The method of mathematical description of the phase composition diagrams

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The method for the mathematical description of phase composition diagrams has been developed. It is based on the balance of distribution of the initial components of the slag or metal over the secondary compounds (phases) formed from them. The equations relating the phase composition to the chemical one are obtained, and a computer program is created on their basis. After setting the chemical composition of the slag from the console and starting it, the computer outputs the phase composition in mass percent, the number of the polytope, its volume, initial and final equations. The method has no restrictions on the number of components considered in the system under study and allows describing five or more component systems that cannot be correctly displayed in three-dimensional space on a plane. Examples of using the model are given. Calculations using the obtained model established that deterioration in the production of carbonaceous ferrochromium from Kazakh ores is due to the movement of slags within the $SiO_2 - Al_2O_3 - MgO$ triple diagram from the region of magnesia spinel ($MgO{\cdot}Al_2O_3$) to the region of predominant forsterite crystallization ($2MgO{\cdot}SiO_2$) during transition to use of magnesia ores. A predictive estimation of the phase composition of steel-smelting slags with high basicity is given. It was found out that, on average, they contain high-temperature compounds such as periclase (MgO), dicalcium silicate (Ca_2SiO_4), calcium monoaluminate ($CaAl_2O_4$), and magnesia spinel ($MgAl_2O_4$) as phase components. All of them are high-temperature compounds, which determine refractoriness of the slag. Presence of Ca_2SiO_4 in the slag in a large amount (74 %), capable of polymorphic transformation with a volume change by 12 %, can cause decomposition of slags with formation of dispersed dust, which is hazardous to the environment. The calculation results are confirmed by X-ray phase analysis of the slag. The proposed mathematical model also allows solving inverse problems, i.e. to find the composition of the charge to obtain a product with the desired phase composition. It is recommended to load charge containing 68.48 % CaO, 25.10 % SiO_2 and 6.43 % Al_2O_3 into the kiln to obtain high quality white Portland cement clinker with the following composition: 45 % of $3CaO{\cdot}SiO_2$, 38 % of $2CaO{\cdot}SiO_2$ and 17 % of $3CaO{\cdot}Al_2O_3$.
Key words: slag, oxides, metal, elements, phase, diagram, oxide distribution, mathematical model, computer program.
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Introduction

Raw materials and finished products in research and production activities are often characterized by their chemical composition. It is considered that metallurgical slag or cement clinker contain e.g. calcium and silicon oxides (CaO, SiO_2), while iron, steel and ferroalloys contain such elements as Fe, C, Si, Cr and other [1]. Indeed, raw materials that were subjected to natural or technological heat treatment (sintering, melting) can't contain free basic (CaO) and acidic (SiO_2) oxides. When reacting with each other, they produce the salts of corresponding acids, e.g. $3CaO{\cdot}SiO_2$, $2CaO{\cdot}SiO_2$. Only definite combination of such phases as tri- and dicalcium silicate makes its possible to obtain, for example, high-quality Portland cement clinker [2].

In the same way, to obtain wear-resistant cast iron, it is necessary to provide forming of Cr_7C_3 carbide in it, not only presence of definite chromium amount [3-5]. Operating the chemical composition is a rather suitable tool for calculation of charges and taking into account loading of materials in industrial units. Activity of enterprises is based on their aim to obtain products with required phase composition, which determines products quality. In this connection the aimed forming and control of phase composition of manufacturing products is rather actual.

The method of experimental determination of materials phase composition via X-ray, petrographic or other instrumental analytical method is the most widely distributed technique. E.g., mastering of the pelletizing technology for iron ores in CIS countries is mainly based on these methods [6]. However, designing of the new technological process, which considers tens and hundreds of kinds of new ores and fluxes for determining their optimal correlation, requires essential material and temporal expenses. This method is quite not applicable, if development of raw materials is still not conducted, and a researcher has only chemical composition of geological samples.

Phase composition can be determined via phase equilibrium diagrams. But they are mainly triple-component ones,

while charge materials and their processing products are multi-component systems. Additionally, it is very difficult to measure the exact numerical value of any parameter from the state equilibrium diagrams and to use it for development of the technology as well as in the process automatic control systems.

In this connection, the theoretical methods are interesting. They are realized within the framework of such computer programs as как SGT, Thermo-Calc, HSC, Astra, TERRA and other [7, 8], which are widely distributed in the research practice [9-12]. Presence of thermodynamic data of all participants of the examining process is a mandatory condition that can't be always provided.

To make practical calculations more suitable, it seems expedient to create mathematical models, which connect phase composition of a product with its chemical composition. It will also allow to use them in the automatic control systems for technological processes. Such method, which was based on mathematical approach, was proposed in 1957 [13]. Its use is complicated owing to exceed of the number of determining phases over the required number of equations; the exit from this situation via equalizing of any phase amount to zero is insufficiently evident.

Research methods and discussion of the results

This research proposes the method of mathematical description of phase composition diagrams, which is based on the balance of distribution of initial substances (oxides, elements) of the researching material via forming phases. Such approach is suggested not for the first time. It is available for description of the phase composition diagrams, which are presented in the technical literature. If necessary, they can be obtained via well-known methods [14]. Such diagrams differ from the state equilibrium diagrams and constitute a set of elementary polytopes of co-existing phases. These are triangles in a triple-component system, tetrahedron in a 4-component system, pentatopes in a 5-component system etc. of co-existing phases. It should be taken into account, that the phase diagram on the plane in 3D space in more than 4-component systems can't provide graphically correct reflection. Only mathematical model allows the required calculations with such multi-component systems, because it can operate in multi-dimensional space. If we know dimensionality k of the studied system, the required space dimensionality N is determined as $N = k - 1$. So, for the 4-component system the required space dimensionality $N = 4 - 1 = 3$, while for 6- component system $N = 6 - 1 = 5$.

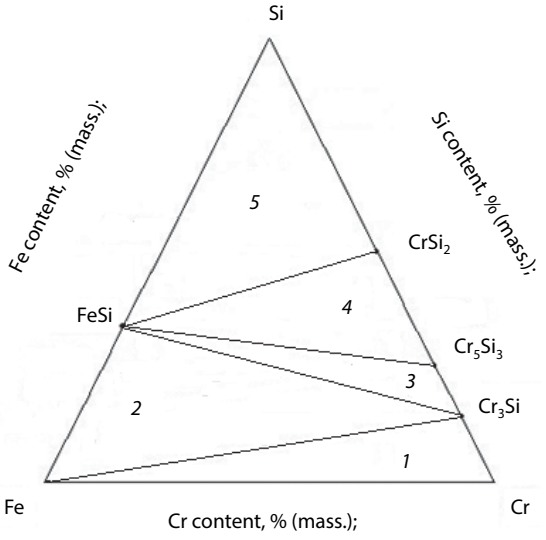

Fig. 1. Diagram of the phase composition of the Fe – Si – Cr system

Table 1. **Coordinates of phases of Fe – Cr_3Si – FeSi triangle**

No.	Phase	Composition, % (mass.)		
		Fe	Si	Cr
1	Fe	100		
2	Cr_3Si		15.26	84.74
3	FeSi	66.54	33.46	

According to the proposed method, the mathematical model is created for each elementary polytopes which are forming the phase composition diagram. The phase composition diagram of congruently melting compounds of the Fe – Si – Cr system is displayed on the **Fig. 1**.

It is divided via usual triangulation by 5 elementary polytopes (triangles) of the co-existing phases: Fe – Cr_3Si – Cr (1), Fe – Cr_3Si – FeSi (2), FeSi – Cr_3Si – Cr_5Si_3 (3), FeSi – Cr_5Si_3 – $CrSi_2$ (4), FeSi – $CrSi_2$ – Si (5). **Table 1** includes the coordinates of triangle 2 phases in % (mass.) as an example.

According to the proposed method, at first the balance of distribution of iron (Fe_0), silicon (Si_0) and chromium (Cr_0) of the examined metal is recorded for the forming phases. For example, iron balance is described using the column 3 in the Table 1, i.e. taking into account the chemical phase composition:

$$Fe_0 = 1 \cdot Fe + 0.6654 \cdot FeSi$$

Silicon and chromium balance is written in the same way:

$$Si_0 = 0.1526 \cdot Cr_3Si + 0.3346 \cdot FeSi \quad (2)$$

$$Cr_0 = 0.8474 \cdot Cr_3Si \quad (3)$$

Solving the equations 1-3 relating to unknown phases allows to obtain the mathematical model for calculation of the amount of all phases in the elementary triangle 2:

$$Fe = Fe_0 - 1.9886 \cdot Si_0 + 0.3582 \cdot Cr_0 \quad (4)$$

$$Cr_3Si = 1.1801 \cdot Cr_0 \quad (5)$$

$$FeSi = 2.9886 \cdot Si_0 - 0.5383 \cdot Cr_0 \quad (6)$$

Distribution of above-presented calculations for all 5 elementary triangles of the co-existing phases allows to obtain the mathematical model of phase composition of Fe-Si-Cr

system (see Fig. 1). The computer program was created on the base of this model. After setting the task of metal chemical composition (Fe_0, Si_0, Cr_0) and switching on by the operator from a console, a computer finds a field (elementary triangle) where metal is located, identifies its number and sends information about phase composition in % (mass.) to a monitor or for printing. Then it is not difficult to find a field for a triple-component system, because visualization according to the graphic diagram (see Fig. 1) is possible. However, 5- or 6-component systems, which contain 100-120 elementary polytopes, can't be reflected correctly in graphical mode on a plane; that's why search of the required polytopes (where metal is located) is carrying out by computer applying to the sign of positive value of amount of phases, with their sum equal to 100 %. Only one polytopes from totality of polytopes in this system can meet the requirements for a metal with concrete composition.

Screenshot of the program for calculation of phase composition in the 6-component system $CaO - SiO_2 - Al_2O_3 - MgO - FeO - Fe_2O_3$ is displayed on the **Fig. 2**. Its applying features are wide, covering ironmaking, steelmaking, production of cement clinker, refractories, copper, ceramics etc.

Its mathematical model was created using above-described balance method via solving of 6 equations with 6 indeterminates in each hexatope. The computer program (see Fig. 2) was developed on the base of these equations. Initial oxides are designated there for short as C_0 (CaO), S_0 (SiO_2), A_0 (Al_2O_3), M_0 (MgO), F'_0 (FeO), F_0 (Fe_2O_3), while the phases which are forming from these oxides are designated as M (MgO), F/ (FeO), C_2S (Ca_2SiO_4), F/ F (Fe_3O_4) etc.

The program can be used for calculation of the phase composition not only in 6-component system, but also in binary, triple, 4- and 5-component systems. It was established via calculations using the obtained model that deterioration

Расчет фазового состава в системе $CaO - SiO_2 - Al_2O_3 - MgO - FeO - Fe_2O_3$

Исходные данные для расчета:

C_0: = 54.1 S_0: = 25.6 A_0: = 12.3 M_0: = 8 F_0: = 0 F_0: = 0

Результаты расчета: str = " "

Номер политопа: N = 11

Состав фаз, %:

faz 1 = " M " 7.711

faz 2 = " F " 0.000

faz 3 = " C2S " 73.352

faz 4 = " CA " 17.911

faz 5 = " MA " 1.026

faz 6 = " F ´ F " 0.000 SUMMA = 100.000

Fig. 2. Screenshot of the program for calculation of phase composition

Table 2. **Composition of carbonaceous ferrochromium slags**

No.	Years	Chemical composition, %			Phase composition, %		
		SiO_2	Al_2O_3	MgO	$MgO{\cdot}Al_2O_3$	SiO_2	$2MgO{\cdot}SiO_2$
1	1942-1945	39.5	29.0	31.5	40.4	24.6	35.0
2	1950-1952	32.7	28.5	38.8	39.8	12.2	47.9
3	1960-1963	34.9	23.9	41.2	33.4	11.2	55.4
4	1968-1969	33.4	21.9	44.7	30.6	6.5	62.9
5	1987-2000	35.1	18.0	46.9	25.0	5.0	70.0

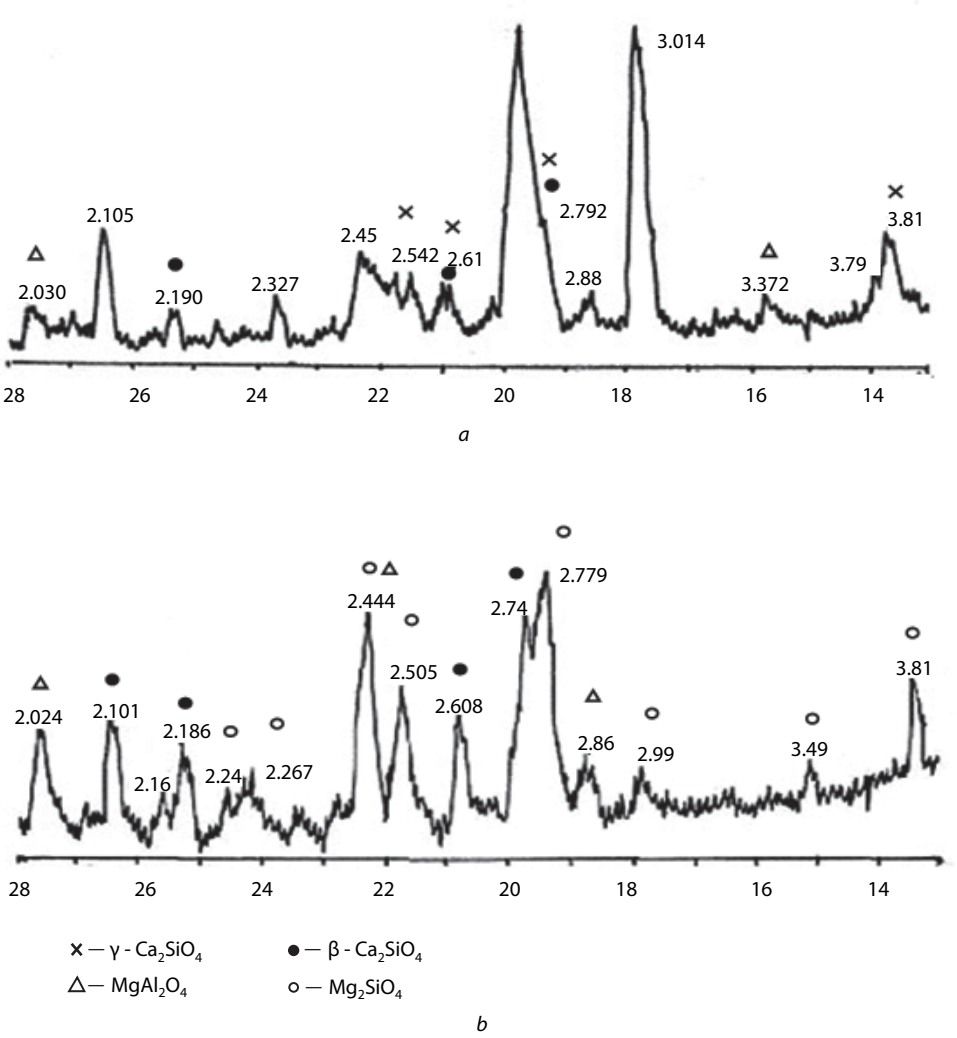

Fig. 3. X-ray of slag after decomposition (*a*) and stabilized slag (*b*)

of production parameters of carbonaceous ferrochromium form Kazakh ores is stipulated by transfer of slags within the range of the triple diagram $SiO_2 - Al_2O_3 - MgO$ from the region of magnesia spinel ($MgO \cdot Al_2O_3$) to the region of preferential crystallization of forsterite ($2MgO \cdot SiO_2$), during transition to use of magnesia ores (**Table 2**).

Steelmaking slags in electric arc furnaces contain in average the following components, % (mass.): 54.1 CaO, 25.6 SiO_2, 12.3 Al_2O_3 and 8 MgO. Calculations using the proposed model show the following content of phase components, % (mass.): 7.71 MgO, 73.35 Ca_2SiO_4, 17.91 $CaAl_2O_4$ and 1.03 $MgAl_2O_4$ (see Fig. 2). All of them are high-temperature components, what determines slag refractoriness, while presence of γ-form of Ca_2SiO_4 (**Fig. 3*a***), capable for polymorphic transformation with a volume change by 12 %, can cause decomposition of slags with formation of dispersed dust, which is hazardous to the environment. Stabilization of high-temperature β-form of Ca_2SiO_4, which is not subjected to decomposition, is achieved by addition of borate ore in it (Fig. 3***b***). It allows to produce road metal from stabilized slag (**Fig. 4**) [15].

The proposed models are suitable for solving also inverse problems, i.e. to calculate composition of the charge material for obtaining a product with the definite phase composition. The initial balance equations (1) – (3) are used for this purpose. It is recommended, for example, to obtain high quality white Portland cement clinker with the following composition: 45 % of $3CaO \cdot SiO_2$, 38 % of $2CaO \cdot SiO_2$ and 17 % of $3CaO \cdot Al_2O_3$.

Use of the following initial equations for the triple system $CaO - SiO_2 - Al_2O_3$ (within the range of a 6-component system), which was concluded by the authors, allows to establish that the charge should contain 68.48 % C_0 (CaO), 25.10 % S_0 (SiO_2) and 6.43 % A_0 (Al_2O). If we know the chemical analyses of limestone, quartzite and alumina at the enterprise, it is possible to reveal their consumption in charge,

$$C_0 = +0.737 \cdot C_3S + 0.65 \cdot C_2S + 0.622 \cdot C_3A \quad (7)$$

$$S_0 = +0.263 \cdot C_3S + 0.349 \cdot C_2S \quad (8)$$

$$A_0 = +0.378 \cdot C_3A \quad (9)$$

a *b*

Fig. 4. Panorama of polygon with slag after decomposition (*a*) and stabilized slag (road metal) (*b*)

Conclusion

The method of mathematical description of phase composition diagrams in multi-component systems is developed. It is based on the balance of distribution of metal (slag) initial components by the phases which are forming from these components. The equations connecting phase composition with chemical one are obtained, the computer program is developed on their base. This method is not restricted by number of considering components in a studying system and allows to describe the systems with 5 and more components, which can't be correctly reflected in 3D space on a plane. The examples of use of this model for revealing the causes of slags refractoriness in melting of carbonaceous ferrochromium, decomposition of slags with high basicity, more detailed calculation of charge in production of Portland cement clinker are given.

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