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PHASE DIAGRAM OF A METALLIC SYSTEM CR-FE-AL-SI IN ANALYTICAL EXPRESSIONS

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Abstract. The article considers the phase diagram of the four-component metallic system Cr-Fe-Al-Si obtained using the method of thermodynamic-diagram analysis (TDA). This method, developed at the Zh. Abishev Chemical Institute, allows analyzing complex multicomponent systems without extensive and labor-intensive thermodynamic calculations, which is especially important when designing new alloys with predetermined properties. A phase diagram of the Cr-Fe-Al-Si system is constructed, which is graphically represented as a tetrahedron with four three-component faces (Fe-Al-Si, Fe-Si-Cr, Si-Al-Cr and Fe-Al-Cr). As a result of the calculations, 24 elementary tetrahedra were identified, for which relative volumes were determined and coefficients of the transformation equations were calculated using the Heath method. The sum of the relative volumes of the tetrahedra is close to unity (0.9978), which confirms the correctness of the partitioning of the system.

Using the example of a complex alloy of aluminosilicon chrome (Cr-25; Fe-20; Al-15; Si-40), the phase composition was calculated, it was shown that this alloy is modeled by tetrahedron No. 13 ($CrSi_2$–Si–$FeSi_2$–$FeAl_3$). The obtained data allow us to describe the phase distribution in the studied alloy: 51.9% $CrSi_2$, 3.4% Si, 19.2% FeSi2 and 25.3% $FeAl_3$. The results of the study demonstrate that the TDA method is an effective tool for predicting the phase state of metal systems and optimizing the composition of the charge to increase the productivity of smelting units and the quality of finished products. The constructed diagrams can serve as a basis for further experimental studies and the development of new technologies for smelting aluminosilicon chrome and other complex alloys.

Key words: Cr-Fe-Al-Si system, phase diagram, thermodynamic diagram analysis (TDA), aluminosilicochrome, tetrahedral model, transformation coefficients, phase composition, mathematical modeling.

Introduction

When designing new types of alloys (with predetermined properties), it is necessary to consider dozens of types of charge materials, more rationally and economically evaluate the phase composition of the initial raw materials and products of their processing by calculation methods, subjecting the optimal compositions to subsequent experimental verification. Less attention is paid to the study of the phase composition of materials, although factors such as high-performance operation of the smelting unit, the release of high-quality products, etc. depend on it. To assess the phase composition, the practice of using X-ray phase and petrographic analysis methods is common. But they are used for solidified, solid materials and the results obtained cannot be fully used in high-temperature melts in a liquid state. Therefore, it is advisable to use a theoretical method to determine the phase composition.

Conventional thermodynamic studies of processes in multicomponent systems are quite complex and require extensive mathematical calculations and are directly related to the need to determine the thermodynamic functions of a large number of independent reactions. In many ways, some data on the properties of substances necessary to determine the Gibbs free energy of reactions are limited or completely absent, which in such cases excludes the applicability of thermodynamic analysis to the study of multicomponent systems.

An alternative to the classical thermodynamic study of processes in metallurgy is the method of analyzing geometric thermodynamics, developed at the Zh. Abishev Chemical Institute – thermodynamic-diagram analysis of complex systems (TDA). This method is especially effective in terms of application to metallurgical technology, since it allows identifying the features of the phase structure of raw materials involved in metallurgical processing, changes in their composition as they are reduced, and the state of the final products obtained from them. The final result of such studies is a phase structure diagram of a single system that is closest to the compositions of the corresponding metallurgical products. Using this diagram, one can clearly trace the evolution of phase transformations in metal systems and predict their final state.

Materials and methods of research

The phase composition of the complex alloy of aluminosilicon chromium is characterized by a four-component metallic system Cr-Fe-Al-Si.

Based on the calculated thermodynamic data, a diagram of the four-component system Cr-Fe-Al-Si [1] was constructed and a mathematical model of its phase structure was created. Figure 1 shows the phase diagram of the four-component system Cr-Fe-Al-Si that we obtained. It is graphically depicted as a tetrahedron. Its faces are three-component systems: 1. Fe-Al-Si; 2. Fe-Si-Cr; 3. Si-Al-Cr and 4. Fe-Al-Cr, which are also shown in the figure. As a result of the calculations, it turned out that the system consists of 24 elementary tetrahedra, which are listed in Table 1. The breakdown of the overall system is carried out taking into account congruent and incongruent compounds. The sum of the relative volumes of the elementary tetrahedra is almost equal to one (0.9978), which confirms the correctness of the tetrahedration.

Table 1 – List of tetrahedra of the Cr-Fe-Al-Si system

№	Tetrahedron	Volume
1	$Si – Al – FeAl_3 – CrSi_2$	0,1967
2	$FeAl_3 – FeSi_2 – FeSi – Cr_2Al$	0,0779
3	$FeSi – Fe_5Si_3 – Fe_2Al_5 – Cr_2Al$	0,0440
4	$Fe_2Al_5 – Fe_5Si_3 – Fe_2Si – Cr_2Al$	0,0133
5	$Cr – Fe_2Si – Cr_3Si – Cr_2Al$	0,0255
6	$Cr_3Si – Fe_2Si – Cr_5Si_3 – Cr_2Al$	0,0156
7	$Cr_5Si_3 – Fe_2Si – Fe_5Si_3 – Cr_2Al$	0,0168
8	$Cr_5Si_3 – Fe_5Si_3 – FeSi – Cr_2Al$	0,0161
9	$Cr_5Si_3 – FeSi – FeSi_2 – Cr_2Al$	0,0264
10	$Cr_5Si_3 – FeSi_2 – CrSi – FeAl_3$	0,0310
11	$CrSi – FeSi_2 – CrSi_2 – FeAl_3$	0,0499
12	$Fe – Cr – Cr_2Al – Fe_2Si$	0,0420
13	$CrSi_2 – FeSi_2 – Si – FeAl_3$	0,1421
14	$Fe – Cr_2Al – FeAl – Fe_2Si$	0,0513
15	$FeAl – Cr_2Al – Fe_2Al_5 – Fe_2Si$	0,0350
16	$Fe_2Al_5 – Cr_2Al – FeAl_3 – FeSi$	0,0115
17	$FeAl_3 – Cr_2Al – Cr_5Al_8 – Cr_5Si_3$	0,0244
18	$FeAl_3 – Cr_5Al_8 – Cr_4Al_9 – Cr_5Si_3$	0,0085
19	$FeAl_3 – Cr_4Al_9 – CrAl_4 – Cr_5Si_3$	0,0255
20	$FeAl_3 – CrAl_4 – Cr_2Al_{11} – CrSi_2$	0,0140
21	$FeAl_3 – Cr_2Al_{11} – CrAl_7 – CrSi_2$	0,0091
22	$FeAl_3 – CrAl_7 – Al – CrSi_2$	0,0458
23	$CrAl_4 – CrSi_2 – CrSi – FeAl_3$	0,0466
24	$CrAl_4 – Cr_5Si_3 – CrSi – FeAl_3$	0,0289
Total		**0,9978**

The well-known work [2] presents the simplest and most accessible for manual calculation method of deriving transformation equations expressing any secondary system through the primary components of the base system. The criterion for the location of a given melt composition in one of the quasi-systems is the positive values of all coefficients of the n-th number of secondary components of a certain polytope (tetrahedron), calculated using the Heath equation. Taking into account the above, Table 2 contains the coefficients calculated by us using the method [2] for each secondary component of 24 congruently and incongruently melting quasi-systems of the base tetrahedron.

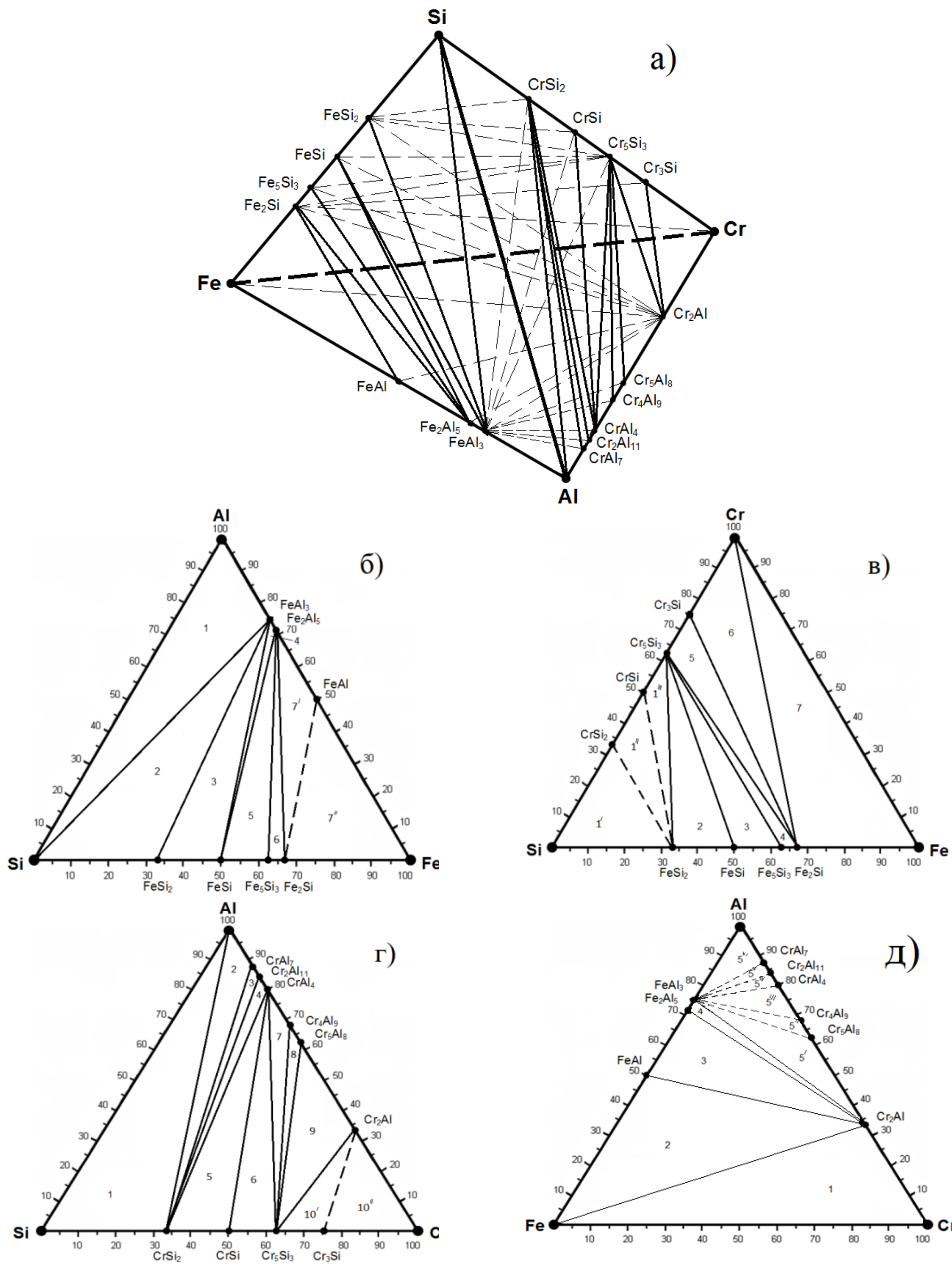

Figure 1. - Phase diagram a) Cr-Fe-Al-Si and elementary triangles of the system: b) Fe-Al-Si; c) Fe-Si-

Cr; d) Si-Al-Cr and d) Fe-Al-Cr

Results and discussion

The practical application of the results of TDA to the smelting of a complex alloy of aluminosilicon chrome comes down to finding elementary tetrahedra, within which their compositions are limited, and the normative distribution of primary phases between secondary compounds for them is equal to 100% of the tetrahedron in question.

To determine the processability of the alloys formed during the melting process, their average weighted material compositions were recalculated into four main elements of the Cr-Fe-Al-Si system, which are given in Table 3.

The phase composition in each of the tetrahedra given in Table 1 can be described by substituting the corresponding coefficients from Table 2 into the equation, which is the Heath transformation equation [3]:

$$X_i = a_iCr + b_iFe + c_iAl + d_iAnd,$$

where X is the amount of secondary phase formed;

a_i, b_i, c_i and d_i– transformation coefficients;

Cr, Fe, Al, Si – the amount of primary metallic components in the metal.

When analyzing the compositions of aluminosilicon chrome smelted from screenings of high-carbon ferrochrome and high-ash Borlin coals from the position of the obtained transformation equations, it was established that:

The composition of the aluminosilicon chrome alloy (Cr-25; Fe-20; Al-15; Si-40) is modeled by tetrahedron №13 $CrSi_2$-Si-$FeSi_2$-$FeAl_3$(relative volume V=0.142136), for which the transformation equations for calculating the equilibrium ratios of secondary components through the primary component according to Table 3 are written as a system of four linear expressions. The phase composition of the tetrahedron found will be as follows, wt.%:

$CrSi_2 = a_1Cr + b_1Fe + c_1Al + d_1Si = 2.079\cdot25 + 0\cdot20 + 0\cdot15 + 0\cdot40 = 51.975$;

$Si = a_2Cr + b_2Fe + c_2Al + d_2Si = -1.079\cdot25 – 1.0\cdot20 + 0.69205\cdot15 + 1.0\cdot40=3.40575$;

$Respond_2 = a_3Cr + b_3Fe + c_3Al + d_3Si = 0\cdot25 + 2.0\cdot20 - 1.38409\cdot15 + 0\cdot40 = 19.23865$;

$FeAl_3 = a_4Cr + b_4Fe + c_4Al + d_4Si = 0\cdot25 + 0\cdot20 + 1.69205\cdot15 + 0\cdot40 = 25.38075$.

From the calculation given it can be seen that this aluminosilicochrome contains 51.9% $CrSi_2$; 3.4% Si; 19.2% $FeSi_2$ and 25.3% $FeAl_3$ [4].

Table 2 – List of elementary tetrahedra, their volumes and coefficients of equations for calculating the equilibrium ratios of secondary components of the Cr-Fe-Al-Si system

Source components	Odds	Pentatopes, their volumes and transformation ratios											
		1	2	3	4	5	6	7	8	9	10	11	12
		Al-Si-$FeAl_3$-$CrSi_2$	$FeSi_2$-FeSi-$FeAl_3$-Cr_2Al	Fe_5Si_3-FeSi-Fe_2Al_5-Cr_2Al	Fe_5Si_3-Fe_2Si-Fe_2Al_5-Cr_2Al	Fe_2Si-Cr-Cr_3Si-Cr_2Al	Fe_2Si-Cr_5Si_3-Cr_3Si-Cr_2Al	Fe_2Si-Cr_5Si_3-Fe_5Si_3-Cr_2Al	FeSi-Cr_5Si_3-Fe_5Si_3-Cr_2Al	Cr_5Si_3-FeSi-$FeSi_2$-Cr_2Al	Cr_5Si_3-CrSi-$FeSi_2$-$FeAl_3$	$CrAl_4$-$CrSi_2$-CrSi-$FeAl_3$	$CrSi_2$-CrSi-$FeSi_2$-$FeAl_3$
Volumes		0,196729	0,077971	0,044077	0,013396	0,025536	0,015624	0,016854	0,016172	0,026478	0,031028	0,046657	0,049939
Cr	a1	0	-0,36682	0,7187	-1,42027	0	0	8,04978	-2,4465	1,3245	3,33333	0	-2,07101
	a2	-1,079	0,55078	-0,49856	1,64041	1	-1,63441	1,3245	1,3245	0,97157	-2,33333	-2,07101	3,07101
	a3	0	-0,44978	-0,48596	-0,48596	0	2,63441	-8,37428	2,122	-1,29607	0	3,07101	0
	a4	2,079	1,26582	1,26582	1,26582	0	0	0	0	0	0	0	0
Fe	b1	-1,44499	-1,99401	3,26471	-6,45161	1,25	1,25	7,45161	-2,26471	0	6,19048	-2,14072	-3,84615
	b2	0	2,99401	-2,26471	7,45161	1,39474	-2,27957	0	0	2,99401	-7,19048	-1,44087	2,84615
	b3	2,44499	0	0	0	-1,64474	2,02957	-6,45161	3,26471	-1,99401	2	2,13661	2
	b4	0	0	0	0	0	0	0	0	0	0	2,44499	0
Al	c1	1	1,37995	-2,70368	5,34293	0	0	-30,28249	9,2035	-4,98266	-4,2841	1,48148	2,66172
	c2	0	-2,072	1,87552	-6,17108	-3,7619	6,14849	-4,98266	-4,98266	-3,65494	4,97615	0,99715	-1,96967
	c3	0	1,69205	1,82815	1,82815	0	-9,91039	31,50324	-7,98275	4,87569	-1,38409	-1,47863	-1,38409

	c4	0	0	0	0	4,7619	4,7619	4,7619	4,7619	4,7619	1,69205	0	1,69205
Si	d1	0	3,99401	-6,53922	25,80645	0	0	-24,80645	7,53922	0	-6,19048	0	3,84615
	d2	1	-2,99401	7,53922	-24,8064	-5,57895	9,11828	0	0	-2,99401	7,19048	3,84615	-2,84615
	d3	0	0	0	0	6,57895	-8,11828	25,80645	-6,53922	3,99401	0	-2,84615	0
	d4	0	0	0	0	0	0	0	0	0	0	0	0

Source components	Odds	Pentatopes, their volumes and transformation ratios											
		13	14	15	16	17	18	19	20	21	22	23	24
		$CrSi_2$- Si- $FeSi_2$- $FeAl_3$	Fe- Cr- Cr_2Al- Fe_2Si	Fe- FeAl- Cr_2Al- Fe_2Si	Fe_2Al_5- FeAl- Cr_2Al- Fe_2Si	$FeAl_3$- Cr_2Al- Fe_2Al_5- FeSi	$FeAl_3$- Cr_2Al- Cr_5Al_8- Cr_5Si_3	$FeAl_3$- Cr_4Al_9- Cr_5Al_8- Cr_5Si_3	$FeAl_3$- Cr_4Al_9- $CrAl_4$- Cr_5Si_3	$FeAl_3$- Cr_2Al_{11}- $CrAl_4$- $CrSi_2$	$FeAl_3$- Cr_2Al_{11}- $CrAl_7$- $CrSi_2$	$CrAl_4$- Cr_5Si_3- CrSi- $FeAl_3$	$FeAl_3$- Al- $CrAl_7$- $CrSi_2$
Volumes		0,142136	0,042	0,05135	0,035076	0,011575	0,02445	0,008517	0,025534	0,01401	0,009128	0,028988	0,045851
Cr	a1	2,079	0	0,55209	-0,80825	-2,73677	0	0	0	0	0	0	0
	a2	-1,079	1	-0,81792	0,54242	1,26582	1,86066	-5,34118	4,96323	-10,2272	18,23256	3,33333	-3,62963
	a3	0	0	1,26582	1,26582	2,47094	-0,86066	6,34118	-3,96324	11,22728	-17,2325	-2,33333	4,62963
	a4	0	0	0	0	0	0	0	0	0	0	0	0
Fe	b1	0	1	1	-1,46396	-12,43182	2,44499	2,44499	2,44499	2,44499	2,44499	-2,14072	2,44499
	b2	-1	0	0	2,46396	0	3,23346	-9,28192	3,45309	-7,11547	7,25855	2,31912	-1,44499
	b3	2	0	0	0	13,43181	-4,67844	7,83693	-4,89808	5,67049	-8,70353	-1,62338	0
	b4	0	0	0	0	0	0	0	0	0	0	2,44499	0
Al	c1	0	0	-2,07692	3,04054	10,29545	0	0	0	0	0	1,48148	0
	c2	0,69205	-3,7619	3,07692	-2,04054	0	-2,2377	6,42353	-2,38971	4,92424	-5,02326	-1,60494	1
	c3	-1,38409	4,7619	0	0	-9,29545	3,2377	-5,42353	3,38971	-3,92425	6,02325	1,12346	0
	c4	1,69205	0	0	0	0	0	0	0	0	0	0	0
Si	d1	0	4	-4	5,85586	24,90096	0	0	0	0	0	0	0
	d2	1	0	0	-9,85586	0	-5,73386	16,45955	-15,2948	9,47846	-16,8976	-6,19048	3,36388
	d3	0	0	0	0	-26,90396	2,65222	-19,5411	12,21323	-10,4052	15,97082	7,19048	-4,29066
	d4	0	5	5	5	3,003	4,08163	4,08163	4,08163	1,92678	1,92678	0	1,92678

The chronology of the movement of low- and high-percentage aluminosilicochrome compositions according to their Cr content takes place in the CrSi tetrahedron$_2$-Si-$FeSi_2$-$FeAl_3$. Table 3 shows the average weighted chemical composition of aluminosilicochrome, as well as the phase composition of the tetrahedron under study. The above tetrahedron has the second value in relative volume among the eleven tetrahedrons found. In turn, the large volume of the tetrahedron provides the most favorable conditions for the implementation of the smelting process, i.e. free regulation of the composition of the charge [5].

Table 3 – Average weighted chemical composition of aluminosilicon chrome and phase composition of the tetrahedron in which the alloy is located – aluminosilicon chrome.

Alloy	Metal composition, %							
	chemical				phase			
	Cr	Fe	Al	And	$CrSi_2$	And	Respond$_2$	$FeAl_3$
№ 1	25	20	15	40	51,9	3,4	19,2	25,3

Conclusions

Thus, in this paper, a phase diagram of congruently melting compounds of the Cr-Fe-Al-Si system and its mathematical model are shown, which allow, based on the chemical analysis of the obtained metal, to find their phase composition and, in combination with their other properties, to optimize the technological process.

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МЕТАЛЛДЫҚ ЖҮЙЕНІҢ ФАЗАЛЫҚ ДИАГРАММАСЫ CR-FE-AL-SI АНАЛИТИКАЛЫҚ ӨРНЕКТЕРДЕ

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Аңдатпа. Мақалада Cr-Fe-Al-Si төрт компонентті металлдық жүйесінің фазалық диаграммасы қарастырылады, ол термодинамикалық-диаграммалық талдау (ТДТ) әдісі арқылы алынған. Ж. Әбішев атындағы ХМИ-де әзірленген бұл әдіс күрделі көпкомпонентті жүйелерді кең және еңбек сыйымды термодинамикалық есептеулер жүргізбей талдауға мүмкіндік береді, бұл алдын ала берілген қасиеттері бар жаңа қорытпаларды жобалауда ерекше маңызды. Cr-Fe-Al-Si жүйесінің фазалық құрылысының диаграммасы салынды және ол төрт үшкомпонентті қыры бар тетраэдр түрінде графикалық түрде көрсетілді (Fe-Al-Si, Fe-Si-Cr, Si-Al-Cr және Fe-Al-Cr). Есептеулер нәтижесінде 24 элементарлы тетраэдр бөлініп алынды, олардың салыстырмалы көлемдері анықталып, Хиз әдісі бойынша түрлендіру теңдеулерінің коэффициенттері есептелді. Тетраэдрлердің салыстырмалы көлемдерінің қосындысы бірге жақын (0,9978), бұл жүйені бөлудің дұрыстығын растайды.

Кешенді алюмосиликохром қорытпасының (Cr-25; Fe-20; Al-15; Si-40) фазалық құрамы есептелді, бұл қорытпа №13 тетраэдрмен ($CrSi_2$–Si–$FeSi_2$–$FeAl_3$) модельденетіні көрсетілді. Алынған деректер зерттелетін қорытпадағы фазалардың бөлінуін сипаттауға мүмкіндік береді: 51,9% $CrSi_2$, 3,4% Si, 19,2% $FeSi_2$ және 25,3% $FeAl_3$. Зерттеу нәтижелері ТДТ әдісі металлдық жүйелердің фазалық күйін болжау және балқыту агрегаттарының өнімділігін арттыру мен дайын өнім сапасын жақсарту үшін шихта құрамын оңтайландыруда тиімді құрал болып табылатынын көрсетті. Құрылған диаграммалар алюмосиликохромды және басқа да күрделі легірленген қорытпаларды балқыту бойынша жаңа технологияларды әзірлеуге және әрі қарайғы эксперименттік зерттеулерге негіз бола алады.

Түйін сөздер: Cr-Fe-Al-Si жүйесі, фазалық диаграмма, термодинамикалық-диаграммалық талдау (ТДТ), алюмосиликохром, тетраэдрлік модель, түрлендіру коэффициенттері, фазалық құрамы, математикалық модельдеу.

ФАЗОВАЯ ДИАГРАММА МЕТАЛЛИЧЕСКОЙ СИСТЕМЫ CR-FE-AL-SI В АНАЛИТИЧЕСКИХ ВЫРАЖЕНИЯХ

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Аннотация. В статье рассматривается фазовая диаграмма четырехкомпонентной металлической системы Cr-Fe-Al-Si, полученная с использованием метода термодинамически-диаграммного анализа (ТДА). Данный метод, разработанный в ХМИ им. Ж. Абишева, позволяет проводить анализ сложных многокомпонентных систем без проведения обширных и трудоемких термодинамических расчетов, что особенно важно при проектировании новых сплавов с заранее заданными свойствами. Построена диаграмма фазового строения системы Cr-Fe-Al-Si, которая графически представлена в виде тетраэдра с четырьмя трехкомпонентными гранями (Fe-Al-Si, Fe-Si-Cr, Si-Al-Cr и Fe-Al-Cr). В результате расчетов выделено 24 элементарных тетраэдра, для которых определены относительные объемы и рассчитаны коэффициенты уравнений трансформации по методу Хиза. Сумма относительных объемов тетраэдров близка к единице (0,9978), что подтверждает корректность разбиения системы.

На примере комплексного сплава алюмосиликохрома (Cr-25; Fe-20; Al-15; Si-40) проведен расчет фазового состава, показано, что данный сплав моделируется тетраэдром №13 ($CrSi_2$–Si–$FeSi_2$–$FeAl_3$). Полученные данные позволяют описать распределение фаз в исследуемом сплаве: 51,9% $CrSi_2$, 3,4% Si, 19,2% $FeSi_2$ и 25,3% $FeAl_3$. Результаты исследования демонстрируют, что метод ТДА является эффективным инструментом прогнозирования фазового состояния металлических систем и оптимизации состава шихты для повышения производительности плавильных агрегатов и качества готовой продукции. Построенные диаграммы могут служить основой для дальнейших экспериментальных исследований и разработки новых технологий выплавки алюмосиликохрома и других сложнолегированных сплавов.

Ключевые слова: Cr-Fe-Al-Si система, фазовая диаграмма, термодинамически-диаграммный анализ (ТДА), алюмосиликохром, тетраэдрическая модель, коэффициенты трансформации, фазовый состав, математическое моделирование.