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THERMODYNAMIC-DIAGRAM ANALYSIS OF THE Fe-Si-Al-Mn SYSTEM WITH THE CONSTRUCTION OF DIAGRAMS OF PHASE RELATIONS

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In the practice of complex theoretical studies of multicomponent systems, the so-called thermodynamic-diagram analysis method is known, which greatly simplifies the study of the features of phase transformations in multicomponent systems by dividing them into thermodynamically stable elementary partial subsystems of the same dimension as the main one. Thermodynamic-diagram analysis combines a thermodynamic assessment of the chemical interaction of components in the system under study with a geometric diagram. Such a combination, as studies of the physico-chemical bases of the production of refractories and ferroalloys have shown, turns out to be productive when interpreting chemical interactions in complex systems.

Key words: Fe-Si-Al-Mn, thermodynamic diagram, Gibbs energy, phases, mathematical model.

INTRODUCTION

Thus, a thermodynamic-diagrammatic analysis of the Fe-Si-Al-Mn system was carried out with the construction of diagrams of phase relationships. Diagrams of phase relationships of individual parts in the Fe-Si-Al-Mn system have been constructed. Triangulation of the Fe-Si-Al-Mn system based on the calculation of the energy of possible reactions made it possible to identify a set of stable triangles of coexisting phases with the determination of the main areas of crystallization of aluminum silicomanganese for industrial compositions [1, 2].

The effective compositions of complex alloys based on iron, manganese, chromium and aluminum are established in the form of mathematical models for each tetrahedron. The results obtained will subsequently make it possible to determine the phase composition of metal products during the smelting of various grades of aluminosilicomanganes e and the maximum residual content of silicon and aluminum in them, while using the latter in the processes of reducing manganese from manganese ore [3].

RESEARCH METHODOLOGY

In the present work, the task of constructing a diagram of the phase structure of the Fe-Si-Al-Mn system only at a temperature (298 K) is posed. The Gibbs energy of a compound is calculated from the reference values of the enthalpy and entropy of the reactants. The missing thermodynamic constants of binary compounds are assumed in leaflet [4, 5].

The used thermodynamic parameters of the FeSi-Al-Mn compounds are shown in Table 1.

Table 1 **Initial thermodynamic data in the Fe-Si-A-Mn system**

Phases	ΔH^0_{298} / kJ/mol	S^0_{298} / J / (mol·K)	ΔG^0_{298} / kJ / mol
1	2	3	4
$FeAl_2$	- 78,24	83,37	- 103,08
FeSi	- 76,57	46,02	- 76,58
1	2	3	4
$FeSi_2$	- 76,15	55,23	- 73,29
Fe_2Si_5	- 81,97	78,14	- 105,25
$MnAl_4$	- 106,69	146,35	- 150,30
$MnAl_6$	- 87,86	194,58	- 145,85
Mn_5Si_3	- 273,22	235,56	- 278,89
MnSi	- 77,82	47,07	- 76,70

The theoretical (calculation) method of constructing diagrams was used in the work. Thermodynamic-diagram methods, which are widely used in research practice [6]. For the mathematical description of the phase composition diagram, an own balance method was used [7]. The use of the above approach makes it possible to remove restrictions on the number of considered components, since the mathematical model operates not only in three-dimensional space, where diagrams are usually depicted, but also in multidimensional space [8].

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RESULTS RESEARCH

The Additive method was used to calculate the standard Gibbs energy (Table 2) below the specified, unknown ternary phases:

$Mn_4Al_3Si_2$: $MnAl_3$ + Mn_2Si + MnSi =

- 152,525 + (- 92,23) + (- 76,70) = - 321,455

When studying the metal system Fe-Si-Al-Mn by the method of thermodynamic diagram analysis (TDA) [9, 10], it is necessary to proceed from the division of boundary subsystems into elementary tetrahedra. This requires, first of all, to describe the metal compounds of varying complexity that make up the system under consideration. The accepted coordinates (based on the mass fraction x1000) of congruent and incongruent compounds of the Fe-Si-Al-Mn system 30 simple and complex compounds are formed in the system. Thus, 30 simple and complex compounds must be taken into account.

Table 2 **Calculate the standard Gibbs energy with Additive method**

Phases	ΔG^0_{298} / kJ/mol
$Mn_4Al_3Si_2$	- 321,455
Mn_2Al_9Si	- 561,735
Mn_3Al_9Si	- 375,075
Fe_2Al_2Si	- 179,86
$FeAl_2Si$	- 99,79
$FeAl_3Si$	- 141,47
$Fe_3Al_{11}Si_6$	- 753,77
$Fe_3Al_{14}Si_3$	- 886,17

As a result of the triangulation of the Fe-Al-Si subsystem, taking into account the resulting complex compounds, it was found that 15 regions can exist in it, such as: Fe-$FeAl_2$-Fe_2Al_2Si, Fe-Fe_2Al_2Si-FeSi, FeSi-Fe_2Al_2Si-FeSi-$FeAl_2Si$, $FeAl_2Si$-FeSi- $Fe_3Al_{11}Si_6$ $FeAl_2$-Fe_2Al_2Si-$FeAl_2Si$ $FeAl_2$-$FeAl_2Si$-$FeAl_3Si$ $FeAl_2Si$-$FeAl_3Si$-$Fe_3Al_{11}Si_6$ $FeAl_2$-$FeAl_3Si$-$Fe_3Al_{11}Si_3$ $FeAl_3Si$-$Fe_3Al_{11}Si_3$-$Fe_3Al_{11}Si_6$ Si-$Fe_3Al_{11}Si_3$-Fe_2Si_5, Fe_2Si_5-$Fe_3Al_{11}Si_6$, $FeSi_2$-$Fe_3Al_{11}Si_3$-FeSi.

As a result of the triangulation of the Fe–Al–Mn subsystem, taking into account the resulting complex compounds, it was found that 4 regions can exist in it, such as: Fe-$FeAl_2$-Mn, Mn-$FeAl_2$-$MnAl_4$, $MnAl_4$-Fe-Al_2-$MnAl_6$, $FeAl_2$-$MnAl_6$- Al.

Figure 1 shows the result of tetrahedra of congruently and incongruently melting compounds of the analyzed system Fe - Si - Al - Mn.

The breakdown of the overall system was carried out taking into account congruently melting compounds and combining metastable connodes of incongruent components into stable tetrahedra. The sum of the relative volumes of elementary tetrahedra is equal to unity (1), which confirms the correctness of the tetrahedra carried out.

Thus, based on the tetrahedra of four particular three-component systems Fe-Si-Al, Fe-Mn-Al, Fe-Mn-Si and Mn-Al-Si, a diagram of the phase composition of the four-component Fe-Si-Al-Mn system was constructed.

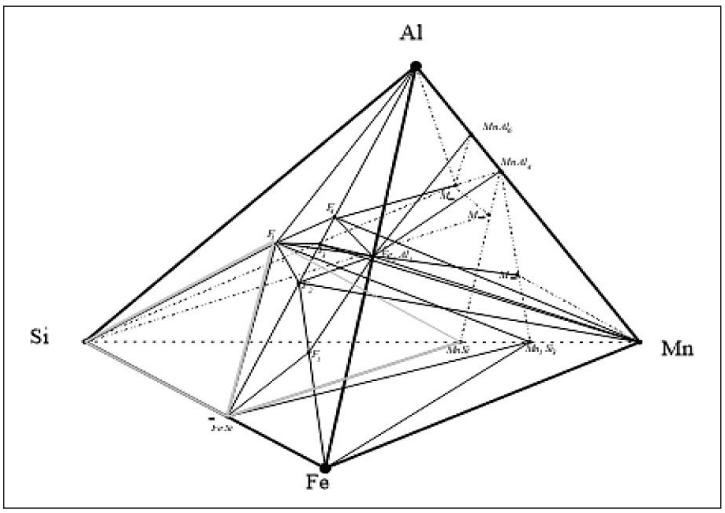

Figure 1 Tetrahedra of the metal system Fe-Si-Al-Mn

It is necessary to find the elementary tetrahedra that make up this system. There are two methods for constructing a phase composition diagram. The first method is geometric, very difficult for a given tetrahedron due to the large number of phases formed. It is extremely difficult to draw all the connodes correctly and not miss or not see the intersection of the borders of the triangles. Therefore, we applied one of the methods for closing a triangle on a tetrahedron.

It consists in searching for triangles that have two identical phases "if two triangles from the nearest triple private system have two identical phases, then they form a tetrahedron, and so on." Next, it consider the phase compositions of the second and third columns. It also repeat finding two identical phases, etc. Following this method, eight tetrahedron were obtained:

- Fe-FeSi-Fe_2Al_2Si-Mn
- $Fe_3Al_{11}Si_6$-Si-MnSi
- Fe_2Si_5-$FeSi_2$-$Fe_3Al_{11}Si_6$-MnSi
- FeSi-$FeSi_2$-$Fe_3Al_{11}Si_6$-MnSi
- Fe-Mn-FeSi-Fe_2Al_5
- $MnAl_6$-Fe_2Al_5-Al-Mn_2Al_9Si
- $MnAl_4$-$MnAl_6$-Fe_2Al_5-Mn_2Al_9Si
- Mn-$MnAl_4$-Fe_2Al_5-$Mn_4Al_3Si_2$

Thus, the presented information and the results of the calculations performed confirm the reliability of the tetrahedra of the phase structure diagram of the considered system. This will subsequently make it possible to determine the phase composition of metal products during the smelting of various grades of aluminosilicomanganese and the maximum residual content of silicon and aluminum in them, while using the latter in the processes of reducing manganese from manganese ore. The calculation of the sum of the relative volumes of tetrahedra was calculated by the method of manual derivation of equations, through the primary components of the base system of the n-th number of components.

Table 3 **List of tetrahedra in the Fe-Si-Al-Mn system and their volumes relative to the total volume of the initial quaternary system, equal to 1 in conventional units**

Tetrahedrons	Elementary volumes (relative to the volume of the total system, equal to 1 unit)
Fe-FeSi-Fe_2Al_2Si-Mn	0,0924
Fe_2Si_5-$Fe_3Al_{11}Si_6$-Si-MnSi	0,136488
Fe_2Si_5-$FeSi_2$-$Fe_3Al_{11}Si_6$-MnSi	0,018612
FeSi-$FeSi_2$-$Fe_3Al_{11}Si_6$-MnSi	0,052734
Fe-Mn-FeSi-Fe_2Al_5	0,1815
$MnAl_6$-Fe_2Al_5-Al-Mn_2Al_9Si	0,07875
$MnAl_4$-$MnAl_6$-Fe_2Al_5-Mn_2Al_9Si	0,02835
Mn-$MnAl_4$-Fe_2Al_5-$Mn_4Al_3Si_2$	0,04752
FeSi-Fe_2Al_2Si-$Fe_3Al_{11}Si_6$-Mn_5Si_3	0,055825
Fe_2Al_5-Fe_2Al_2Si-$FeAl_2Si$-Mn_5Si_3	0,02156
Fe_2Al_5- $FeAl_2Si$-$Fe_3Al_{14}Si_3$-Mn_5Si_3	0,023716
$FeAl_2Si$-$Fe_3Al_{11}Si_6$- $Fe_3Al_{14}Si_3$-Mn_5Si_3	0,015631
Si-$Fe_3Al_{11}Si_6$-Al-MnSi	0,1716
$Fe_3Al_{11}Si_6$-Al-$Fe_3Al_{14}Si_3$-$Mn_4Al_3Si_2$	0,024242
Mn_5Si_3-Mn-$Mn_4Al_3Si_2$-Fe_2Al_5	0,034155
Fe_2Al_5-$Fe_3Al_{14}Si_3$-Al-Mn_2Al_9Si	0,01957
Total	1,000000

Table 3 summarizes the coefficients calculated by the above method for each component of the tetrahedron.

According to the diagram of real ratios in the Fe-Si-Al-Mn system, it can be seen that when melting aluminosilicomanganese with a high and medium silicon content and with a high manganese content in the alloy composition, it is necessary to strive to the region of the Fe_2Si_5 - $Fe_3Al_{11}Si_6$ - Si - MnSi tetrahedron, which has the largest volume 0,136488.

Further, according to the Gauss method, it introduce the transformation coefficients and obtain the mathematical dependences of each substance included in this tetrahedron.

It is possible to find the phase composition of the metal according to the using geometric constructions, but it is very difficult, and for more than four-component systems it is almost impossible. The work uses the Gaussian matrix method, according to which the mathematical dependences of the tetrahedron vertices on the initial components are obtained. For example, the initial balance equations are written as follows:

$$Fe_0 = 1 \cdot Fe + 0,67 \cdot FeSi + 0,58 \cdot Fe_2Al_2Si + + 0 \cdot Mn_5Si_3$$

$$Si_0 = 0 \cdot Fe + 0,33 \cdot FeSi + 0,15 \cdot Fe_2Al_2Si + + 0,23 \cdot Mn_5Si_3$$

$$Al_0 = 0 \cdot Fe + 0 \cdot FeSi + 0,27 \cdot Fe_2Al_2Si + + 0 \cdot Mn_5Si_3$$

CONCLUSION

For the first time, the triangulation of the phase structure diagram of the Fe-Al-Si-Mn system for the solid state with the participation of complex chemical compounds: Fe_2Al_2Si, $FeAl_2Si$, $FeAl_3Si$, $Fe_3Al_{11}Si_6$, $Fe_3Al_{14}Si_3$, $Mn_4Si_2Al_3$, α-Mn_2SiAl_9 and β-Mn_3SiAl_9 was carried out and it was determined that it consists of 16 thermodynamic stable tetrahedron.

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Note: The responsible translator for English language is Abdirashit Assylbek, Temirtau, Kazakhstan