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THERMODYNAMIC MODELING OF PHASE COMPOSITION FOR Fe-Ca-Si-Al SYSTEM

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In this paper, theoretical studies on the construction of phase structure diagrams of the Fe-Ca-Si-Al system as modeling composition of alloy by Thermodynamic-diagram analysis (TDA) were carried out. TDA analysis allows predicting the optimal composition of alloys using phase structure diagrams of the multicomponent systems. TDA excludes complex mathematical apparatus. Also, TDA allows to obtaine data for the Fe-Ca-Si-Al system, a diagram of phase relationships, each elementary subsystem of which is independent. By analyzing the binary systems, the state diagram of Fe-Ca-Si-Al metal system was constructed, which simulates the final phase composition of the ferroalloy. The reliability of the effectiveness of these methods is confirmed by large-scale laboratory melting tests.

Keywords: ferroalloys, Fe-Ca-Si-Al system, thermodynamic-diagram analysis, phase composition, alkaline earth metals

INTRODUCTION

Complex ferroalloys with alkaline earth metals such as calcium, magnesium, barium and other metals are important for the metallurgical industry. A number of authors prove the efficiency of using multicomponent ferroalloys with alkaline-earth metals for deoxidation and modification of steel [1-3].

In the practice of complex theoretical studies of multicomponent systems, the TDA method of analysis is known, which greatly simplifies the study of the peculiarities of phase transformations in multicomponent systems by dividing them into thermodynamically stable elementary partial subsystems of the same dimension as the main one. In this paper thermodynamic-diagram analysis was provided for Fe-Ca-Si-Al system for determination the phase composition in final ferroalloy and construction of the phase composition diagram of congruent compounds for a four-component system under the study.

RESEARCH METHODOLOGY

The initial charge materials used for smelting a complex ferroalloy based on Fe-Ca-Si-Al consist mainly of silicon, calcium, aluminum, iron oxides (blast furnace slag and coal ash) and solid carbon - a reducing agent (high-ash coal and coal sludge). Therefore, in order to clarify the phase regularities in metallic systems to predict the final phase composition of the alloy, in this work, theoretical studies have been carried out to plot the phase structure diagram of the Fe-Ca-Si-Al system as a modeling composition of the final alloy by the method of thermodynamic diagram analysis (TDA).

TDA allows obtaining data for the system in the form of a phase diagram, each elementary subsystem in this diagram is independent. Subsystem can be regarded as a quasi-system.

Fairly simple and accurate method for deriving equations for calculating the phase composition of oxide systems was proposed by A.A. Akberdin (Chemical and Metallurgical Institute named after J. Abishev). It is based on the balance of the distribution of the initial oxides over the formed phases [4].

Topographically, the four-component Fe-Ca-Si-Al system is a tetrahedron, on the vertices of which are located pure chemical elements: iron, silicon, aluminum and calcium, respectively.

The triangulation method was used for the study. Also, the principle of minimizing the Gibbs free energy was used. In the absence of the values of the standard Gibbs energies, it is possible to determine using the well-known Gibbs-Helmholtz equation [5-7].

The complete calculation of the thermodynamic constants of the reactions (occurring in these systems) was carried out using the Gibbs software complex.

The number of elementary triangles of co-existing phases into which the system under study is divided can be pre-determined by formula 1.

$$X_3 = \sum C_2 + 2\sum C_3 + 1 \quad (1)$$

where X_3 – number of elementary triangles in the system under study; $\sum C_2$ – number of binary connections; $\sum C_3$ – the number of triple phases.

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RESULTS RESEARCH AND DISCUSSION

The study of the phase composition diagram of the four-component system Fe-Ca-Si-Al began with particular three-component systems, identifying binary and ternary phases in them using reference data.

Thus, to consider the four-component system Fe-Ca-Si-Al, it can be divided into the following three-component systems: Fe-Si-Al; Fe-Si-Ca; Fe-Al-Ca; Si-Al-Ca.

The Fe-Si-Al system consists of three private binary systems. They are Fe-Si, Fe-Al and Al-Si. According to the literature [8-10], the existence of the following phases was established in the Fe-Si binary system: α – and γ- iron-based solid solutions, α_2 - phase, Fe_3Si (α_1), Fe_2Si, Fe_5Si_3, FeSi, Fe_2Si_5, $FeSi_2$. Phases were applied on the composition triangle (Figure 1).

Five stable phases are formed in the Fe-Al system, each of which has a certain area of homogeneity. In the ternary system Fe-Si-Al there are two stable (FeSi and Fe_2Al_5) binary compounds, there are no ternary ones.

The Si-Al binary system belongs to a simple eutectic type with a low solubility of the components in each other in the solid state.

The Fe-Si-Ca system consists of three binary private subsystems. They are Fe-Si, Fe-Ca and Si-Ca. They were determined by using formula 1 and are shown in Figure 2.

Calcium silicide Ca_2Si exists at temperatures < 910 ºC in solid equilibrium melts containing more than 60 % of Ca. In the Fe-Si-Ca system three stably binary compounds have been established. They are FeSi, CaSi and $CaSi_2$.

The system Fe-Al-Ca consists of three binary private subsystems. They are Fe-Si, Fe-Ca, Si-Ca and they are shown in Figure 3.

The system contains two compounds. They are Al_4Ca and Al_2Ca. The Al_2Ca compound melts congruently at a temperature of 1079 °C. In the Fe-Al-Ca system are two stable binary compounds Al_2Ca and Fe_2Al_5.

The Si-Al-Ca system consists of three binary private subsystems. They are Al-Si, Si-Ca, Al-Ca. Three

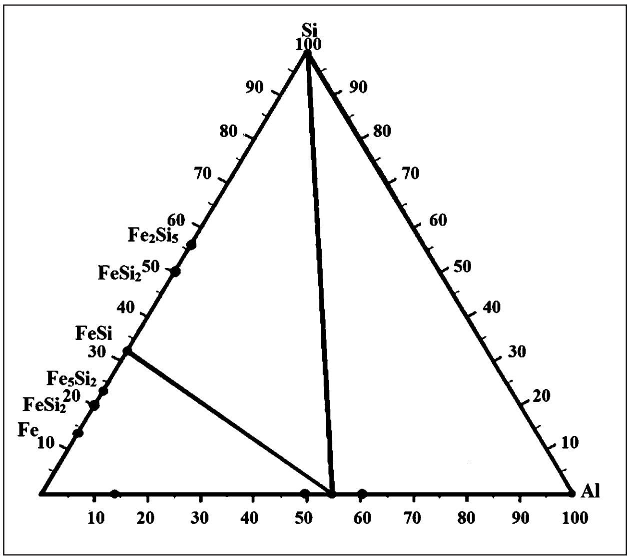

Figure 1 Congruent connections of Fe-Si-Al subsystem

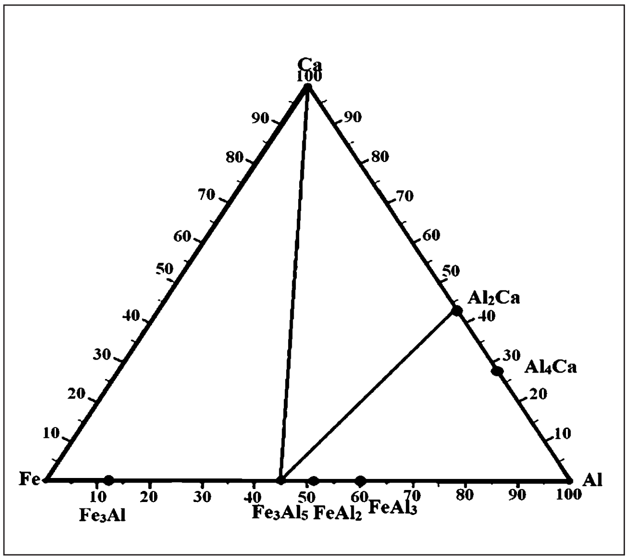

Figure 3 Congruent connections of Fe-Al-Ca subsystem

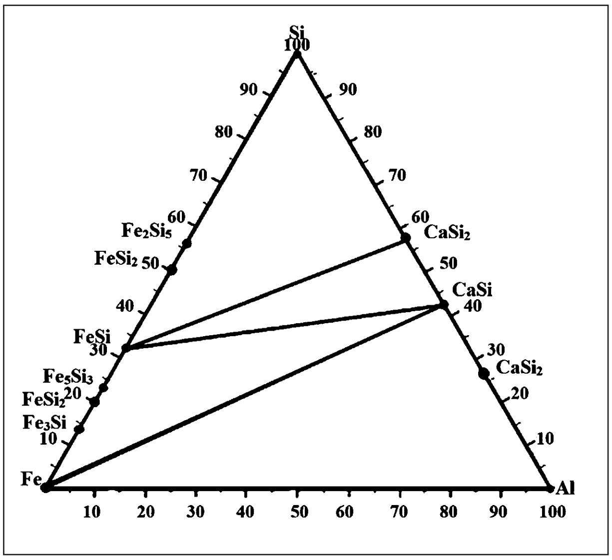

Figure 2 Congruent connections of Fe-Si-Ca subsystem

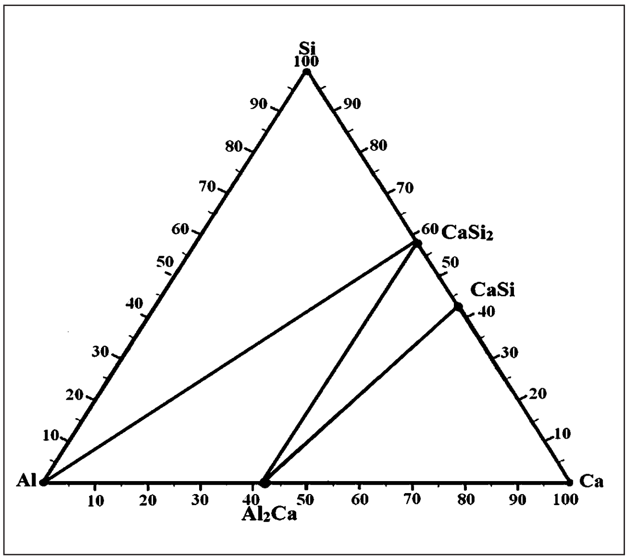

Figure 4 Congruent connections of Al-Si-Ca subsystem

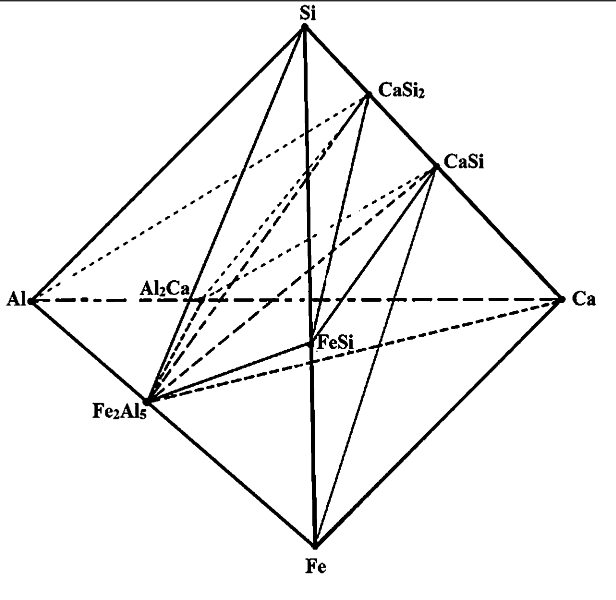

Figure 5 Diagram of the phase composition of congruent compounds of a four-component Fe-Ca-Al-Si system

stable binary compounds have been established: $CaSi_2$, CaSi and Al_2Ca. Established phases were plotted on the Figure 4. In the Si-Al-Ca system are four triangles of phases coexisting.

Phase composition diagrams of particular three-component systems makes possible to break down the four-component Fe-Ca-Si-Al system into elementary tetrahedrons by the method of "closing triangles" into a tetrahedron by comparing their compositions. In the investigated four-component system Fe-Ca-Si-Al was determined seven tetrahedrons. They are presented in the Table 1.

Thus, on the basis of the data obtained above, it is possible to construct a graphical image of the phase composition diagram of the Fe-Ca-Al-Si system in elementary tetrahedrons of coexisting phases. The diagram of the phase composition of congruent compounds of the four-component system Fe-Ca-Al-Cu is shown in Figure 5.

The breakdown of the overall system is carried out taking into account congruent connections. The sum of the relative volumes of elementary tetrahedron is equal to one (0,999999), which confirms the correctness of the tetrahedration performed in Table 1.

Table 1 **List of tetrahedrons of the Fe-Ca-Si-Al system**

№	Tetrahedron	Elementary volumes
1	Ca-CaSi-Fe_2Al_5-Fe	0,252132
2	CaSi-FeSi-Fe-Fe_2Al_5	0,120033
3	CaSi-$CaSi_2$-FeSi-Fe_2Al_5	0,069996
4	$CaSi_2$-Fe_2Al_5-FeSi-Si	0,170097
5	CaSi-$CaSi_2$-Al_2Ca-Fe_2Al_5	0,050030
6	$CaSi_2$-Al_2Ca-Al-Fe_2Al_5	0,126081
7	$CaSi_2$-Fe_2Al_5-Al-Si	0,211630
Total amount		0,999999

The performed thermodynamic diagrammatic analysis of the four-component system Fe-Ca-Al-Si gives a predicted estimate of the coexistence of phase regions. The obtained results of the study show the applicability of this method as a method for carrying out thermodynamic-diagrammatic analysis of a complex ferroalloy based on the Fe-Ca-Si-Al system.

It was found that, topographically, the four-component system Fe-Ca-Si-Al is a tetrahedron, at the vertices of which are located pure chemical elements: iron, silicon, aluminum and calcium, respectively. There are double connections on the edges of the tetrahedron, and triple ones on the edges.

The triangulation method was used to break down the ternary systems into elementary triangles of coexisting phases.

Seven stable tetrahedrons were identified by plotting the state diagram of the Fe-Ca-Si-Al metal system. They are: 1.Ca-CaSi-Fe_2Al_5-Fe; 2. CaSi-FeSi-Fe-Fe_2Al_5; 3. CaSi-$CaSi_2$-FeSi-Fe_2Al_5; 4. $CaSi_2$-Fe_2Al_5-FeSi-Si; 5. CaSi-$CaSi_2$-Al_2Ca-Fe_2Al_5; 6. $CaSi_2$-Al_2Ca-Al-Fe_2Al_5; 7. Fe_2Al_5-Al-Si-$CaSi_2$.

It was also found that the phase composition of the ferroalloy under study is characterized by the compounds CaSi, $CaSi_2$, Al_2Ca, Fe_2Al_5 and FeSi. Tetrahedron No. 1 (Ca-CaSi-Fe_2Al_5-Fe) is the most voluminous, which characterizes the final composition of the alloy, and a large volume of the tetrahedron provides favorable conditions for the process of smelting a calcium-containing ferroalloy.

The reliability of the effectiveness of these methods is confirmed by tests carried out on a large-scale laboratory and pilot-industrial scale. Earlier, the authors of this work developed a pilot batch of a complex ferroalloy with calcium, barium and magnesium with the following chemical composition / %: Ca – 11-15, Si - 50-55, Al – 12-20, P – 0,06, S – 0,02, Mg – 1,2, Ba – 1,3 and the rest is iron. Ferroalloy was obtained as a result of large-scale laboratory tests simulating industrial conditions at the experimental site of the Chemical and Metallurgical Institute named after J. Abishev. In the course of physicochemical studies of the properties of a new complex ferroalloy with alkaline-earth metals, it was found that the phase composition of the alloy is presented in the form of $CaAl_2Si_{1,5}$ and free silicon Si, and is also characterized by the compounds CaSi, $CaSi_2$, Al_2Ca, Fe_2Al_5 and FeSi [11].

Thus, the region where the compositions of complex alloys based on Fe-Ca-Si-Al are located is characterized by a combination the above tetrahedrons.

CONCLUSION

Based on the results of theoretical studies carried out by the method of thermodynamic-diagrammatic analysis, the following results were obtained:

- analyzing binary systems, a diagram of the state of the Fe-Ca-Si-Al metal system was constructed, which simulates the final phase composition of the calcium-containing ferroalloy, which consists of seven stable tetrahedrons;

- the phase composition of the calcium-containing ferroalloy is characterized by the compounds CaSi, $CaSi_2$, Al_2Ca, Fe_2Al_5 and FeSi. Tetrahedron No. 1 (Ca-CaSi-Fe2Al5-Fe) is the most voluminous, which characterizes the final composition of the alloy, and the large volume of the tetrahedron provides favorable conditions for the process of smelting a calcium-containing ferroalloy.

In the studied system, using formula 1, the number of elementary triangles of coexisting phases was calculated.

On the basis of the data obtained above, the image of the phase composition diagram of the Fe-Ca-Al-Si system in elementary tetrahedrons of coexisting phases was constructed.

Obtained data on thermodynamic diagrammatic analysis made it possible to identify the optimal phase regions for a complex ferroalloy based on Fe-Ca-Si-Al.

Thus in this paper, theoretical studies on the construction of phase structure diagrams of the Fe-Ca-Si-Al system as modeling composition of alloy by thermodynamic-diagram analysis were carried out.

The performed TDA of the four-component system Fe-Ca-Al-Si gives a predicted estimate of the coexistence of phase regions. However, the most detailed study of coexisting condensed phases requires additional thermodynamic calculations; with the help of such calculations, it is possible to determine the distribution of the elements that make up the final phase regions over the existing phases. Therefore, within the framework of this scientific work, it is planned to carry out a thermodynamic analysis of individual subsystems that make up a four-component system using the Terra software package.

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