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Technology of smelting complex alloys using high-ash coals and modeling of the possibilities of their application in the production of steel and ferroalloys

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Abstract. 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-Cr-C, Cr-Si-C, 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

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

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 [1].

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 [2].

In many cases, the ideal model allows us to adequately describe the process or phenomenon under study.

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 [3].

In connection with the intensification of steel smelting processes, the practice of deoxidation and alloying of metal in a ladle is becoming increasingly widespread. In the production of stainless-steel grades, a relatively refractory ferrochrome alloy is added to the bucket. The use of ferrochrome is associated with certain difficulties; therefore, it is preferable to use complex alloys with lower melting points. An additional decrease in the melting point of chromium-containing ferroalloys can be achieved by introducing some amounts of aluminum into the alloy. Considering all the advantages of complex alloys over standard ferroalloys, the analysis of the technologies developed to date for their smelting and application in the production of steel and ferroalloys was made.

2. Materials and methods

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.

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 [4].

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).

In practice, the isolation condition means that the processes of establishing equilibrium proceed much faster than changes occur at the boundaries of the system (i.e., changes in conditions external to the system) and the system exchanges matter and energy with the environment [5].

And so on, let's consider modeling the production of a complex alloy based on Cr-Si-Al-C using the «Terra» software package.

The «Terra» program is designed to calculate the composition of phases, thermodynamic and transport properties of arbitrary systems with chemical and phase transformations.

It allows you to model extremely equilibrium states using an ideal gas model. Condensed phases can be described in the approximation of immiscible single-component phases, ideal or regular solutions. The «Terra» program is designed to simulate extremely equilibrium states of complex systems.

The calculation method used does not allow finding the «place» of transition to the equilibrium state.

Therefore, as the initial data determining the chemical composition of the system, it is sufficient to specify only the mass content of chemical elements.

The method and algorithm for calculating the composition of phases in complex multi-element systems implemented in the Terra program allows you to perform a series of calculations with a change in the content of primary substances. Multiple calculations for all possible relationships make it possible to represent a region with the same set of single-component condensed phases.

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 [6].

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). 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.

Aluminum-chromium-silicon alloys have been tested as a reducing agent of chromium ore oxides during the smelting of refined ferrochrome. Experimental melting was carried out in a two-electrode electric furnace with a capacity of 80 kW. As a result, ferrochrome was obtained with a content, %: chromium - 65-68; silicon - 0.4-0.6; phosphorus - 0.02-0.05; carbon - 1-3.5; sulfur - 0.003-0.008.

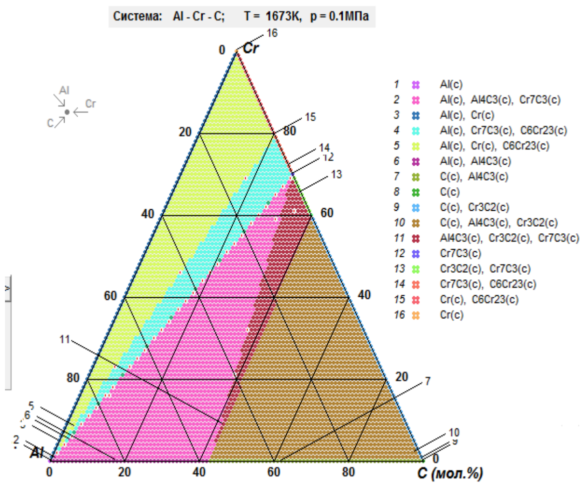
3. Results and discussion

After analyzing the above technologies for the production of complex alloys, the following positive points can be identified:

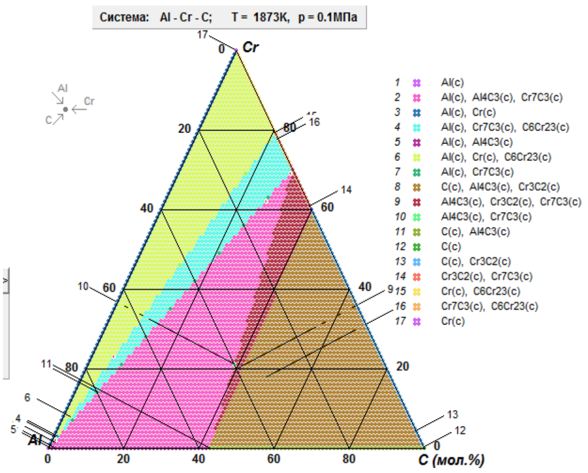
1. In the smelting process, the complex use of substandard, cheap and easily accessible raw materials is ensured with the production of highly efficient complex alloys with a wide range of content of the main deoxidizing and alloying elements. They are an alternative replacement for traditional types 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 [7].

In all the considered and industrially implemented methods, ferrosilicochrome is widely used as a reducing agent in the smelting of refined ferrochrome.

With the help of the Triangle software package, the data obtained from the phase state diagram of the triple Al-Cr-C system was determined and presented. The state of thermodynamic changes in the temperature range 1673-1873 of the specified triple metal system is investigated [8-9]. Thermodynamic modeling of the triple Al-Cr-C system in the temperature range of 1673, 1873K revealed the main phases of the system and their molar fractions. Stable atmospheric pressure and a temperature scale of 1673, 1873K were taken as initial data.



a)



b)

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

In Figure 1(a) Al-Cr-C triple system forms 16 compounds at a temperature of 1673K: 1)Al(c); 2)Al(c);Cr_7C_3(c);Al_4C_3(c); 3)Al(c);Cr(c); 4)Al(c);Cr_7C_3(c);C_6Cr_{23}(c); 5)Al(c);Cr(c); C_6Cr_{23}(c); 6)Al(c); Al_4C_3(c); 7)C(c); Al_4C_3(c); 8)C(c); 9)C(c); Cr_3C_2(c); 10)C(c); Cr_3C_2(c); Al_4C_3(c); 11)Al_4C_3(c); Cr_3C_2(c); Cr_7C_3(c); 12)Cr_7C_3(c); 13)Cr_3C_2(c); Cr_7C_3(c); 14)Cr_7C_3(c); C_6Cr_{23}(c); 15)Cr(c);C_6Cr_{23}(c); 16)Cr(c). Al-Cr-C 50% of the triple system C(c); Cr(c); C_6Cr_{23}(c); Cr_3C_2(c); 30% of the triple system Al(c);Cr_7C_3(c); the remaining 20% make up the remaining compounds of the triple system.

In Figure 1(b) Al-Cr-C triple system forms 17 compounds at a temperature of 1873K: 1)Al(c); 2)Al(c);Cr_7C_3(c);Al_4C_3(c); 3)Al(c);Cr(c); 4)Al(c);Cr_7C_3(c);C_6Cr_{23}(c); 5)Al(c); Al_4C_3(c); 6)Al(c);Cr(c);C_6Cr_{23}(c); 7)Al(c); Cr_7C_3(c); 8)C(c); Cr_3C_2(c); Al_4C_3(c); 9)Al_4C_3(c); Cr_3C_2(c); Cr_7C_3(c); 10)Cr_7C_3(c); Al_4C_3(c); 11)C(c); Al_4C_3(c); 12)C(c); 13)C(c); Cr_3C_2(c); 14)Cr_3C_2(c); Cr_7C_3(c); 15)Cr(c);C_6Cr_{23}(c); 16)Cr_7C_3(c);C_6Cr_{23}(c); 17)Cr(c). Al-Cr-C 50% of the triple system C(c); Cr(c); C_6Cr_{23}(c); Cr_3C_2(c); 30% of the triple system Al(c);Cr_7C_3(c); the remaining 20% make up the remaining compounds of the triple system.

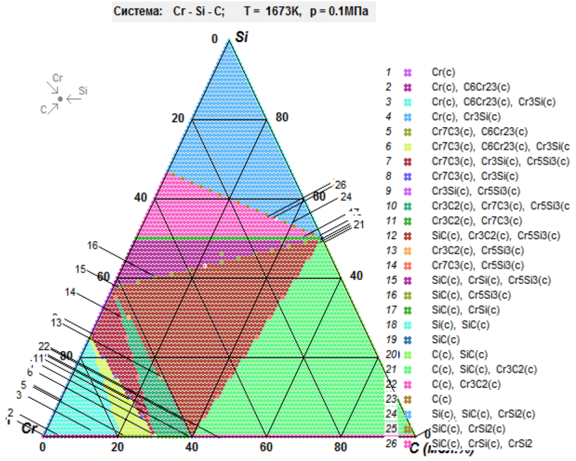
The Cr(c) phase consists of Al-0%, Cr-100%, C-0% percentage and a mole fraction of 5.4392 mol/kg. Phase C(c) consists of Al-0%, Cr-0%, C-100% percentage and a Mole fraction of 35.6045 mol/kg. It was found that the Al(c) phase consists of Al-100%, Cr-0%, C-0% in percentage composition and with a mole fraction of 17.9057 mol/kg.

The system under consideration has phases that undergo special changes. It is established that the Cr(c), Cr_7C_3(c) phase is formed at a temperature of 1573K and when the temperature reaches 1673K, the phase persists, in the future the temperature scale increases, and the indicators when the temperature reaches 1773, 1873K destroy the specified phase composition [10]. At temperature of 1873K, a new phase Al_4C_3(c); Cr_3C_2(c); Cr_7C_3(c) is formed in the triple Al-Cr-C system. In an amount of about 1%, the Cr_3C_2(c) phase; Cr_7C_3(c) occurs at a temperature of 1773-1873K. The phase that changes the following composition due to an increase in temperature is Cr_3C_2(c), Cr_7C_3(c), C_6Cr_{23}(c). It is known that this phase at a temperature of 1873 K spreads in the composition of the system in question in an amount of about 7%. Further, it was proved that Cr_3C_2(c) Cr_7C_3(c);C_6Cr_{23}(c) are destroyed by increasing the temperature scale of 1973K. When studying thermodynamic changes at a temperature of 1873K in the Al-Cr-C metal system, it was found that the Al_4C_3(c) phase spreads in an amount of about 1% and eliminates the composition of the phase with increasing temperature.

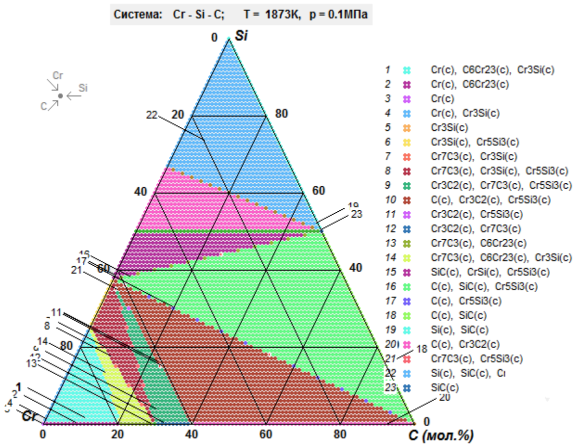
In Figure 2(a) at a temperature of 1673K, the Cr-Si-C triple system shows that it forms 26 compounds:

1)Cr(c); 2)Cr(c);C_6Cr_{23}(c); 3)Cr(c);C_6Cr_{23}(c);Cr_3Si(c); 4)Cr_7C_3(c);C_6Cr_{23}(c);Cr_3Si(c); 5)Cr_7C_3(c);Cr_3Si(c);Cr_5Si_3(c); 6)SiC(c);Cr_3C_2(c);Cr_5Si_3(c);7)C(c);SiC(c);Cr_3C_2(c) 8)Cr_3Si(c); Cr_7C_3(c);Cr_5Si_3(c); 9)C(c);Cr_3C_2(c); 10)C(c);SiC(c); 11)SiC(c);Cr_5Si_3(c); 12)Cr_7C_3(c);C_6Cr_{23}(c); 13)SiC(c); 14)SiC(c);CrSi(c);$CrSi_2$(c); 15)Si(c);SiC(c);$CrSi_2$(c); 16)SiC(c); $CrSi_2$(c); 17)SiC(c);CrSi(c); 18)SiC(c);CrSi(c);Cr_5Si_3(c); 19)Si(c);SiC(c); 20)Cr_7C_3(c);Cr_5Si_3(c); 21)Cr_7C_3(c);Cr_3Si(c); 22)Cr_3C_2(c);Cr_5Si_3(c); 23)Cr(c);Cr_3Si(c); 24)Cr_3C_2(c);Cr_7C_3(c); 25)Cr_3C_2(c);Cr_5Si_3(c); 26)C(c). 90% of this triple system Cr-Si-C belongs to compounds such a Cr_7C_3(c);Cr_5Si_3(c); Cr_3Si(c); 7% is C_6Cr_{23}(c);CrSi(c);$CrSi_2$(c);C(c), the remaining 3% is the remaining compounds.

In Figure 2(b) at a temperature of 1873K, the Cr-Si-C triple system shows that it forms 23 compounds: 1)Cr(c); 2)Cr(c);C6Cr_{23}(c); 3)Cr(c);C_6Cr_{23}(c);Cr_3Si(c); 4)Cr_7C_3(c); C_6Cr_{23}(c); Cr_3Si(c); 5)Cr_7C_3(c);Cr_3Si(c);Cr_5Si_3(c); 6)SiC(c); Cr_3C_2(c);Cr_5Si_3(c); 7)C(c);SiC(c);Cr_3C_2(c) 8)Cr_3Si(c); Cr_7C_3(c);Cr_5Si_3(c); 9)C(c);Cr_3C_2(c); 10)C(c);SiC(c); 11)SiC(c); Cr_5Si_3(c); 12)SiC(c);Cr_3C_2(c); 13)SiC(c); 14)SiC(c); CrSi(c);$CrSi_2$(c); 15)Si(c);SiC(c);$CrSi_2$(c); 16)SiC(c);$CrSi_2$(c); 17)SiC(c);CrSi(c); 18)SiC(c);CrSi(c);Cr_5Si_3(c); 19)Si(c); SiC(c); 20)Cr_7C_3(c);Cr_5Si_3(c); 21)Cr_7C_3(c);Cr_3Si(c); 22)Cr_3C_2(c); Cr_5Si_3(c); 23)Cr(c);Cr_3Si(c). 66% of this triple system of Cr-Si-C is SiC(c); Cr_5Si_3(c); Cr_3Si(c); 21% C_6Cr_{23}(c);CrSi(c);$CrSi_2$(c);C(c), the remaining 13% make up the remaining compounds.



a)



b)

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

Components of the triple system Cr-Si-C the Cr(c) phase consists of Si-0%, Cr-100%, C-0% percentage and a mole fraction of 3.5458 mol/kg. Phase C(c) consists of Si -0%, Cr-0%, C-100% percentage and a mole fraction of 27.5134 mol/kg. It was found that the Si(c) phase consists of Si-100%, Cr-0%, C-0% in percentage composition and with a mole fraction of 15.3576 mol/kg.

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

4. Conclusions

To study the formation and change of compounds, it is important to study thermodynamic changes that allow using a software package and determine the composition of a ferrosilicochrome alloy.

In accordance with the tasks set, phase transformations in chromium-based metal systems and the establishment of composition regions in complex metal melts are determined, theoretical studies on the determination of phase-structural features in the Cr-Si-Al-C metal system are relevant in this work.

In accordance with the purpose of the work, the following tasks were solved:

-Determination of phase-structural features in the Cr-Si-Al-C metal system by thermodynamic-diagram analysis;

-Determination of molar fractions and percentages of the main components of the compounds of the metal system Cr-Si-Al-C using the integrated program «Triangle».

Based on the data obtained, graphs of the temperature dependence of the composition of the phases were compiled. Using the complex program «Triangle», the mole proportions and percentages of the main constituent phases of the Cr-Si-Al-C metallic system were determined and it was proved that the phase-forming compounds have the dynamics of changes in accordance with the previous chapters.

In the course of the analysis of the results obtained, it was found that the triple systems Al-Cr-Si and Si-Cr-C, 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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Күлі жоғары көмірді пайдалана отырып кешенді қорытпаларды балқыту технологиясы және олардың болат және ферроқорытпалар өндірісінде қолданылуы мүмкіндіктерін модельдеу

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Аңдатпа. Мақалада көп компонентті 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-Cr-C, Cr-Si-C, 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.*

Технология выплавки комплексных сплавов с использованием высокозольных углей и моделирование возможностей их применения в производстве стали и ферросплавов

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Аннотация. 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-Cr-C, Cr-Si-C. 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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