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Study of the possibilities of obtaining a complex alloy using high-ash coals by thermodynamic modeling using a computer program

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Abstract. The content of the leading elements in the technical composition of high-ash coals on the territory of Kazakhstan makes it possible to obtain a complex alloy. In accordance with this, a comprehensive study of the possibilities of obtaining an Aluminium-chromium-silicon alloy, which can be a complex deoxidizer and reducing agent, is among the topical issues. The article presents the results of a study of the thermodynamic-diagram analysis of the Cr-Si-Al-C multicomponent system, where, on the basis of thermodynamic data, the boundary ternary systems of the basic four-component Cr-Si-Al-C system are constructed. As a result, the components of the condensed phases of a multicomponent system were determined. Descriptions are given for each of the defined phases, with the help of which it is possible to create an accurate model of the general system of compositions of chromium-containing melts with the calculation of their normative phase compositions. Triangles of the Cr-Si-Al-C system have been established, modulating the compositions of the resulting compositions of metal products during the smelting of the aluminosilicochrome alloy using high-ash coals. As a result of modeling, the main components of the phase of three-component systems Al-Si-C, Al-Cr-Si, were revealed. Volumes and color integrals indicating condensed and gaseous phases are determined. The technology of obtaining silicon-aluminum alloys is based on the reduction of oxides from the ash of high-ash coal with its own carbon in ore-thermal furnaces.

Keywords: *high-ash coals, ferrosilicochromium, four-component system, thermodynamic-diagram, carbon, volume.*

1. Introduction

Technologies for the production of complex alloys can be distinguished by the following positive aspects:

1. In the smelting process, the complex use of substandard, cheap and easily accessible raw materials is ensured with the production of highly efficient complex alloys with a wide range of content of the main deoxidizing and alloying elements. They are an alternative replacement for traditional types of ferroalloys, such as ferrosilicochrome, ferrosilicon and aluminum.

2. When using low-grade high-ash coals as a reducing agent, the cost of alloys is noticeably reduced by excluding the use of expensive coke from the technological chain and subsequently predetermines a reduction in the cost of deoxidized steel.

3. When using complex alloys in the production of standard ferroalloys, in particular refined ferrochrome grades, a number of technological problems associated with the scattering of slag into fine dust are solved.

4. When deoxidizing steel with complex alloys, there is no need to use significant amounts of ferrosilicon, as well as scarce and expensive ingot aluminum [1].

To obtain high-quality complex alloys, it is necessary to conduct various studies. One of the research methods is computer modeling.

Thermodynamic modeling is a kind of mathematical modeling. Its main stages are

1. Creation of a thermodynamic model;
2. Development of a mathematical model;
3. Algorithm development and software implementation;
4. Preparation of initial data;
5. Carrying out the calculation;
6. Analysis of the results of calculations.

In solving many scientific and technical problems, the issues of studying high-temperature processes with physicochemical transformations play a significant role [2-4].

Experimental methods of studying processes of this kind are usually expensive, and often not feasible at all.

Under these conditions, a computational experiment performed using a computer acquires special importance, which allows analyzing states and processes and drawing conclusions about the behavior of the objects under study based on model representations.

The main assumption in this case is the assumption of the existence of a local equilibrium in the system, which makes it possible to carry out calculations using the mathematical apparatus of equilibrium thermodynamics.

The most common methods of equilibrium thermodynamics are used in combination with the so-called ideal model, according to which the behavior of the gas phase is described by the equation of state of an ideal gas, and all solutions are ideal.

The main advantages of the ideal model are its simplicity, versatility and availability of information: if a chemically reacting heterogeneous system is being investigated, then the parameters of the model are actually only the thermodynamic properties of individual substances. However, in a situation where the forces of intermolecular interaction play an essential role (dense gases, highly ionized plasma, concentrated solutions of condensed substances), the ideal model becomes unsuitable.

As an example, high-temperature processes, combustion of fuel, energy materials in a closed volume, processes at the detonation wave front, metallurgical, chemical-technological, geochemical processes can be cited [5-8].

For a long period of time, fossil coal had no worthy competitors among energy carriers and played a huge role in global development as energy for fuel power plants, in the metallurgical industry and in the household sector. There are coal deposits in more than 70 countries, including Kazakhstan, which ranks among the top ten countries in coal production, second only to China, the USA, India, Australia, Russia, South Africa, and Ukraine. Reserves of both energy and coking coal will be sufficient for hundreds of years, even with an active increase in production.

In order to increase production efficiency, improve technology and improve technical and economic indicators in the ferrous metallurgy, it is necessary to expand the production and use of complex ferroalloys. In order to expand the range of alloys currently used in the production of steel and ferroalloys, it is necessary to search for new high-quality types of complex alloys. The most acceptable is the selection of complex alloys characterized by an optimal chemical composition and a single-stage method of obtaining from high-ash coals, which is the cheapest method for smelting similar types of alloys [9,10].

2. Materials and methods

The main task of modeling thermodynamic equilibrium is to determine the phase and chemical composition, as well as the values of the thermodynamic parameters of the system under study.

The object of thermodynamic analysis is a thermodynamic system – a conditionally isolated material region whose interaction with the environment is reduced to the exchange of matter and energy.

As a rule, it is assumed that the influence of gravitational and electromagnetic fields, as well as the action of surface tension forces, can be neglected, and the only kind of work that the system can perform is expansion work.

Thermodynamic equilibrium is the limiting state to which a thermodynamic system isolated from external influences tends, i.e., thermal, mechanical and chemical equilibrium is established at each point of the system (temperature and pressure equalize, and all kinds of chemical reactions proceed to the end) [11].

The main complexity of such an approach to thermodynamic modeling consists in the labor intensity of creating visual graphic images. The «Triangle» program allows you to simplify the process of performing serial calculations and building three-phase diagrams. As the three primary substances, there can be both individual chemical elements and arbitrary compounds.

In the practice of a comprehensive theoretical study of multicomponent systems, the method of thermodynamic modeling is known, which much simplifies the study of the features of Phase turns in multicomponent systems by dividing them into thermodynamically resistant simple subsystems by the size of the main system. A graphical method was used to determine the phase composition of a metal system based on Al-Cr-Si-C. During the calculation, a tetrahedron of a multicomponent system was constructed and the component phases were determined using coordinate lattices in this tetrahedron [12].

3. Results and discussion

Aluminum-chromium-silicon alloy. The technology of smelting this chromium–containing alloy is based on the complex processing of poor chromium ores and the use of high-ash coals instead of a relatively expensive reducing agent - metallurgical coke. Experimental tests for the production of alloys of this type using poor chrome ores of the «Don deposit» and high-ash «Ekibastuz» coal have been carried out repeatedly. The alloy was smelted in a continuous slag-free way to obtain an alloy of silicon, aluminum and chromium.

According to the Concept of development of the coal industry of the Republic of Kazakhstan until 2020, the total geological reserves and projected coal resources are estimated at 150 billion tons. Off-balance sheet coal reserves by basins and deposits, as of January 1, 2007, amount to 28.6 billion tons, including 3.2 billion tons of hard coal, 25.4 billion tons of brown coal [13].

The complex program «Triangle» makes it possible to simplify the process of constructing three-phase diagrams. In addition, to calculate the equilibrium phase composition, it can be carried out in two modes. That is, firstly, for the isothermal case, when the equilibrium of the system is given by the values of temperature (T, K) and pressure (p, MPa). And secondly, for the cases of changes in the adiabatic equilibrium (gorenje), expressed at each point of calculation by the values of pressure (p, MPa) and enthalpy (enthalpy of formation of the starting materials) (I, kJ/kg).

With the help of the «Triangle» program, Al-Si-C, Al-Cr-Si the triple component system and the chemical compounds included in them were studied at temperature intervals of 1673-1873K.

In Figure 1(a) Al-Si-C triple system forms 12 compounds at a temperature of 1673K: 1)Si(c);SiC(c);Al(c); 2)Al(c); 3)C(c); 4)Si(c);SiC(c); 5)C(c); SiC(c);Al4C3(c); 6)C(c);SiC(c); 7)C(c);Al4C3(c); 8)Al(c);Al4C3(c); 9)SiC(c);Al(c); Al4C3(c); 10)SiC(c);Al(c); 11)SiC(c);Al(c); 12)SiC(c). Al-Si-C 50% of the triple system C(c);SiC(c); 30% of the triple system SiC(c), the remaining 20% make up the remaining compounds of the triple system.

In Figure 1(b) Al-Si-C triple system forms 12 compounds at a temperature of 1873K: 1)Si(c);SiC(c);Al(c); 2)Al(c); 3)C(c); 4)Si(c);SiC(c); 5)C(c); SiC(c);Al4C3(c); 6)C(c);SiC(c); 7)C(c);Al4C3(c); 8)Al(c);Al4C3(c); 9)SiC(c);Al(c); Al4C3(c); 10)SiC(c);Al(c); 11)SiC(c);Al(c); 12)SiC(c). Al-Si-C 50% of the triple system C(c);SiC(c); 30% of the triple system SiC(c), the remaining 20% make up the remaining compounds of the triple system.

In Figure 2(a) at a temperature of 1673K, the Al-Cr-Si triple system shows that it forms 19 compounds: 1)Al(c); 2)Si(c); 3)Al(c);CrSi(c);Cr5Si3(c); 4)Al(c);CrSi(c); 5) Al(c); CrSi(c);CrSi2(c); 6)Al(c);Cr(c); 7)Si(c);Al(c);CrSi2(c); 8)Si(c);Al(c); 9)Al(c);Cr(c);Cr3Si(c); 10)Cr(c); 11)Cr(c); Cr3Si(c); 12)Cr3Si(c); Cr5Si3(c); 13)Al(c); Cr3Si(c); Cr5Si3(c); 14)CrSi(c);Cr5Si3(c); 15)CrSi(c); 16)CrSi(c); CrSi2(c); 17)Si(c);CrSi2(c); 18)Al(c);CrSi(c);Cr5Si3(c). 35% of this triple system Al-Cr-Si belongs to compounds such a CrSi(c);Cr5Si3(c); 20% is Si(c);CrSi2(c); 20% is Si(c);Al(c); the remaining 25% is the remaining compounds.

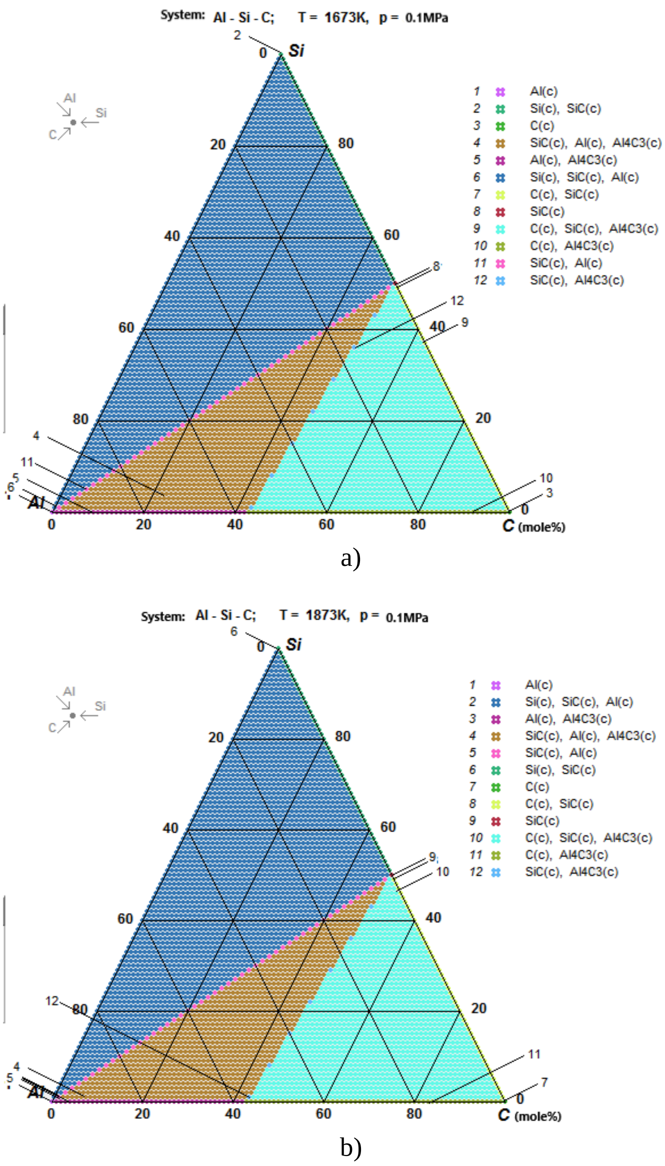

Figure 1. Diagram of the phase composition of the triple system Al-Si-C at temperatures: 1673K(a), 1873K(b)

In Figure 2(b) at a temperature of 1873K, the Al-Cr-Si triple system shows that it forms 20 compounds: 1)Al(c); 2)Al(c);Cr3Si(c); 3)Al(c);CrSi(c);Cr5Si3(c); 4)Al(c);CrSi(c); 5)Al(c);CrSi(c);CrSi2(c); 6)Al(c);Cr(c); 7)Si(c);Al(c); CrSi2(c); 8)Si(c);Al(c); 9)Al(c);Cr(c);Cr3Si(c); 10)Cr(c); 11)Cr(c);Cr3Si(c); 12)Cr3Si(c); Cr5Si3(c); 13)Al(c); Cr3Si(c); Cr5Si3(c); 14)CrSi(c);Cr5Si3(c); 15)Al(c); CrSi2(c); 16)CrSi(c);CrSi2(c); 17)Si(c);CrSi(c); 18)Al(c); Cr5Si3(c); 19)Cr3Si(c); 20)CrSi(c);CrSi2(c). of this triple system Al-Cr-Si belongs to compounds such a CrSi(c);Cr5Si3(c); 20% is Si(c);CrSi2(c); 20% is Si(c);Al(c); the remaining 25% is the remaining compounds.

Ferrosilicochrome with a silicon content of ~48% is obtained by carbothermic method in ore-thermal furnaces with a transformer with a capacity of 10-20 MWA by a continuous process. The charge is loaded constantly, in small portions on the surface of the grate in the zones adjacent to the electrodes. According to the smelting process and depending on the grade of the alloy obtained, there are two methods for producing ferrosilicochrome: single-stage (slag) and two-stage (slag-free). In the one-stage method, the charge consists of chromium ore, quartzite and a carbon-containing reducing agent (coke, semi-coke, briquetted peat, brown coal, graphitization waste, etc.), and in the two-stage method - of quartzite, carbonaceous (transfer) ferrochrome and carbon-containing reducing agent (coke, semi-coke, special coke and coal) [11-13].

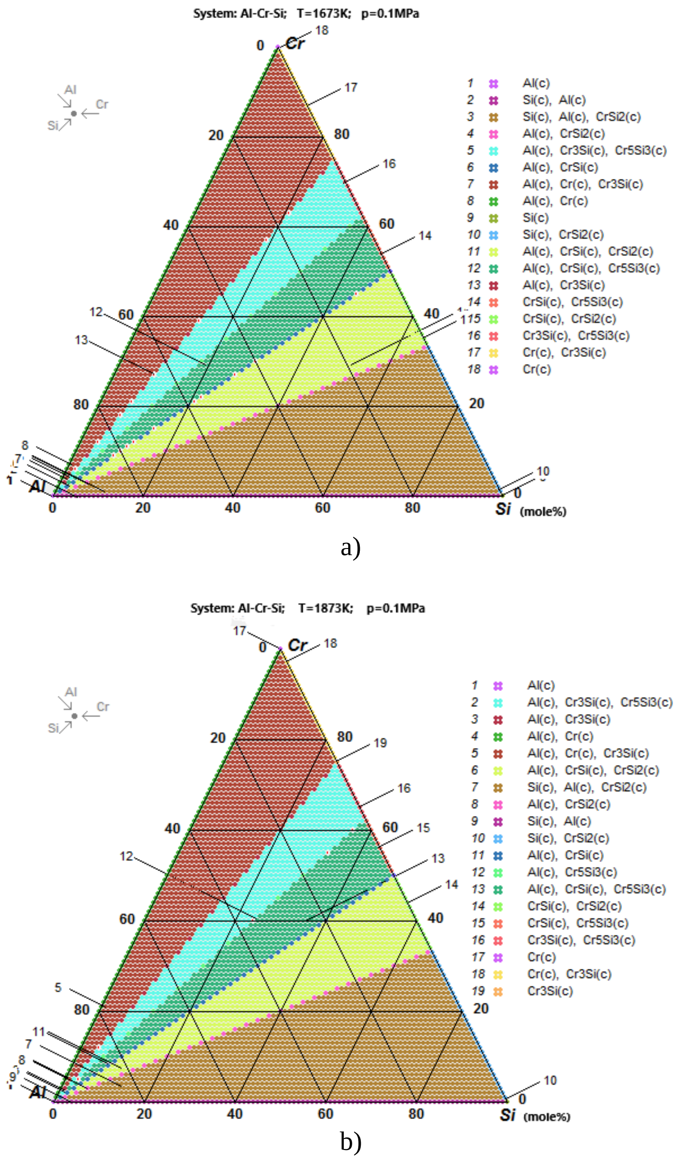

Figure 2. Diagram of the phase composition of the triple system Al-Cr-Si at temperatures: 1673K(a), 1873K(b)

Currently, both methods are practiced. The indicators and advantages of each of them are characterized to a large extent by the degree of refinement of the technology and the consumption of electricity. The economic efficiency of ferrosilicochrome production depends on the cost of charge materials and on the content of target elements in the alloy: chromium and silicon. The advantage of the single-stage method of ferrosilicochrome production is the increased extraction of chromium into the alloy, however, the total electricity consumption for ferrosilicochrome smelting (48-50%) with the two-stage method is lower (6700-7300 KW·h) than with the single-stage (8200-8855 KW·h).

Table 1. Chemical composition of the starting materials

Chrome Ore, %	
Cr_2O_3	51.73
SiO_2	7.76
CaO	0.53
MgO	17.75
Al_2O_3	8.32
Fe_{total}	9.42
S	0.012
Puncture loss	2.10
Al-Cr-Si, %	
Cr	36.92
Si	25.11
Al	14.41
C	1.48
Fe	rest

The composition of the briquetted charge is as follows:
- chrome ore (0-0.5 mm) - 69.1%;
- Aluminosilicochrome (0-0.5 mm) - 30.9%.

As a binder, liquid glass was used in an amount of 6-7% of the dry weight of the charge. The density of liquid glass is 1.46-1.48g/cm^3, silicate modulus SiO_2/Na_2O = 2.64-2.84. Before briquetting, the raw materials, first in a dry state, and then with a binder in the specified ratio, were thoroughly mixed and briquettes in the form of cylinders with a diameter of 10 mm and a height of 10-15 mm were obtained. The briquetted charge was dried in a laboratory muffle furnace at a temperature of 200-250°C for a duration of 3 hours. The chemical composition of the briquettes is given in Table 2. Lime with a CaO content of ≥ 95% was used as a fluxing material.

The resulting alloy in chemical composition met the requirements of the standard. The results of the smelting are shown in Table 2. As can be seen from the table, the slag compositions were characterized by different basicity values. The amount of reducing agent varied to find the optimal value.

In terms of carbon content, the resulting metal corresponds to the grades of medium-carbon ferrochrome according to GOST 4757-91. Table 2 shows that the use of a silicon-aluminum reducing agent - Alumosilicochrome in the process of metallothermy of refined ferrochrome leads to the formation of alumina-containing slags. The concentration of alumina in them ranges from 15.07-30.55%, while according to standard technology it is 5-7%. Consequently, there is a significant change in the chemical composition of the slags. In this regard, it became necessary to study the features of the slags obtained by the new technology [9].

Table 2. Chemical composition of melting products

№	Metal				Slag						CaO/SiO_2
	Cr	Fe	Si	C	Cr_2O_3	CaO	SiO_2	MgO	Al_2O_3	FeO	
1	66.88	29.05	1.22	1.96	5.26	31.87	23.43	13.59	30.55	0.55	1.36
2	68.08	27.82	0.66	2.33	6.31	33.69	24.23	11.43	27.29	0.62	1.38
3	63.24	33.47	0.42	0.77	5.43	33.52	23.44	13.65	18.98	0.71	1.43
4	68.72	26.79	0.39	3.24	5.67	31.88	20.50	13.22	14.90	1.08	1.55
5	67.22	28.29	1.05	1.18	5.11	37.59	24.06	13.07	18.07	1.12	1.56
6	67.28	28.31	1.02	1.31	2.17	32.62	20.46	10.07	21.07	0.82	1.59
7	66.38	30.58	1.03	1.13	4.25	39.98	24.53	13.03	17.17	0.93	1.63
8	67.48	29.81	1.06	1.25	5.07	39.75	23.66	14.11	16.09	1.04	1.68
9	67.26	28.34	0.20	3.20	5.68	34.54	21.69	14.26	15.07	1.23	1.73
10	68.87	26.01	0.78	2.94	6.26	41.43	23.18	11.16	15.32	2.05	1.79

4. Conclusions

A model of the Alumosilicochrome alloy was constructed by computer modeling. The data obtained by calculation showed the correctness of the molten metal-containing alloy. All identified phases were obtained by thermodynamic modeling during the melting process. This shows the correctness of the calculations.

In the course of the analysis of the results obtained, it was found that the triple systems Al-Si-C, Al-Cr-Si, which are the main components of the studied metallic system Al-Cr-Si-C, undergo large-scale changes in the composition and number of phases. Although the decline in quality and impoverishment of ores and raw materials is a serious problem, it is known that the demand and requirements for metallurgical charge materials are growing. Therefore, the ways to fully study the materials involved in metallurgical production and expand the possibilities of obtaining the necessary alloys are relevant. The results of the work presented in the article do not allow the processes of melting the initial products without preliminary research. The computer program used allows you to choose the right charge materials to assess the composition and quality of the products being smelted. The presented simulation results correctly and accurately reflect the phases that form the basis of the Aluminium-chromium-silicon alloy when using high-ash coals. the number and volumes of condensed phases and the processes of obtaining alloys in accordance with state standards are determined.

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Компьютерлік бағдарлама көмегімен термодинамикалық модельдеу әдісі арқылы жоғары күлді көмірлерді қолданып кешенді қорытпа алу мүмкіндіктерін зерттеу

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Аңдатпа. Қазақстан территориясындағы жоғары күлді көмірлердің техникалық құрамындағы жетекші элементтердің мөлшері кешенді қорытпа алуға мүмкіндік береді. Осыған сәйкес, кешенді қышқылсыздандырғыш және тотықсыздандырғыш бола алатын АХС қорытпасын алу мүмкіндіктерін жан-жақты зерттеу өзекті мәселелер қатарында. Ұсынылған мақалада Cr-Si-Al-C жүйесінің термодинамикалық диаграммаларын талдаудың зерттеу нәтижелері келтірілген, мұнда термодинамикалық мәліметтер негізінде негізгі төрт компонентті Cr-Si-Al-C жүйесінің шекаралық үштік жүйелері салынған. Белгілі бір фазалардың әрқайсысы үшін сипаттамалар берілген, олардың көмегімен хром бар балқымалар құрамдарының жалпы жүйесінің нақты моделін олардың нормативтік фазалық құрамдарын есептей отырып жасауға болады. Cr-Si-Al-C жүйесінің үшбұрыштары орнатылды, олар күлі жоғары көмірді қолдана отырып, алюминий силикохром қорытпасын балқыту кезінде алынған металл бұйымдарының құрамдарын модуляциялады. Модельдеу нәтижесінде Al-Si-C, Al-Cr-Si, үш компонентті жүйелерінің фазаларының негізгі компоненттері анықталды. Конденсацияланған және газ тәрізді фазаларды көрсететін көлемдер мен түс интегралдары анықталады. Кремний алюминий қорытпаларын өндіру технологиясы жоғары күл көмірінің күлінен оксидтерді кен термиялық пештердегі өз көміртегімен тотықсыздандыруға негізделген.

Негізгі сөздер: *жоғары күлді көмір, ферросиликохром, төрт компонентті жүйе, термодинамикалық диаграмма, көміртек, көлем.*

Изучение возможностей получения комплексного сплава с использованием высокозольных углей методом термодинамического моделирования с помощью компьютерной программы

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Аннотация. Содержание ведущих элементов в техническом составе высокозольных углей на территории Казахстана позволяет получить комплексный сплав. В соответствии с этим, комплексное изучение возможностей получения сплава АХС, который может быть комплексным раскислителем и восстановителем, находится в числе актуальных вопросов. В статье представлены результаты исследования анализа термодинамических диаграмм многокомпонентной системы Cr-Si-Al-C, где на основе термодинамических данных построены граничные тройные системы базовой четырехкомпонентной системы Cr-Si-Al-C. В результате были определены компоненты конденсированных фаз многокомпонентной системы. Даны описания для каждой из определенных фаз, с помощью которых можно создать точную модель общей системы составов хромсодержащих расплавов с расчетом их нормативных фазовых составов. Были установлены треугольники системы Cr-Si-Al-C, модулирующие составы получаемых композиций металлических изделий при выплавке алюмосиликохромового сплава с использованием высокозольных углей. В результате моделирования были выявлены основные составляющие фазы трехкомпонентных систем Al-Si-C, Al-Cr-Si. Определяются объемы и цветовые интегралы, указывающие на конденсированную и газообразную фазы. Технология получения кремнийалюминиевых сплавов основана на восстановлении оксидов из золы высокозольного угля собственным углеродом в руднотермических печах.

Ключевые слова: *высокозольные угли, ферросиликохром, четырехкомпонентная система, термодинамическая диаграмма, углерод, объем*.

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