



REGULAR ARTICLE

Estimation of Al – Si System Melts Structure Transformations Possibility by Thermodynamic Data

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Currently, one of the promising methods of silumins mechanical properties improving is a melt thermal time treatment. Its effect is most often associated with changes in the structure during melt overheating and aging and with positive effect of these changes on alloy structure after crystallization. Although the fact that a certain close-order structure is realized in metal melts is now considered indisputable, the problem of transformations possibility in melts structure remains debatable. In previous studies, the thermodynamic parameters of Al–Si system melts were determined based on experimentally determined equilibrium compositions of the liquid and solid phases at different temperatures. The results of the analysis gave reason to assume that the structure of specified system melts may change, depending on the composition and temperature. In this paper, in order to further clarify the issue of the possibility of structural micro-heterogeneity and transformations of Al–Si system melts structure, the experimentally established values of components activities has been compared with the known calculated data obtained under the assumption of melts structure immutability. It has been established that at significantly higher than the liquidus temperature, the specified calculated parameters of the liquid phase are no longer able to adequately describe the experimentally established concentration dependences of Al–Si system melt components activities. This fact may indicate the possibility of changes in the structure of aluminum-silicon melts when the temperature changes. In addition, the results of analysis of experimental data on the concentration dependence of Al–Si system melt integral enthalpy of mixing do not contradict the idea of possibility of structure changing of this system melts when the silicon content in them changes. The results obtained provide grounds for further research of Al–Si system melt structure changes possibility using the analysis of temperature-concentration dependences of their associative composition and experimental research of temperature dependences of structurally sensitive properties (for example, electrical resistance).

**Keywords:** Partial molar free energy, Activity, Integral enthalpy of mixing.

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## 1. INTRODUCTION

The study of the physical and chemical characteristics of metal melts is an important part of modern metallurgy. However, many issues regarding the structure and properties of melts of metal systems require further research. The fact that a particular close-order structure is realized in metal melts is considered indisputable. However, the question of the possibility of transformations in the structure of melts remains debatable. Therefore, based on ideas about the micro-heterogeneity of melts of eutectic systems (on the example of the Al–Si system), an assessment of the thermodynamic probability of transformations of the structure of melts upon changing temperature and composition becomes relevant.

The liquidus line of a binary state diagram of the eutectic type can be presented as the result of the

mutual intersection of two "cigars", which appear when the equilibria between the liquid phase and each of the two solid solutions are considered independently [1]. Therefore, in [2], for the Al–Si system, these two types of equilibrium were considered independently (liquid phase – aluminum-based solid solution and liquid phase – silicon-based solid solution). According to the methodology [2], the thermodynamic parameters of the phases were determined by the experimentally established coordinates of the points that belong to the corresponding branches of the liquidus line and solidus lines. It should be noted that the data [2] were obtained only based on information about the equilibrium compositions of the phases. They are consistent with generally accepted information about the temperature-concentration dependences of the Gibbs potentials of the phases of the Al–Si system [3].

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It was established that when considering the equilibrium between the melt and the aluminum-based solid solution independently, the calculated values of the coefficients of the interaction parameter in the liquid phase coincide with the values obtained in [2] during the joint analysis of the equilibria between the melt and two solid solutions. At the same time, when independently considering the equilibrium between the melt and the silicon-based solid solution, two solutions were found for the parameters of the liquid phase. The first solution (the value of the coefficients of the interaction parameter in the liquid phase) entirely coincides with the solution obtained in [2] under the assumption that the structure of the melt does not depend on its composition and temperature. For the second solution, the calculated values of the interaction parameters in the liquid phase differ significantly from those obtained in the first case. Therefore, for these two cases, the concentration dependences of the free energy of the liquid phase are also significantly different. On the curve of the concentration dependence of the free energy of the liquid phase obtained from the equilibrium between the silicon-based solid solution and the melt, a noticeable upward bulge appears at the melting temperature of silicon. This indicates the structural heterogeneity of the melt. This gave reason to assume that the structure of melts of the Al-Si system may change depending on the composition and temperature [2].

To further clarify the issue of structural microheterogeneity and the possibility of structural transformations in melts of the Al-Si system, it seems appropriate to compare the experimentally established values of partial molar free energies and activities of components [3-9] with calculated data.

## 2. MATERIALS AND METHODS

Melts of pure components are chosen as standard states. Therefore, the expression of the temperature-concentration dependence of the free energy of the liquid phase takes the form:

$$G(x, T) = x(1-x)G_0(x, T) + R \cdot T \cdot [x \ln x + (1-x) \ln(1-x)] \quad (1)$$

where  $x$  – content of silicon in the phase, mol. particles;  $T$  – absolute temperature, K;  $x(1-x) \cdot G_0(x, T)$  – free energy of mixing in the liquid phase;  $R$  – universal gas constant.  $R = 8,31$  J/mol K;  $G_0(x, T)$  – temperature-concentration dependence of the interaction parameter in the liquid phase [2].

$$G_0(x, T) = -15046.6 + 0,759T + 4549.8 \cdot x - 3.33 \cdot T \cdot x + 4022 \cdot x^2 - 2.76 \cdot T \cdot x^2 \quad (2)$$

The paper calculated the concentration dependences of the partial molar free energies of the melt components at the corresponding temperatures from the expression for the free energy of the liquid phase:

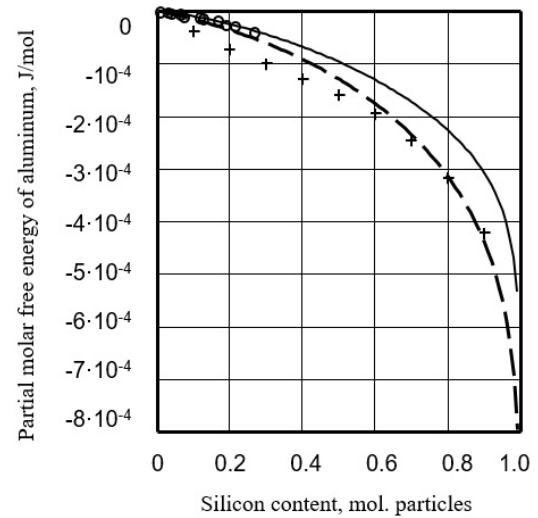
$$\begin{aligned} \text{for aluminum: } G_{Al}(x) &= G(x) - x \partial G(x) / \partial x \\ \text{for silicon: } G_{Si}(x) &= G(x) + (1-x) \partial G(x) / \partial x \end{aligned}$$

The concentration dependences of the activities of the components  $a_{Al}(x)$  and  $a_{Si}(x)$  at a given temperature of the melt were determined through their partial molar free energies:

$$\begin{aligned} a_{Al}(x) &= \exp(G_{Al}(x)/R \cdot T) \\ a_{Si}(x) &= \exp(G_{Si}(x)/R \cdot T). \end{aligned}$$

## 3. RESULTS AND DISCUSSION

There is a coincidence of the experimentally obtained values of activities and partial molar free energies of aluminum and silicon with those calculated during the analysis of the concentration dependences of the thermodynamic parameters of the melt components of the Al-Si system (Figs. 1-3).



**Fig. 1** – Concentration dependences of the partial molar free energy of aluminum in melts of the Al-Si system: — — — — calculated at a temperature of 827 °C; - - - - calculated at a temperature of 1427 °C; ○ – experimental data at a temperature 827 °C; + – experimental data at a temperature 1427 °C

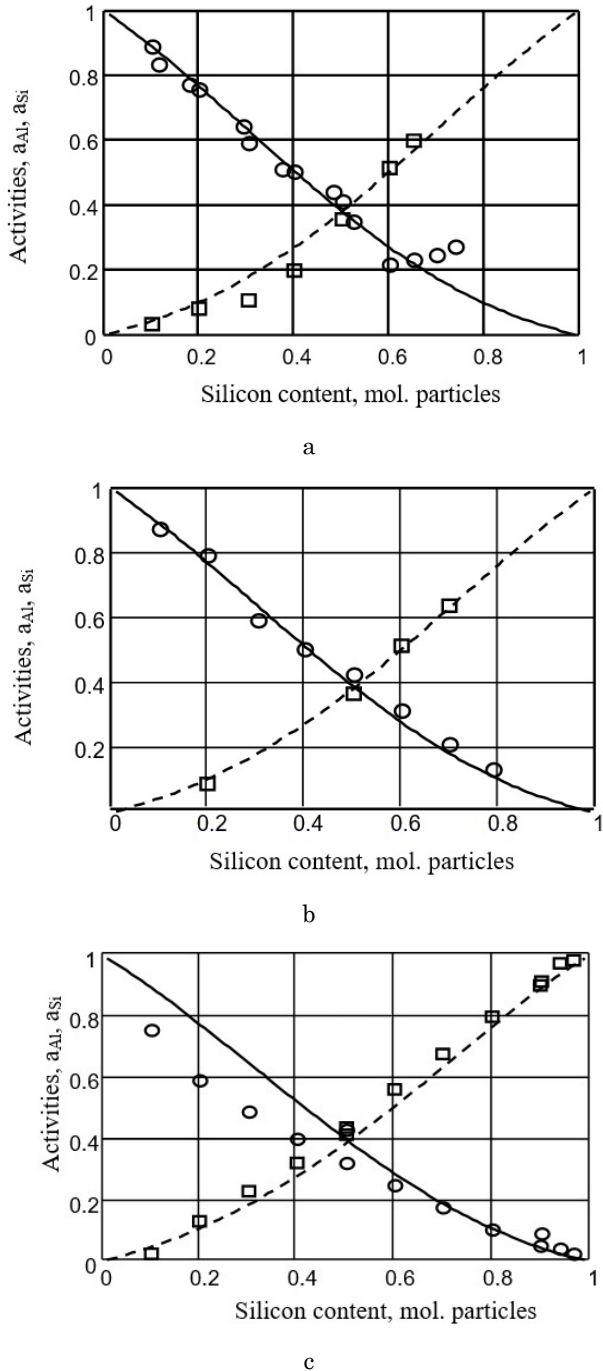
This coincidence is characteristic of the temperature range in which both branches of the liquidus line of the Al-Si system are determined (from the eutectic 577 °C to the melting temperature of silicon 1414 °C. In turn, at temperatures exceeding the melting temperature of silicon, there are significant discrepancies between the experimentally determined and calculated values (Fig. 2, 3).

The calculation model cannot adequately describe the liquid phase under conditions of significant overheating (over 1414 °C). That is, changes in the structure of melts of the Al-Si system, which occur during overheating above the liquidus temperature, are not taken into account by the adopted model. It should be especially emphasized that the calculation model (1) includes the temperature-concentration dependences of the mixing parameters in the phases.

In turn, thermodynamic parameters were calculated based on experimental data at equilibrium compositions of solid and liquid phases in the range of temperatures at which the liquidus line was experimentally determined. Therefore, the applied model can implicitly consider possible changes in the structure of melts in the specified temperature range. At the same time, the functions

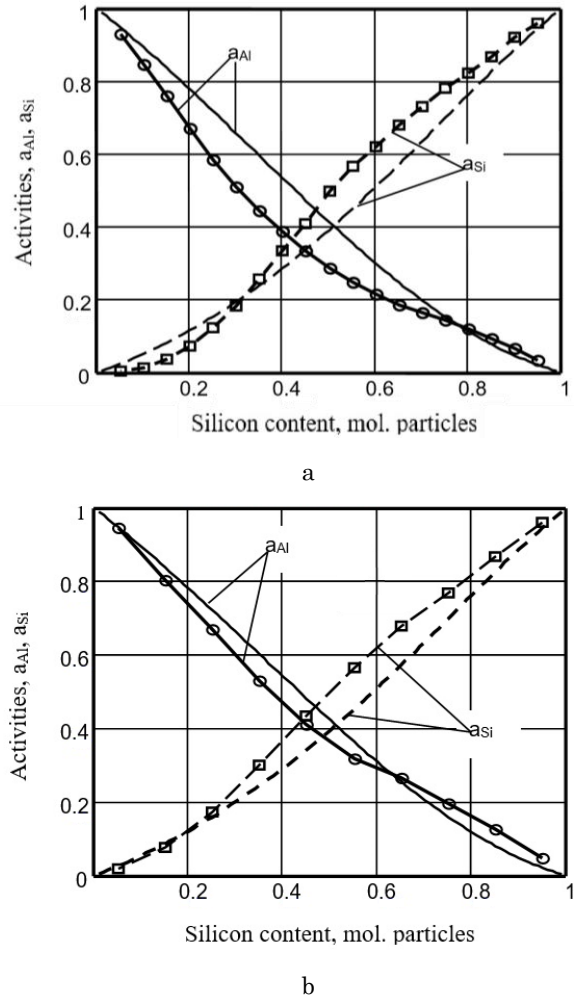
describing the thermodynamic parameters of the phases can level out sharp changes in the thermodynamic parameters of the phases.

Its apparent continuity is due to the initial assumption that there are no changes in the structure of the melt, as well as the natural desire when building a thermodynamic model to obtain functions in which at least the first derivative is continuous. It should be noted that sharp changes in thermodynamic parameters indicate changes in phase structures.



**Fig. 2** – Concentration dependence of activities aluminum and silicon in the melts of the system Al – Si: a – at a temperature 1200 °C; b – at a temperature 1300 °C; c – at a temperature 1427 °C; ○ – experimental values of aluminum activity; □ – experimental values of silicon activity

Experimentally determining the activity of melt components with continuous changes in composition and temperature (or at least with a relatively small step) is also impossible. Therefore, in this case, we obtain smooth dependencies as well. In any case, with a high degree of probability, it can be stated that the reason for the significant discrepancy between the experimental and calculated values of the activities of the components at temperatures exceeding 1414 °C is a change in the structure of the melt.



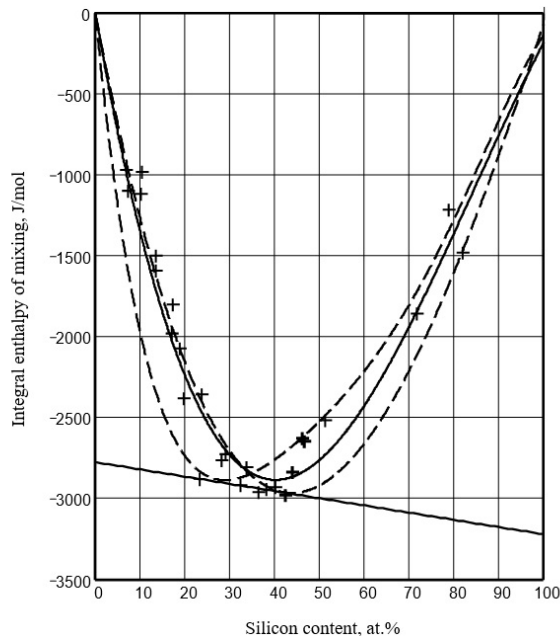
**Fig. 3** – Concentration dependences of the activities of aluminum and silicon in melts of the Al–Si system at temperatures 1700 °C (a) and 1900 °C (b)  
 ○ – experimentally determined values of aluminum activity; □ – experimentally determined values of silicon activity;  
 — — — activity of aluminum, calculated from the equilibrium compositions of the phases;  
 - - - - activity of silicon, calculated from the equilibrium compositions of the phases

At lower temperatures, structural transformations in the melt are also possible. However, due to the reasons described, it is impossible to draw an unequivocal conclusion on this matter.

It should be noted that the results of the analysis of experimental data on the concentration dependence of the integral enthalpy of mixing in the Al–Si system [4] also do not contradict the above conclusions. This is evidenced, in particular, by the presence (in the area of silicon content from 24 to 42 at. %) of a group of points

located practically on the same straight line (Fig. 4).

Based on the assumption of a homogeneous structure of the melts, in [3] the array of experimental data on the integral enthalpy of mixing was approximated by a smooth downward convex curve (Fig. 4, thick solid line).



**Fig. 4** – Concentration dependence of the integral enthalpy of mixing in melts of the system Al – Si: + – data of calorimetric measurements; ———— – approximation of experimental data; - - - - - – approximation of experimental data in this work

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In our work, based on the thesis about the possibility of a microheterogeneous state of the melt, the experimental data are approximated by two curves having a common tangent that passes through the indicated group of points (Fig. 4, dotted lines). The approximation was carried out so that the total root mean square error did not exceed the errors when approximating the experimental data [3].

Therefore, it can be assumed that the results of calorimetric studies do not contradict the thesis about the microheterogeneous structure of melts of the Al–Si system in the range of silicon content from 24 to 42 % and the possibility of structural changes in them.

In the future, it seems appropriate to evaluate the possibility of structural transformations in the melts of the Al–Si system employing studying the temperature dependences of structurally sensitive properties (for example, electrical resistance), as well as to analyze the temperature-concentration dependences of the associative composition.

## 4. CONCLUSIONS

Thus, the results of the thermodynamic analysis give reason to believe that melts of the Al-Si system can exist in a microheterogeneous state and undergo structural transformations.

Presumably, these melts were formed by at least two types of cytotoxic groups. Its own composition and structure characterize each of the types. It is possible to assert only the microheterogeneity of the melt because no noticeable delamination of the melt is observed under normal conditions.

**Оцінка можливості перетворень будови розплавів системи Al – Si за термодинамічними даними**В. Христенко<sup>1</sup>, М. Аршук<sup>1</sup>, О. Доній<sup>1</sup>, С. Котляр<sup>1</sup>, З. Остапчук<sup>2</sup>, Н. Харченко<sup>3</sup>, Т. Говорун<sup>3</sup><sup>1</sup> *Навчально-науковий інститут матеріалознавства та зварювання імені Є.О. Патона, Національний технічний університет України «КПІ ім. І. Сікорського», 03056 Київ, Україна*<sup>2</sup> *Інститут проблем матеріалознавства ім. І.М.Францевича НАН України, 03142 Київ, Україна*<sup>3</sup> *Сумський державний університет, 40007 Суми, Україна*

Наразі достатньо перспективним методом покращення механічних властивостей силумінів є термомасова обробка розплаву. Її дію найчастіше пов'язують зі зміною будови при перегріванні і витримці розплаву і позитивному впливі зазначених змін на структуру сплаву після кристалізації. Хоча на тепер і вважається безсумнівним той факт, що в металевих розплавах реалізується певна структура близького порядку, питання про можливість перетворень будови розплавів залишається дискусійним. В попередніх дослідженнях визначали термодинамічні параметри розплавів системи Al–Si, ґрунтуючись на експериментально встановлених рівноважних складах рідкої і твердих фаз при різних температурах. Результати аналізу дали підстави припустити, що будова розплавів зазначеної системи може змінюватись, залежно від складу і температури. В даній роботі, для подальшого прояснення питання про можливість структурної мікронеоднорідності і перетворень будови розплавів системи Al–Si, порівнювали експериментально встановлені значення активностей компонентів із відомими розрахунковими даними, отриманими в припущенні про сталість будови розплавів. Встановлено, що при температурах, які помітно перевищують температуру ліквідусу, зазначені розрахункові параметри рідкої фази вже не в змозі адекватно описати експериментально встановлені концентраційні залежності активностей компонентів розплавів системи Al–Si. Зазначений факт може свідчити про можливість змін будови алюмінієво-кремнієвих розплавів при зміні температури. Окрім того, результати аналізу експериментальних даних про концентраційні залежності інтегральної ентальпії змішування в розплавах системи Al–Si не суперечать уявленню про можливість зміни будови розплавів цієї системи при зміні вмісту кремнію в них. Отримані результати дають підстави для подальшого дослідження можливості змін будови розплавів системи Al–Si за допомогою аналізу температурно-концентраційних залежностей їх асоціативного складу та експериментального дослідження температурних залежностей структурно-чутливих властивостей (наприклад, електричного опору).

**Ключові слова:** Парціальна молярна вільна енергія, Активність, Інтегральна ентальпія змішування.