Calc бағдарламалық пакетін (TCW8 нұсқасы, TTAL 8.2 дерекқоры) пайдалану арқылы Al-Fe-Si фазалық диаграммасы талданды. Легірлеуші компонент ретінде марганец қосылған Al-Fe-Si жүйесінің политемиялық бөлімі құрастырылды және талданды. Құрам қисықтарының көмегімен  $\alpha$  ( $Al_8Fe_2Si$ ) және  $\alpha_{Mn}$  ( $Al_{15}Si_2Mn_4$ ) фазаларының түзілуіне қажетті марганецтің оңтайлы концентрациясы анықталды. Сондай-ақ, салқындату қисықтарын пайдалана отырып, құрамында Fe бар фазалардың бастапқы кристалдарының пайда болу шекаралары анықталды. Алынған нәтижелер негізінде Al-Fe-Si жүйесінің қорытпасын марганецпен легірлеудің тиімділігін бағалау мүмкіндігі көрсетілген. Thermo-Calc бағдарламалық пакетіндегі модельдеу нәтижелері (TCW8, TTAL8.2 дерекқор нұсқасы) фазалық түрлендіру температураларын үлкен дәлдікпен болжауға және сол арқылы оңтайлы термиялық өңдеу режимін белгілеуге мүмкіндік береді. Тәжірибелік тұрғыдан алғанда, ұсынылған зерттеулер кешені алюминий негізіндегі қорытпалардан және берілген құрылымы бар функционалдық материалдардан жартылай фабрикаттар мен дайын өнімдерді өндіру мен өңдеудің жаңа технологияларын ғылыми негіздеуге және дамытуға мүмкіндік береді.

**Кілт сөздер:** алюминий қорытпасы, фаза, кристалдану, политемиялық кесу, легірлеуші элемент.

### **Влияние марганца на фазообразование в системе Al-Fe-Si**

<sup>1</sup>\*АНДРЕЯЩЕНКО Виолетта Александровна, PhD, руководитель ИЛИП, Vi-ta.z@mail.ru,  
<sup>1</sup>ТОЛЕУОВА Айнагуль Рымкуловна, PhD, доцент, rymkul.ainagul@mail.ru,  
<sup>1</sup>АЛИНА Арайлым Алтынбековна, PhD, старший преподаватель, altynbekovna\_21@mail.ru,  
<sup>1</sup>НАО «Карагандинский технический университет имени Абылкаса Сагинова», пр. Н. Назарбаева, 56, Караганда, Казахстан,  
\*автор-корреспондент.

**Аннотация.** С помощью программного комплекса Thermo-Calc (версия TCW8, база дан-

ных ТТАЛ 8.2) проанализирована фазовая диаграмма Al-Fe-Si. Построен и проанализирован политермический разрез системы Al-Fe-Si с добавлением марганца в качестве легирующего компонента. С помощью кривых состава определена оптимальная концентрация марганца, необходимая для образования фаз  $\alpha$  ( $Al_8Fe_2Si$ ) и  $\alpha_{Mn}$  ( $Al_{15}Si_2Mn_4$ ). Также с помощью кривых охлаждения определены границы появления первичных кристаллов Fe-содержащих фаз. На основе полученных результатов показана возможность оценки эффективности легирования сплава системы Al-Fe-Si марганцем. Результаты моделирования в программном комплексе Thermo-Calc (версия TCW8, база данных ТТАЛ8.2) дают возможность с большой точностью предсказывать температуры фазовых превращений и тем самым назначать оптимальный режим термической обработки. С практической точки зрения комплекс предлагаемых исследований позволит научно обосновать и разработать новые технологии получения и обработки полуфабрикатов и готовых изделий из сплавов на основе алюминия и функциональных материалов с заданной структурой.

**Ключевые слова:** алюминиевый сплав, фаза, кристаллизация, политермический разрез, легирующий элемент.

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