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Study of the Fe-Si-Al-Ba system using the thermodynamic-diagrammatic analyses method

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Abstract. The article presents the results of a study of the thermodynamic-diagram analysis of the Fe-Si-Al-Ba multicomponent system, where, on the basis of thermodynamic data, the boundary ternary systems of the basic four-component Fe-Si-Al-Ba system are constructed. As a result, it was determined that the system consists of 12 elementary tetrahedra. For each of the tetrahedra, analytical equations are determined, with the help of which it is possible to establish the location in the factor space of the general system of the compositions of various metal melts with the calculation of their normative phase compositions. The correctness of the breakdown into elementary tetrahedra can be seen due to the volumes of the same tetrahedra, where the sum of these volumes is equal to one (1.00000). The quasi-volumes in the system Fe-Si-Al-Ba, simulating the compositions of the resulting metal products during the smelting of an alloy of ferrosilicoaluminum with barium in the process of reduction, have been established. As a result, it turned out that the Fe-Si-Al-Ba system does not include ternary and quaternary compounds, with the exception of interstitial solid solutions containing Fe-Si and Fe-Al phases doped with barium, as well as silicon-barium-aluminum containing eutectic. In this case, the region of the composition of the alloy with a barium content of 8-10% will be the most optimal. Further, with an increase in the concentration of barium in the alloy above 10%, it leads to the loss of barium with atmospheric oxygen, and also leads to a violation of the melting process.

Keywords: *barium, ferrosilicoaluminum, four-component system, thermodynamic-diagram analysis, quasi-volume, tetrahedra.*

1. Introduction

The state diagrams of various systems contain valuable information about the composition and structure of the proposed smelting products and serve to obtain melts as close as possible to the specified compositions and a certain temperature zone of the process, thereby predicting their properties and methods of technological modes of production.

In modern scientific and applied metallurgy, an important place is occupied by the study of the structure of liquid melts obtained by pyrometallurgical processing of various raw materials. As a rule, the initial raw material, whether it is an ore or a concentrate, contains in its composition compounds that are not stable in a liquid state, i.e. decaying into stable constituent parts after overcoming their liquidus temperature. The generally accepted thermodynamic studies of processes in multicomponent systems are quite complex and require the use of 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 absent, which in such cases excludes the applicability of thermodynamic analysis to study multicomponent systems.

Designed and developed in KhMI im. Zh. Abisheva, thermodynamic diagram analysis (TDA) of complex systems, has established itself as the simplest and at the same time accurate method for studying phase patterns in comparison with classical thermodynamic studies of metallurgy processes. The effectiveness of the method, as an application to metallurgical technology, is the ability to reveal the features of the phase structure of the resulting melts in the process of metallurgical processing of various raw materials. Based on the results of such studies, phase composition diagrams are constructed that allow one to trace phase metamorphism and predict the final state of a single system that simulates the composition of the melt under study.

2. Materials and methods

To study the production technology of ferrosilicoaluminum with barium, as well as during deoxidation and partial alloying of steel, it is necessary to know the thermodynamic parameters of the components and the properties of the Fe-Si-Al-Ba system.

This article discusses the possibility of constructing a phase structure diagram for the Ba-Fe-Al-Si system, simulating the compositions of barium-based alloys using thermodynamic diagram analysis. To carry out triangulation or breakdown of a metallic system into phase triangles of coexisting phases, it is necessary to determine the values of the Gibbs energy (ΔG_{298}) of all compounds formed between the components of the system. Reference data on ΔG_{298} for some compounds of the system are taken from [1-3]. However, ΔG_{298} values are not available for almost many compounds. The value of the standard Gibbs energy of any compound at any temperature can be determined

using the well-known Gibbs-Helmholtz equation with known and (the index T indicates the temperature dependence) [5]:

$$\Delta G_T^0 = \Delta H_T^0 - T\Delta S_T^0 \quad (1)$$

Since for many compounds of the system not only the values are not available, but also information about their heat capacity in both solid and liquid states, the article posed the problem of constructing a diagram of the phase structure of the Fe-Si-Al-Ba system only at standard temperature (298 TO). This also makes it possible to simulate the direction of reactions for various combinations of components and compounds in the Fe-Si-Al-Ba system.

The Hertz method was used to determine the $S°_{298}$ values for compounds for which there are no data in reference books [5, 6]. This method is based on the empirical formula established by Hertz for elements and inorganic compounds:

$$S_{298}^0 = K_z \cdot \left(M/C_{p,298}\right)^{1/3} \cdot m \quad (2)$$

where, K_g - Hertz constant (20.5); M - molecular weight; $C_{p,298}$ - molar heat capacity at 298 K; m is the number of atoms in the compound.

Due to the fact that the Hertz method with a fixed value of Kg = 20.5 does not allow obtaining high accuracy, the authors of [5] improved it and found that there is a good relationship between the average values of the Hertz constant (Kg) and the molar mass (Ma) of the element, which is the role of the anion in the compound:

$$K_z = 33{,}5 \cdot \frac{x^2 \cdot e^x}{(e^x - 1)^2} \quad (3)$$

where, x - 42.4 / Ma.

The calculation of the heat capacity of solids was carried out according to the Debye theory. The method is based on quantum concepts of atomic vibrations in the crystal lattice of a solid. The method provides a fairly accurate calculation of the heat capacity of simple solids. Its capabilities as applied to solid compounds have hardly been studied, although the method for calculating Cp of complex substances is well known [7].

The initial calculation data are the characteristic (Debye) temperatures of the elements forming the compounds, as well as the melting temperatures of the elements and compounds (Table 1). The characteristic temperatures of the QD elements are currently determined experimentally, so there is no need to calculate them using the Lindemann formula. It is only necessary to correct them for the test compound using the Koref formula:

$$Q_D^{/} = Q_D \sqrt{T_{mel}^{/} / T_{mel}} \quad (4)$$

where, $T_{mel}^{/}$ and T_{mel} are the melting points of the compound and the element, respectively.

Table 1. Melting points (Tm) and characteristic temperatures (QD) of substances in the crystalline state

№ n/e	Element	T_m, K	Q_D, K
1.	Ba	1000	424
2.	Fe	1808	373
3.	Al	933	390
4.	Si	1700	689

Next, we calculate the argument of the Debye function using the following formula:

$$C_v = Q_D^{/} / T \quad (5)$$

After that, using the Debye function table, we find the isobaric heat capacity of the elements (Table 2) and summing them up according to the Neumann-Kop rule, determining the isochoric heat capacity of the compound.

Table 2. Values of the Debye heat capacity, J/mol K

№ n/e	Q_D/T	C_v	№ n/e	Q_D/T	C_v	№ n/e	Q_D/T	C_v
1	2	3	4	5	6	7	8	9
1	0	24.94	26	2.5	18.58	51	5,0	9.20
2	0.1	24.94	27	2.6	18.16	52	5,2	8.62
3	0.2	24.89	28	2.7	17.74	53	5,4	8.12
4	0.3	24.85	29	2.8	17.32	54	5,6	7.61
5	0.4	24.77	30	2.9	16.90	55	5,8	7.11
6	0.5	24.64	31	3.0	16.51	56	6,0	6.61
7	0.6	24.52	32	3.1	16.07	57	6,2	6.19
8	0.7	24.35	33	3.2	15.65	58	6,4	5.77
9	0.8	24.18	34	3.3	15.27	59	6,6	5.44
10	0.9	24.02	35	3.4	14.85	60	6,8	5.10
11	1.0	23.76	36	3.5	14.43	61	7,0	4761
12	1.1	23.51	37	3.6	14.06	62	7,5	4.05
13	1.2	23.22	38	3.7	13.68	63	8,0	3.477
14	1.3	22.97	39	3.8	13.30	64	9,0	2.665
15	1.4	22.68	40	3.9	12.93	65	10	1.887
16	1.5	22.38	41	4.0	12.56	66	12	1.117
17	1.6	22.05	42	4.1	12.18	67	14	0.703
18	1.7	21.71	43	4.2	11.84	68	16	0.473
19	1.8	21.34	44	4.3	11.51	69	18	0.330
20	1.9	20.96	45	4.4	11.17	70	20	0.243
21	2.0	20.58	46	4.5	10.84	71	22	0.181
22	2.1	20.21	47	4.6	10.50	72	24	0.140
23	2.2	19.83	48	4.7	10.17	73	26	0.1096
24	2.3	19.46	49	4.8	9.83	74	28	0.0883
25	2.4	19.04	50	4.9	9.50	75	30	0.0720

The next step is to convert the isochoric to isobaric heat capacity, which can be done using the semi-empirical Nernst-Lindemann formula:

$$C_p = C_v + 0{,}0051 \cdot T \cdot C_p^2 / T_{\text{mel}} \quad (6)$$

All the thermodynamic parameters of the compounds in the Fe-Si-Al-Ba system obtained as a result of the calculation are shown in Table 3.

Table 3. Results of calculation of thermodynamic parameters

№ n/e	Connections	ΔG_{298}	ΔS_{298}	Cp_{298}
		kJ/mol	J/mol	
1	FeAl	-53.333	65.98	47.41
2	Fe_2Al_5	-203.912	206.37	197.76
3	$FeAl_3$	-114.51	121.57	100.14
4	$FeAl_2$	-78.2408	-	-
5	Fe_3Al	-98.7	-	-
6	FeSi	-76.5798	46.024	48.53
7	Fe_3Si	-84.59	-	-
8	Fe_5Si_3	-197.6396	209.62	199.6
9	$FeSi_2$	-73.2911	55.23	66.11
10	Fe_2Si	-82.887	104.01	72.06
11	BaSi	-242.38	-	-
12	$BaSi_2$	-258.68	-	-
13	BaAl	-62.7	-	-

3. Results and discussion

Diagram of the phase structure of the Fe-Si-Al system. The Fe-Si-Al system (Figure 1) consists of three binary systems Fe-Al, Fe-Si and Si-Al. There are 5 double compounds in the Fe-Al system - Fe_3Al, Fe_2Al_5, FeAl, $FeAl_2$, $FeAl_3$. The Fe-Si system also contains 5 binary compounds - Fe_3Si, Fe_2Si, Fe_5Si_3, FeSi, $FeSi_2$, of which only FeSi is stable in the liquid state. There are no double compounds in the Si-Al system.

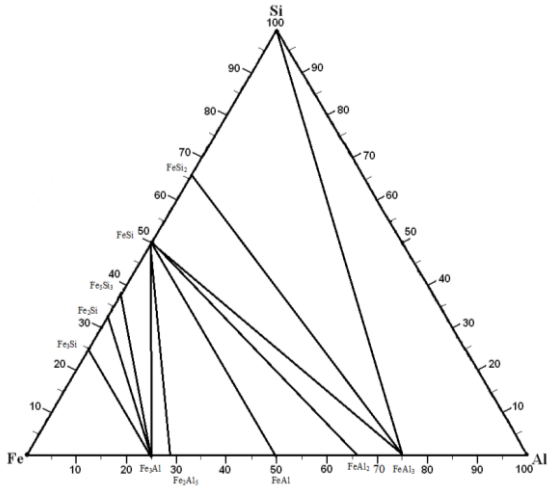

Figure 1. Fe-Si-Al system

In general, the Fe-Si-Al ternary system consists of three simple elements and 10 double compounds. Triangulation of the Fe-Si-Al system was carried out using the Hess law:

$$\Delta Gp = \sum con - \sum sou, \quad (7)$$

At a positive value of the Gibbs energy of the reaction, the points corresponding to the initial compounds were connected on the state diagram. At a negative value of the Gibbs energy of the reaction, the reaction products were combined. In this way, the triple system is divided into stable triangles of coexisting phases. Using this method, the Fe-Si-Al system was divided into 11 stable triangles. Moreover, all components of a single stable triangle do not interact with each other. The areas of interest to us for the composition of the FSA alloy with barium in relation to the Fe-Si-Al system will be in the Si-$FeAl_3$-$FeSi_2$ and $FeSi_2$-$FeAl_3$-FeSi phase regions. This indicates that when the composition of the alloy falls into the range of these compositions, the alloy will contain free silicon.

Diagram of the phase structure of the Ba-Fe-Si system. When triangulating the Ba-Fe-Si subsystem, 8 thermodynamically stable triangles of coexisting phases were formed (Figure 2). In the Ba-Si binary system, the most stable compound is $BaSi_2$ with a melting point of 1180°C. It is reported in [8, 9, 10] that the $BaSi_2$ compound has a rhombic lattice with the following parameters: a = 8.92 A; b = 6.80 A; c = 11.58 A.

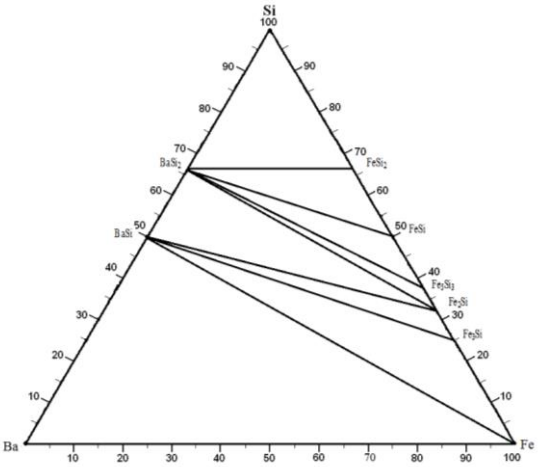

Figure 2. Ba-Fe-Si system

Thus, the Ba-Si system undoubtedly contains $BaSi_2$ compounds (congruent melting T_m = 1180°C - barium disilicide and BaSi (incongruent melting T_m = 840°C - barium silicide. The melting point of barium, according to sources [4] is 710°C, and sources - 725°C. The melting point of silicon (α - quartz) T_{melt} = 1690K, 1688K and 1685K.

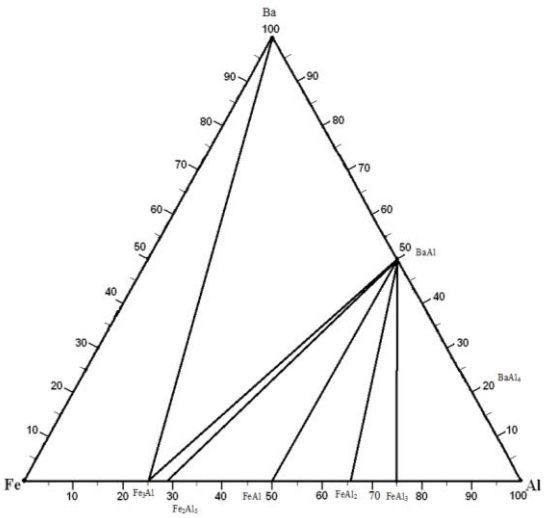

Figure 3. Fe-Al-Ba system

Phase structure diagram of the Fe-Al-Ba system (Figure 3). This system contains three elements and 7 binary compounds, and in the Fe-Al binary system, 5 double compounds are known - Fe_3Al, Fe_2Al_5, FeAl, $FeAl_2$ and $FeAl_3$, and in the Ba-Al binary system there are two compounds BaAl and $BaAl_4$.

As a result of triangulation, the Fe-Al-Ba system was divided into 8 stable coexisting phase triangles. On the Al-Ba side, the most stable compound is BaA_{l4}.

Figure 4. Al-Si-Ba system

Diagram of the phase structure of the Al-Si-Ba system (Figure 4). The system contains four double compounds - BaSi, $BaSi_2$, BaAl, BaA_{l4}, there are no ternary compounds in the system. This system is interesting from the standpoint of determining the composition of the alloy at a constant iron content of around 20%. Then, in the section at 20% iron, when converted to the content of barium, aluminum and silicon, an alloy with a content of 68% Si, 22% Al and 10% Ba will be formed. This composition is in the Al-Si-$BaSi_2$ region, which implies the precipitation of a free silicon phase during crystallization. Aluminum will be in the composition of the alloy in the form of a free phase, but possibly alloyed with iron. This assumption was refined during the study of the microcomponent composition of FSA and FSA alloys with barium by the method of imprinting with a diamond pyramid.

4. Conclusions

Thus, no ternary and quaternary compounds were found in the Fe-Si-Al-Ba system, with the exception of interstitial solid solutions containing Fe-Si and Fe-Al phases doped with barium, as well as silicon-barium-aluminum containing eutectic.

In general, the macrostructure of the FSA alloy with barium is represented by a highly porous surface. The main matrix of the alloy is silicon, which is released in free form during crystallization.

The most optimal is the region of the composition of the alloy with a content of 8-10% barium. Exceeding the content of barium over 10% will lead to its increased losses in the form of oxidation by atmospheric oxygen - the pyroelectric effect increases. In addition, the technological parameters of the smelting of the FSA alloy with barium, when 10% of barium in the alloy is exceeded, somewhat decrease. This is due to an increase in the number of slag-forming compounds coming together with barite ore and the possible transition of the smelting process to the so-called slag mode, which disrupts the normal operation of the furnace.

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Термодинамикалық-диаграммалық талдау арқылы Fe-Si-Al-Ba жүйесін зерттеу

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Аңдатпа. Мақалада Fe-Si-Al-Ba көп компонентті жүйесінің термодинамикалық-диаграммалық талдауын зерттеу нәтижелері келтірілген, мұнда термодинамикалық мәліметтер негізінде Fe-Si-Al-Ba базалық төрт компонентті

жүйесінің шекаралық үштік жүйелері салынған. Нәтижесінде жүйе 12 қарапайым тетраэдрден тұратындығы анықталды. Тетраэдрлердің әрқайсысы үшін аналитикалық теңдеулер анықталады, олардың көмегімен әртүрлі металл балқымаларының құрамдарының жалпы жүйесінің факторлық кеңістікте орналасуын, олардың нормативтік фазалық құрамдарын есептеу арқылы орнатуға болады.

Қарапайым тетраэдрлерге бөлудің дұрыстығын сол тетраэдрлердің көлеміне байланысты көруге болады, мұнда осы көлемдердің қосындысы (1.00000) бірлікке тең.

Тотықсыздану үрдісінде ферросиликоалюминий қорытпасын бариймен балқыту кезінде түзілетін металл өнімдерінің құрамын модельдейтін Fe-Si-Al-Ba жүйесінде квази көлемдер орнатылған. Нәтижесінде Fe-Si-Al-Ba жүйесі бариймен легірленген Fe-Si және Fe-Al фазалары бар қатты енгізу ерітінділерін, сондай-ақ құрамында эвтектика бар кремний-барий-алюминийді қоспағанда, үш және төрт қосылыстарды қамтымайтыны анықталды. Бұл жағдайда барий мөлшері 8-10% болатын қорытпаның құрамы ең оңтайлы болады. Әрі қарай, қорытпадағы барий концентрациясының 10%-ға жоғарылауымен ауаның оттегімен барийдің жоғалуына, сонымен қатар балқытудың технологиялық үрдісінің бұзылуына әкеледі.

Негізгі сөздер: *барий, ферросиликоалюминий, төрт компонентті жүйе, термодинамикалық-диаграммалық талдау, квазиъем, тетраэдрация.*

Изучение системы Fe-Si-Al-Ba методом термодинамическо-диаграммного анализа

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Аннотация. В статье приведены результаты исследования термодинамически-диаграммного анализа многокомпонентной системы Fe-Si-Al-Ba, где на основе термодинамических данных построены граничные тройные системы базовой четырехкомпонентной системы Fe-Si-Al-Ba. В результате определили, что система состоит из 12 элементарных тетраэдров. Для каждого из тетраэдров определены аналитические уравнения, с помощью которых можно установить месторасположение в факторном пространстве общей системы составы различных металлических расплавов с вычислением их нормативных фазовых составов.

Правильность разбивки на элементарные тетраэдры, можно увидеть за счет объемов этих же тетраэдров, где сумма этих объемов равна единице (1.00000).

Установлены квазиобъемы в системе Fe-Si-Al-Ba, моделирующие составы образующихся металлических продуктов при выплавке сплава ферросиликоалюминия с барием в процессе восстановления. В результате выяснилось, что система Fe-Si-Al-Ba не включает тройные и четверные соединения, за исключением твердых растворов внедрения, содержащих фазы Fe-Si и Fe-Al легированных барием, а также кремний-барий-алюминий содержащую эвтектику. При этом наиболее оптимальным будет являться область состава сплава с содержанием бария 8-10%. Далее с увеличением концентрации бария в сплаве свыше 10% приводит к потере бария с кислородом воздуха, а также приводит нарушению технологического процесса плавки.

Ключевые слова: *барий, ферросиликоалюминий, четырехкомпонентная система, термодинамический-диаграммный анализ, квазиобъем, тетраэдрация*.

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